United States Patent & Trademark Office
Patent Full-Text/APS

Customer Information Services Group
Electronic Information Products Division
June 1985
with revisions through February 1997

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2/25/97

Update 3 - Patent Full-Text/APS, June 1985

The following pages to the Patent Full-Text/APS File technical documentation are being changed as indicated. Change bars identify new and/or changed information.

Pages	Explanation
77, 78 and 78.1	Include the appearance of the Locarno International Classification for Design Patents.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNDERSECRETARY OF COMMERCE FOR INTELLECTUAL PROPERTY AND
DIRECTOR OF THE UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON D.C. 20231
WWW.USPTO.GOV

November 22, 1993

Special Update:

The following changes are being made to the Patent Full-Text/APS file (a.k.a. Green Book).

Effective with the January 4, 1994 issue International Classification can appear in the Field of Search and the Foreign Reference Cited.

Example #1 – Shows the elements appearing on the front page of patent document 5,235,703.

Example #2 – Shows the elements appearing in the Patent Full-Text/APS (Green Book) format of the front page of patent document 5,235,703.

(1 of 3) - the new field “FSI” within the logical group “CLAS”.
(2 of 3) - the new field “ICL” within the logical group “FREP”.
(3 of 3) - the field “OCL” becomes an optional field within the logical group “FREP”.

Example #3 – Shows the format of the International Classification of the new field “FSI” within the logical group “CLAS” and the new field “ICL” within the logical group “FREP”.

45818 2001 400 25-05-15 49412

28-10-93 141115 181470 05235703 2000

United States Patent [19]

Maynard

[11] **Patent Number:** 5,235,703

[45] **Date of Patent:** Aug. 17, 1993

[54] SHOCK ABSORBING BODY PROTECTOR

[76] Inventor: **Robert Maynard**, 315 W. Bradley
Ave., El Cajon, Calif. 92020

[21] Appl. No.: **793,577**

[22] Filed: **Nov. 18, 1991**

[51] **Int. Cl.**^{5} **A41D 13/00**
[52] **U.S. Cl.** 2/2; 2/45; 2/268; 2/DIG. 3
[58] **Field of Search** .... 2/2, DIG. 3, 267, 268, 2/DIG. 10, 92, 2.5, 44, 45, 413; 36/29; B02D 1/00, 2/00, 3/00; K01L 33/00

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,664,043	5/1972	Polumbus, Jr.	36/71
3,771,170	11/1973	Leon	2/2
3,866,241	2/1975	Grant	2/2
3,999,220	12/1976	Keltner	2/2
4,453,271	6/1984	Donzis	2/2
4,467,475	8/1984	Gregory et al.	2/2
4,700,403	10/1987	Vacanti	2/DIG. 3
4,724,549	2/1988	Herder et al.	2/411
4,730,403	3/1988	Walkhoff	36/93
4,991,230	2/1991	Vacanti	2/45
5,007,111	4/1991	Adams	2/2
5,074,765	12/1991	Pekar	36/29

FOREIGN PATENT DOCUMENTS

153082	8/1985	European Pat. Off.	2/2
1111111	1/1993	European Pat. Off.	B01K 1/00
3608585	2/1987	Fed. Rep. of Germany	2/2
22222	2/1998	Japan	K01L 1/00
3530397	3/1987	Fed. Rep. of Germany	2/2
2272615	1/1974	France	2/2
2177892	2/1987	United Kingdom	2/2

Primary Examiner—Clifford D. Crowder
Assistant Examiner—Amy Brooke Vanatta
Attorney, Agent, or Firm—Brown, Martin, Haller & McClain

[57] ABSTRACT

A body protector for athletes, particularly those engaged in motocross or motorcycle racing, having an outer semirigid plastic shell and an inner layer of air cell material for absorbing the impact of a fall or collision. The air cell material comprises a closed network of cells that are interconnected with channels. The channels slow the air movement away from the impact area, thereby distributing the energy of the impact throughout the cell network. An integral pump allows the wearer to maintain the air cell material at the desired pressure. An inflation indicator allows the wearer to estimate the pressure level of the air cells.

2 Claims, 2 Drawing Sheets

Example #1

```
      PATENT NUMBER - 05235703       ISSUE DATE - 08/17/93        DATE OF LISTING - 11/12/93       PAGE NUMBER    1


PATN
WKU  052357031
SRC  7
APN  7935773
APT  1
ART  247
APD  19911118
TTL  Shock absorbing body protector
ISD  19930817
NCL  2
ECL  1
EXA  Vanatta; Amy Brooke
EXP  Crowder; Clifford D.
NDR  2
NFG  6
INVT
NAM  Maynard; Robert
STR  315 W. Bradley Ave.
CTY  El Cajon
STA  CA
ZIP  92020
CLAS
OCL     2   2
XCL     2 45
XCL     2268
XCL     2DIG3
EDF  5
ICL  A41D 1300
FSC     2
FSS  2;DIG. 3;267;268;DIG. 10;92;2.5;44;45;413
FSC    36
FSS  29                                 1
UREF
PNO  3664043
ISD  19720500
NAM  Polumbus, Jr.
OCL    36 71
UREF
PNO  3771170
ISD  19731100
NAM  Leon
OCL     2   2
UREF
PNO  3866241
ISD  19750200
NAM  Grant
OCL     2   2
UREF
PNO  3999220
ISD  19761200
NAM  Kellner
OCL     2   2
UREF
PNO  4453271
ISD  19840600
NAM  Donzis
```

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[1] The Field of Search International Patent Classification(s) (FSI) would appear following the Field of Search U.S. Classification(s).

```
FSI    B02D     100
FSI    B02D     200
FSI    B02D     300
FSI    K01L    3300
```

Example #2 (1 of 3)

```
        PATENT NUMBER - 05235703        ISSUE DATE - 08/17/93        DATE OF LISTING - 11/12/93        PAGE NUMBER    2

OCL     2  2
UREF
PNO   4467475
ISD   19840800
NAM   Gregory et al.
OCL     2  2
UREF
PNO   4700403
ISD   19871000
NAM   Vacanti
OCL     2DIG.3
UREF
PNO   4724549
ISD   19880200
NAM   Horder et al.
OCL     2411
UREF
PNO   4730403
ISD   19880300
NAM   Walkhoff
OCL    36 93
UREF
PNO   4991230
ISD   19910200
NAM   Vacanti
OCL     2 45
UREF
PNO   5007111
ISD   19910400
NAM   Adams
OCL     2  2
UREF
PNO   5074765
ISD   19911200
NAM   Pekar
OCL    36 29
FREF
PNO   153082
ISD   19850800
CNT   EPX
OCL     2  2                        1
-----------------------------------
FREF
PNO   3608585
ISD   19870200
CNT   DEX
OCL     2  2                        2
-----------------------------------
FREF
PNO   3530397
ISD   19870300
CNT   DEX
OCL     2  2
FREF
PNO   2272615
ISD   19740100
CNT   FRX
OCL     2  2
```

Foreign Reference (FREF) citing an International Patent Classification (IPC).

```
1 FREF
  PNO    1111111
  ISD    19930100
  CNT    EPX
  ICL    B01K      100

2 FREF
  PNO    22222
  ISD    19980200
  CNT    JPX
  ICL    K01L      100
```

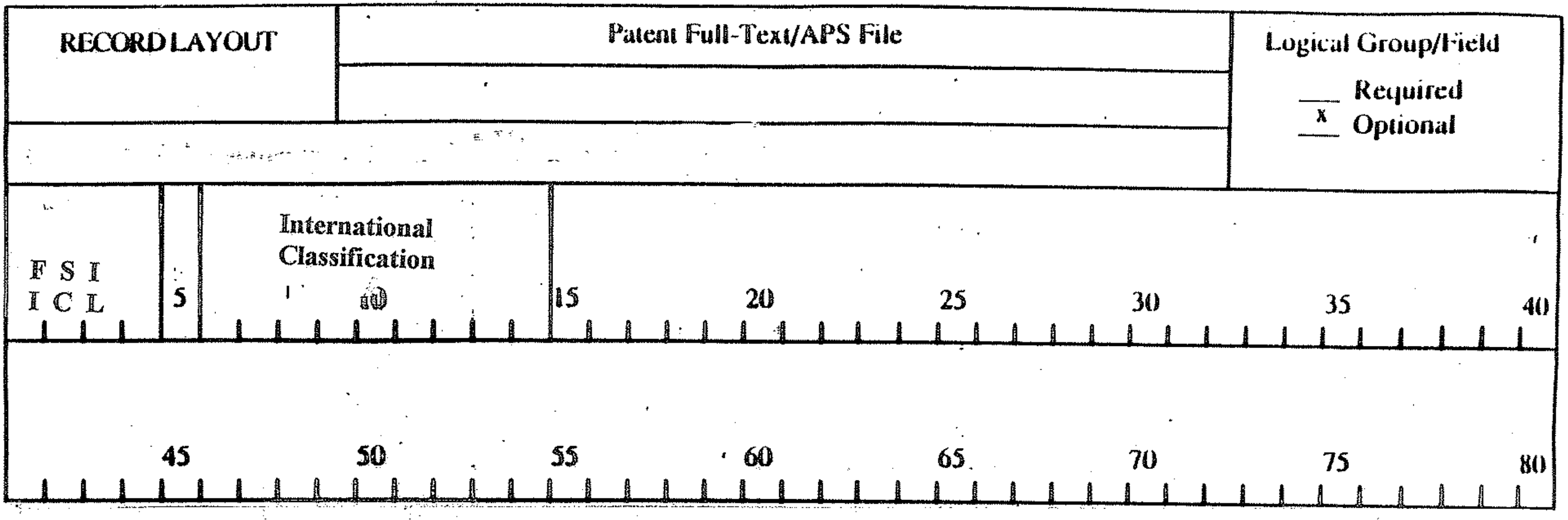
Example #2 (2 of 3)

```
     PATENT NUMBER - 05235703        ISSUE DATE - 08/17/93          DATE OF LISTING - 11/12/93        PAGE NUMBER    3


FREF
PNO  2177892
ISD  19870200
CNT  GBX
OCL    2  2
LREP
FRM  Brown, Martin, Haller & McClain
ABST
PAL  A body protector fbr athletes, particularly those engaged in motocross or
      motorcycle racing, having an outer semirigid plastic shell and an inner
      layer of air cell material for absorbing the impact of a fall or
      collision. The air cell material comprises a closed network of cells that
      are interconnected with channels. The channels slow the air movement away
      from the impact area, thereby distributing the energy of the impact
      throughout the cell network. An integral pump allows the wearer to
      maintain the air cell material at the desired pressure. An inflation
      indicator allows the wearer to estimate the pressure level of the air
      cells.
```

Example #2 (3 of 3)

Example #3



The ID Code (Positions 1-4) will contain FSI or ICL identifying the record as a Field of Search International Patent Classification record or an International Classification record.

Position 6 will begin a variable length alphanumeric field appearing as follows:

- **position 1 - Section - 1 character alphabetic.**
- **position 2-3 - Class - 2 character numeric.**
- **position 4 - Subclass - 1 character alphabetic.**
- **position 5-7 - Group - 3 character numeric, right justified, leading zeros.**
- **position 8-14 - Subgroup - Maximum of 7 characters alphanumeric (including punctuation).**

The International Classification for Designs will appear in the following manner:

- **position 1 - Section - 1 character alphabetic containing a "D".**
- **position 2-3 - Class - 2 character numeric, right justified, with a leading zero when required for a single digit class.**
- **position 4-5 - Subclass - 2 character numeric, right justified, with a leading zero when required for a single digit class.**

The remainder of the record, through position 80, contains spaces.

6/27/88

Update 2 - Patent Full-Text/APS File, June 1985

SPECIAL INSTRUCTIONS:

Update 2 to the Patent Full-Text/APS File technical reference is being published to include the appearance of text data for tables and "in-line" equations on the file.

The following pages will be updated as indicated. Change bars identify new and/or changed information.

Page	Explanation
A-1	Include an explanation for the use of a FNT ID Code in a table.
A-2	Three additional ID Codes are being established to support table and equation text data.
B-1	Include an explanation for table data records.
B-2, B-3	The addition of a call-out identifier for verical spacing.
D, D-51 thru D-275	Include machine-readable patent documents having tables and "in-line" equations.
E, E-1, E-2 E-44 thru E-273	Include printed patent documents having tables and "in-line" equations.

6/20/88

Update 1 - Patent Full-Text/APS File, June 1985

The following pages to the Patent Full-Text/APS File will be updated as indicated. Change bars identify new and/or changed information.

Page	Explanation
20	The addition of Series Code 7.
52	Include a NOTE identifying the use of the first position of ASSG/COD.
101	Change the NOTE explaining the appearance of LREP/ATT record(s).
115	Correct the ID Code (positions 1-4) of the PCT Publication Date from PCT to PCD.
C-1 thru C-10	The entire Appendix C - Special Characters is being replaced. Changes only apply to patents issued January 1971 thru December 1974. The changes are being made to Column 1 - +290 thru +299 and +338 thru +489. Column 2 of these items will have the last character appearing after the period (.).

Purpose

The purpose of this technical reference is to provide a detailed description of the organization, content and use of the patent full-text/APS file.

Patent Full-Text/APS File

The files resides on a 9-track, ASCII 6250 BPI, magnetic tape. Reference Figure 1 - American National Standard Code for Information Interchange. The data records on the file will be 80 characters in length, blocked 25, for a block size of 2000 characters. The contents of the file will appear as follows:

a. Standard Header Labels

b. Control Header Record A control header record will appear as the first record on the file. This record will contain information pertinent to the APS system, to include the issue date of the file.

c. Data Records The data records are 80 characters in length, consisting of data elements as defined in this technical reference. The first data element to appear will be a logical group. Each logical group identifies a section of a patent, such as the bibliographic data, the abstract and the claims. Within each logical group its associated data will be present. This data can appear as a fixed length field containing bibliographic data or variable length containing bibliographic or text data. All data within a logical group will be identified with ID Codes.

Logical Group ID Codes will contain a four-position alpha identifier. ID Codes identifying data fields will contain a three-position alpha identifier followed by a space. Some types of data will require continuation records. The ID Code in continuation records will contain spaces. Reference Appendix B - The Appearance of Text, for additional information.

The following appendices are included that define the appearance of data on the patent full-text/APS file.

Appendix A - Definition of Paragraph ID Codes.
Appendix B - The Appearance of Text.
Appendix C - Special Characters.
Appendix D - Example of Patent Documents as they appear in machine-readable form.
Appendix E - Example of Patent Documents as they appear when issued and printed.

d. Standard Trailer Labels

The following is a summary of the logical groups and the data fields within each logical group. This summary is presented in the sequence that the data on the file will appear.

Logical Group: Patent Bibliographic Information ID CODE: PATN

REQUIRED

Description : Contains the bibliographic information that appears on the front page of a patent.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Patent Number	WKU	8	A/N	R
Series Code	SRC	1	N	R
Application Number	APN	6	N	R
Application Type	APT	1	N	R
Publication Level	PBL	2	A	O
Art Unit	ART	3	N	R
Application Filing Date	APD	8	N	R
Title of Invention	TTL	V(255)	A/N	R
Issue Date	ISD	8	N	O
Number of Claims	NCL	V(4)	N	R
Exemplary Claim Number(s)	ECL	V(14)	A/N	R
Assistant Examiner	EXA	V	A/N	O
Primary Examiner	EXP	V	A/N	R
Number of Drawing Sheets	NDR	V(4)	N	O
Number of Figures	NFG	V(4)	N	O
Disclaimer Date	DCD	8	N	O
Number of Pages of Specifications	NPS	V(4)	N	O
Term of Patent	TRM	V(4)	N	O

Logical Group: INVENTOR

ID CODE: INVT

REQUIRED

Description : This group contains information of the inventor.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Inventor Name	NAM	V	A/N	R
Street	STR	V	A/N	O
City	CTY	V	A/N	R
State	STA	2	A	O
Country	CNT	3	A	O
Zip Code	ZIP	5	N	O
Rule 47 Indicator	R47	1	N	O
Inventor Descriptive Text	ITX	V	A/N	O

Logical Group: ASSIGNEE

ID CODE: ASSG

OPTIONAL

Description : Contains the data identifying the assignee(s) of an invention at the time of issue.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Assignee Name	NAM	V	A/N	R
City	CTY	V	A/N	O
State	STA	2	A	O
Country	CNT	3	A	O
Zip Code	ZIP	5	N	O
Assignee Type Code	COD	2	N	R
Assignee Descriptive Text	ITX	V	A/N	O

Logical Group: FOREIGN PRIORITY

ID CODE: PRIR

OPTIONAL

Description : Contains the data indicating in which foreign countries an application claims priority.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Country Code	CNT	3	A	R
Priority Application Date	APD	8	N	R
Priority Application Number	APN	V	A/N	R

Logical Group: REISSUE

ID CODE: REIS

OPTIONAL

Description : Contains the data describing the reissue of a patent.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Reissue Code	COD	2	N	R
Application Number	APN	6	N	R
Application Filing Date	APD	8	N	R
Patent Number	PNO	9	A/N	R
Issue Date	ISD	8	N	R

Logical Group: RELATED U.S. APPLICATION DATA ID CODE: RLAP

OPTIONAL

Description : Contains the coded version of parent case/continuation data of prior applications related to this patent.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Parent Code	COD	2	N	R
Application Number	APN	6	N	R
Application Filing Date	APD	8	N	O
Patent Status Code	PSC	1	N	R
Patent Number	PNO	8	A/N	O
Issue Date	ISD	8	N	O

Logical Group: CLASSIFICATION ID CODE: CLAS

REQUIRED

Description : Provides the U.S. and International classification codes for patents.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
US Classification	OCL	V(9)	A/N	R
Cross Reference	XCL	V(9)	A/N	O
Unofficial Reference	UCL	V(9)	A/N	O
Digest Reference	DCL	V(9)	A/N	O
Edition Field	EDF	1	N	O
International Classification	ICL	V(14)	A/N	O
Field of Search Class	FSC	3	A/N	O
Field of Search Subclasses	FSS	V	A/N	O

Logical Group: U.S. REFERENCE

ID CODE: UREF

OPTIONAL

Description : Contains the data identifying patents which are referenced as prior art.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Patent Number	PNO	V(9)	A/N	R
Issue Date	ISD	8	N	R
Patentee Name	NAM	V	A/N	R
US Classification	OCL	V(9)	A/N	O
Cross Reference	XCL	V(9)	A/N	O
Unofficial Reference	UCL	V(9)	A/N	O

Logical Group: FOREIGN REFERENCE

ID CODE: FREF

OPTIONAL

Description : Contains the data identifying the foreign patents cited as references.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Foreign Patent No.	PNO	V	A/N	R
Issue Date	ISD	8	N	R
Country Code	CNT	3	A	R
Classification	OCL	V(9)	A/N	R

Logical Group: OTHER REFERENCE

ID CODE: OREF

OPTIONAL

Description : Contains data for other referenced cited as prior art.

Field Name	ID Code
Reference Paragraphs Text Data	PAL

Logical Group: LEGAL INFORMATION ID CODE: LREP

OPTIONAL

Description : Contains data describing the attorneys or representative representing an applicant's patent.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Legal Firm Name	FRM	V	A/N	O
Principal Attorney Name	FR2	V	A/N	O
Associate Attorney Name	AAT	V	A/N	O
Agent's Name	AGT	V	A/N	0
Attorney Name	ATT	V	A/N	O
Registration Number	REG	5	N	O
Representative Name	NAM	V	A/N	O
Street	STR	V	A/N	O
City	CTY	V	A/N	O
State	STA	2	A	O
Country	CNT	3	A	O
Zip Code	ZIP	5	N	O

Logical Group: PCT INFORMATION ID CODE: PCTA

OPTIONAL

Description : Provides the descriptive data for related PCT information.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
PCT Number	PCN	14	A/N	R
PCT 371 Date	PD1	8	N	R
PCT 102 (e) Date	PD2	8	N	R
PCT Filing Date	PD3	8	N	R
PCT Publication No.	PCP	8	N	O
PCT Publication Date	PCD	8	N	O

Logical Group: ABSTRACT

ID CODE: ABST

OPTIONAL

Description : Contains the abstract section from a patent.

Field Name	ID Code
Abstract Paragraphs Text Data	PAx

Logical Group: GOVERNMENT INTEREST

ID CODE: GOVT

OPTIONAL

Description : Contains data describing the Government's interest in a patent.

Field Name	ID Code
Paragraphs Text Data	PAx

Logical Group: PARENT CASE

ID CODE: PARN

OPTIONAL

Description : Contains the text of parent case/continuation data of prior applications related to this patent.

Field Name	ID Code
Paragraphs Text Data	PAx

Logical Group: BRIEF SUMMARY

ID CODE: BSUM

REQUIRED

Description : Contains the summary description of the invention.

Field Name	ID Code
Paragraphs Text Data	PAx

Logical Group: DRAWING DESCRIPTION

ID CODE: DRWD

OPTIONAL

Description : Identifies the drawing(s) presented in a patent.

Field Name	ID Code
Paragraphs Text Data	PAx

Logical Group: DETAIL DESCRIPTION

ID CODE: DETD

OPTIONAL

Description : Contains the detailed technical specification from a patent.

Field Name	ID Code
Paragraphs Text Data	PAx

Logical Group: CLAIMS INFORMATION

ID CODE: CLMS

REQUIRED

Description : Contains the claim(s) information from a patent.

Field Name	ID Code	Field Size (Max.)	Field Type	Required or Optional
Claims Statement	STM	V	A/N	O
Claims Number	NUM	V(4)	N	R
Claim Text Data Paragraphs	PAx			

Logical Group: DESIGN CLAIM

ID CODE: DCLM

OPTIONAL

Description : Contains the claim information for a design patent.

Field Name	ID Code
Text Data Paragraphs	PAx

NOTE: PAx that appears throughout this summary represents the paragraph ID Code that appear in Appendix A.

American National Standard Code for Information Interchange

b7 b6 b5 Bits					0 0 0	0 0 1	0 1 0	0 1 1	1 0 0	1 0 1	1 1 0	1 1 1
b4	b3	b2	b1	COLUMN / ROW	0	1	2	3	4	5	6	7
0	0	0	0	0	NUL	DLE	SP	0	@	P	`	p
0	0	0	1	1	SOH	DC1	!	1	A	Q	a	q
0	0	1	0	2	STX	DC2	"	2	B	R	b	r
0	0	1	1	3	ETX	DC3	#	3	C	S	c	s
0	1	0	0	4	EOT	DC4	$	4	D	T	d	t
0	1	0	1	5	ENQ	NAK	%	5	E	U	e	u
0	1	1	0	6	ACK	SYN	&	6	F	V	f	v
0	1	1	1	7	BEL	ETB	'	7	G	W	g	w
1	0	0	0	8	BS	CAN	(	8	H	X	h	x
1	0	0	1	9	HT	EM	)	9	I	Y	i	y
1	0	1	0	10	LF	SUB	*	:	J	Z	j	z
1	0	1	1	11	VT	ESC	+	;	K	[	k	{
1	1	0	0	12	FF	FS	,	<	L	\	l	|
1	1	0	1	13	CR	GS	–	=	M	]	m	}
1	1	1	0	14	SO	RS	.	>	N	^	n	~
1	1	1	1	15	SI	US	/	?	O	_	o	DEL

FIGURE 1

FORM TP075-10 U.S. DEPT. OF COMMERCE
(REV. 11-76)
(FORMERLY PTO-1053)

ANSI-VOLUME-LABEL - VOL1

Volume-Header Label (VOL1)

CP	Field Name	L	Content
1 to 3	Label Identifier	3	VOL
4	Label Number	1	1
5 to 10	Volume Identifier	6	"a" characters. Assigned permanently by the owner to identify this volume.
11	Accessibility	1	"a" character. Indicates restrictions on access to the information in this volume. Space means no restrictions. The numeric characters and all special characters of the "a" set are reserved for operating system definition. "A" through "Z" are reserved for installation assignment.
12 to 37	Reserved for Future Standardization	26	Spaces.
38 to 51	Owner Identifier	14	"a" characters. Identifies the owner of the volume. Identifiers are not specified in this standard.
52 to 79	Reserved for Future Standardization	28	Spaces.
80	Label-Standard Version	1	Indicates the version of this standard to which the labels and data formats on this volume conform. "3" means this version.

"a" characters = alphanumeric. "n" characters = numeric.

If a numeric (n) value is shorter than the field, then the value is right-adjusted and unused positions f d with zeros. If an alphanumeric (a) value is shorter than the f then the value is left-adjust d unused positions filled with spaces.

FORM TP075-10 U.S. DEPT. OF COMMERCE
(REV. 11-76)
(FORMERLY PTO-1053)

ANSI-STANDARD-LABEL - HDR1

First File-Header Label (HDR1)

CP	Field Name	L	Content
1 to 3	Label Identifier	3	HDR
4	Label Number	1	1
5 to 21	File Identifier	17	"a" characters. Assigned by the originator to identify the file.
22 to 27	File-Set Identifier	6	"a" characters. Identifies this file set among other file sets.
28 to 31	File Section Number	4	"n" characters. Identifies this section among the sections of this file.
32 to 35	File Sequence Number	4	"n" characters. Identifies this file among the files of this file set.
36 to 39	Generation Number	4	"n" characters. Distinguishes among successive generations of this file.
40 to 41	Generation Version Number	2	"n" characters. Distinguishes among successive iterations of the same generation.
42 to 47	Creation Date	6	One space followed by two "n" characters for the year followed by three "n" characters for the day (001 to 366) within the year. Indicates date on which this file was created. Space followed by five zeros means that no creation date is specified.
48 to 53	Expiration Date	6	Same format as Creation Date. Indicates date on which this file may be overwritten. Space followed by five zeros means that this file is expired.
54	Accessibility	1	"a" character. Indicates restrictions on access to the information in this file. Space means no restrictions. The numeric characters and all special characters of the "a" set are reserved for operating system definition (see System Code (CP 61-73)). "A" through "Z" are reserved for installation assignment.
55 to 60	Block Count	6	000000
61 to 73	System Code	13	"a" characters. Identifies the system that recorded this file. Identifiers are not specified in this standard. Spaces means that system-defined controls on file access, buffer offset, Reserved for System Use, and Other System Labels should not be used.
74 to 80	Reserved for Future Standardization	7	Spaces

ANSI-STANDARD-LABEL - HDR2

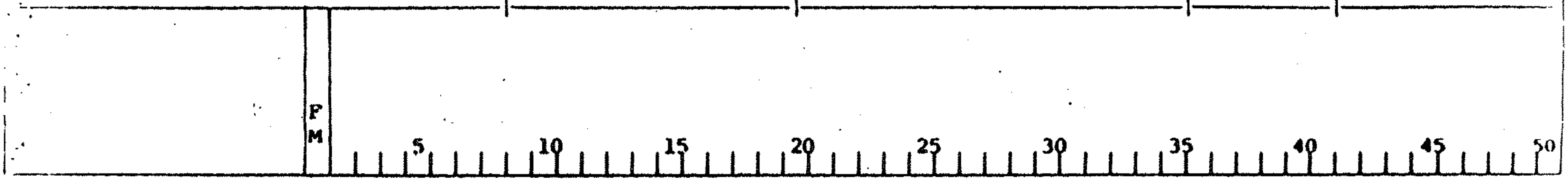
Second File-Header Label (HDR2)

CP	Field Name	L	Content
1 to 3	Label Identifier	3	HDR
4	Label Number	1	2
5	Record Format	1	F - FIXED LENGTH D - VARIABLE LENGTH IN DECIMAL IN FIRST 4 CHAR. V - VARIABLE LENGTH IN BINARY IN FIRST 2 CHAR. U - UNDEFINED I - VARIABLE LENGTH IN REC AT FIXED LOCATION L - LINKS
6 to 10	Block Length	5	"n" characters. Specifies the maximum number of characters per block.
11 to 15	Record Length	5	"n" characters. Specifies the record length in conjunction with Record Format (CP 5). If Record Format is F, this field contains the actual record length. If Record Format is D, this field contains the maximum record length including the count field. If Record Format is S, this field contains the maximum record length, excluding all the Segment Control Words. In this case, 00000 indicates that the maximum record length may be greater than 99999.
16	DENSITY	1	0 800 2 200 1 556 3 1600 4 6250

CP	Field Name	L	Content
17 18	Reserved for Future Standardization	2	Spaces
19	External Form	1	4 - EBCDIC, 5 ASCII
20 to 50	Reserved for System Use	31	"a" characters. Not intended for use in an interchange environment.
51 to 52	Buffer-Offset Length	2	"n" characters. Specifies the length in characters of any additional field inserted before the first record in a data block.
53 to 80	Reserved for Future Standardization	28	Spaces

FORM TP075-10 U.S. DEPT. OF COMMERCE
(REV. 11-76)
(FORMERLY PTO-1053)

File Mark



A 1-position file mark will follow the HDR2 header label and the last data record on the file.
Two file marks will follow the EOF2 (End-of-file) label record.

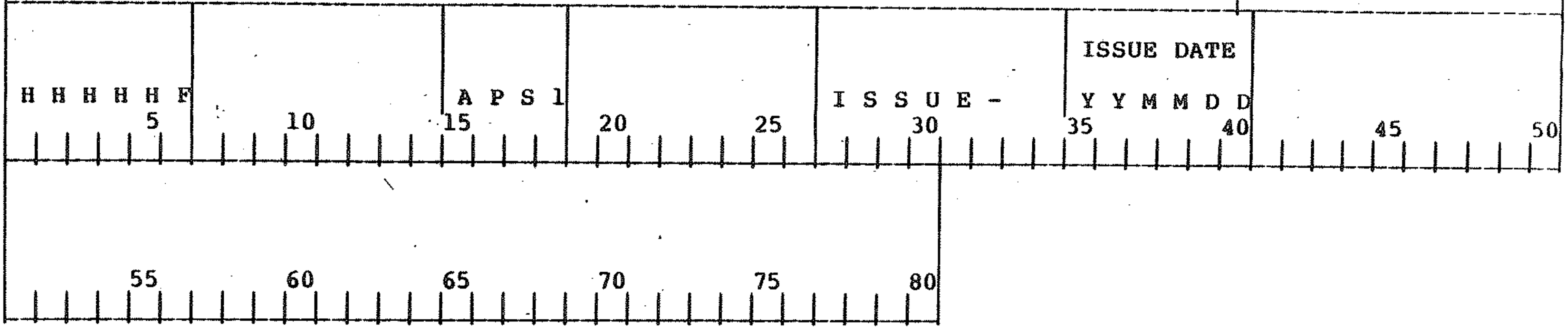
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

x Required
___ Optional

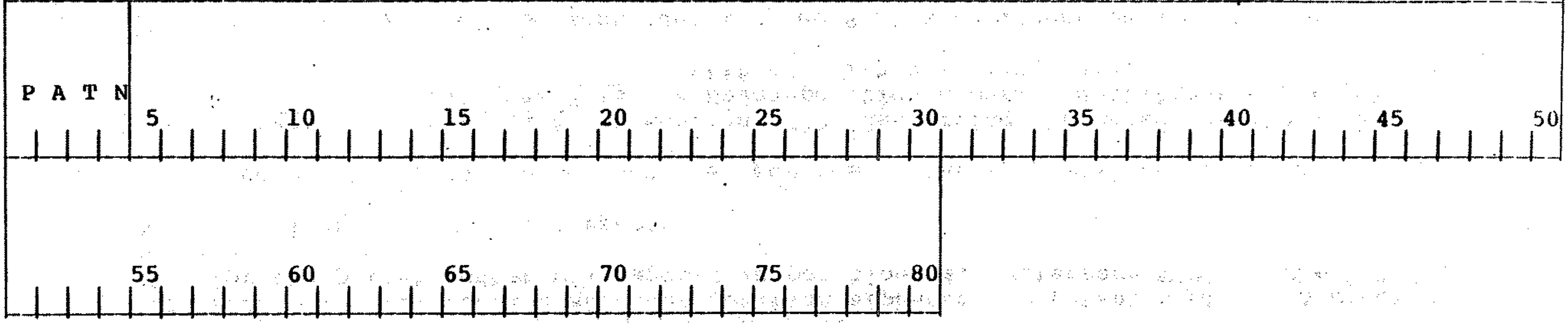
Control Header Record



Each file will contain the patents issued for a given week. The first data record on the file will be a control header record identifying the system.

Positions 1-6 will contain: HHHHHF
Positions 15-18 will contain: APS1
Positions 27-34 will contain: ISSUE-
Positions 35-40 will contain the issue date in the format YYMMDD
Positions 7-14, 19-35 and 41-80 will contain spaces.

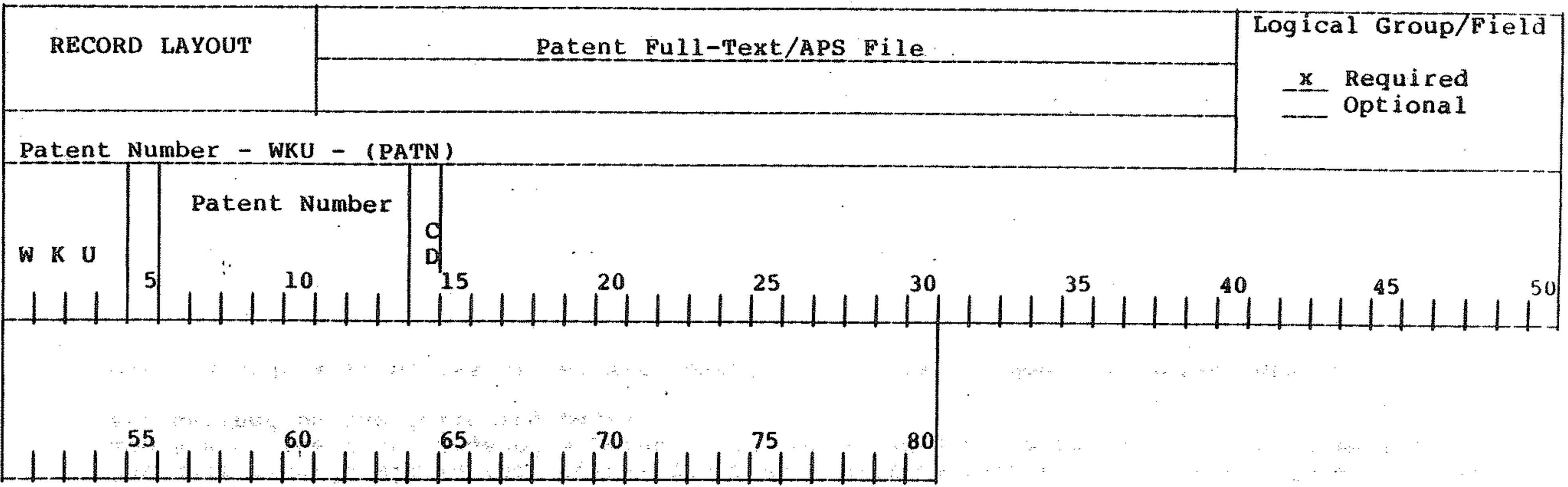
RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional
Logical Group - PATN - Patent bibliographic Information		



The ID Code (Positions 1-4) will contain: PATN identifying logical group Patent Bibliographic Information. Positions 5-80 will contain spaces.

The data records within the logical group PATN will contain bibliographic information that appears on the front page of a patent. ID Codes and associated data for the PATN logical group are defined on the following pages.

Data records will be associated with every type of patent document unless otherwise specified.



The ID Code (Positions 1-4) will contain WKU identifying the record as a Patent Number record.

Position 5 in all records will contain a space.
Positions 6-13 will contain an eight-position alphanumeric patent number. A check digit (CD) for the patent number will appear in position 14. Reference Table-1 Check Digit Modulus 11.
Positions 15-80 will contain spaces.

The appearance of the patent number and the sequence of the file will be as follows:

- <u>Design Patents</u> - <u>Position 6</u> - A constant "D" identifying the patent as a Design.
  <u>Positions 7-13</u> - A Seven-position numeric identification, right justified, with a leading zero.

The following three types of document identify the Statutory Invention Registration (SIR) that could be present on the file:

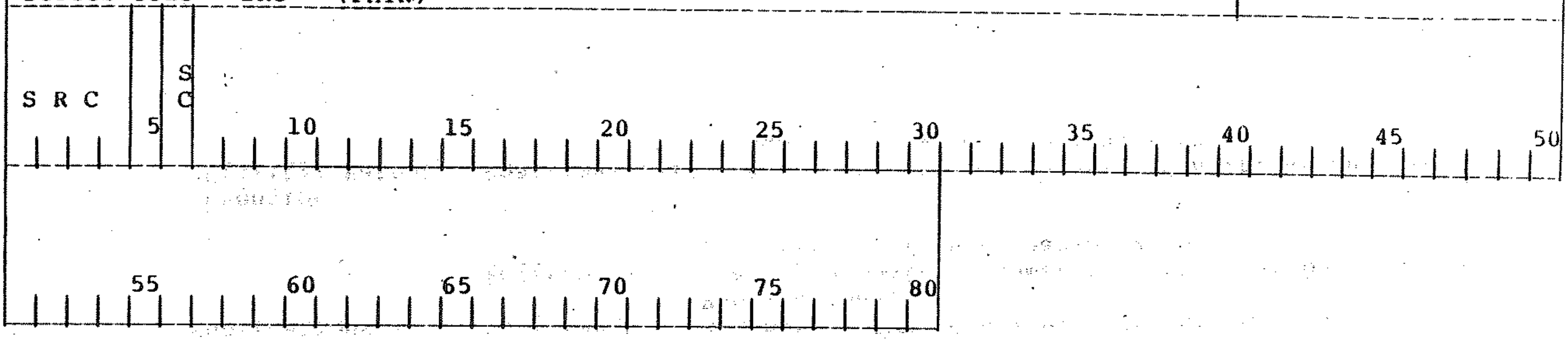
- <u>Design SIR</u> - <u>Positions 6-7</u> - A constant "HD" identifying the SIR document as a Design.
  <u>Positions 8-13</u> - A six-position numeric identification, right justified, with leading zero.
- <u>Plant SIR</u> - <u>Positions 6-7</u> - A constant "HP" identifying the SIR document as a Plant.
  <u>Positions 8-13</u> - A six-position numeric identification, right justified, with leading zeros.

Patent Number - WKU - (PATN) - (continued)

- Invention SIR (Utility)	Position 6	- A constant"H" identifying the SIR document as a Utility SIR.
	Positions 7-13	- A seven-position numeric identification, right justified with leading zeros.
- Plant Patents -	Positions 6-7	- A two-position constant "PP" identifying the patent as a Plant.
	Positions 8-13	- A six-position numeric identification, right justified, with a leading zero.
- Reissue Patents -	Positions 6-7	- A two-position constant "RE" identifying the patent as a Reissue
	Positions 8-13	- A six-position numeric identifying, right justified, with a leading zero.
- Defensive Publications -	Position 6 -	A constant "T" identifying the document as a Defensive Publications.
	Position 7-13	- A seven-position numeric identification, right justified, with a leading zero.
- Invention - (Utility) Patent -	Positions 6-13	- An eight-position numeric identification, right justified, with a leading zero.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional

Series Code - SRC - (PATN)



The ID Code (Positions 1-4) will contain SRC identifying the record as a Series Code record.

Position 6 (SC) will contain a numeric series code identifying the filing date of the applications.

Code	Series	Filing Dates
2	Pre-1948	Earlier then Jan. 1, 1948
3	1948	Jan. 1, 1948 - Dec. 31, 1959
4	1960	Jan. 1, 1960 - Dec. 31, 1969
5	1970	Jan. 1, 1970 - Dec. 31, 1978
6	1980	Jan. 1, 1979 - Dec. 31, 1986
7		Jan. 1, 1987 - Current

Positions 7-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional
Application Number - APN - (PATN)		

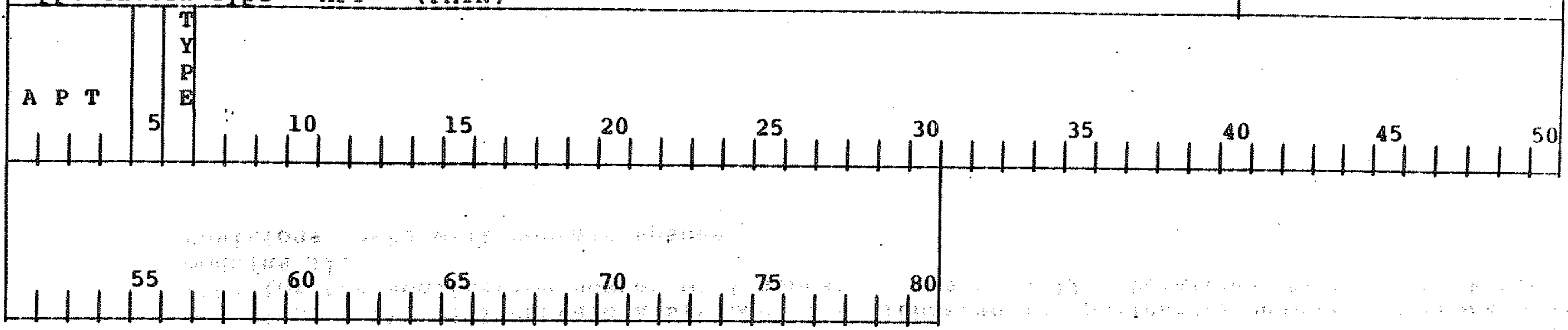
A P N		Application Number	C D	
1–4	5	6–11	12	13–80

The ID Code (Positions 1-4) will contain APN identifying the record as an application number record.

Positions 6-11 will contain a six-position alphanumeric application number. A check digit (CD) for the application number will appear in position 12. Reference Table-1 Check Digit Modulus 11.

Positions 13-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional
Application Type - APT - (PATN)		



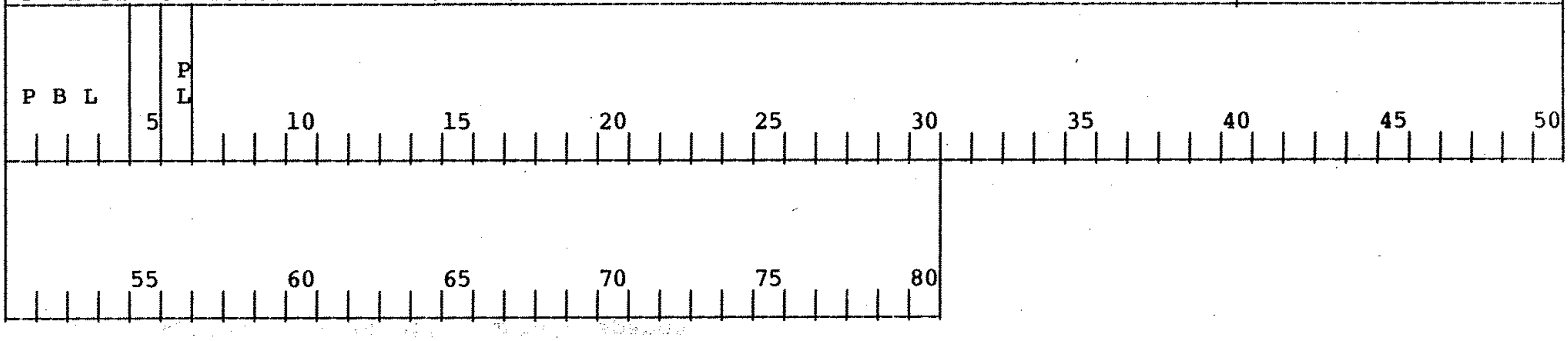
The ID Code (Positions 1-4) will contain APT identifying the record as an application type record.

Position 6 will contain a one-position numeric application type as defined below:

1 - Invention (Utility) Patent
2 - Reissue Patent
3 - TVPP Application (if present)
4 - Design Patent
5 - Defensive Publication
6 - Plant Patent
7 - Statutory Invention Registration (SIR)

Positions 7-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Publication Level - PBL ~ (PATN)		



ID Code (Positions 1-4) will contain PBL identifying the record as a publication level record. A PBL record will only be present for Reissue patents and Defensive Publications.

Position 6 (PL) will contain "E" for Reissues and "H" for Defensive Publications.
Positions 7-80 will contain spaces.

NOTE: The publication level will only appear in patents issued on or after July 1, 1975.

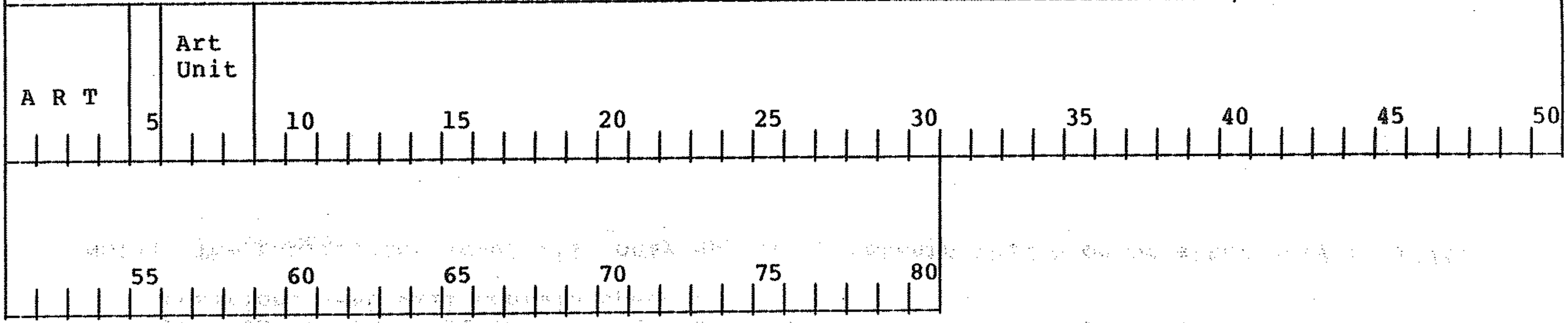
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

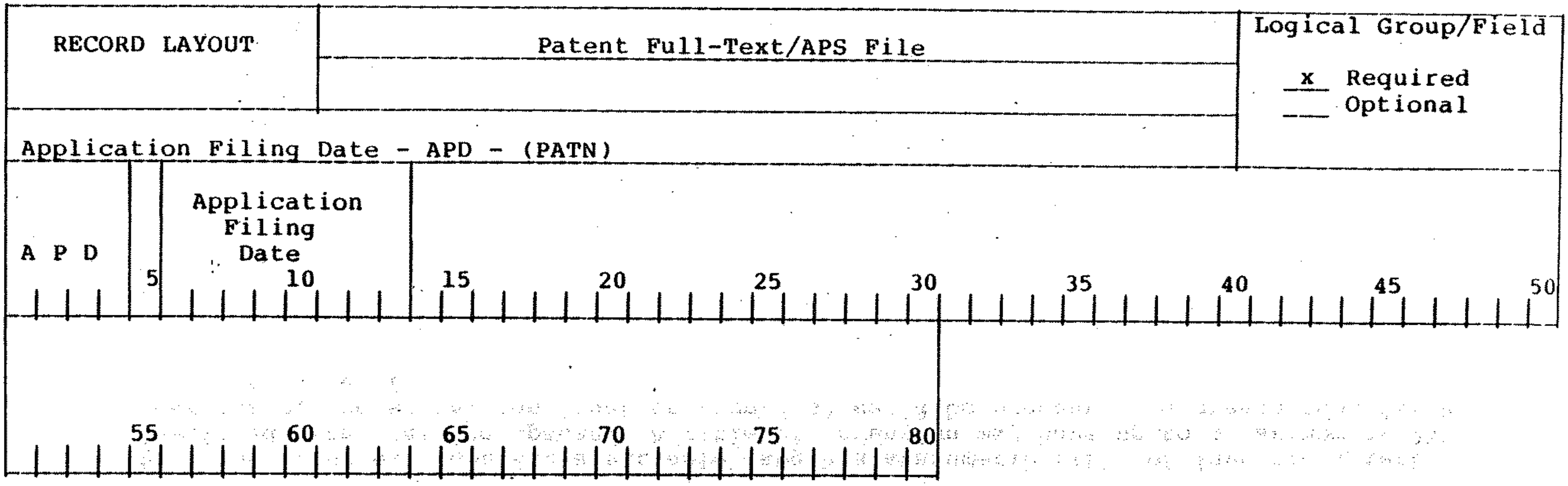
x Required
__ Optional

Art Unit - ART - (PATN)



ID Code (Positions 1-4) will contain ART identifying the record as an Art Unit record.

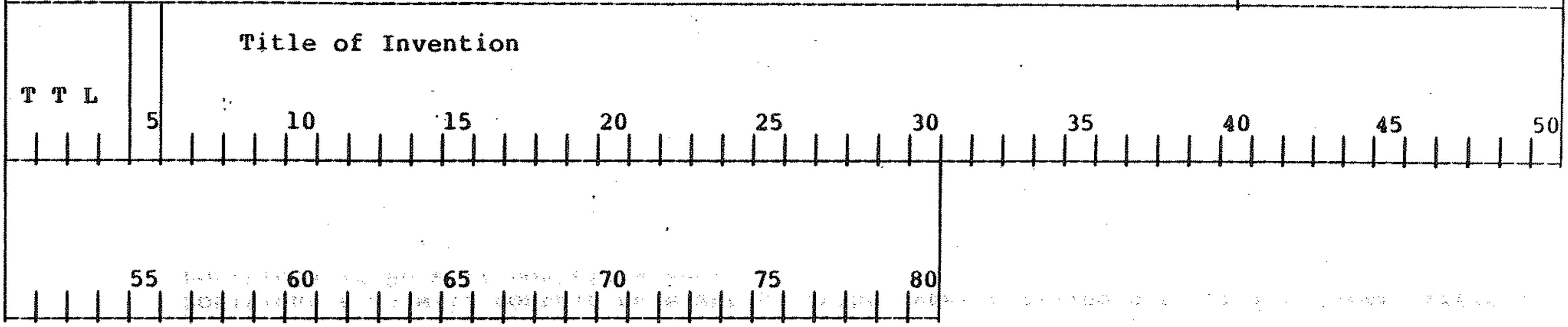
Positions 6-8 will contain a three-position numeric art unit.
Positions 9-80 will contain spaces.



The ID Code (Positions 1-4) will contain APD identifying the record as an Application Filing Date record.

Positions 6-13 will contain an eight-position numeric filing date in the format YYYYMMDD. Positions 14-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional
Title of Invention - TTL (PATN)		



The ID Code (Positions 1-4) will contain TTL identifying the record as a Title of Invention record.

Positions 6-80 will contain a variable length alphanumeric title of invention, left justified with trailing spaces. A title of invention may have up to a maximum of 255 characters, therefore, continuation record(s) could be present. Reference Appendix B - The Appearance of Text.

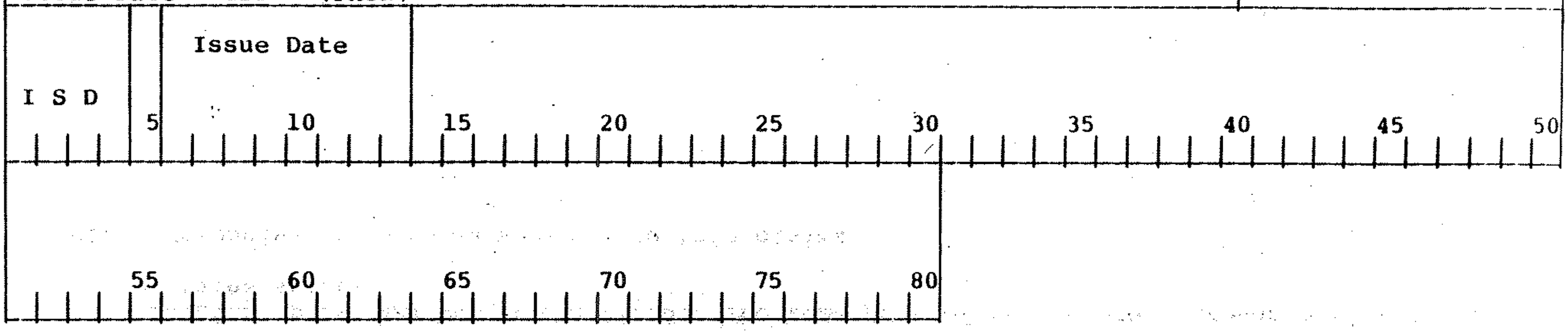
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

x Required
Optional

Issue Date - ISD - (PATN)



The ID Code (Positions 1-4) will contain ISD identifying the record as an Issue Date record.

Positions 6-12 will contain an eight-position numeric issue date in the format YYYYMMDD.
Positions 14-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional
Number of Claims - NCL - (PATN)		

N C L		No. of Claims
1–4	5	6

Positions: 5 10 15 20 25 30 35 40 45 50

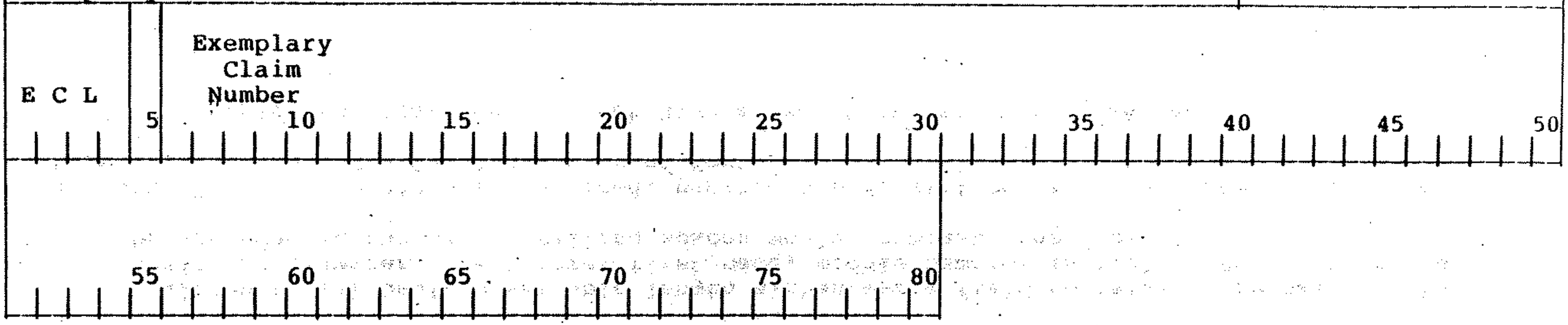
55 60 65 70 75 80

The ID Code (Postions 1-4) will contain NCL identifying the record as a Number of Claims record.

Position 6 will begin a variable length numeric field defining the number of claims. A trailing space terminates the field. The remainder of the record, through position 80, contains spaces.

NOTE: Defensive Publications do not contain claims.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional
Exemplary Claim Number - ECL - (PATN)		



The ID Code (Positions 1-4) will contain ECL identifying the record as an Exemplary Claim Number record.

Position 6 will begin a variable length alphanumeric field defining the claim number(s) for the claim(s) that is the primary claim(s). A trailing space would terminate the field. If, more than one claim number appears in this field each claim number would be separated by a comma. The remainder of the record, through position 80, contains spaces.

NOTE: Defensive Publications do not contain Claims.

Since the issue date 10/1/74 the exemplary claim(s) have appeared in the Official Gazette.

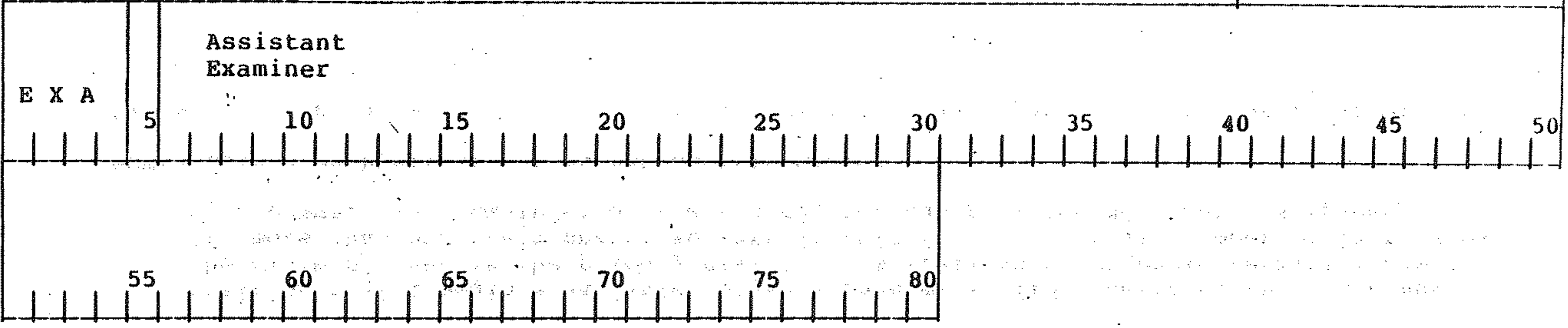
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

___ Required
_x_ Optional

Assistant Examiner - EXA - (PATN)



The ID Code (Positions 1-4) will contain EXA identifying the record as an Assistant Examiner record. This record will only be present if the patent had an Assistant Examiner.

Position 6 will begin a variable length alphanumeric field containing the name of the assistant examiner, (Last name; first name, middle name/or initial). Punctuation would be included in the name, trailing spaces would terminate the field.

If continuation record(s) are required, positions 6-80 will contain the continuation data. Reference Appendix B - The Appearance of Text.

NOTE: Defensive Publications will not have a Assistant Examiner - EXA record.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional
Primary Examiner - EXP - (PATN)		

E X P		Primary Examiner
1-4	5	6-80

5 10 15 20 25 30 35 40 45 50

55 60 65 70 75 80

The ID Code (Positions 1-4) will contain EXP identifying the record as a Primary Examiner record.

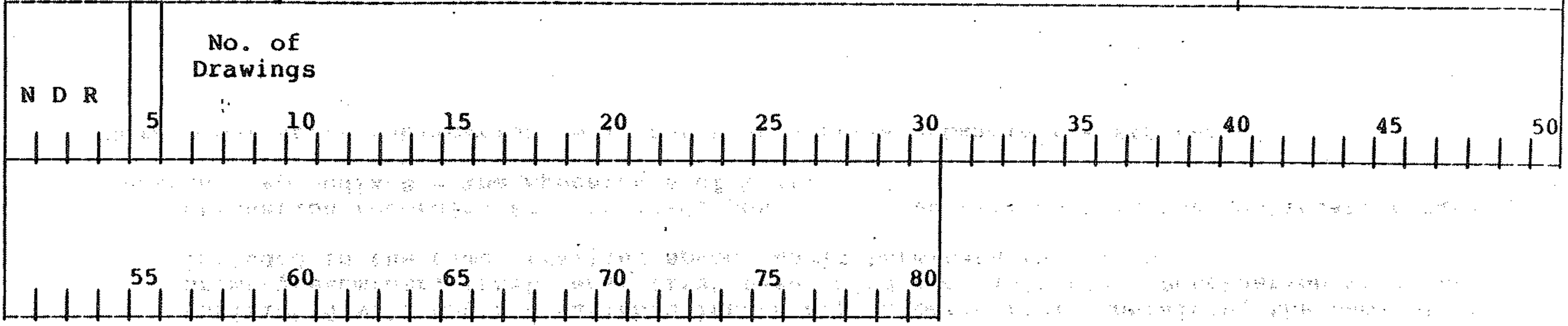
Position 6 will begin a variable length alphanumeric field containing the name of the primary examiner, (Last name; first name, middle/or initial). Punctuation would be included in the name, trailing spaces would terminate the field.

If continuation record(s) are required, positions 6-80 will contain the continuation data. Reference Appendix B - The Appearance of Text.

NOTE: Defensive Publications will not have a Primary Examiner - EXP record.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Number of Drawing Sheets - NDR - (PATN)

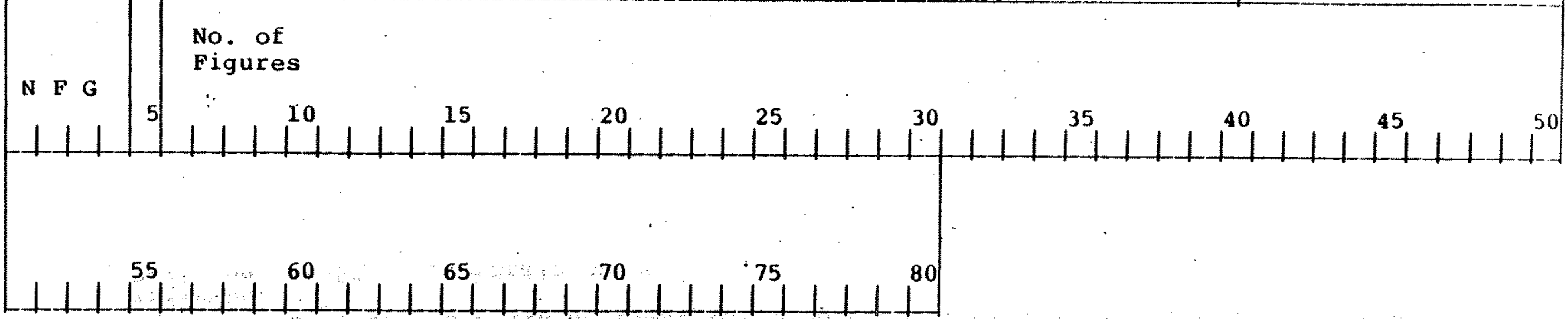


The ID Code (Positions 1-4) will contain NDR identifying the record as a Number of Drawing Sheets record.

Position 6 will begin a variable length numeric field containing the number of drawing within the patent. A trailing space would terminate the field. The remainder of the record, through position 80, contains spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Number of Figures - NFG - (PATN)



The ID Code (Positions 1-4) will contain NFG identifying the record as a Number of Figures record.

Position 6 will begin a variable length numberic field containing the number of figures within the patent. A trailing space would terminate the field. The remainder of the record, through position 80, contains spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Disclaimer Date - DCD - (PATN)		
D C D	Disclaimer Date	

5 10 15 20 25 30 35 40 45 50

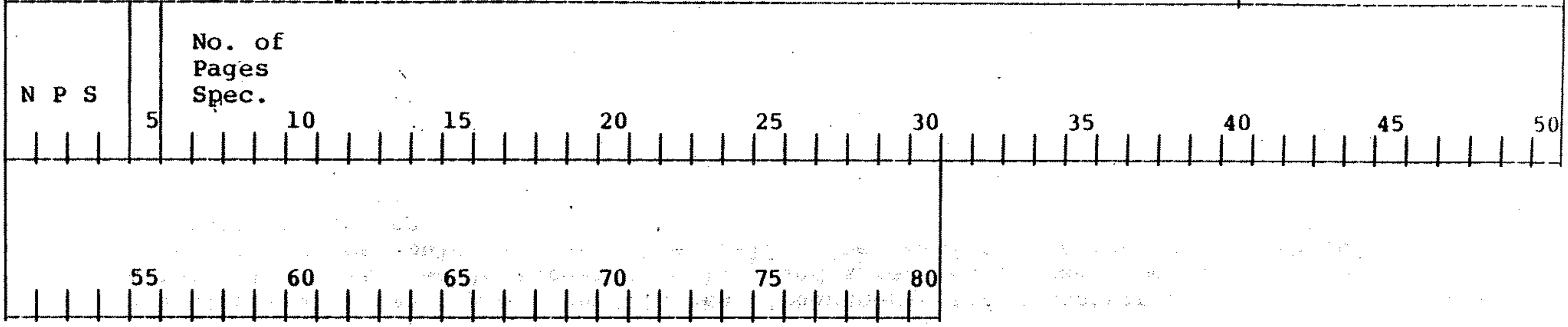
55 60 65 70 75 80

The ID Code (Positions 1-4) will contain DCD identifying the record as a Disclaimer Date record.

Positions 6-13 will contain an eight-position numeric disclaimer date in the format YYYYMMDD.

Positions 14-80 will contain spaces.

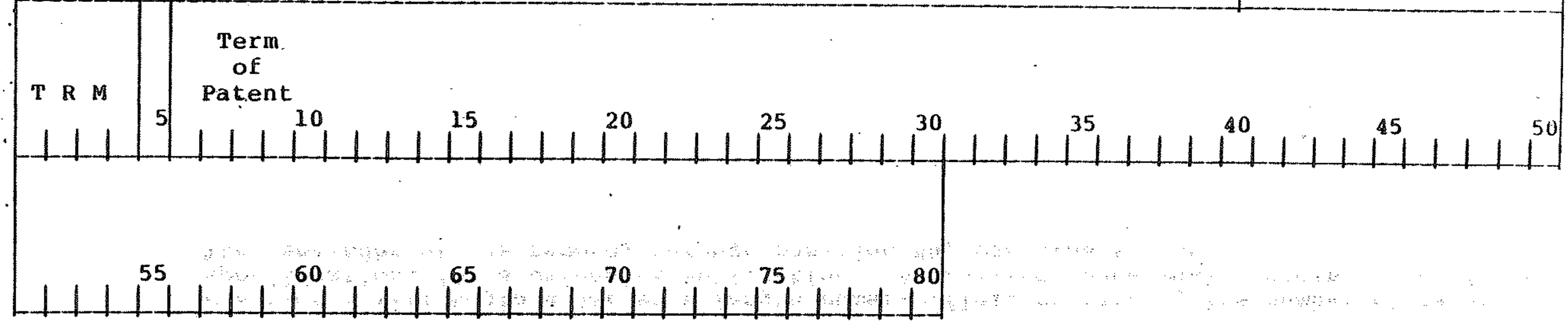
RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Number of Pages of Specifications - NPS - (PATN)		



The ID Code (Positions 1-4) will contain NPS identifying the record as a Number of Pages of Specifications record. A NPS record will only be present for Defensive Publications.

Position 6 will begin a variable length numeric field containing the number of pages of specifications for a Defensive Publication. A trailing space would terminate the field. The remainder of the record, through position 80, contains spaces.

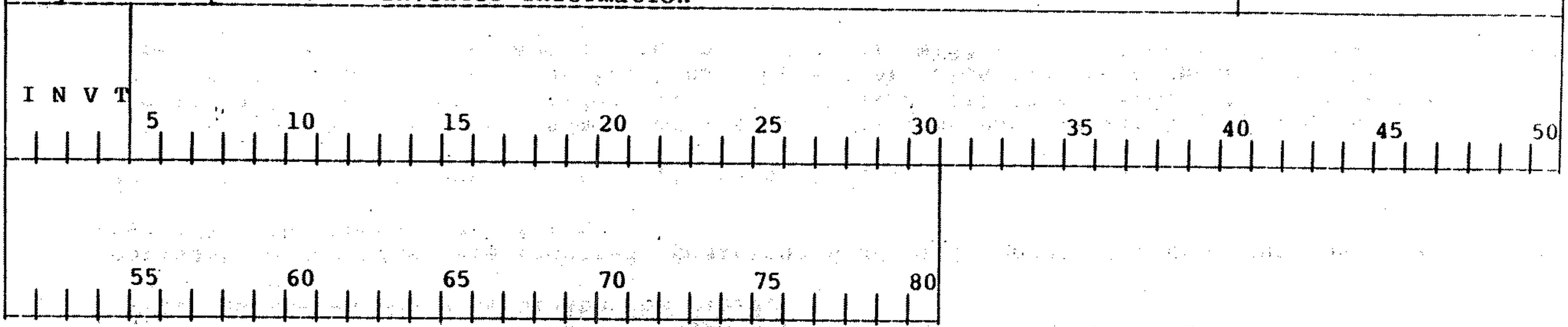
RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Term of Patent - TRM - (PATN)		



The ID Code (Positions 1-4) will contain TRM identifying the record as a Term of Patent record. A TRM record will only be present for Design Patents.

Position 6 will begin a variable length alphanumeric field containing the term of patent. A term of 14 years would appear as - 14 - and a term of 3½ years would appear as - 3.5. A trailing space would terminate the field. The remainder of the record, through position 80, contains spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional
Logical Group - INVT - Inventor Information		

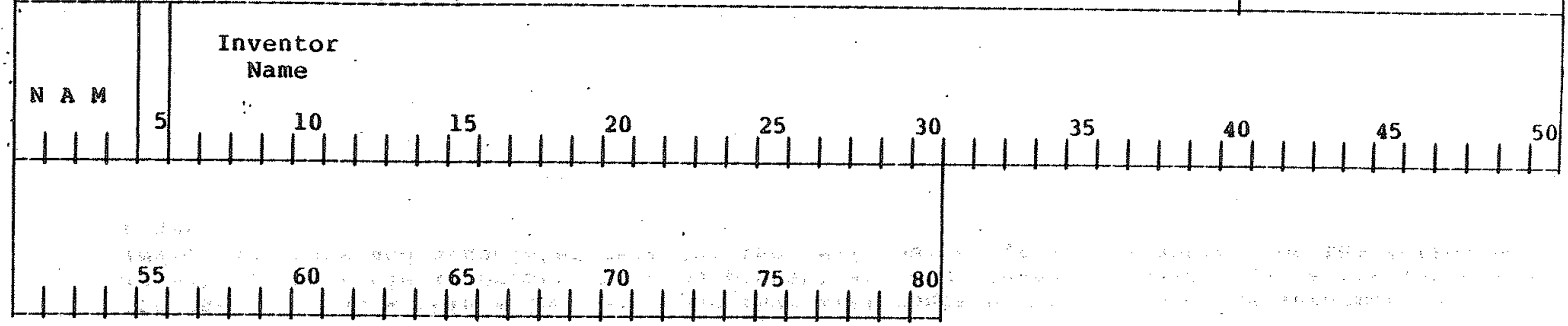


The ID Code (Positions 1-4) will contain INVT identifying logical group Inventor Information. Positions 5-80 will contain spaces.

The data records within a logical group INVT will contain name and address information on an Inventor. Multiple inventors could be present and each inventor would begin a new logical group INVT. ID Codes and associated data for the INVT logical group are defined on the following pages.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional

Inventor Name - NAM - (INVT)



The ID Code (Positions 1-4) will contain NAM identifying the record as an Inventor Name record.

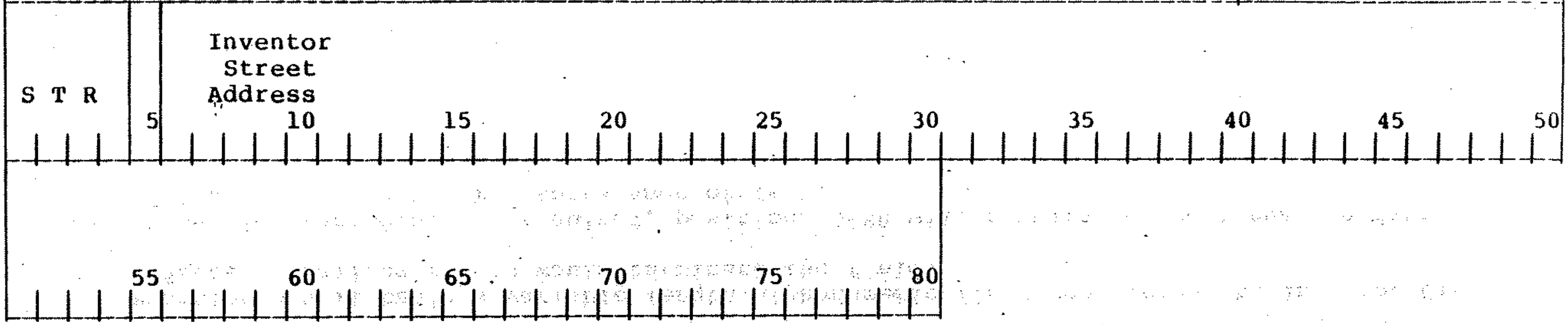
Position 6 will begin a variable length alphanumeric field containing the Inventor Name. Trailing spaces would terminate the field.

If continuation record(s) are required, positions 6-80 will contain the continuation data. Reference B - The Appearance of Text.

The appearance of the Inventor's Name will be as follows:

<u>Inventor's Name</u> - 1) Last name, (Jr., etc.); the last name is first separated by a coma if additional description is needed, i.e., Jr., Senior, III (the third), etc. The entire surname is separated from the first name by a semi-colon (;) and a space. 2) First - A space follows the first name of the inventor. 3) Middle initial or middle name.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required x Optional
Inventor Street Address - STR - (INVT)		



The ID Code (Positions 1-4) will contain STR identifying the record as an Inventor Street Address record.

Position 6 will begin a variable length alphanumeric field containing the Inventor Street Address. Trailing spaces would terminate the field.

If the continuation record(s) are required, positions 6-80 will contain the continuation data. Reference Appendix B - The Appearance of Text.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional

Inventor City Address - CTY - (INVT)

C T Y

Inventor
City
Address

5 10 15 20 25 30 35 40 45 50

55 60 65 70 75 80

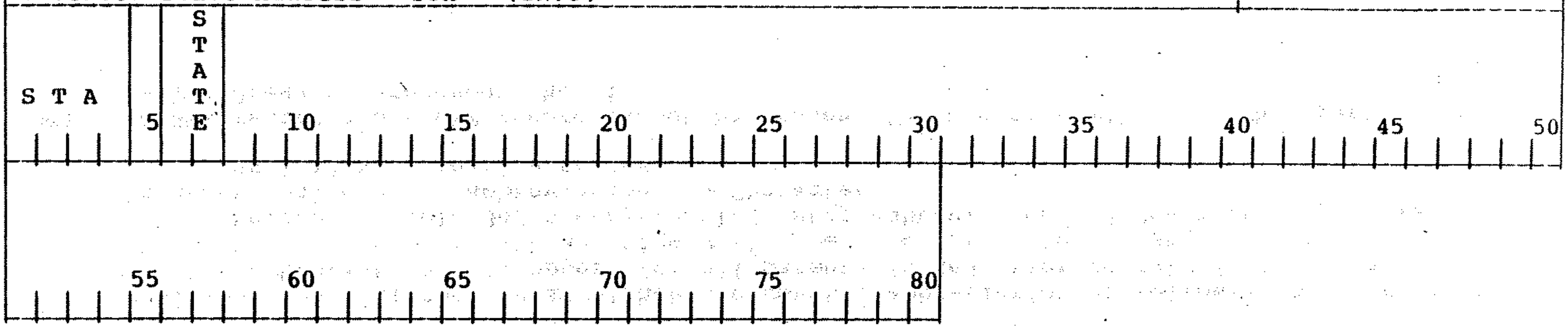
The ID Code (Positions 1-4) will contain CTY identifying the record as an Inventor City Address record.

Position 6 will begin a variable length alphanumeric field containing the Inventor City Address. Trailing spaces would terminate the field.

If continuation record(s) are required, positions 6-80 will contain the continuation data. The Reference Appendix B - The Appearance of Text.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Inventor State Address - STA - (INVT)

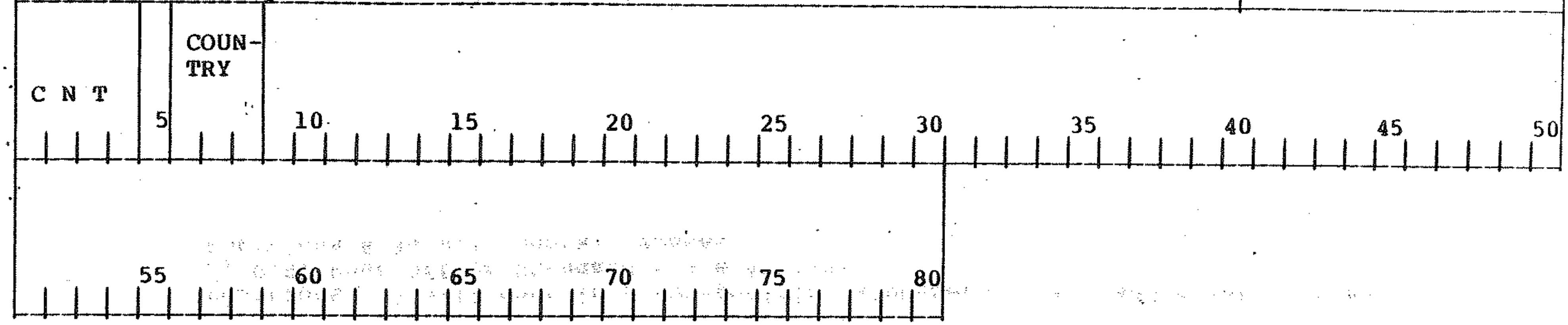


The ID Code (Positions 1-4) will contain STA identifying the record as an Inventor State Address record.

Positions 6-7 will contain a two-position alphabetic state addreviation. Reference Table 2, U.S. Post Office Standard State Abbreviations.
Positions 8-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Inventor Country Address - CNT - (INVT)



The ID Code (Positions 1-4) will contain CNT identifying the record as an Inventor Country Address record.

Positions 6-8 will contain an alphabetic country abbreviation as follows: A two-character country abbreviation will appear for all patents issued prior to July 4, 1978. A three-character country abbreviation will appear for all patents issued on or after July 4, 1978. Reference Table 3A International Country Abbreviation - 2-Character and Table 3B International Country Abbreviation - 3-Character.
Positions 9-80 will contain spaces.

NOTE: A STA record and a CNT record cannot be present for the same address. This pertains to all addresses throughout the file.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Inventor Zip Code Address - ZIP - (INVT)		

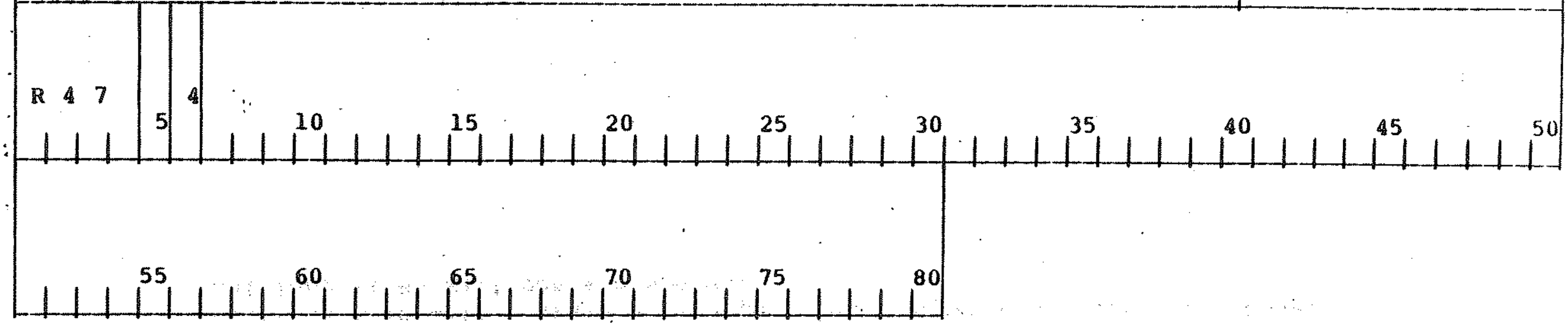
Positions 1-4	Position 5	Positions 6-10	Positions 11-80
Z I P		Zip Code	

Position scale: 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80

The ID Code (Positions 1-4) will contain ZIP identifying the record as an Inventor Zip Address record.

Positions 6-10 will contain a five-position numeric U.S. Postal Zip Code.
Positions 11-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Rule 47 Indicator - R47 - (INVT)		



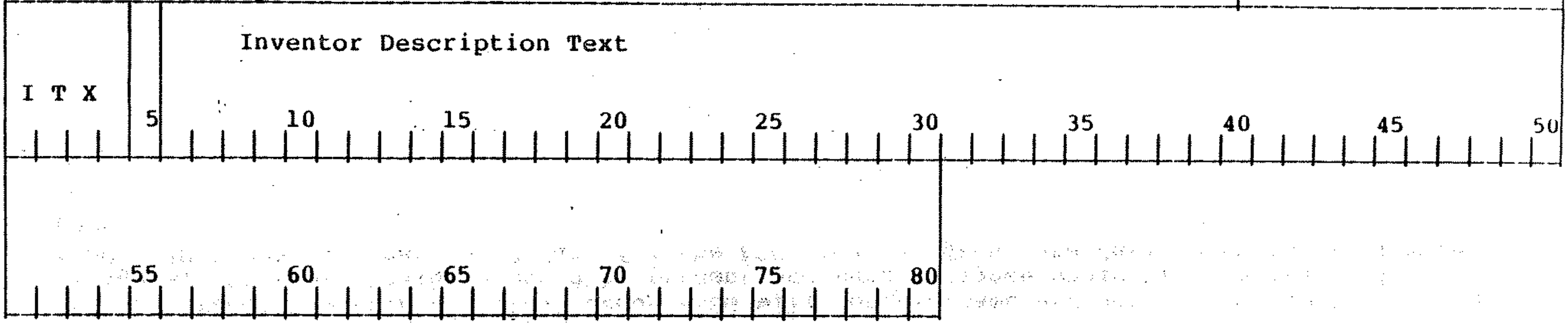
The ID Code (Positions 1-4) will contain R47 identifying the record as a Rule 47 Indicator record.

Position 6 would contain a "4" denoting that the application was filed under Rule 47. Positions 7-80 would contain spaces.

NOTE: Rule 47 applies when an Inventor is deceased, mentally or otherwise incapacitated, or refuses to execute an application or cannot be found after diligent efforts.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Inventor Descriptive Text - ITX - (INVT)



The ID Code (Positions 1-4) will contain ITX identifying the record as an Inventor Descriptive Text record.

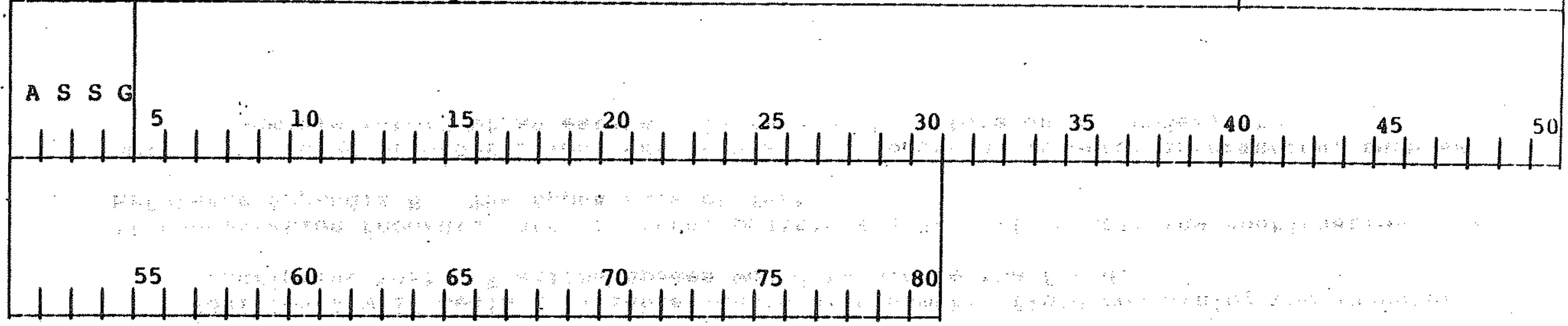
Position 6 will begin a variable length alphanumeric field containing the Inventor Descriptive Text. Trailing spaces would terminate the field.

If continuation record(s) are required, positions 6-80 will contain the continuation data. Reference Appendix B - The Appearance of Text.

NOTE: The Inventor Description Text is used in support of inventor information, such as "administrator" of an estate, "in respect to", foreign zip codes, etc.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Logical Group - ASSG - Assignee Information



The ID Code (Positions 1-4) will contain ASSG identifying logical group Assignee Information. Positions 5-80 will contain spaces.

The data records within a logical group ASSG will contain name and address information on an Assignee. Multiple Assignee could be present and each assignee would begin a new logical group ASSG. ID Codes and associated data for the ASSG logical group are defined on the following pages.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required __ Optional

Assignee Name - NAM - (ASSG)

1-4	5	6-80
N A M		Assignee Name

5 10 15 20 25 30 35 40 45 50

55 60 65 70 75 80

The ID Code (Positions 1-4) will contain NAM identifying the record as an Assignee Name record.

Position 6 will begin a variable length alphanumeric field containing the name of the assignee. Punctuation would be included in the name, trailing spaces would terminate the field.

If continuation record(s) are required, positions 6-80 will contain the continuation data. Reference Appendix B - The Appearance of Text.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

C T Y		Assignee City Address
1–4	5	6–80

5 10 15 20 25 30 35 40 45 50

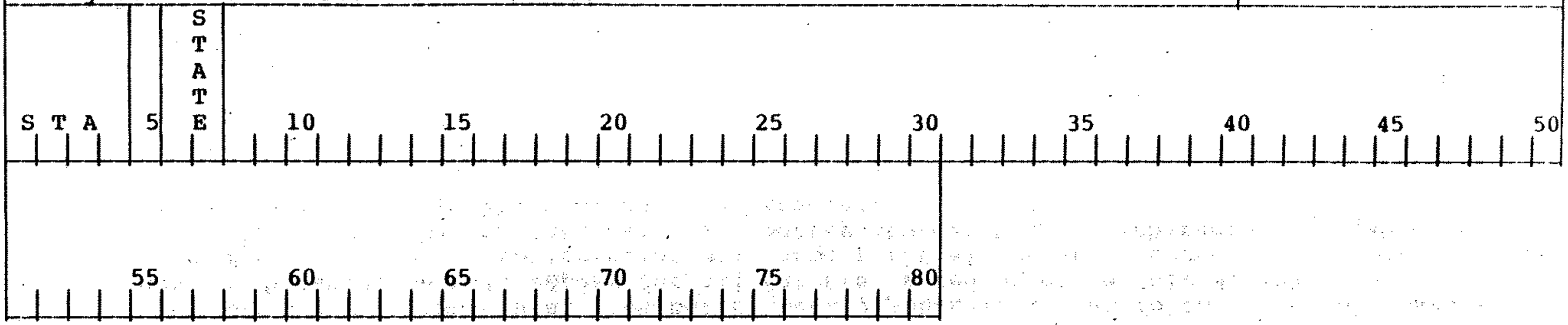
55 60 65 70 75 80

The ID Code (Positions 1-4) will contain CTY identifying the record as an Assignee City Address record.

Position 6 will begin a variable length alphanumeric field containing the Assignee City Address. Trailing spaces would terminate the field.

If continuation record(s) are required, positions 6-80 will contain the continuation data. Reference Appendix B - The Appearance of Text.

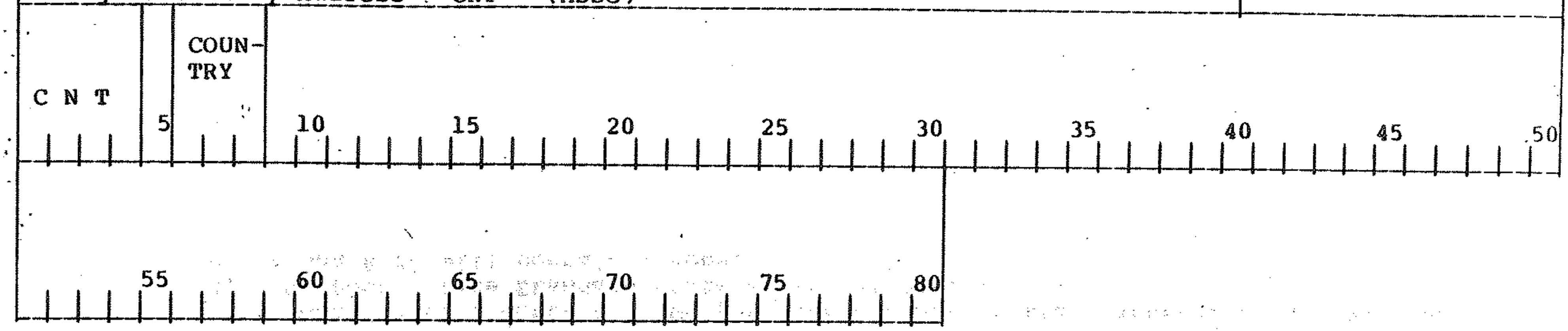
RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Assignee State Address - STA - (ASSG)		



The ID Code (Positions 1-4) will contain STA identifying the record as an Assignee State Address record.

Positions 6-7 will contain a two-position alphabetic state abbreviation. Reference Table 2, U.S. Post Office Standard State Abbreviations.
Positions 8-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Assignee Country Address - CNT - (ASSG)		



The ID Code (Positions 1-4) will contain CNT identifying the record as an Assignee Country Address record.

Positions 6-8 will contain an alphabetic country abbreviation as follows: A two-character country abbreviation will appear for all patents issued prior to July 4, 1978. A three-character country abbreviation will appear for all patents issued on or after July 4, 1978. Reference Table 3A International Country Abbreviation - 2-character and Table 3B International Country Abbreviation - 3-character.

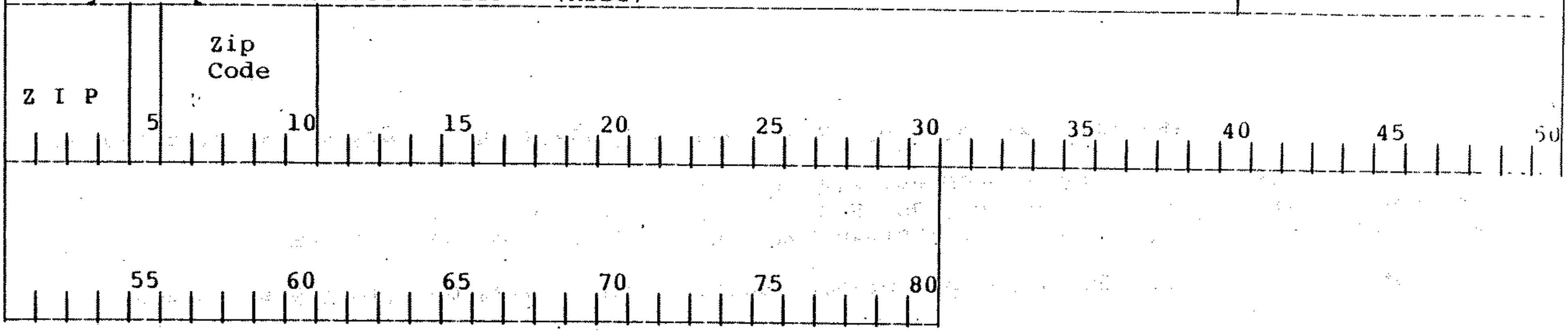
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

___ Required
_x_ Optional

Assignee Zip Code Address - ZIP - (ASSG)



The ID Code (Positions 1-4) will contain ZIP identifying the record as an Assignee Zip Code Address record.

Positions 6-10 will contain a five-position numeric U.S Postal Zip Code.
Positions 11-80 will contain spaces.

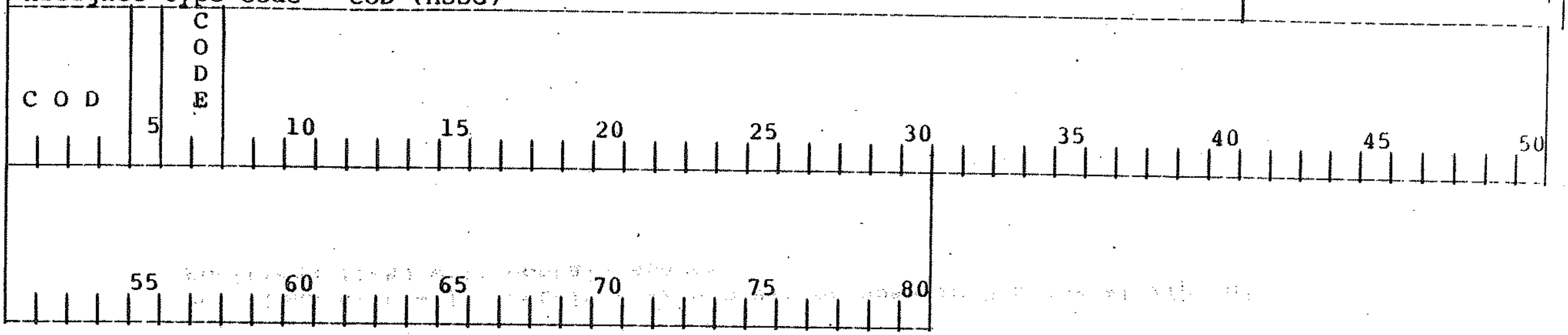
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

___ Required
_x_ Optional

Assignee Type Code - COD (ASSG)



The ID Code (Positions 1-4) will contain COD identifying the record as an Assignee Type Code record.

Positions 6-7 will contain a two-position numeric code defining the type of assignment.

02 - To U.S. Company or Corporation
03 - To Foreign Company or Corporation
04 - To U.S. Individual
05 - To Foreign Individual
06 - To U.S. Government
07 - To Foreign Government
08 - To County Government
09 - To State Government (US)

NOTE: A "1" appearing in the first position would identify part interest.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Assignee Descriptive Text - ITX - (ASSG)		

I T X		Assignee Descriptive Text
1-4	5	6-80

The ID Code (Positions 1-4) will contain ITX identifying the record as an Assignee Descriptive Text record.

Position 6 will begin a variable length alphanumeric field containing the Assignee Descriptive Text. Trailing spaces would terminate the field.

If continuation record(s) are required, positions 6-80 will contain the continuation data. The ID Code (Positions 1-4) will contain spaces in continuation records.

NOTE: The Assignee Descriptive Text is used in support of assignee information.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Logical Group - PRIR - Foreign Priority

P	R	I	R	5	10	15	20	25	30	35	40	45	50

55	60	65	70	75	80

The ID Code (Positions 1-4) will contain PRIR identifying logical group Foreign Priority. Positions 5-80 will contain spaces.

The data records within logical group PRIR will contain the data indicating in which foreign countries an application was filed. Multiple foreign priorities could be present and each one would begin a new logical group PRIR.

ID Codes and associated data for the PRIR logical group are defined on the following pages.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional

Priority Country - CNT - (PRIR)

C N T		COUN-TRY

5 10 15 20 25 30 35 40 45 50

55 60 65 70 75 80

The ID Code (Positions 1-4) will contain CNT identifying the record as a priority country record.

Positions 6-8 will contain an alphabetic country abbreviation as follows: A two-character country abbreviation will appear for all patents issued prior to July 4, 1978. A three-character country abbreviation will appear for all patents issued on or after July 4, 1978. Reference Table 3A International Country Abbreviation - 2-character and Table 3B International Country Abbreviation - 3-character.

RECORD LAYOUT	APS Application Text Input Standard	Logical Group/Field _x_ Required ___ Optional

Priority Application Date - APD - (PRIR)

A P D		Priority Application Date	
1-4	5	6-13	14-80

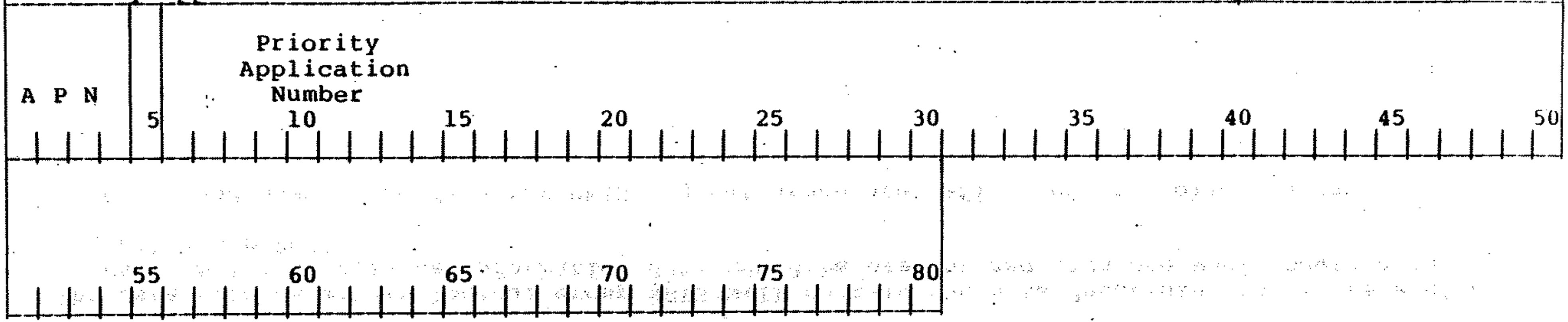
5 10 15 20 25 30 35 40 45 50

55 60 65 70 75 80

The ID Code (Positions 1-4) will contain APD identifying the record as a priority application filing date record.

Positions 6-13 will contain an eight-position numeric application date in the format YYYYMMDD.
Positions 14-80 will contain spaces.

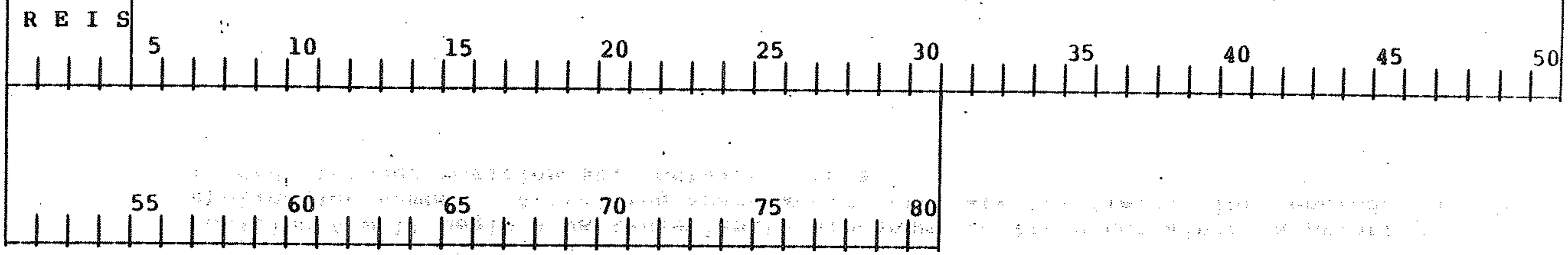
RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional
Priority Application Number - APN - (PRIR)		



The ID Code (Positions 1-4) will contain APN identifying the record as a priority applicaton number record.

Position 6 will begin a variable length alphanumeric field containing a priority application number. A trailing space would terminate the field. The remainder of the record, through position 80, contains spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Logical Group - REIS - Reissue Information Data		



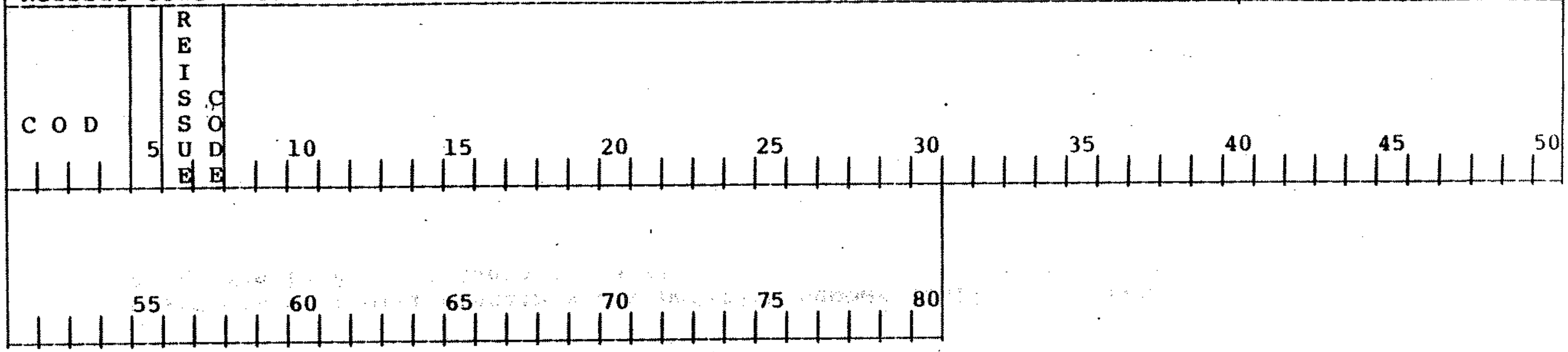
The ID Code (Positions 1-4) will contain REIS identifying logical group Reissue Information Data. Positions 5-80 will contain spaces.

The data records within logical group REIS will contain the data describing the reissue of a patent. Mulitple reissue information data could be present and each one would begin a new logical group REIS.

ID Codes and associated data for REIS logical group are defined on the following pages.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional

Reissue Code - COD - (REIS)



The ID Code (Positions 1-4) will contain COD identifying the record as a reissue code record.

Positions 6-7 will contain a two-position numeric reissue code as defined below:

REISSUE CODES

Reissue Codes	Condition	Publication Level
50	Reissue of	First Reissue (Second Publication)
51	Which is a Reissue of	Second Reissue (Third Publication)
52	Which is a Reissue of	Third Reissue (Fourth Publication)

Positions 8-80 will contain spaces.

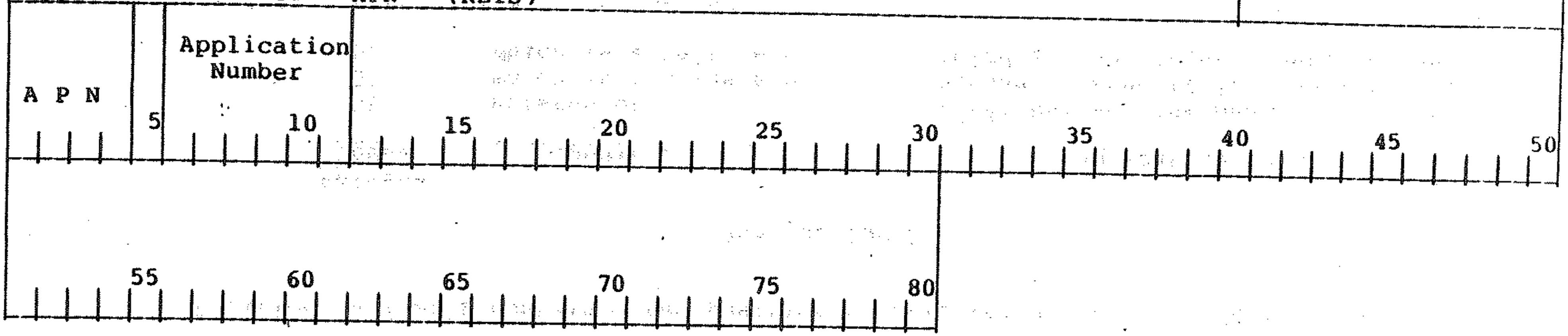
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

_x_ Required
___ Optional

Application Number - APN - (REIS)

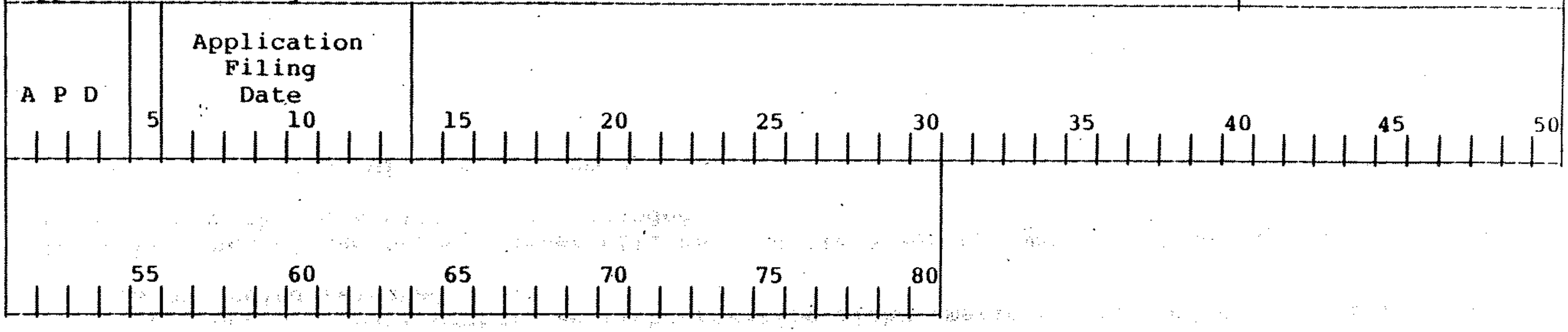


The ID Code (Positions 1-4) will contain APN identifying the record as an application number record.

Positions 6-11 will contain a six-position number application number
Positions 12-80 will contain spaces

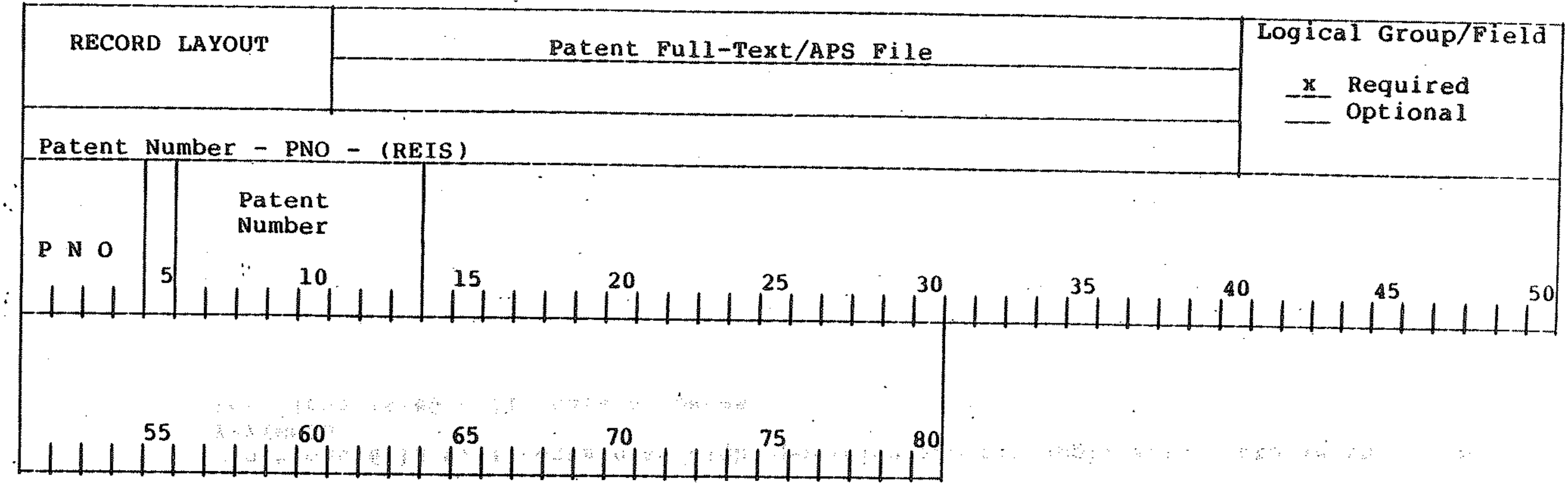
RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional

Application Filing Date - APD - (REIS)



The ID Code (Positions 1-4) will contain APD identifying the record as an application filing date record.

Positions 6-13 will contain an eight-position numeric application date in the format YYYYMMDD
Positions 14-80 will contain spaces



RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

_x_ Required
___ Optional

Patent Number - PNO - (REIS)

The ID Code (Positions 1-4) will contain PNO identifying the record as a Patent Number record.

Positions 6-13 will contain an eight-position alphanumeric patent number identifying the patent being reissued.

The appearance of the patent number will be as defined for the WKU record within logical group PATN (the check digit will not be included).

Positions 14-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional
Issue Date - ISD - (REIS)		

I S D		Issue Date	

5 10 15 20 25 30 35 40 45 50

55 60 65 70 75 80

The ID Code (Positions 1-4) will contain ISD identifying the record as an issue date record.

Positions 6-13 will contain an eight-position numeric issue date in the format YYYYMMDD.
Positions 14-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Logical Group - RLAP - Related U.S. Application Data		

R L A P	5	10	15	20	25	30	35	40	45	50
	55	60	65	70	75	80				

The ID Code (Positions 1-4) will contain RLAP identifying logical group Related U.S. Application Data. Positions 5-80 will contain spaces.

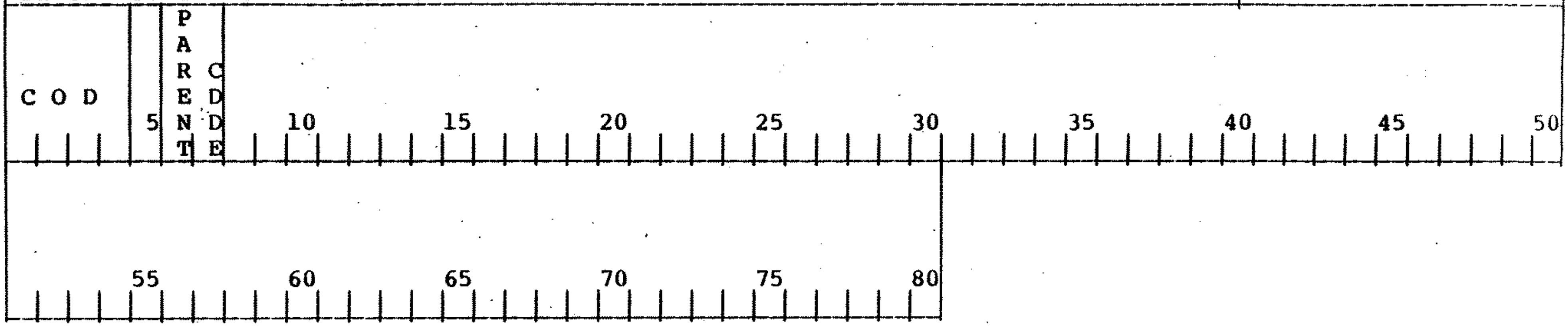
The data records within logical group RLAP will contain the coded version of parent case/continuation data of prior applications related to this patent.

Multiple related U.S. Application Data could be present and each one would begin a new logical group RLAP.

ID codes and associated data for the RLAP logical group are defined on the following pages.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional

Parent Code - COD - (RLAP)



The ID Code (Positions 1-4) will contain COD identifying the record as a parent code record.

Positions 6-7 will contain a two-position numeric parent code as defined below:

Parent Code and Definitions

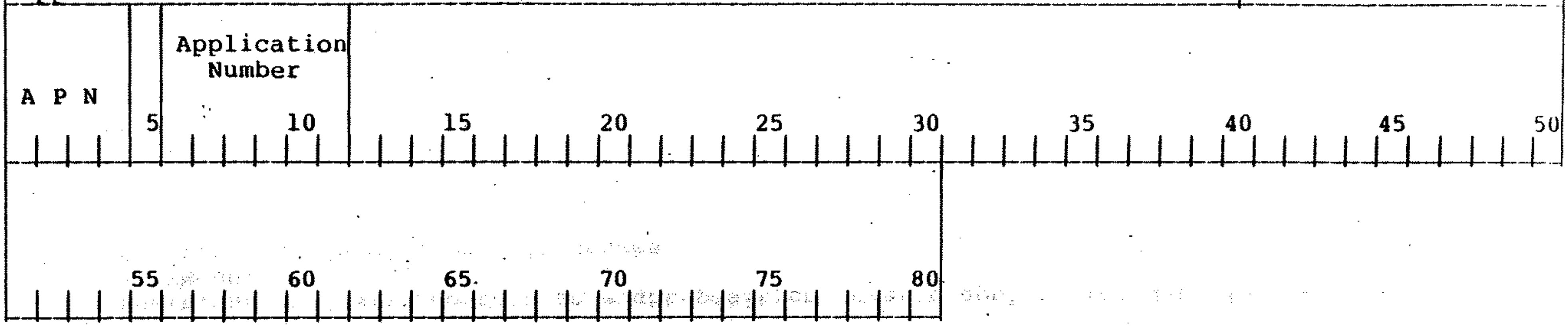
71	Continuation of (including streamline cont.)
72	Continuation-in-part of
73	A substitute for
74	Divison of
81	Which is a continuation of
82	Which is a continuation-in-part of
84	Which is a division of
86	, said
89	Ser. No.
90	And
91	And a continuation of
92	, each

Parent Code - COD - (RLAP) (continued)

Note: When the codes 86 and 92 are used, they must be followed by a code in the 80 series (81, 82, or 84); the conditions beginning with "which is ...", the work "which" is automatically dropped.

All codes 71-92 automatically generate "Ser. No.".

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional
Application Number - APN - (RLAP)		

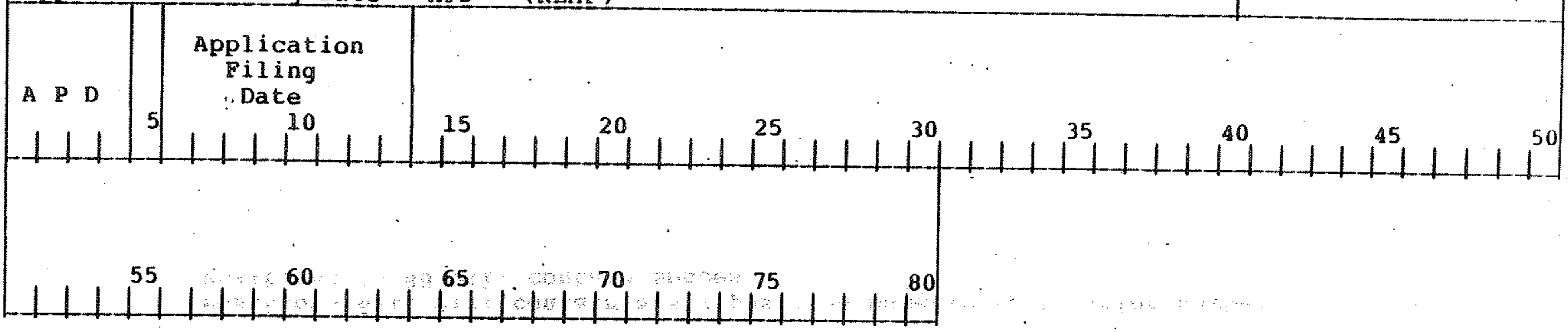


The ID Code (Positions 1-4) will contain APN identifying the record as an application number record.

Positions 6-11 will contain a six-position numeric application number.
Positions 13-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

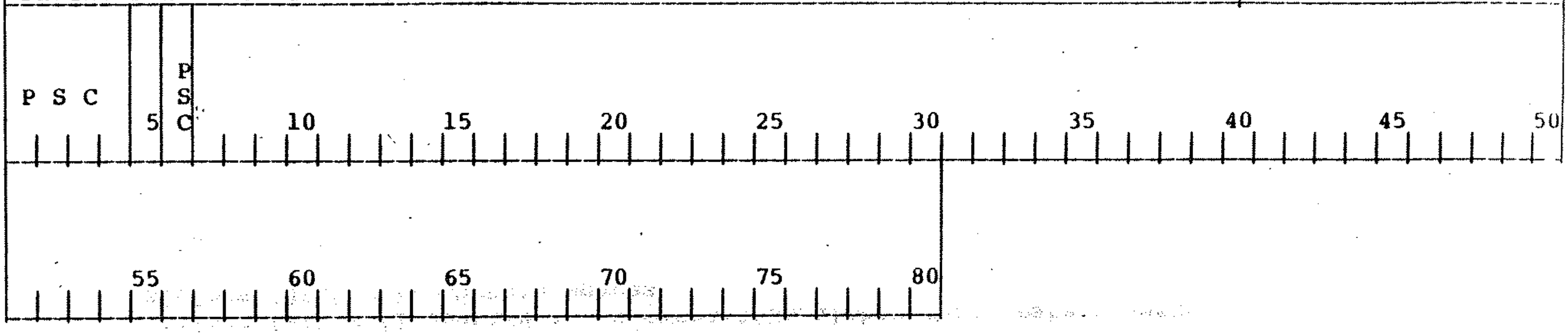
Application Filing Date - APD - (RLAP)



The ID Code (Positions 1-4) will contain APD identifying the record as an application filing date record.

Positions 6-13 will contain an eight-position numeric application date in the format YYYYMMDD.
Positions 14-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional
Parent Status Code - PSC - (RLAP)		



The ID Code (Positions 1-4) will contain PSC identifying the record as a parent status code record.

Position 6 will contain a numeric parent case code as defined below
Positions 8-80 will contain spaces.

Parent Status Code:

1	Now patented
3	Now abandoned
(No Code)	Pending
4	", now Defensive Publication No. _____.

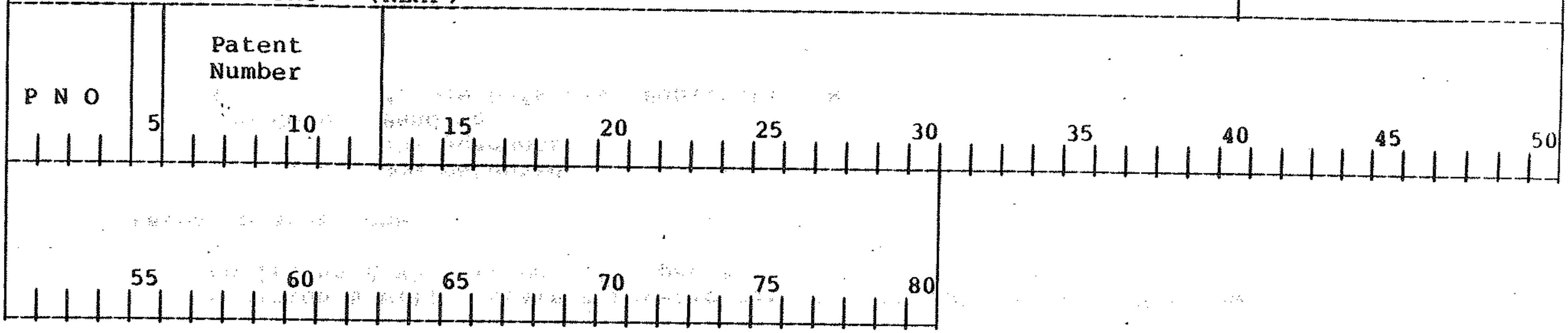
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

___ Required
_x_ Optional

Patent Number - PNO - (RLAP)

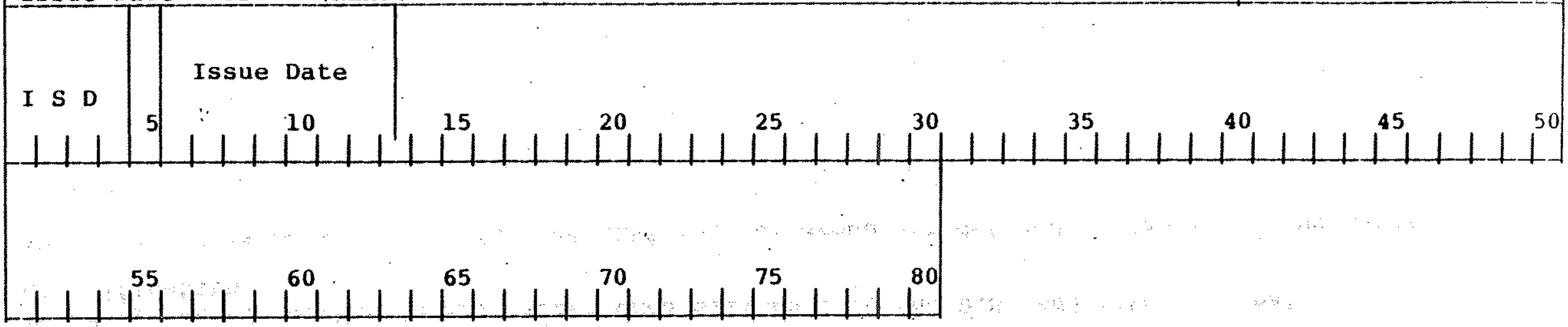


The ID Code (Positions 1-4) will contain PNO identifying the record as a patent number record.

Positions 6-12 will contain a seven-position alphanumeric patent number.
Positions 13-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Issue Date - ISD - (RLAP)

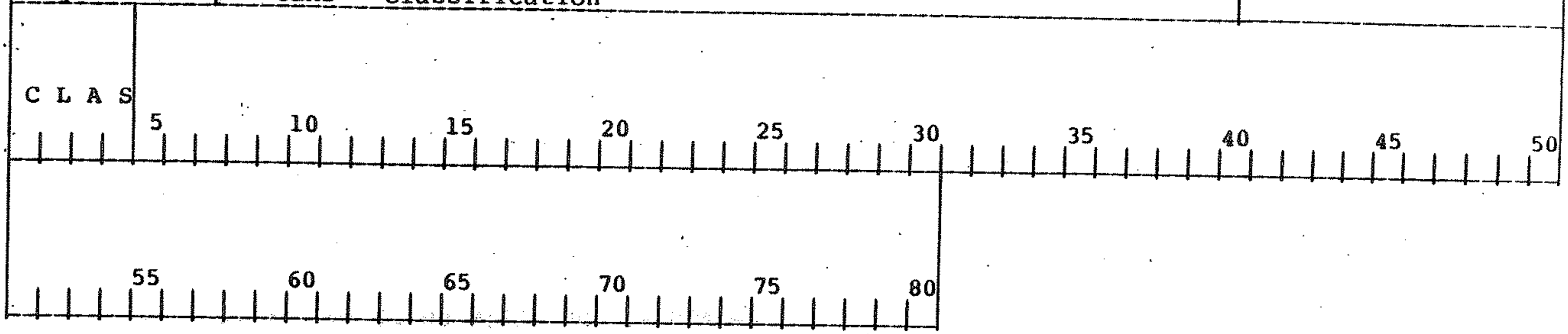


The ID Code (Positions 1-4) will contain ISD identifying the record as an issue date record.

Positions 6-13 will contain an eight-position numeric issue date in the format YYYYMMDD.
Positions 14-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional

Logical Group - CLAS - Classification



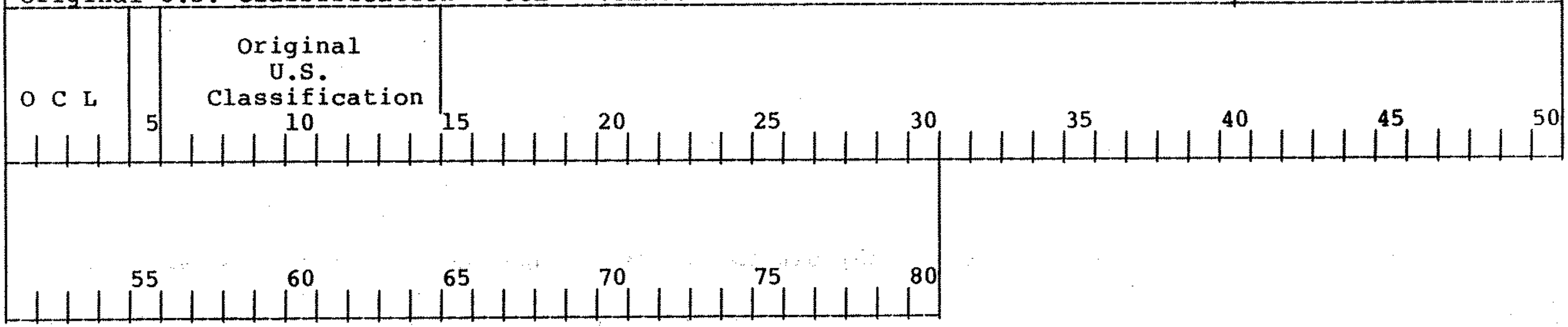
The ID Code (Positions 1-4) will contain CLAS identifying logical group Classification. Positions 5-80 will contain spaces.

The data records within logical group CLAS will contain the U.S. and International Classifications.

ID Codes and associated data for the CLAS logical group are defined on the following pages.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required ___ Optional

Original U.S. Classification - OCL - (CLAS)



The ID Code (Positions 1-4) will contain OCL identifying the record as an original U.S. Classification record.

Position 6 will begin a variable length alphanumeric field appearing as defined below:

- <u>Class</u> - DESIGNS will contain a "D" in the first position. Positions two and three, right justified, with a leading space when required for a single digit class.

  PLANTS - Three alphabetic characters containing "PLT"

  ALL OTHER PATENTS - Three alphanumeric positions, right justified, with leading spaces.

- <u>Sub-Class</u> - ALL PATENTS - Three alphanumeric positions, right justified, leading spaces, and, if present, one to three alphanumeric characters to the right of the decimal point (assumed decimal point on full-text), left justifed.

  A digest entry present as a subclass would appear as follows:

  Three alpha positions containing DIG, and one to three alphanumeric positions, left justified.

NOTE: Only one OCL record will appear within logical group CLAS.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required x Optional
Cross Reference to U.S Classification - XCL - (CLAS)		
X C L	Cross Reference Classification	
5 10 15 20 25 30 35 40 45 50		
55 60 65 70 75 80		

The ID Code (Position 1-4) will contain XCL identifying the record as a Cross Reference to the U.S. Classification record.

Position 6 will begin a variable length alphanumeric field appearing as defined for an OCL record.

NOTE: More than one XCL record may appear within logical group CLAS.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Unofficial Reference to U.S. Classification - UCL - (CLAS)		

U C L		Unofficial Reference Classification	
1–4	5	6–14	15–50

5	10	15	20	25	30	35	40	45	50
55	60	65	70	75	80				

The ID Code (Positions 1-4) will contain UCL identifying the record as an Unofficial Reference to the U.S. Classification record.

Position 6 will begin a variable length alphanumeric field appearing as defined for an OCL record.

NOTE: More than one UCL record may appear within logical group CLAS.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Digest Entry to U.S. Classification - DCL - (CLAS)

D C L		Digest Entry Reference Classification
1–4	5	6–15

5 10 15 20 25 30 35 40 45 50

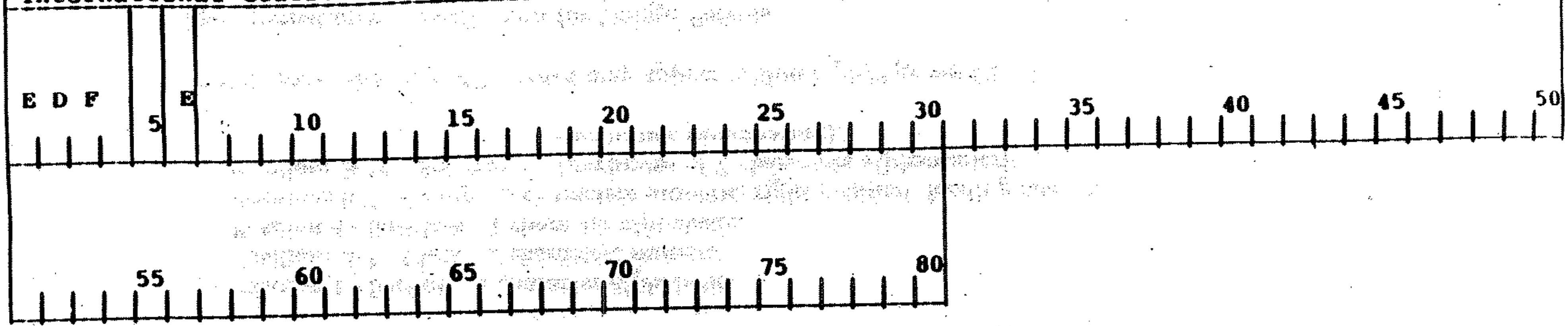
55 60 65 70 75 80

The ID Code (Positions 1-4) will contain DCL identifying the record as a Digest Reference to the U.S. Classification record.

Position 6 will begin a variable length alphanumeric field appearing as defined for an OCL record.

NOTE: More than one DCL record may appear within logical group CLAS.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
International Classification Edition Field - EDF - (CLAS)		



The ID Code (Positions 1-4) will contain EDF identifying the record as the Edition Field of the International Classification.

Position 6 will contain a numeric value as defined below:

A "6" would denote that all subsequent ICL record(s) contain the 6th edition of the International Classification.

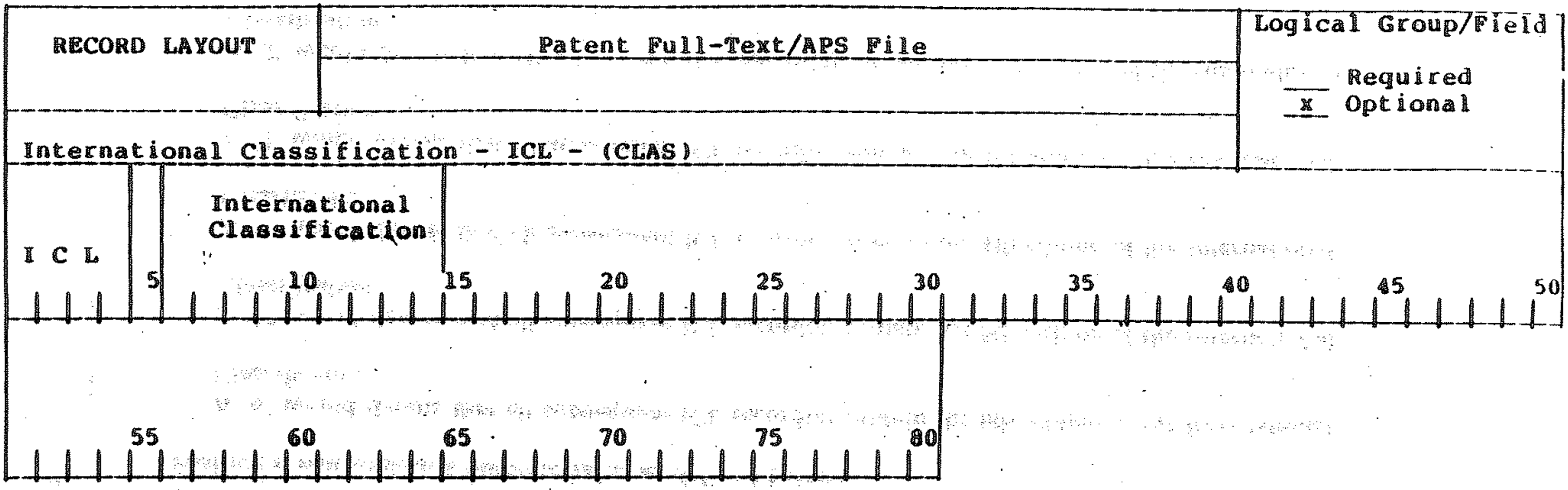
A "5" would denote that all subsequent ICL record(s) contain the 5th edition of the International Classification.

A "4" would denote that all subsequent ICL record(s) contain the 4th edition of the International Classification.

A "3" would denote that all subsequent ICL record(s) contain the 3rd edition of the International Classification.

A "2" would denote that all subsequent ICL record(s) contain the 2nd edition of the International Classification.

If the ICL records are not preceded by an EDF record the International Classification would be the 1st or original edition. An EDF record will always be present for the International (Locarno) Classification



The ID Code (Positions 1-4) will contain ICL identifying the record as the International Classification record.

Position 6 will contain a variable length alphanumeric field appearing as follows:

-Position 1 - Section - 1 character alphabetic.
-Positions 2-3 - Class - 2 characters numeric.
-Position 4 - Subclass - 1 character alphabetic.
-Positions 5-7 - Group - 3 characters numeric, right justified, leading spaces.
-Positions 8-14 - Subgroup - Maximum of 7 characters alphanumeric, (including punctuation).

NOTE: More than one ICL record may appear within logical group CLAS.

The International Classification for Design Patents:

Issue dates January 5, 1971 through March 6, 1984 the International Classification for Design Patents will appear in the following manner:

-Position 1 - Section - 1 character alphabetic containing a "D".
-Positions 2-3 - Class - 2 characters numeric, right justified, with a leading zero when required f[illegible] single digit class.
-Positions 4-5 - Subclass - 2 characters numeric, right justified, with a leading

The International Classification for Design Patents (Continued)

NOTE: Design Patents issued March 13, 1984 through April 29, 1997 will not have an International Classification (ICL).

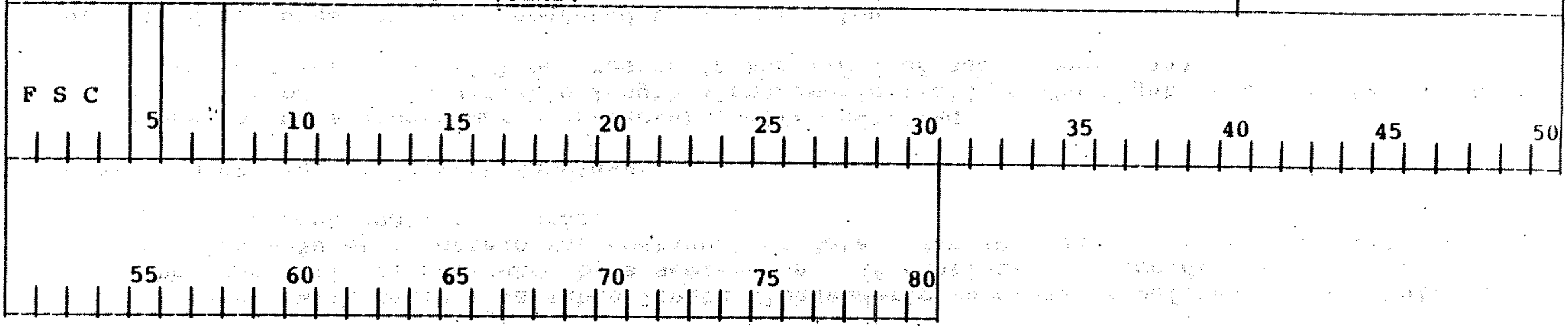
Effective with the issue of May 6, 1997, the International (Locarno) Classification will be present for Design Patents appearing in the following manner:

-Positions 1-2 - Class - 2 characters numeric, right justified with leading zeros.
-Positions 3-4 - Subclass - 2 characters numeric, right justified with leading zeros.

NOTE: Only one International (Locarno) Classification will be present for a Design Patent.

The unused positions of each ICL record, through position 80, will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Field of Search Class - FSC - (CLAS)		

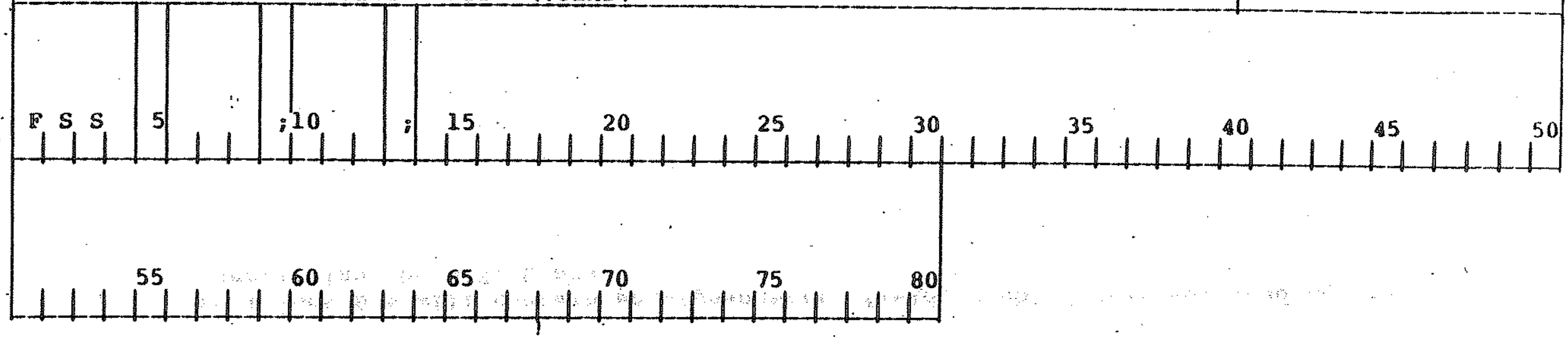


The ID Code (Positions 1-4) will contain FSC identifying the record as a field of search classification record.

Positions 6-8 will contain an alphanumeric field, right justified, leading spaces, identifying the U.S. Class.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Field of Search Subclass - FSS - (CLAS)



The ID Code (Positions 1-4) will contain FSS identifying the record as a field of search subclass record.

Position 6 will begin a variable length alphanumeric subclass as defined below. Multiple subclasses will be separated by a semi-colon. If continuation record(s) are required, position 6-80 will contain the continuation data. The ID Code (Positions 1-4) will contain spaces in continuation records.

Appearance of Field of Search Subclass:

- One to three alphanumeric characters, left justified.
- And, if present, a variable length alphanumeric field to the right of the decimal point (the decimal point will be present in the field of search subclass).

Multiple subclasses would be separated by a semi-colon.
Two spaces would terminate one subclass or the last subclass in a record.

Field of Search Subclass - FSS - (CLAS) (continued)

Examples of FSS records - (¶ = one space character):

Example #1 shows one subclass.

```
FSS 136¶¶
```

Example #2 shows two records each having multiple subclasses

```
FSS 91;92¶¶
FSS 217;238;258¶¶
```

Example #3 shows three records each having multiple subclasses. Each record also includes a subclass with decimal subclass data.

```
FSS 25;30;63.5¶¶
FSS 505.26;495¶¶
FSS 30;63.5;76;174¶¶
```

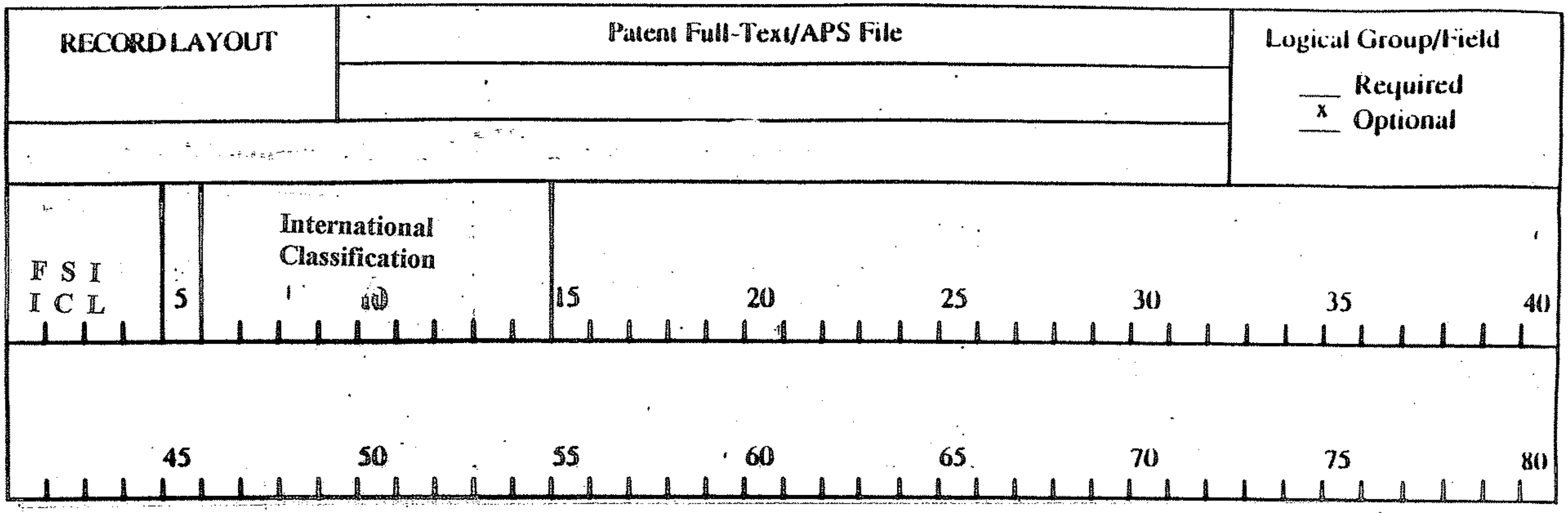
Example #4 shows one subclass record with the decimal subclass containing an alpha character. Note that a single space precedes the alpha character.

```
FSS 39.14¶M¶¶
```

Example #5 shows a subclass record having multiple subclasses including Digest (DIG.) entries

```
FSS 183;300;DIG.¶30;DIG.¶31¶¶
```

Example #3



The ID Code (Positions 1-4) will contain FSI or ICL identifying the record as a Field of Search International Patent Classification record or an International Classification record.

Position 6 will begin a variable length alphanumeric field appearing as follows:

- **position 1 - Section - 1 character alphabetic.**
- **position 2-3 - Class - 2 character numeric.**
- **position 4 - Subclass - 1 character alphabetic.**
- **position 5-7 - Group - 3 character numeric, right justified, leading zeros.**
- **position 8-14 - Subgroup - Maximum of 7 characters alphanumeric (including punctuation).**

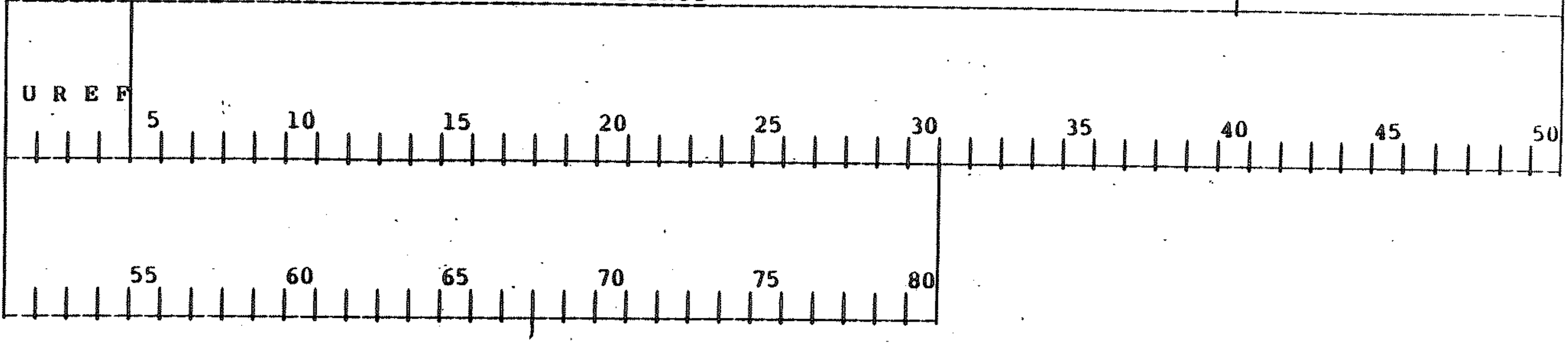
The International Classification for Designs will appear in the following manner:

- **position 1 - Section - 1 character alphabetic containing a "D".**
- **position 2-3 - Class - 2 character numeric, right justified, with a leading zero when required for a single digit class.**
- **position 4-5 - Subclass - 2 character numeric, right justified, with a leading zero when required for a single digit class.**

The remainder of the record, through position 80, contains spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Logical Group - UREF - U.S. Patent Reference



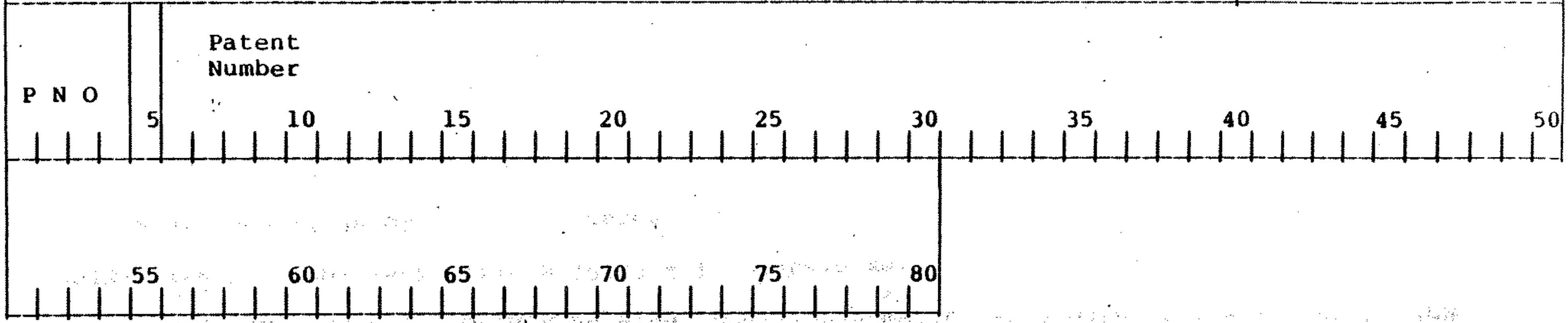
The ID Code (Positions 1-4) will contain UREF identifying logical group U.S. Patent Reference. Positions 5-80 will contain spaces.

The data records within logical group UREF will contain the U.S. Patent Reference(s) tht are being cited.

ID Codes and associated data for the UREF logical group are defined on the following pages.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional

Patent Number - PNO - (UREF)

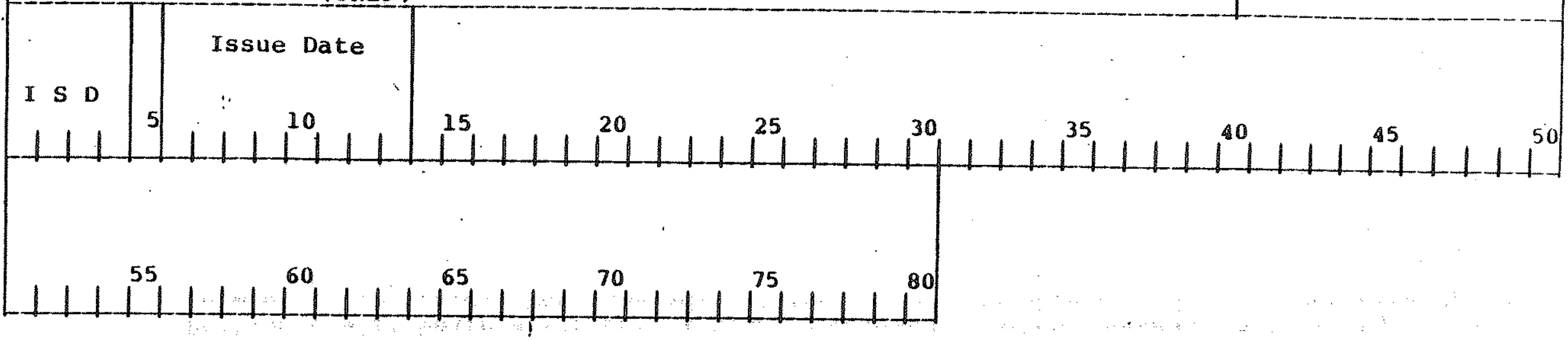


The ID Code (Positions 1-4) will contain PNO identifying the record as a patent number record.

Postion 6 will begin a variable length alphanumeric patent number. A trailing space would terminate the field. The remainder of the record, through position 80, contains spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional

Issue Date - ISD - (UREF)



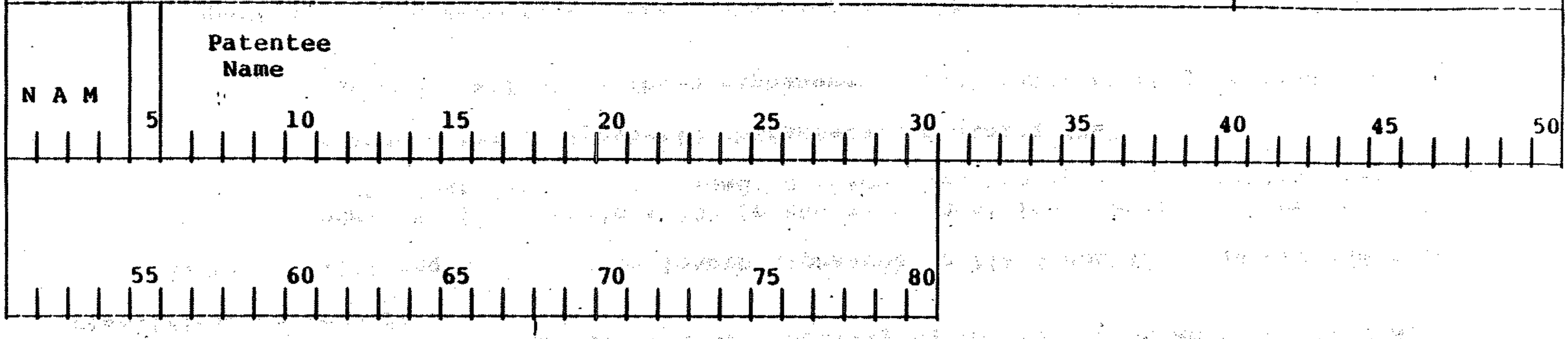
The ID Code (Positions 1-4) will contain ISD identifying the record as an issue date record.

Positions 6-13 will contain an eight-position numeric issue date in the format YYYYMMDD.

NOTE: The Day (DD) in positions 12-13 will contain zeros

Positions 14-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required __ Optional
Patentee Name - NAM - (UREF)		



The ID Code (Positions 1-4) will contain NAM identifying the record as a patentee name record.

Position 6 will begin a variable length alphabetic field containing the last name of the patentee. If more than one patentee exists, "et al" will follow the first patentee name. Two spaces would terminate the field.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Original U.S. Classification - OCL - (UREF)		

OCL		Original US Classification	
1–4	5	6–13	14–80

The ID Code (Positions 1-4) will contain OCL identifying the record as an original U.S. Classification records.

Position 6 will begin a variable length alphanumeric field appearing as defined below:

- <u>Class</u> - DESIGNS will contain a "D" in the first position. Positions two and three, right justified, with a leading space when required for a single digit class.

  PLANTS - Three alphabetic characters containing "PLT"

  ALL OTHER PATENTS - Three alphanumeric positions, right justified, with leading spaces.

- <u>Sub-Class</u> - ALL PATENTS - Three alphanumeric positions, right justified, leading spaces, and, if present, one to there alphanumeric characters to the right of the decimal point (assumed decimal point on-full-text), left justifed.

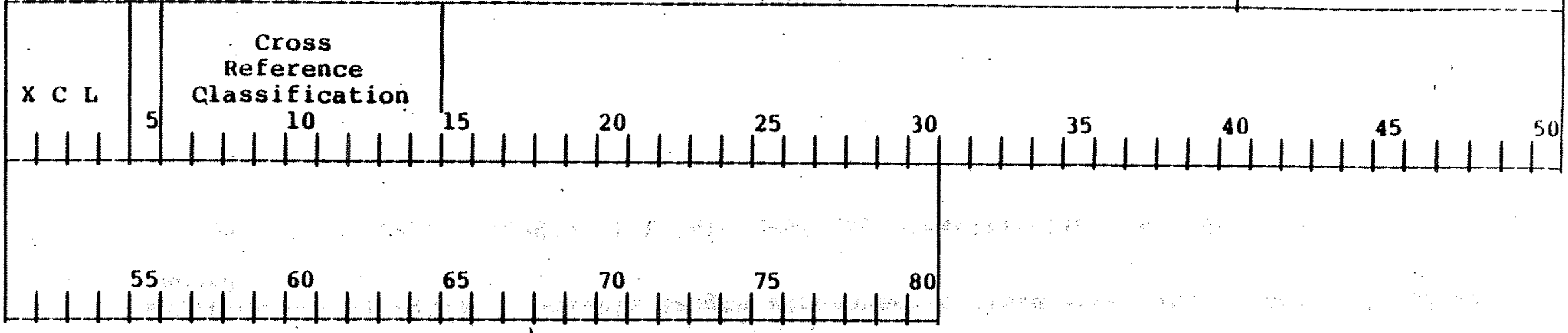
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

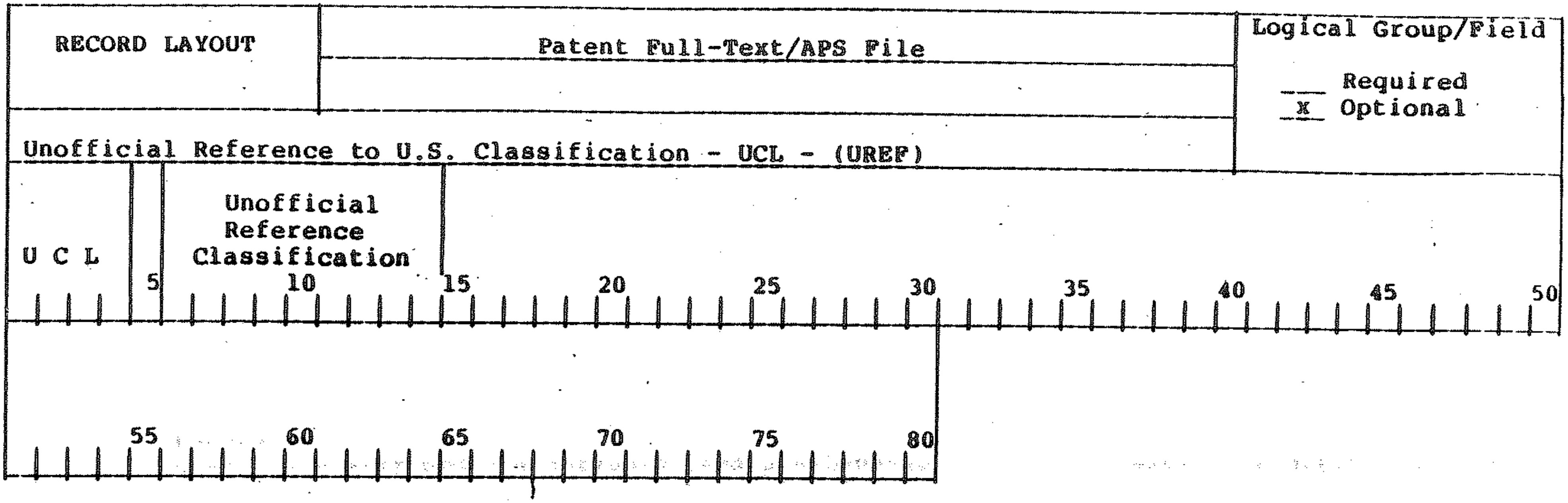
___ Required
_x_ Optional

Cross Reference to U.S. Classification - XCL - (UREF)



The ID Code (Positions 1-4) will contain XCL identifying the record as a Cross Reference.

Position 6 will begin a variable length alphanumeric field appearing as defined for an OCL record.



RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Unofficial Reference to U.S. Classification - UCL - (UREF)		

U C L

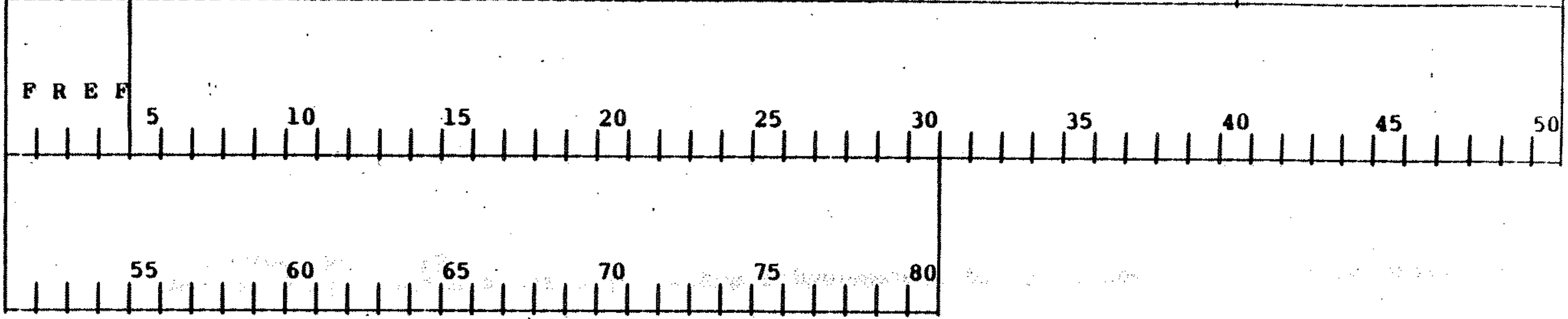
Unofficial Reference Classification

The ID Code (Positions 1-4) will contain UCL identifying the record as a unofficial reference.

Position 6 will begin a variable length alphanumeric field appearing as defined for an OCL record.

NOTE: Each U.S. Reference (UREF) will only have one classification record, a OCL or XCL or UCL.

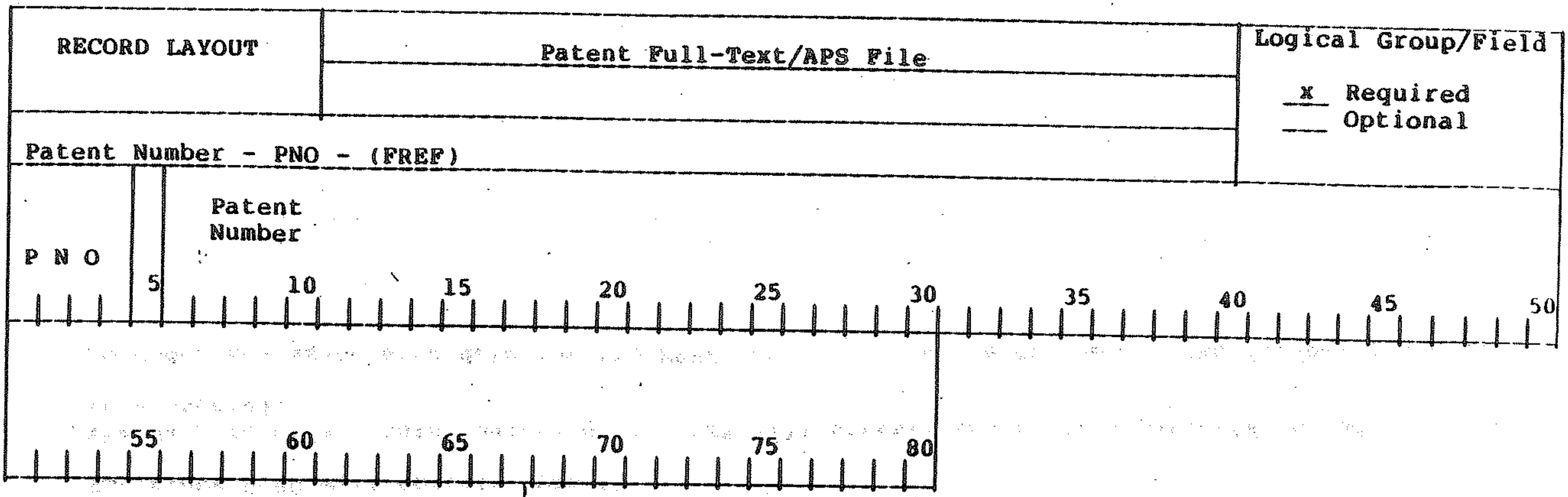
RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required x Optional
Logical Group - FREF - Foreign Reference		



The ID Code (Positions 1-4) will contain FREF identifying logical group Foreign Reference. Positions 5-80 will contain spaces.

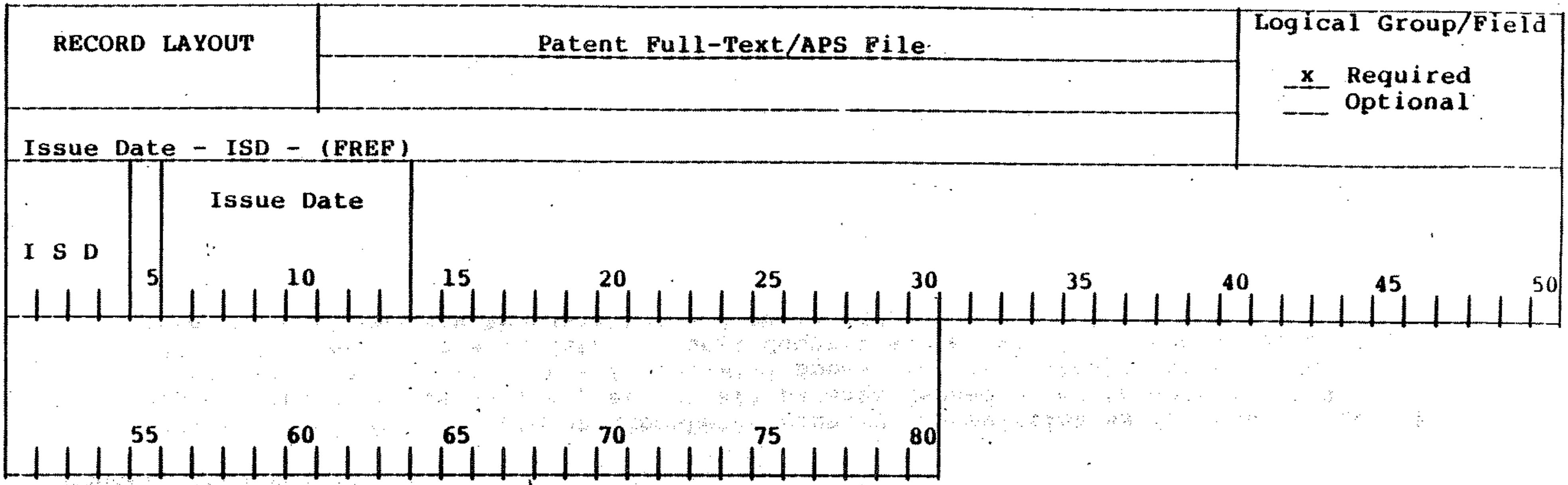
The data records within logical group FREF will contain the foreign patent(s) cited as reference(s).

ID Codes and associated data for the FREF logical group are defined on the following pages.



The ID Code (Positions 1-4) will contain PNO identifying the record as a patent number record.

Postion 6 will begin a variable length alphanumeric patent number. A trailing space would terminate the field.

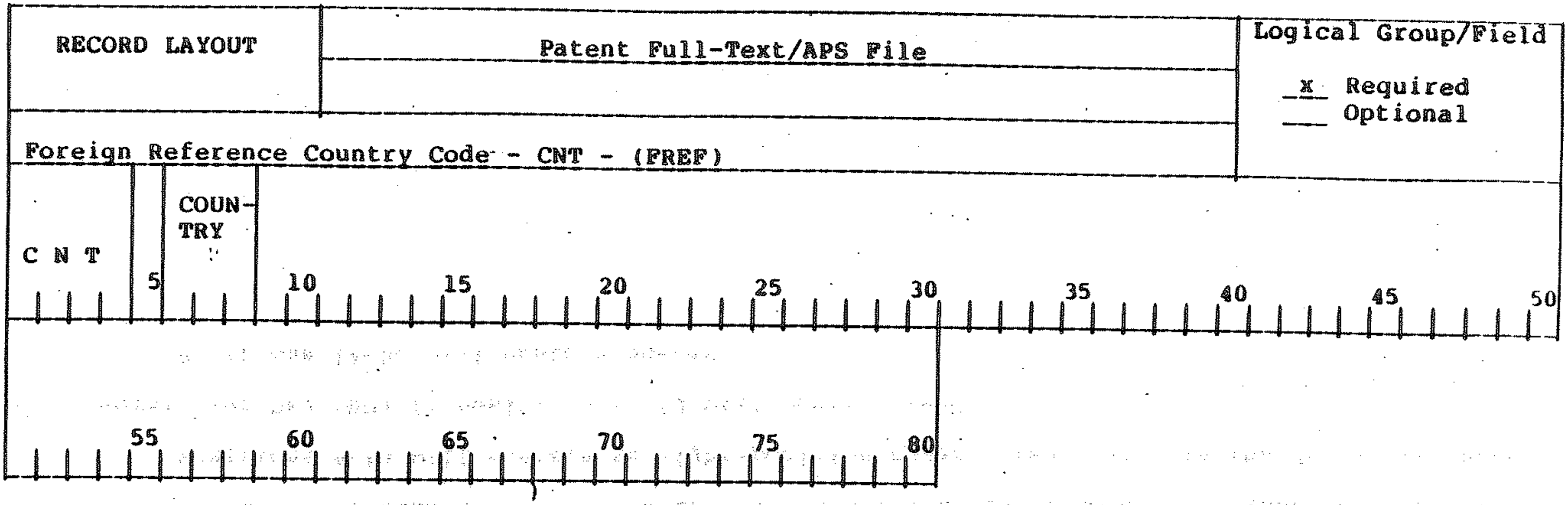


The ID Code (Positions 1-4) will contain ISD identifying the record as an issue date record.

Positions 6-13 will contain an eight-position numeric issue date in the format YYYYMMDD.

NOTE: The Day (DD) in positions 12-13 will contain zeros

Positions 14-80 will contain spaces.

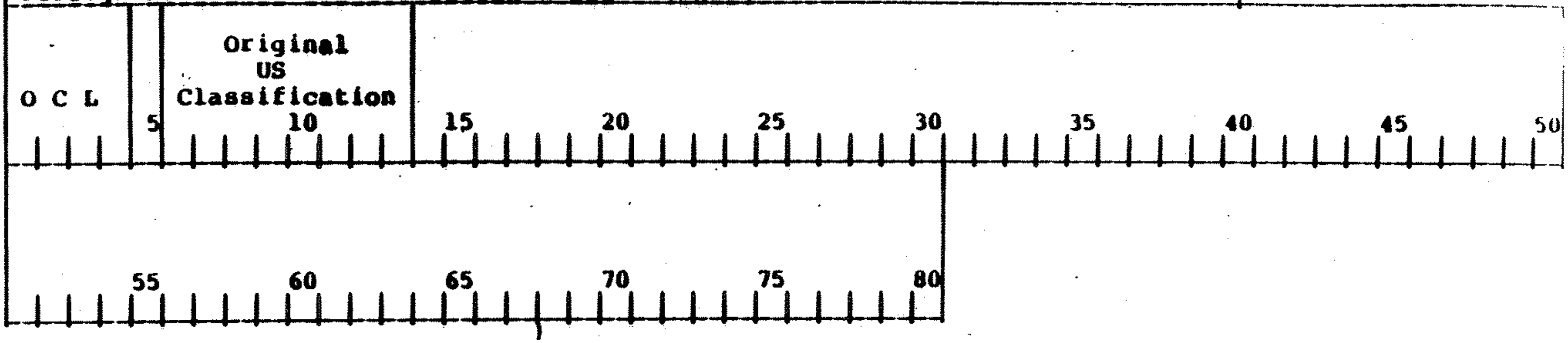


The ID Code (Positions 1-4) will contain CNT identifying the record as a Foreign Reference Country Code record.

Positions 6-8 will contain an alphabetic country abbreviation as follows: A two-character country abbreviation will appear for all patents issued prior to July 4, 1978. A three-character country abbreviation will appear for all patents issued on or after July 4, 1978. Reference Table 3A International Country Abbreviation - 2-character and Table 3B International Country Abbreviation - 3-character.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _X_ Optional

Foreign Reference Classification - OCL - (FREF)



The ID Code (Positions 1-4) will contain OCL identifying the record as an original U.S. Classificabion records.

Position 6 will begin a variable length alphanumeric field appearing as defined below:

- Class - Three alphanumeric positions, right justified, with leading spaces.
- Sub-Class - ALL PATENTS - Three alphanumeric positions, right justified, leading spaces, and, if present, one to there alphanumeric characters to the right of the decimal point (assumed on-full-text), left justifed.

RECORD LAYOUT	Patent Full-Text/APS File		Logical Group/Field ___ Required _x_ Optional
Foreign Reference International Patent Classification - ICL - (FREF)			
I C L	5	International Classification 10	15 20 25 30 35 40
	45	50	55 60 65 70 75 80

The ID Code (Positions 1-4) will contain ICL identifying the record as a foreign reference International Patent Classification record.

Position 6 will begin a variable length alphanumeric field appearing as follows:

- **position 1 - Section - 1 character alphabetic.**
- **position 2-3 - Class - 2 character numeric.**
- **position 4 - Subclass - 1 character alphabetic.**
- **position 5-7 - Group - 3 character numeric, right justified, leading zeros.**
- **position 8-14 - Subgroup - Maximum of 7 characters alphanumeric (including punctuation).**

The International Classification for Designs will appear in the following manner:

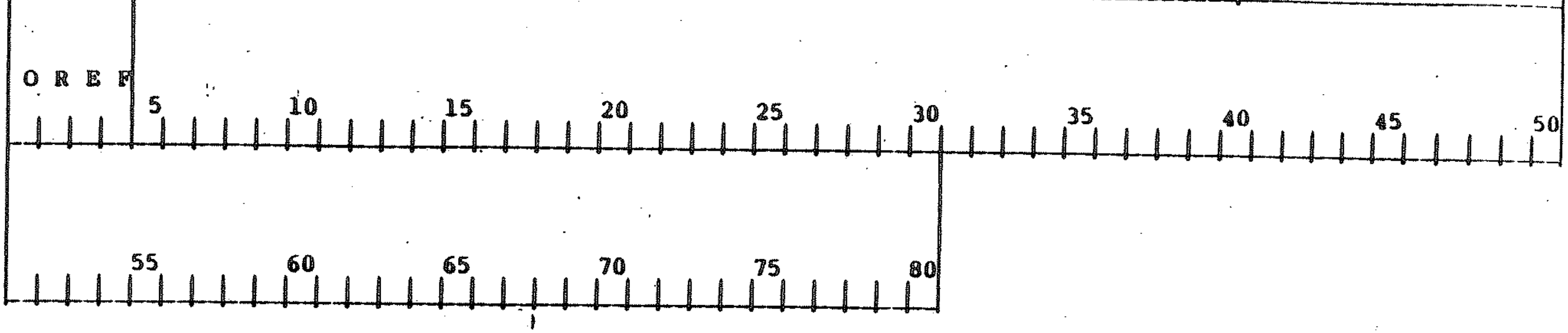
- position 1 - Section - 1 character alphabetic containing a "D".
- position 2-3 - Class - 2 character numeric, right justified, with a leading zero when required for a single digit class.
- position 4-5 - Subclass - 2 character numeric, right justified, with a leading zero when required for a single digit class.

The remainder of the record, through position 80, contains spaces.

NOTE: Effective with the 01/01/94 issue, International Patent Classifications may appear as a Foreign Reference classification.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Logical Group - OREF - Other Reference



The ID Code (Positions 1-4) will contain OREF identifying logical group Other References. Positions 5-80 will contain spaces.

The data records within logical group OREF will contain Other References that are being cited.

Other References - Such as books, pamphlets, trade journals, pages from catalogues, etc., includes name of publication and article (if appropriate), edition and year, volume and issue, publisher, and pertinent pages if less than the entire publication is being relied on. If abstracts, such as Chemical Abstracts, are cited, the name of the abstracting company will also be given. Defensive Publications are cited under this category and are identified with "Def. Pub." before the number (which is preceded by a "T", indicating technical disclosure document, for those published after 12/16/69).

Each Other Reference cited within logical group OREF will begin with PAL as the ID Code (Positions 1-4).

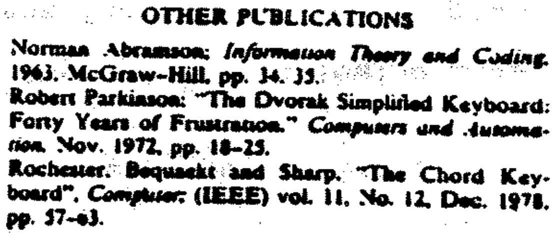
NOTE: PAL defines a new paragraph all lines being left justified on the printed document. Refer to Appendix A Definition of Paragraph ID Codes and Appendix B Appearance of Text

Logical Group - OREF - Other Reference (continued)

Example of Other Reference appearing on APS File:

```
OREF
PAL  Norman Abramson; Information Theory and Coding, 1963, McGraw-Hill, pp. 34,
       35.
PAL  Robert Parkinson; "The Dvorak Simplified Keyboard; Forty Years of
       Frustration," Computers and Automation, Nov. 1972, pp. 18-25.
PAL  Rochester, Bequaekt and Sharp, "The Chord Keyboard", Computer; (IEEE) vol.
       11, No. 12, Dec. 1978, pp. 57-63.
```

Example of Other Reference appearing on printed document:



OTHER PUBLICATIONS

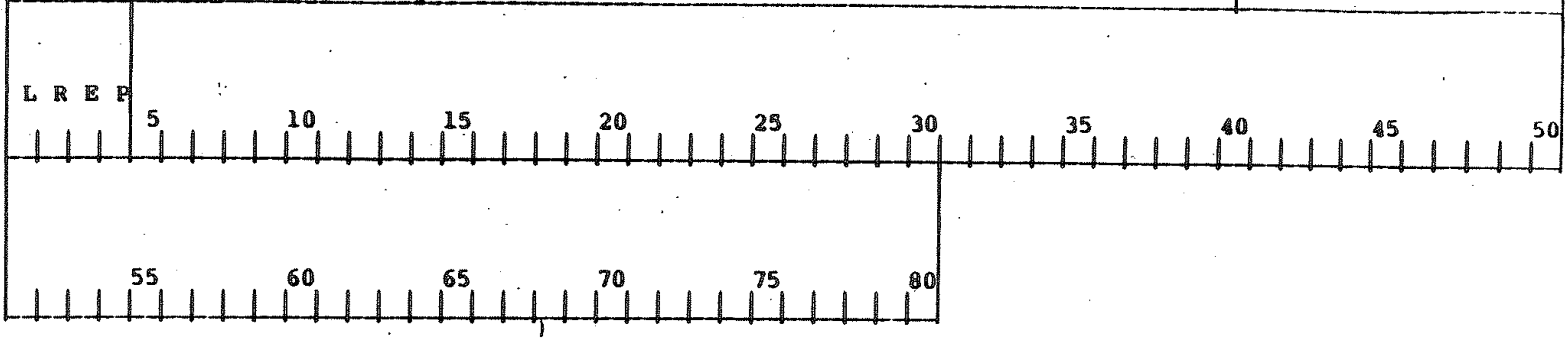
Norman Abramson; *Information Theory and Coding*, 1963, McGraw-Hill, pp. 34, 35.

Robert Parkinson; "The Dvorak Simplified Keyboard: Forty Years of Frustration," *Computers and Automation*, Nov. 1972, pp. 18–25.

Rochester, Bequaekt and Sharp, "The Chord Keyboard", *Computer*; (IEEE) vol. 11, No. 12, Dec. 1978, pp. 57–63.

NOTE: The two examples are from the same patent.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Logical Group - LREP - Legal Information		



The ID Code (Positions 1-4) will contain LREP identifying logical group Legal Information. Positions 5-80 will contain spaces.

The data records within logical group LREP will describe the attorney, agent, firm or legal representative representing an applicants patent.

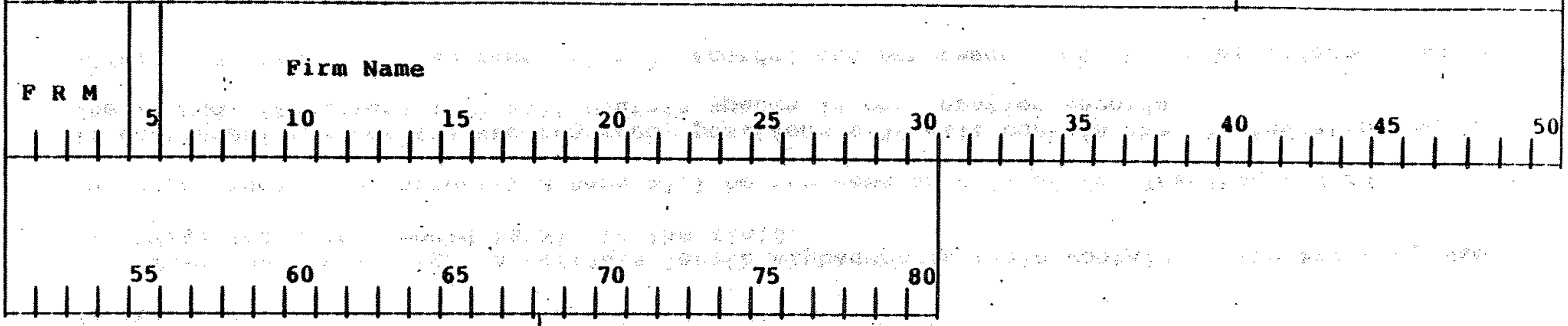
ID Codes and associated data for the FREF logical group are defined on the following pages.

Only one of the following Legal Information types will be present for logical group LREP

TYPE

FRM
FR2
AGT
AAT
ATT
NAM & Address

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Legal Firm - FRM - (LREP)		



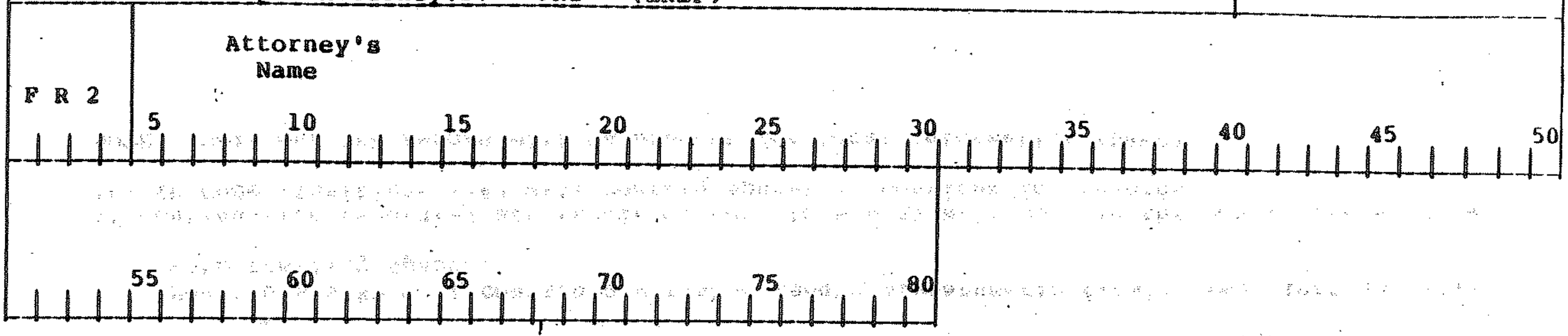
The ID Code (Positions 1-4) will contain FRM identifying the record as a Legal Firm record.

Positions 6-80 will contain a variable length alphanumeric firm's name, left justified with trailing spaces.

If continuation record(s) are required, positions 6-80 will contain the continutation data. The ID Code (Positions 1-4) will contain spaces in continuation records.

NOTE: Only one FRM record will be present for Legal Information (LREP).

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Combined Principal Attorney(s) - FR2 - (LREP)		



The ID Code (Positions 1-4) will contain FR2 identifying the record as a Principal Attorney record.

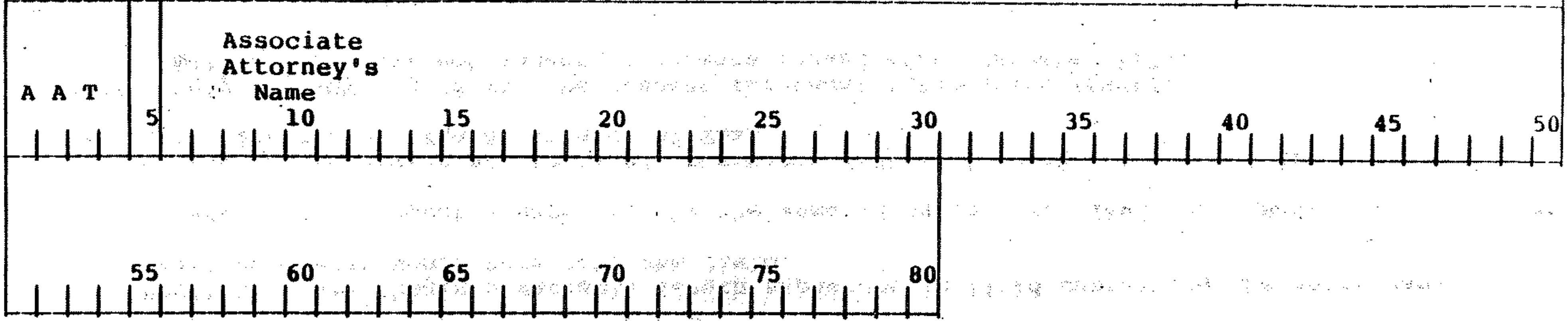
Position 6 will begin a variable length alphanumeric field containing the Attorney Name. Trailing spaces would terminate the field.

The appearance of an attorney's name will be the same as defined for Inventor's Name.

If continuation record(s) are required, positions 6-80 will contain the continutation data. The ID Code (Positions 1-4) will contain spaces in continuation records.

NOTE: A maximum of three names (3 FR2 records) can be present for the Legal Information LREP.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Associate Attorney - AAT - (LREP)		



The ID Code (Positions 1-4) will contain AAT identifying the record as an Associate Attorney record.

Position 6 will begin a variable length alphanumeric field containing the Associate Attorney's Name. Trailing spaces would terminate the field.

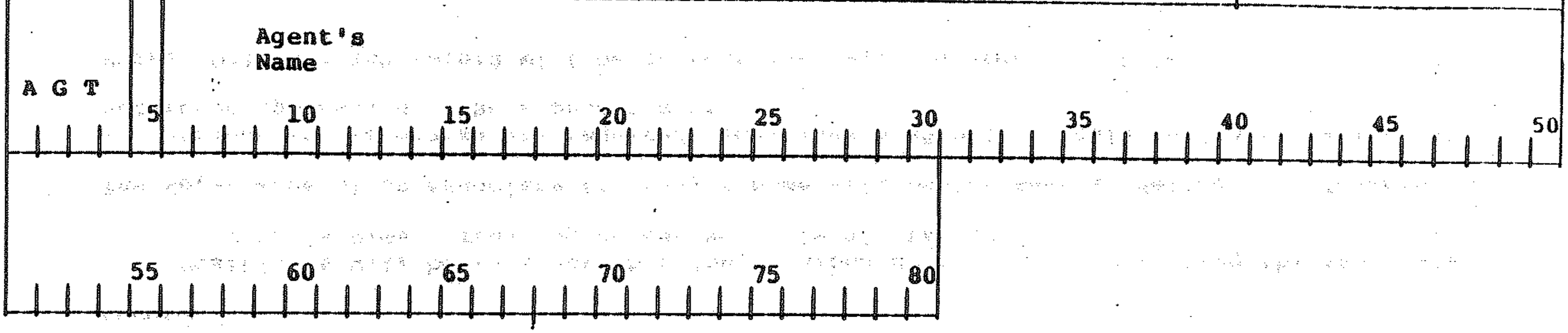
The appearance of an Associate Attorney's Name will be the same as defined for Inventor's Name

If continuation record(s) are required, positions 6-80 will contain the continuation data. Reference Appendix B - The Appearance of Text.

NOTE: Only one AAT record will be present for Legal Information (LREP).

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Agent - AGT - (LREP)



The ID Code (Positions 1-4) will contain AGT identifying the record as an Agent record.

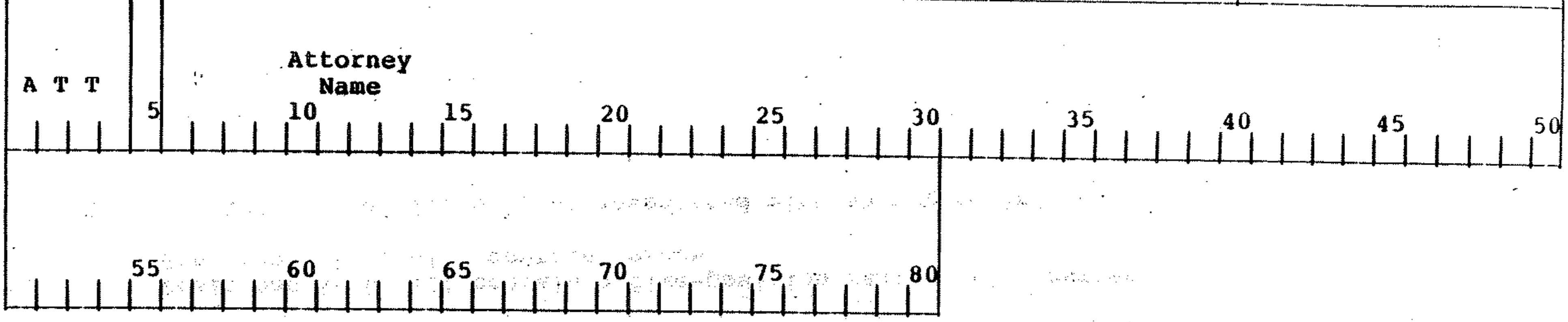
Position 6 will begin a variable length alphanumeric field containing the Agent Name. Trailing spaces would terminate the field.

The appearance of an Agent's name will be the same as defined for Inventor's Name.

If continuation record(s) are required, positions 6-80 will contain the continuation data. Reference Appendix B - The Appearance of Text.

NOTE: Only one AGT record will be present for Legal Information (LREP).
AGT records will not appear in patents issued after December 1973.

RECORD LAYOUT	Patent Full-Text/APS Files	Logical Group/Field ___ Required _x_ Optional
Attorney Name - ATT - (LREP)		



The ID Code (Positions 1-4) will contain ATT identify the record as an Attorney Name record.

Position 6 will begin a variable length alphanumeric field containing the Attorney's Name. Trailing spaces would terminate the field.

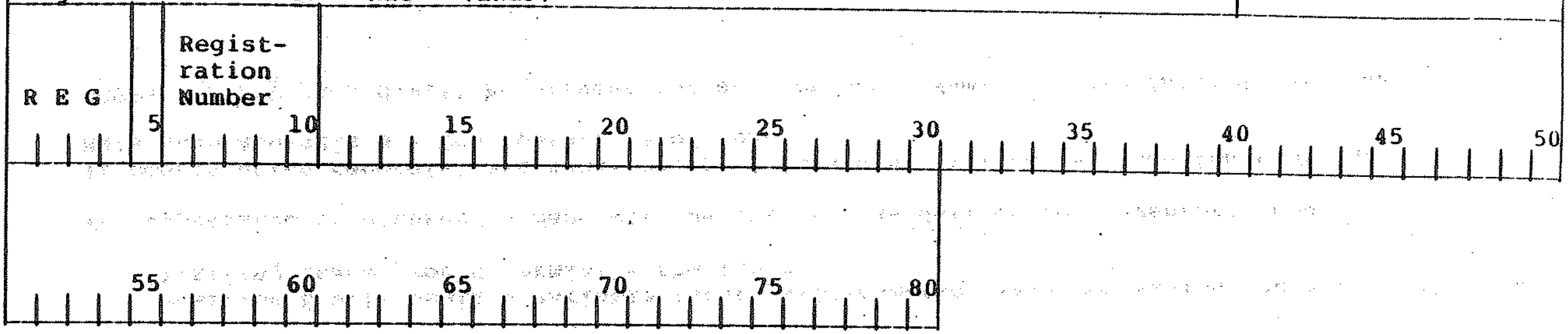
The appearance of Attorney's Name will be the same as defined for Inventor's Name.

If continuation record(s) are required, positions 6-80 will contain continuation data. Reference Appendix B - The Appearance of Text

NOTE: An ATT record will be present for each Attorney Name in Legal Information (LREP).

RECORD LAYOUT	Patent Full-Text/APS Files	Logical Group/Field ___ Required _x_ Optional

Registration Number - REG - (LREP)

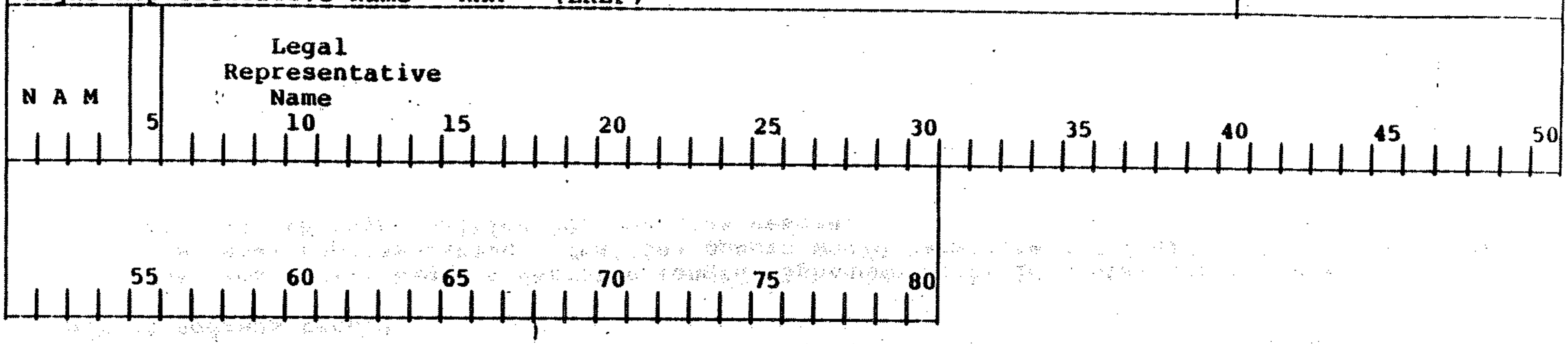


The ID Code (Positions 1-4) will contain REG identifying this as a Registration Number record.

Positions 6-10 will contain a five-position registration number.
Positions 11-80 will contain spaces.

NOTE: A REG record will only be associated with an ATT record.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Legal Representative Name - NAM - (LREP)		



The ID Code (Positions 1-4) will contain NAM identifying the record as a Legal Representative Name record.

Position 6 will begin a variable length alphanumeric field containing the name of the legal representative. Trailing spaces would terminate the field.

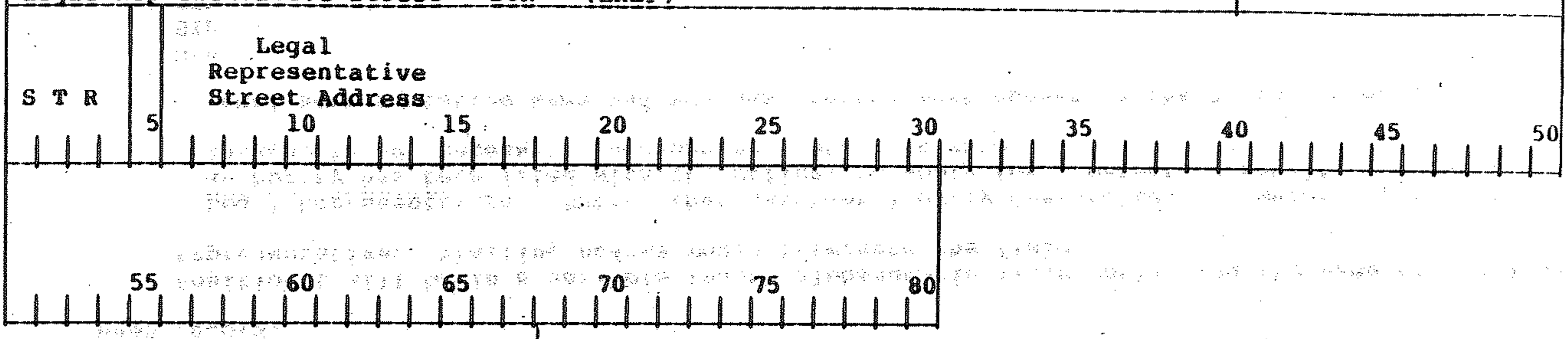
- <u>Legal Representative</u> - Entity that has been legally designated, and which a proof of authority has been filed with the Office, to apply for a patent on behalf of a legally incapacitated (deceased, incompentent, etc.) inventor.

Legal Representative Name and Address records must appear in the following order:

NAM
STR
CTY
STA or CNT
ZIP

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

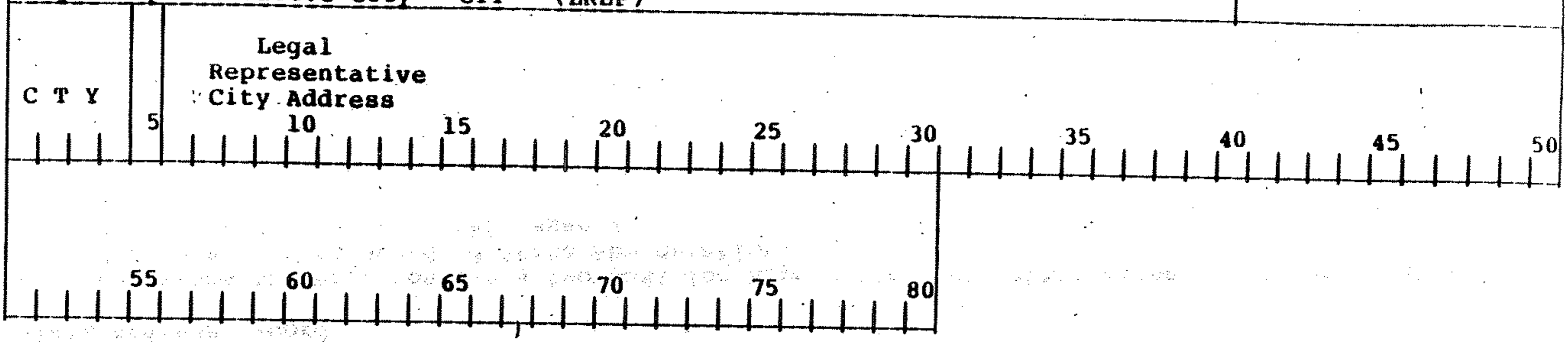
Legal Representative Street - STR - (LREP)



The ID Code (Positions 1-4) will contain STR identifying the record as a Legal Representative Street Address record.

Position 6 will begin a variable length alphanumeric field containing the street address of the legal representative. Trailing spaces would terminate the field. The remainder of the records, through position 80, contains spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Legal Representative City - CTY - (LREP)		

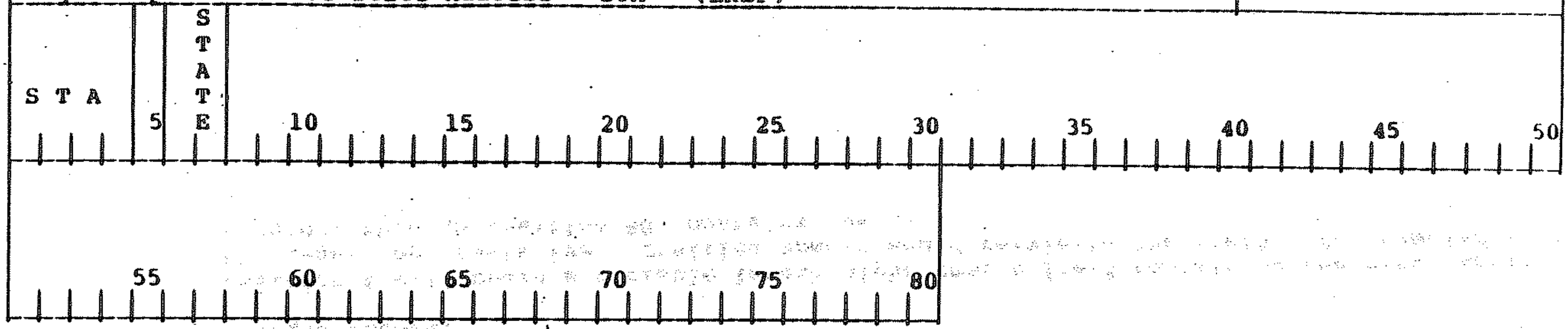


The ID Code (Positions 1-4) will contain CTY identifying the record as a Legal Representative City Address record.

Position 6 will begin a variable length alphanumeric field containing the city, address of the legal representative. Trailing spaces would terminate the field. The remainder of the records, through position 80, contains spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Legal Representative State Address - STA - (LREP)



The ID Code (Positions 1-4) will contain STA identifying the record as a Legal Representative State Address record.

Positions 6-7 will contain a two-position alphabetic state abbrevation. Reference Table 2, U.S. Post Office Standard State Abbreviation.
Positions 8-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Legal Representative Country Address - CNT - (LREP)		

1–4	5	6–8
C N T		COUN-TRY

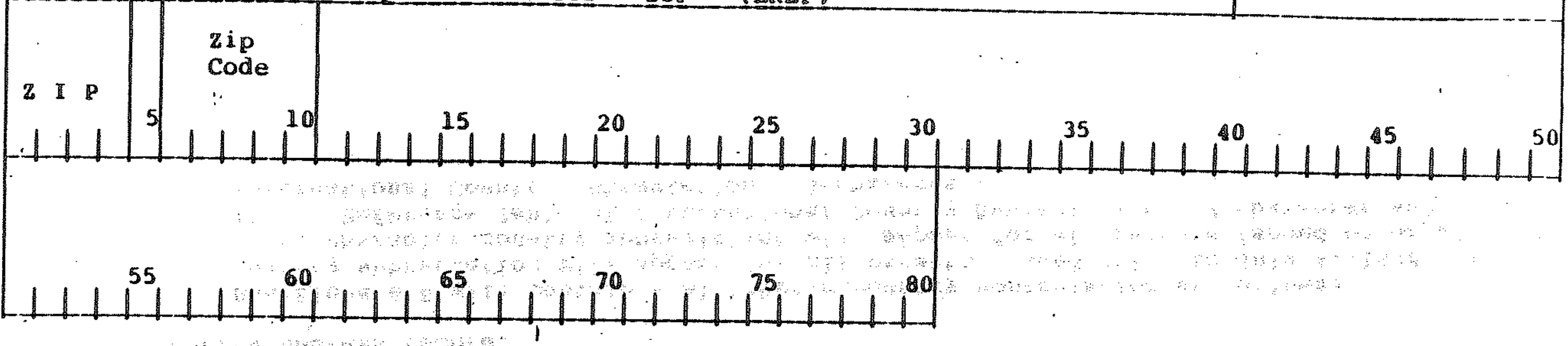
Positions: 5 10 15 20 25 30 35 40 45 50

55 60 65 70 75 80

The ID Code (Positions 1-4) will contain CNT identifying the record as a Legal Representative Country Address record.

Positions 6-8 will contain a alphabetic country abbreviation as follows: country abbreviation will appear for all patents issued prior to July 4, 1978. A three-character country abbreviation will appear for all patents issued on or after July 4, 1978. Reference Table 3A International Country Abbreviation - 2-character and Table 3B International Country Abbreviation - 3-character.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Legal Representative Zip Code Address - ZIP - (LREP)		



The ID Code (Positions 1-4) will contain ZIP identifying the record as an Assignee Zip Code Address record.

Positions 6-10 will contain a five-position numeric U.S Postal Zip Code.
Positions 11-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Logical Group - PCTA - PCT Information		

P C T A

5 10 15 20 25 30 35 40 45 50

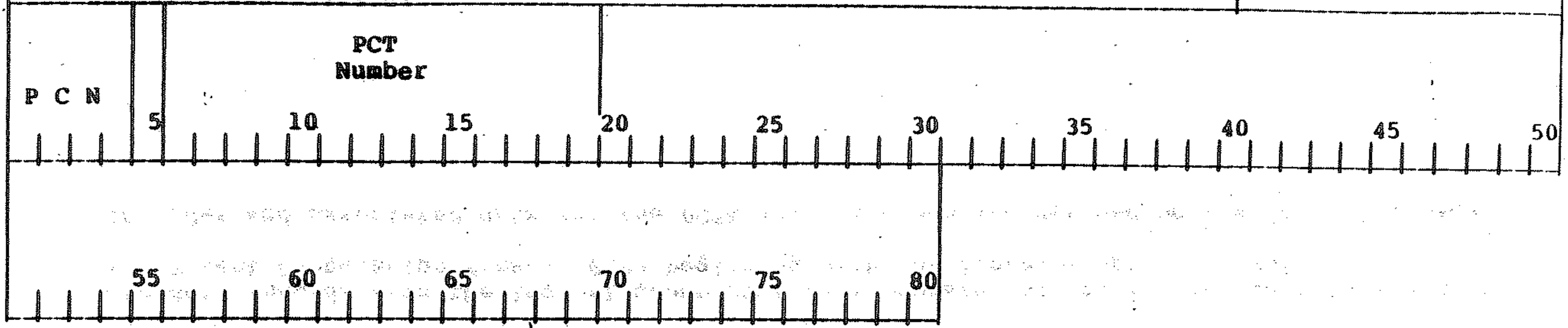
55 60 65 70 75 80

The ID Code (Positions 1-4) will contain PCTA identifying logical group PCT Information. Positions 5-80 will contain spaces.

The data records with the logical group PCTA will contain information for patents issued under the Patent Cooperation Treaty (PCT) beginning with the issue of April 1, 1980.

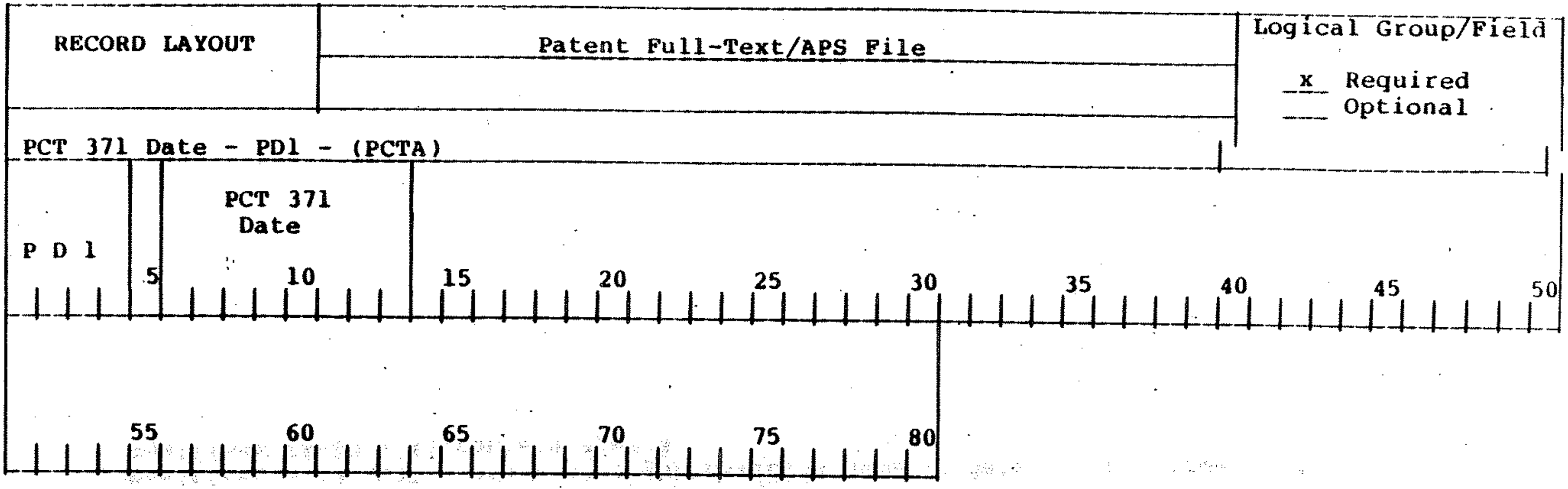
ID codes and associated data for the PCTA logical group are defined on the following pages.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field _x_ Required ___ Optional
PCT Number - PCN - (PCTA)		



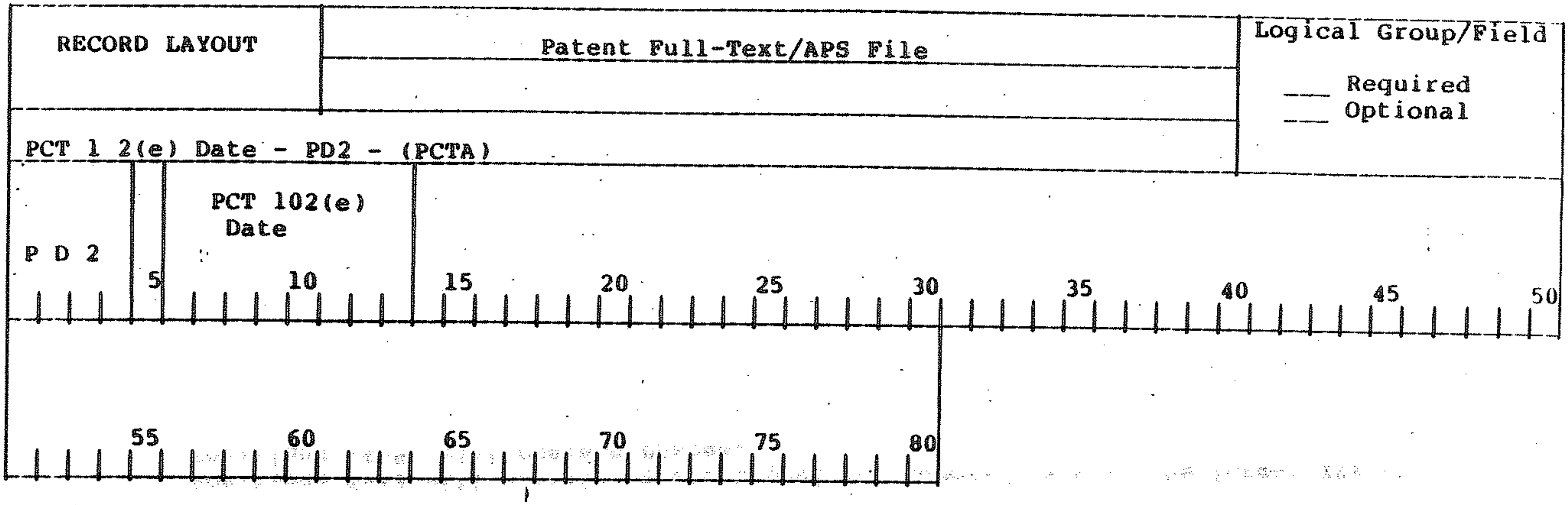
The ID Code (Positions 1-4) will contain PCN identifying the record as a PCT Number record.

Positions 6-19 will contain a fourteen-position alphanumeric PCT Number.
Positions 20-80 will contain spaces.



The ID Code (Positions 1-4) will contain PD1 identifying the record as a PCT 371 Date record.

Positions 6-13 will contain an eight-position numeric date in the format YYYYMMDD.
Positions 14-80 will contain spaces.

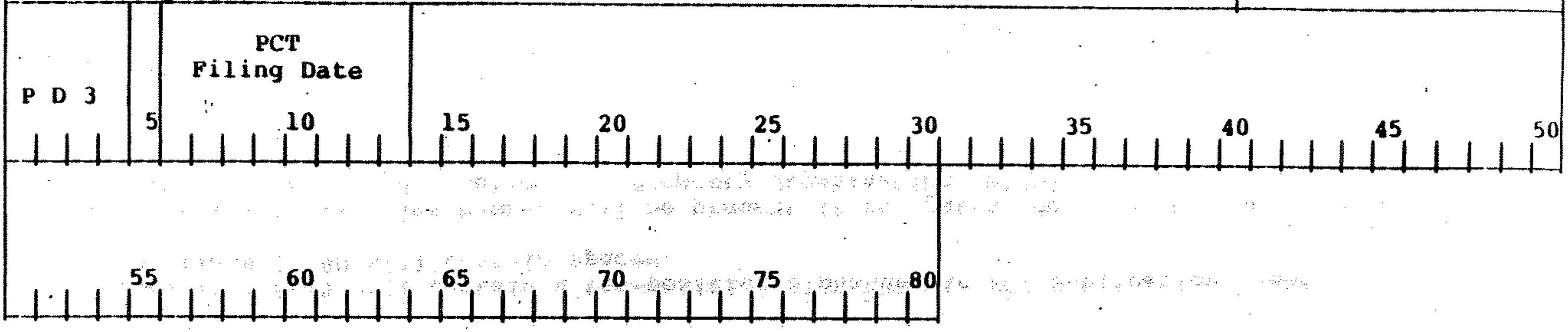


The ID Code (Positions 1-4) will contain PD2 identifying the record as a PCT 102(e) Date record.

Positions 6-13 will contain an eight-position numeric date in the format YYYYMMDD.
Positions 14-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required Optional

PCT Filing Date - PD3 - (PCTA)



The ID Code (Positions 1-4) will contain PD3 identifying the record as a PCT Filing Date record.

Positions 6-13 wil contain an eight-position numeric date in the format YYYYDDMM.
Positions 14-80 will contain spaces.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required x Optional
PCT Publication Number - PCP - (PCTA)		

P C P		PCT Publication Number	
1-4	5	6-15	16-80

The ID Code (Positions 1-4) will contain PCP identifying the record as a PCT Publication Number record.

Positions 6-15 will contain a ten-position alphanumeric PCT Publication Number.
Positions 16-80 will contain spaces.

NOTE: The PCT Publication Number will be present if the patent document has been published through the World Intellectual Property Organization (WIPO).

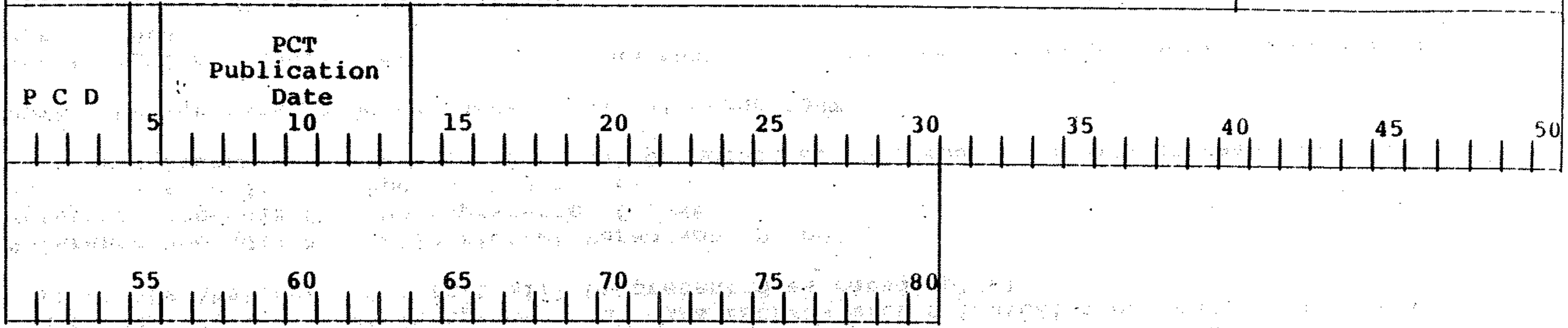
RECORD LAYOUT

Patent Full-Text/APS File

Logical Group/Field

___ Required
x Optional

PCT Publication Date - PCD - (PCTA)



The ID Code (Positions 1-4) will contain PCD identifying the record as a PCT Publication Date record.

Positions 6-13 will contain an eight-position numeric date in the format YYYYMMDD. Positions 14-80 will contain spaces.

NOTE: The PCT Publication Date will be present if the patent document has been published through the World Intellectual Property Organization (WIPO).

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional
Logical Group - ABST - Abstract		

```
A B S T  5    10   15   20   25   30   35   40   45   50
|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|

         55   60   65   70   75   80
|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|_|
```

The ID Code (Positions 1-4) will contain ABST identifying logical group Abstract. Positions 5-80 will contain spaces. The data records within logical group ABST will contain the text of the Abstract. The text will be presented as paragraph(s).

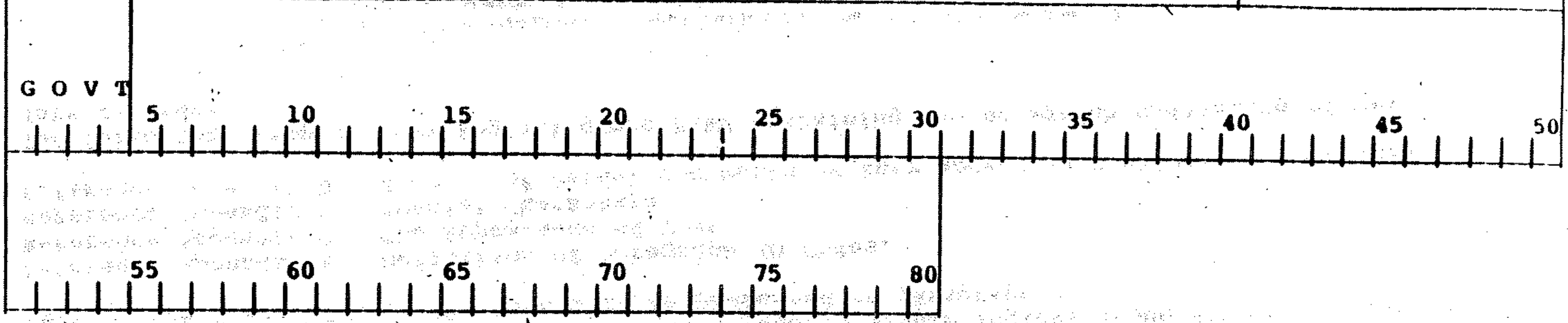
Reference Appendix A - Definition of Paragraph ID Codes.
Reference Appendix B - The Appearance of Text.
Reference Appendix C - Special Characters.
Reference Appendix D - Example of Patent Documents as they appear in machine-readable form.

NOTE: Design Patents do not have a logical group ABST.

The following example shows logical group ABST containing one paragraph consisting of fifteen data records:

```
ABST
PAL  A novel acute care cerebral support system and method for treating severly
      ischemic brains is disclosed wherein an oxygenated nutrient emulsion is
      circulated through at least a portion of the ventriculo-subarachnoid
      spaces. The nutrient emulsion contains an oxygenatable non-aqueous
      component, an aqueous nutrient component, an emulsification component, and
      other components which render physiologic acceptability to the nutrient
      emulsion. The disclosed system and method have been shown to effectively
      exchange oxygen, carbon dioxide, glucose, and other metabolites in
      severely stroked brains. Significant restoration of oxidative metabolism
      and electrographic activity result from the disclosed treatment. Methods
      for producing the nutrient emulsion and a system for delivering that
      emulsion to the cerebrospinal pathway   ce also disclosed. Additionally,
      novel diagnostic methods for diagnos    the physiologic state of
      hypoxic-ischmeic and other diseased r   ologic tissue during treatment are
      provided.
```

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required x Optional
Logical Group - GOVT - Government Interest		



The ID Code (Positions 1-4) will contain GOVT identifying logical group Government Interest. Positions 5-80 will contain spaces. The data records within logical group GOVT will contain the text of the Statement of Government Interest. The text will be presented as paragraph(s).

Reference Appendix A - Definition of Paragraph ID Codes.
Reference Appendix B - The Appearance of Text.
Reference Appendix C - Special Characters.
Reference Appendix D - Example of Patent Documents as they appear in machine-readable form.

The statement of government interest is present when the patent was issued as result of government financed research, etc.

The following example shows logical group GOVT containing two paragraph consisting of four data records:

```
GOVT
PAC  STATEMENT OF GOVERNMENT INTEREST
PAR  The invention described herein may be manufactured and used by or for the
      Government of the United States of America for governmental purposes
      without the payment of any royalties thereon or therefor.
```

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Logical Group - PARN - Parent Case Text		

P A R N

5 10 15 20 25 30 35 40 45 50

55 60 65 70 75 80

The ID Code (Positions 1-4) will contain PARN identifying logical group Parent Case Text. Positions 5-80 will contain spaces. The data records within logical group PARN will contain the text of the Parent Case. The text will be presented as paragraph(s).

Reference Appendix A - Definition of Paragraph ID Codes.
Reference Appendix B - The Appearance of Text.
Reference Appendix C - Special Characters.
Reference Appendix D - Example of Patent Documents as they appear in machine-readable form.

The following example shows logical group PARN containing one paragraph consisting of two data records:

```
PARN
PAR  This is a continuation. of application Ser. No. 713,768 filed Aug. 12.
      1976. now abandoned.
```

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required Optional
Logical Group - BSUM - Brief Summary		

B S U M	5	10	15	20	25	30	35	40	45	50
	55	60	65	70	75	80				

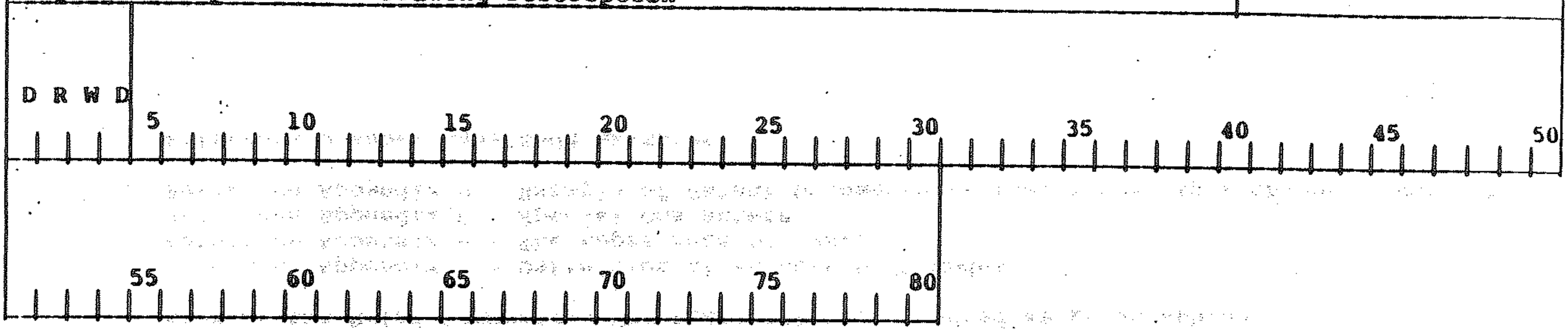
The ID Code (Positions 1-4) will contain BSUM identifying logical group Brief Summary. Positions 5-80 will contain spaces. The data records within logical group BSUM will contain the text of the Brief Summmary. The text will be presented as paragraph(s).

Reference Appendix A - Definition of Paragraph ID Codes.
Reference Appendix B - The Appearance of Text.
Reference Appendix C - Special Characters.
Reference Appendix D - Example of Patent Documents as they appear in machine-readable form.

Reference D shows many BSUM examples.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional

Logical Group - DRWD - Drawing Description



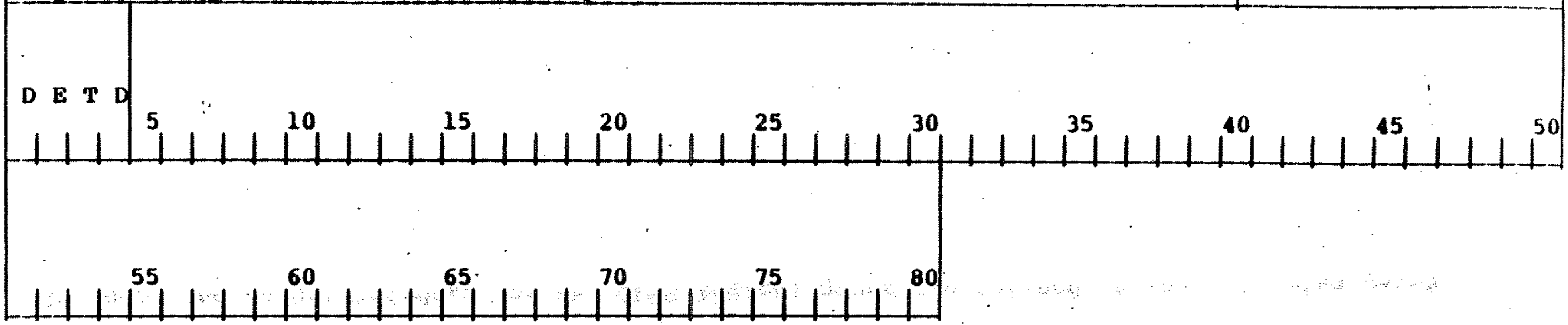
The ID Code (Positions 1-4) will contain DRWD identifying logical group Drawing Description. Positions 5-80 will contain spaces. The data records within logical group DRWD will contain the text describing the drawing. The text will be presented as paragraph(s).

Reference Appendix A - Definition of Paragraph ID Codes.
Reference Appendix B - The Appearance of Text.
Reference Appendix C - Special Characters.
Reference Appendix D - Example of Patent Documents as they appear in machine-readable form.

The following example shows logical group DRWD containing eight paragraphs consisting of sixteen records.

```
DRWD
PAC  BRIEF DESCRIPTION OF THE DRAWINGS
PAR  The accompanying drawings illustrate the invention. In such drawings:
PAR  FIG. 1 is a schematic diagram illustrating a pneumatic starting system for
       a gas turbine machine, and including a pressure regulator system of this
       invention;
PAR  FIG. 2 is a vertical section of a pressure reduction regulator for use in
       the regulator system;
PAR  FIG. 3 is an enlarged fragmented view of the reduction regulator of FIG. 2,
       showing the regulator in a position closed to fluid flow;
PAR  FIG. 4 is an enlarged fragmented view similar to FIG. 3, showing the
       reduction regulator in a position open to fluid flow;
PAR  FIG. 5 is an enlarged fragmented view similar to FIGS. 3 and 4, partially
       exploded, illustrating the interfitting components of the reduction
       regulator valve seat; and
PAR  FIG. 6 is a vertical section, partially fragmented, of an improved solenoid
       valve assembly for use in the system
```

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field ___ Required _x_ Optional
Logical Group - DETD - Detail Description		

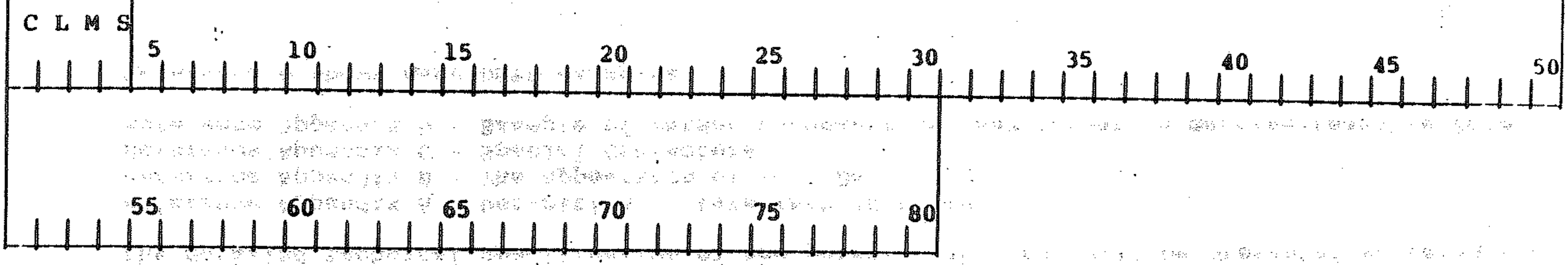


The ID Code (Positions 1-4) will contain DETD identifying logical group Detail Description. Positions 5-80 will contain spaces. The data records within logical group DETD will contain the the detailed technical specification of the patent. The text will be presented as paragraph(s).

Reference Appendix A - Definition of Paragraph ID Codes.
Reference Appendix B - The Appearance of Text Data.
Reference Appendix C - Special Characters.
Reference Appendix D - Example of Patent Documents as they appear in machine-readable form.

Reference D shows many DETD examples.

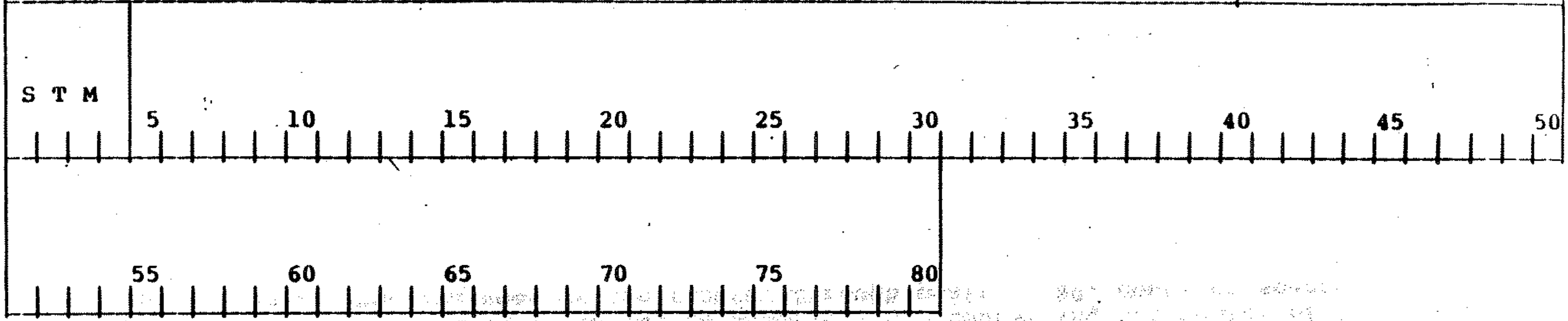
RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required ___ Optional
Logical Group - CLMS - Claims		



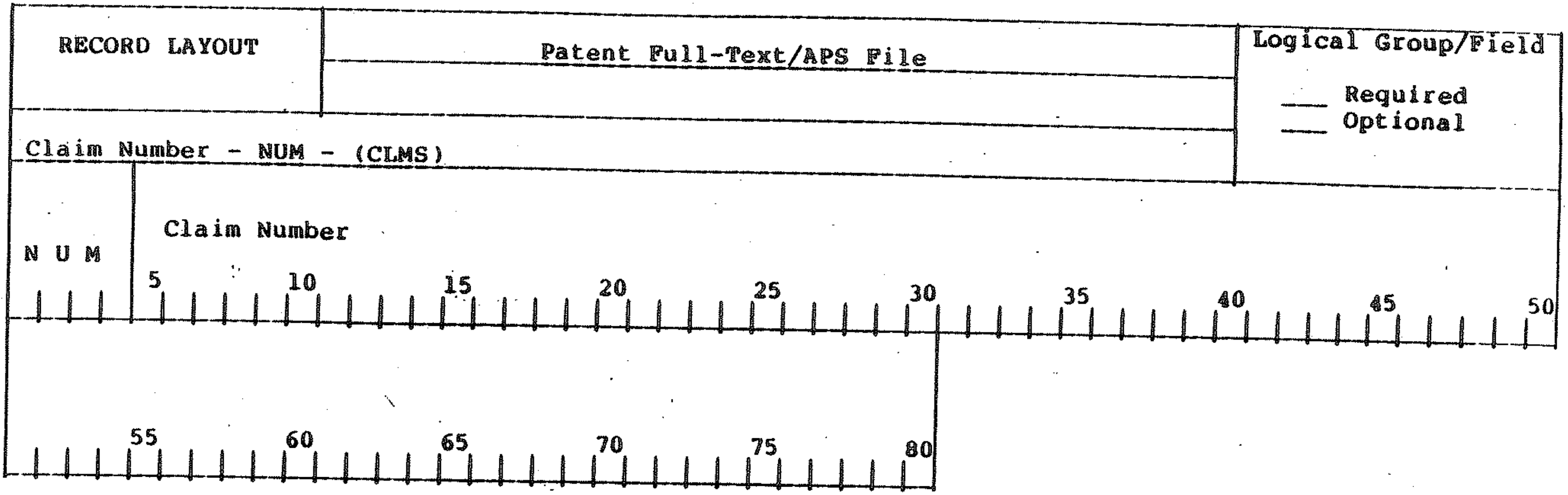
The ID Code (Positions 1-4) will contain CLMS identifying logical group Claims. Positions (5-80) will contain spaces.

ID Codes and associated data for the CLMS logical group are defined on the following pages.

RECORD LAYOUT	**Patent Full-Text/APS File**	**Logical Group/Field** ___ **Required** _x_ **Optional**
Claim Statement - STM - (CLMS)		

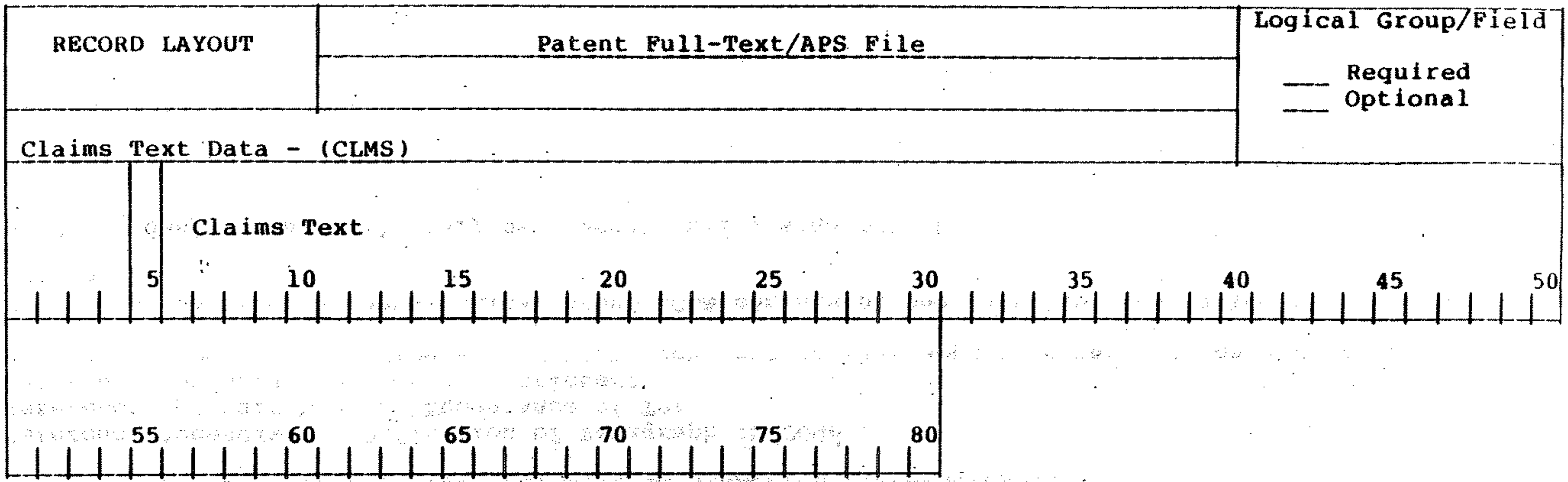


The ID Code (Positions 1-4) will contain STM identifying the record as a claim statement record.



The ID Code (Positions 1-4) will contain NUM identifying the record as a claim number record.

Position 6 will begin a variable length numeric field containing the number of the claim that follows. The remainder of the record, through position 80, contains spaces.



The ID Code (Positions 1-4) will contain the appropriate paragraph ID Code to begin a paragraph of text data. Reference Appendix A - Definition of Paragraph ID Codes.

The text of the claim will begin in position 6 as a variable length alphanumeric field. If continuation record(s) are required, positions 6-80 will contain the continuation data. Reference Appendix B - The Appearance of Text.

Reference Appendix C - Special Characters.
Reference Appendix D - Example of Patent Documents as they appear in machine-readable form.

RECORD LAYOUT	Patent Full-Text/APS File	Logical Group/Field x Required Optional
Logical Group - DCLM - Design Claim		

D C L M

5 10 15 20 25 30 35 40 45 50

55 60 65 70 75 80

The ID Code (Positions 1-4) will contain DCLM identifying logical group Design Claim. Positions 5-80 will contain spaces. The data records within logical group DCLM will contain the text of the design claim. The text will be presented as paragraph(s).

Reference Appendix A - Definition of Paragraph ID Codes.
Reference Appendix B - The Appearance of Text.
Reference Appendix C - Special Characters.
Reference Appendix D - Example of Patent Documents as they appear in machine-readable form.

The following example shows logical group DCLM containing one paragraph consisting of two records.

NOTE: A design claim will only be present in a design patent.

ANSI-STANDARD-LABEL (EOV)

First End-of-Volume Label (EOV1)

CP	Field Name	L	Content
1 to 3	Label Identifier	3	EOV
4	Label Number	1	1
5 to 54	Same as the corresponding fields in HDR1	50	Same as the corresponding fields in HDR1
55 to 60	Block Count	6	"n" characters. Denotes the number of data blocks since the preceding Beginning-of-File-Section Label Group.
61 to 80	Same as the corresponding fields in HDR1	20	Same as the corresponding fields in HDR1

Second End-of-Volume Label (EOV2)

CP	Field Name	L	Content
1 to 3	Label Identifier	3	EOV
4	Label Number	1	2
5 to 80	Same as the corresponding fields in HDR2	76	Same as the corresponding fields in HDR2

NSI-STANDARD-LABEL (EOF1)

First End-of-File Label (EOF1)

CP	Field Name	L	Content
1 to 3	Label Identifier	3	EOF
4	Label Number	1	1
5 to 54	Same as the corresponding fields in HDR1	50	Same as the corresponding fields in HDR1
55 to 60	Block Count	6	"n" characters. Denotes the number of data blocks since the preceding Beginning-of-File-Section Label Group.
61 to 80	Same as the corresponding fields in HDR1	20	Same as the corresponding fields in HDR1

ANSI-STANDARD-LABEL (EOF2)

Second End-of-File Label (EOF2)

CP	Field Name	L	Content
1 to 3	Label Identifier	3	EOF
4	Label Number	1	2
5 to 80	Same as the corresponding fields in HDR2	76	Same as the corresponding fields in HDR2

Table 1

Check Digit Modulus 11

A check digit is established for each patent number and application serial number that appears on the full-text file. The patent number check digit will appear in the 9th position of each record following the patent number. The check digit for the application serial number will appear in the 8th position of the Selected Front Page Information element. The check digit is derived in the following manner:

> Multiply the right most numeric position of the field by 2, the next numeric position to the left by 3, the next by 4, the next by 5, etc.
>
> The products are added and divided by 11. The resulting remainder is subtracted from 11, which produces the check digit. The exception will be if the result is 11, the check digit will be 0, if the result is 10, the check digit will appear as an ampersand (&).

TABLE 2
U.S. POST OFFICE STANDARD STATE ABBREVIATONS

ALASKA	AK	MONTANA	MT
ALABAMA	AL	NEBRASKA	NE
ARKANSAS	AR	NORTH CAROLINA	NC
ARIZONA	AZ	NORTH DAKOTA	ND
CALIFORNIA	CA	NEW HAMPSHIRE	NH
COLORADO	CO	NEW JERSEY	NJ
CONNECTICUT	CT	NEW MEXICO	NM
CANAL ZONE	CZ	NEW YORK	NY
DISTRICT OF COLUMBIA	DC	NEVADA	NV
DELAWARE	DE	OHIO	OH
FLORIDA	FL	OKLAHOMA	OK
GEORGIA	GA	OREGON	OR
HAWAII	HI	PENNSYLVANIA	PA
IOWA	IA	PUERTO RICO	PR
IDAHO	ID	RHODE ISLAND	RI
ILLINOIS	IL	SOUTH CAROLINA	SC
INDIANA	IN	SOUTH DAKOTA	SD
KANSAS	KS	TENNESSEE	TN
KENTUCKY	KY	TEXAS	TX
LOUISIANA	LA	UTAH	UT
MASSACHUSETTS	MA	VIRGINIA	VA
MARYLAND	MD	VIRGIN ISLANDS	VI
MAINE	ME	VERMONT	VT
MICHIGAN	MI	WASHINGTON	WA
MINNESOTA	MN	WISCONSIN	WI
MISSOURI	MO	WEST VIRGINIA	WV
MISSISSIPPI	MS	WYOMING	WY

NOTE: The state abbreviation for Nebraska prior to July 4, 1978 is NB.

Table 3A International Country Abbreviations
(2-Character)

Afganistan	AF
Albania	AN
Algeria	AG
Andorra	AD
Argentina	AR
Australia	AU
Austria	OE
Bahrain	BB
Barbados	BD
Belgium	BE
Bhutan	BH
Bolivia	BO
Botswana	BT
Brazil	BR
Bulgaria	BG
Burma	BU
Burundi	BI
Byelorussian SSR	SB
Cameroon	KA
Canada	CA
Central African Republic	ZR
Chad	TS
Chile	CE
China	RC
Colombia	CO
Congo	CF
Costa Rica	CR
Cuba	CU
Cyprus	CY
Czechoslovakia	CS
Dahomey	DA
Democratic Republic of Viet-Nam	VN
Democratic Yemen	SY
Denmark	DK
Dominican Republic	DR
Ecuador	EC
Egypt	ET
El Salvador	SL
Ethiopia	EA

Finland	SF
France	FR
Gabon	GA
Gambia	GE
German Democratic Republic	DL
Germany, Federal Republic of	DT
Ghana	GH
Greece	GR
Guatemala	GU
Guinea	GI
Guyana	GY
Haiti	HI
Holy See	CV
Honduras	HO
Hungary	HU
Iceland	IS
India	IN
Indonesia	ID
Iran	IR
Iraq	I[illegible]
Ireland	EI
Israel	IL
Italy	IT
Ivory Coast	CI
Jamaica	JM
Japan	JA
Jordan	JO
Kenya	KE
Khmer Republic	CD
Kuwait	KU
Laos	LA
Lebanon	LB
Lesotho	LS
Liberia	LR
Libyan Arab Republic	LY
Liechtenstein	FL
Luxembourg	LU

Table 3A - (continued)

Madagascar	MD
Malawi	MW
Malaysia	MY
Maldives	MV
Mali	MJ
Malta	ML
Mauritania	MT
Mauritius	MS
Mexico	MX
Monaco	MC
Mongolia	MO
Morocco	MA
Nepal	NP
Netherlands	NL
New Zealand	NZ
Nicaragua	NA
Niger	NI
Nigeria	WN
Norway	NO
Oman	OM
Pakistan	PK
Panama	PM
Paraguay	PG
People's Democratic Republic of Korea	KN
Peru	PE
Philippines	RP
Poland	PO
Portugal	PT
Qatar	QA
Republic of China	CT
Republic of Korea	KS
Republic of Viet-Nam	VS
Rhodesia	RH
Romania	RU
Rwanda	RW
San Marino	SM
Saudi Arabia	SA
Senegal	SN
Sierra Leone	WL
Singapore	SG
Somalia	SO
South Africa	ZA
Soviet Union	SU
Spain	ES
Sri Lanka	CL
Sudan	SD
Sweden	SW
Switzerland	CH
Syrian Arab Republic	SR
Thailand	TH
Togo	TO
Trinidad and Tobago	TD
Tunisia	TN
Turkey	TR
Uganda	UG
Ukranian SSR	UU
United Kingdom	GB
United Republic of Tanzania	TA
United States of America	US
Upper Volta	UV
Uruguay	UY
Venezuela	VE
Western Samoa	WS
Yemen	YE
Yugoslavia	YU
Zaire	CB
Zambia	ZB

TABLE 3B

INTERNATIONAL COUNTRY ABBREVIATIONS
(3-Characters)

ICIREPAT COUNTRY CODES AND CODES FOR U.S. AGENCIES

The following are two complete lists of ICIREPAT country codes; country codes to be used for international organizations in the field of industrial property, as well as the country codes to be used or international agreements (such as Benelux, Hague, and Libreville); and a list of codes to be used in the data base to generate the names of certain U.S. Government agencies.

The first list, entitled, "ICIREPAT Country Codes - Alphabetized by Country Name," includes the names of the countries as they are to appear on the printed patent front page.

The second list, entitled, "Country Names - Alphabetized by Country Codes," presents an alphabetical listing by country code.

The third list indicates which country codes to use for international organizations in the field of industrial property, as well as those codes which are applicable for international agreements, such as Benelux, Hague, and Libreville.

The fourth list indicates the codes to use to generate the names of certain U.S. Government agencies.

The following countries do not appear in the first two lists of country codes. These countries were previously assigned their own country codes, but they now form parts of other countries.

Country	Now a Part of
British Antarctic Territory	Antarctica
Byelorussian SSR	U.S.S.R.
Dronning Maud Land	Antarctica
New Guinea	Indonesia and Papua New Guinea
Portuguese Timor	Indonesia
Ryuku Islands	Japan
Sikkim	India
Swann Islands	Honduras
Ukranian SSR	U.S.S.R.

Note that Euratom is no longer listed. Also the Code "KN," which was previously assigned to the British West Indies, is now used to designate the islands of St. Christopher-Nevis-Anquilla. The islands of Jamaica, The Bahamas, Barbados, and Trinidad and Tobago, which previously formed a part of the British West Indies, are now independent and are assigned their own individual codes.

An "X" will appear in the third position of all country codes in the data base (i.e., AFX, ALX, DZX, etc.), with the exception of those locations marked with an asterisk on the following pages.

Locations which do not have their own ICIREPAT country codes are assigned the same code as the higher political or geographic entity of which they form a part or to which they belong. Channel Islands, England, Great Britain, Northern Ireland, Scotland, and Wales, for instance, are all divisions of the United Kingdom and are also assigned the GB country codes. To differentiate these locations from the higher entity, the third position has been designated as a numeral (i.e., Channel Islands is GB1; England is GB2; Great Britain is GB3, etc.). By using the GB2 code, for instance, the correct geographic location can be generated for the inventor and/or the assignee.

ICIREPAT COUNTRY CODES

ALPHABETIZED BY COUNTRY NAME

COUNTRY	CODE*	SPELLING FOR PATENTS
Afghanistan	AF	Afghanistan
Albania	AL	Albania
Algeria	DZ	Algeria
American Samoa	AS	American Samoa
Andorra	AD	Andorra
Angola	AO	Angola
Antarctica	AQ	Antarctica
Antigua	AG	Antigua
Argentina	AR	Argentina
Australia	AU	Australia
Austria	AT	Austria
Bahamas, The (formerly Bahamas)	BS	The Bahamas
Bahrain	BH	Bahrain
Bangladesh	BD	Bangladesh
Barbados	BB	Barbados
Belgium	BE	Belgium
Belize	BZ	Belize
Benin (formerly Dahomey)	BJ	Benin
Bermuda	BM	Bermuda
Bhutan	BT	Bhutan
Bolivia	BO	Bolivia
Botswana	BW	Botswana
Bouvetoya (formerly Bouvet Island)	BV	Bouvetoya
Brazil	BR	Brazil
British Indian Ocean Territory	IO	Br. Indian Ocean Ter.
British Virgin Islands	VG	British Virgin Isls.
Brunei	BN	Brunei
Bulgaria	BG	Bulgaria
Burma	BU	Burma
Burundi	BI	Burundi
Cambodia	KH	Cambodia
Cameroon	CM	Cameroon
Canada	CA	Canada
Canal Zone	PZ	Canal Zone
Canton and Enderbury Islands	CT	Canton/Enderbury Isls.
Cape Verde, Republic of	CV	Rep. of Cape Verde

COUNTRY	CODE	SPELLING FOR PATENTS
Cayman Islands	KY	Cayman Islands
Central African Empire (formerly Central African Republic)	CF	Cen. African Empire
Chad	TD	Chad
*Channel Islands	GB1	Channel Islands
Chile	CL	Chile
China (Taiwan)	TW	Taiwan
China	CN	China
Christmas Island	CX	Christmas Island
Cocos (Keeling) Islands	CC	Cocos (Keeling) Isls.
Colombia	CO	Colombia
Comoros (formerly Comoros Islands)	KM	Comoros
Congo	CG	Congo
Cook Islands	CK	Cook Islands
Costa Rica	CR	Costa Rica
Cuba	CU	Cuba
Cyprus	CY	Cyprus
Czechoslovakia	CS	Czechoslovakia
Denmark	DK	Denmark
Dominica	DM	Dominica
Dominican Republic	DO	Dominican Republic
Ecuador	EC	Ecuador
Egypt	EG	Egypt
El Salvador	SV	El Salvador
*England	GB2	England
Equatorial Guinea	GQ	Equatorial Guinea
Ethiopia	ET	Ethiopia
Faroe Islands (formerly Faeroe Islands)	FO	Faroe Islands
Falkland Islands (Islas Malvinas)	FK	Falkland Islands (I.M.)
Fiji	FJ	Fiji
Finland	FI	Finland
France	FR	France
French Guiana	GF	French Guiana
French Polynesia	PF	French Polynesia

COUNTRY	CODE	SPELLING FOR PATENTS
French Southern and Antarctic Lands	FQ	Fr. So./Antarctic Lands
French Territory of the Afars and Issas	AI	Fr. Terr. Afars/Issas
Gabon	GA	Gabon
Gambia, The (formerly Gambia)	GM	The Gambia
German Democratic Republic	DD	German Democratic Rep.
*Germany, before 1945	DE1	Fed. Rep. of Germany
Germany, Federal Republic of	DE	Fed. Rep. of Germany
Ghana	GH	Ghana
Gibraltar	GI	Gibraltar
Gilbert Islands (formerly Gilbert and Ellice Islands)	GE	Gilbert Islands
*Great Britain	GB3	Great Britain
Greece	GR	Greece
Greenland	GL	Greenland
Grenada	GD	Grenada
Guadeloupe	GP	Guadeloupe
Guam	GU	Guam
Guatemala	GT	Guatemala
Guinea	GN	Guinea
Guinea-Bissau	GW	Guinea-Bissau
Guyana	GY	Guyana
Haiti	HT	Haiti
Heard Island and McDonald Islands	HM	Heard/McDonald Isls.
Honduras	HN	Honduras
Hong Kong	HK	Hong Kong
Hungary	HU	Hungary
Iceland	IS	Iceland
India	IN	India
Indonesia	ID	Indonesia
Iran	IR	Iran
Iraq	IQ	Iraq
Iraq-Saudi Arabia Neutral Zone	NT	Iraq-Saudi Arabia NZ
Ireland	IE	Ireland
*Isle of Man	GB4	Isle of Man
Israel	IL	Israel

COUNTRY	CODE	SPELLING FOR PATENTS
Italy	IT	Italy
Ivory Coast	CI	Ivory Coast
Jamaica	JM	Jamaica
Japan	JP	Japan
Johnston Atoll	JT	Johnston Atoll
Jordan	JO	Jordan
Kenya	KE	Kenya
Korea, Democratic Peoples Republic of	KP	D.P.R. of Korea
Korea, Republic of	KR	Rep. of Korea
Kuwait	KW	Kuwait
Laos	LA	Laos
Lebanon	LB	Lebanon
Lesotho	LS	Lesotho
Liberia	LR	Liberia
Libya	LY	Libya
Liechtenstein	LI	Liechtenstein
Luxembourg	LU	Luxembourg
Macao	MO	Macao
Madagascar (formerly Malagasy Republic)	MG	Madagascar
Malawi	MW	Malawi
Malaysia	MY	Malaysia
Maldives	MV	Maldives
Mali	ML	Mali
Malta	MT	Malta
Martinique	MQ	Martinique
Mauritania	MR	Mauritania
Mauritius	MU	Mauritius
Mexico	MX	Mexico
Midway Islands	MI	Midway Islands
Monaco	MC	Monaco
Mongolia	MN	Mongolia
Montserrat	MS	Montserrat
Morocco	MA	Morocco
Mozambique	MZ	Mozambique
*Muscat	OM1	Muscat
Namibia (formerly South-West Africa)	NA	Namibia

COUNTRY	CODE	SPELLING FOR PATE.
Nauru	NR	Nauru
Navassa Island	NV	Navassa Island
Nepal	NP	Nepal
Netherlands	NL	Netherlands
Netherlands Antilles	AN	Netherlands Antilles
New Caledonia	NC	New Caledonia
New Hebrides	NH	New Hebrides
New Zealand	NZ	New Zealand
Nicaragua	NI	Nicaragua
Niger	NE	Niger
Nigeria	NG	Nigeria
Niue	NU	Niue
Norfolk Island	NF	Norfolk Island
*Northern Ireland	GB5	Northern Ireland
Norway	NO	Norway
Oman	OM	Oman
Pakistan	PK	Pakistan
Panama	PA	Panama
Papua New Guinea	PG	Papua New Guinea
Paracel Islands	PI	Paracel Islands
Paraguay	PY	Paraguay
Peru	PE	Peru
Philippines	PH	Philippines
Pitcairn (formerly Pitcairn Island)	PN	Pitcairn
Poland	PL	Poland
Portugal	PT	Portugal
Puerto Rico	PR	Puerto Rico
Qatar	QA	Qatar
Reunion	RE	Reunion
Romania	RO	Romania
Rwanda	RW	Rwanda
St. Christopher-Nevis-Anguilla	KN	St. Chris.-Nevis-Ang.
St. Helena	SH	St. Helena
St. Lucia	LC	St. Lucia
St. Pierre and Miquelon	PM	St. Pierre/Miquelon
St. Vincent	VC	St. Vincent
San Marino	SM	San Marino
Sao Tome and Principe	ST	Sao Tome/Principe

COUNTRY	CODE	SPELLING FOR PATENTS
Saudi Arabia	SA	Saudi Arabia
*Scotland	GB6	Scotland
Senegal	SN	Senegal
Seychelles	SC	Seychelles
Sierra Leone	SL	Sierra Leone
Singapore	SG	Singapore
Solomon Islands	SB	Solomon Islands
Somalia	SO	Somalia
South Africa	ZA	South Africa
Southern Rhodesia	RH	Southern Rhodesia
Spain	ES	Spain
Spratly Islands	SI	Spratly Islands
Sri Lanka	LK	Sri Lanka
Sudan	SD	Sudan
Surinam	SR	Surinam
Svalbard and Jan Mayen	SJ	Svalbard and Jan Mayen
Swaziland	SZ	Swaziland
Sweden	SE	Sweden
Switzerland	CH	Switzerland
Syria	SY	Syria
Tanzania, United Republic of	TZ	United Rep. of Tanzania
Thailand	TH	Thailand
*Tibet	CN1	Tibet
Togo	TG	Togo
Tokelau Islands	TK	Tokelau Islands
Tonga	TO	Tonga
Trinidad and Tobago	TT	Trinidad and Tobago
Trust Territory of the Pacific Islands (includes Caroline, Mariana, and Marshall Island groups)	PC	Trust Ter. Pacific Isl.
Tunisia	TN	Tunisia
Turkey	TR	Turkey
Turks and Caicos Islands	TC	Turks and Caicos Isls.
Tuvalu (formerly Gilbert and Ellice Islands)	TV	Tuvalu
Uganda	UG	Uganda

COUNTRY	CODE	SPELLING FOR PATENTS
Union of Soviet Socialist Republics	SU	U.S.S.R.
United Arab Emirates	AE	United Arab Emirates
United Kingdom	GB	United Kingdom
United States	US	United States
United States Miscellaneous Pacific Islands (includes Kingman Reef, Howland, Baker and Jarvis Islands, and Palmyra Atoll)	PU	U.S. Misc. Pac. Isls.
Upper Volta	HV	Upper Volta
Uruguay	UY	Uruguay
Vatican City	VA	Vatican City
Venezuela	VE	Venezuela
Vietnam (formerly Democratic Republic of Vietnam and Republic of South Vietnam)	VN	Vietnam
Virgin Islands of the U.S.	VI	Virgin Isls. of U.S.
Wake Island	WK	Wake Island
*Wales	GB7	Wales
Wallis and Futuna	WF	Wallis and Futuna
Western Sahara (formerly Spanish Sahara)	EH	Western Sahara
Western Samoa	WS	Western Samoa
Yemen (Aden)	YD	Yemen (Aden)
Yemen (Sana)	YE	Yemen (Sana)
Yugoslavia	YU	Yugoslavia
Zaire	ZR	Zaire
Zambia (formerly Northern Rhodesia)	ZM	Zambia

COUNTRY NAMES
ALPHABETIZED BY COUNTRY CODES

CODE	COUNTRY
AD	Andorra
AE	United Arab Emirates
AF	Afghanistan
AG	Antigua
*AI	French Territory of the Afars and Issas
*AL	Albania
AN	Netherlands Antilles
AO	Angola
*AQ	Antarctica
AR	Argentina
AS	American Samoa
*AT	Austria
AU	Australia
*BB	Barbados
*BD	Bangladesh
BE	Belgium
BG	Bulgaria
*BH	Bahrain
BI	Burundi
*BJ	Benin
BM	Bermuda
BN	Brunei
BO	Bolivia
BR	Brazil
BS	The Bahamas
*BT	Bhutan
BU	Burma
*BV	Bouvetoya
*BW	Botswana
BZ	Belize
CA	Canada
*CC	Cocos (Keeling) Islands
*CF	Central African Empire
*CG	Congo
CH	Switzerland
CI	Ivory Coast
*CK	Cook Islands
*CL	Chile
*CM	Cameroon

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*These countries were assigned new or revised ICIREPAT Country Codes, effective January 1, 1978.

CODE	COUNTRY
*CN	China
*CN1	Tibet
CO	Colombia
CR	Costa Rica
CS	Czechoslovakia
*CT	Canton and Enderbury Islands
CU	Cuba
CV	Republic of Cape Verde
*CX	Christmas Island
CY	Cyprus
*DD	German Democratic Republic
*DE	Federal Republic of Germany
*DE1	Germany, before 1945
DK	Denmark
*DM	Dominica
*DO	Dominican Republic
*DZ	Algeria
EC	Ecuador
*EG	Egypt
*EH	Western Sahara
ES	Spain
*ET	Ethiopia
*FI	Finland
FJ	Fiji
*FK	Falkland Islands (Islas Malvinas)
*FO	Faroe Islands
*FQ	French Southern and Antarctic Lands
FR	France
GA	Gabon
GB	United Kingdom
*GB1	Channel Islands
*GB2	England
*GB3	Great Britain
*GB4	Isle of Man
*GB5	Northern Ireland
*GB6	Scotland
*GB7	Wales
GD	Grenada
*GE	Gilbert Islands
*GF	French Guiana
GH	Ghana
*GI	Gibraltar
*GL	Greenland
*GM	The Gambia
*GN	Guinea
*GP	Guadaloupe
GQ	Equatorial Guinea
GR	Greece

CODE	COUNTRY
*GT	Guatemala
*GU	Guam
GW	Guinea-Bissau
GY	Guyana
HK	Hong Kong
*HM	Heard Island and McDonald Islands
*HN	Honduras
*HT	Haiti
HU	Hungary
*HV	Upper Volta
ID	Indonesia
*IE	Ireland
IL	Israel
IN	India
*IO	British Indian Ocean Territory
IQ	Iraq
IR	Iran
IS	Iceland
IT	Italy
JM	Jamaica
JO	Jordan
*JP	Japan
*JT	Johnston Atoll
KE	Kenya
*KH	Cambodia
KM	Comoros
KN	St. Christopher-Nevis-Anquilla
*KP	Democratic Peoples Republic of Korea
*KR	Republic of Korea
*KW	Kuwait
*KY	Cayman Islands
LA	Laos
LB	Lebanon
*LC	St. Lucia
*LI	Liechtenstein
*LK	Sri Lanka
LR	Liberia
LS	Lesotho
LU	Luxembourg
LY	Libya
MA	Morocco
MC	Monaco
*MG	Madagascar

CODE	COUNTRY
*MI	Midway Islands
*ML	Mali
*MN	Mongolia
*MO	Macao
*MQ	Martinique
*MR	Mauritania
*MS	Montserrat
*MT	Malta
*MU	Mauritius
MV	Maldives
MW	Malawi
MX	Mexico
MY	Malaysia
MZ	Mozambique
NA	Namibia
NC	New Caledonia
*NE	Niger
*NF	Norfolk Island
*NG	Nigeria
*NH	New Hebrides
*NI	Nicaragua
NL	Netherlands
NO	Norway
NP	Nepal
NR	Nauru
*NT	Iraq-Saudi Arabia Neutral Zone
*NU	Niue
*NV	Navassa Island
NZ	New Zealand
*OM	Oman
*OM1	Muscat
*PA	Panama
PC	Trust Territory of the Pacific Islands
PE	Peru
*PF	French Polynesia
*PG	Papua New Guinea
PH	Philippines
*PI	Paracel Islands
PK	Pakistan
*PL	Poland
*PM	St. Pierre and Miquelon
*PN	Pitcairn
PR	Puerto Rico
PT	Portugal
*PU	United States Miscellaneous Pacific Islands
*PY	Paraguay
PZ	Canal Zone

CODE	COUNTRY
QA	Qatar
*RE	Reunion
RH	Southern Rhodesia
*RO	Romania
RW	Rwanda
SA	Saudi Arabia
*SB	Solomon Islands
SC	Seychelles
SD	Sudan
*SE	Sweden
SG	Singapore
*SH	St. Helena
*SI	Spratly Islands
*SJ	Svalbard and Jan Mayen
*SL	Sierra Leone
SM	San Marino
SN	Senegal
SO	Somalia
SR	Surinam
ST	Sao Tome and Principe
SU	Union of Soviet Socialist Republics
*SV	El Salvador
*SY	Syria
SZ	Swaziland
*TC	Turks and Caicos Islands
*TD	Chad
*TG	Togo
TH	Thailand
*TK	Tokolau Islands
TN	Tunisia
*TO	Tonga
TR	Turkey
*TT	Trinidad and Tobago
*TV	Tuvalu
*TW	China (Taiwan)
*TZ	United Republic of Tanzania
UG	Uganda
US	United States
UY	Uruguay
*VA	Vatican City
*VC	St. Vincent
VE	Venezuela
*VG	British Virgin Islands
VI	Virgin Islands of the U.S.
*VN	Vietnam

CODE	COUNTRY
*WF	Wallis and Futuna
*WK	Wake Island
WS	Western Samoa
*YD	Yemen (Aden)
YE	Yemen (Sana)
YU	Yugoslavia
ZA	South Africa
*ZM	Zambia
*ZR	Zaire

CODING FOR U.S. AGENCIES

The following U.S. Government agencies will be coded in the data base as shown:

Agency	Code
U.S. Air Force	USF
U.S. Army	USA
U.S. Navy	USN
NASA	USS
ERDA	USE

COUNTRY CODES FOR INTERNATIONAL ORGANIZATIONS IN THE FIELD OF INDUSTRIAL PROPERTY

World Intellectual Property Organization (WIPO). . . . . WO*

European Patent Organization (EPO) . . . . EP*

International Patent Institute (IIB) . . . . IB*

African Intellectual Property Organization (OAPI). . . . OA

COUNTRY CODES FOR INTERNATIONAL AGREEMENTS

The following Country Codes have been assigned to international agreements (or treaties) entered into by various Convention countries:

Benelux Designs Convention (printed on the patent front page as "Benelux") . . . . XB

Hague Agreement Concerning the International Deposit of Industrial Designs (printed on the patent front page as "Hague") . . . . XH

Libreville Agreement (printed on the patent front page as "Libreville"). This Country Code is the same as African Intellectual Property Organization, above. . . . . OA

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*As of January 24, 1978, the Patent Cooperation Treaty (PCT) went into effect. Applications filed under that treaty are designated as World Intellectual Property Organization (WIPO) applications, and are coded "WO". Applications filed with the European Patent Organization (EPO), a separate administrative and technical organization involving nine countries, became effective January 1, 1978, and are coded "EP". The International Patent Institute (IIB), which is a searching authority for the EPO, also became effective January 1, 1978. (There is only a remote possibility, however, that an application will ever be filed with the IIB.)

Appendix A - Definition of Paragraph ID Codes

The following information defines the types of paragraph ID Codes that may appear in data records containing text. The definition identifies the appearance of the printed document.

ID Code (positions 1-4) of data records)	Definition
PAR	This ID Code begins a new paragraph with an indented first line and all subsequent lines justified to the left margin.
PAC	This ID Code begins data that is centered and is generally used in text headings or titles.
PAL	This ID Code begins a new paragraph with all lines justified to the left margin.
PA0	This ID Code begins a new paragraph with the first line left justified and all subsequent lines indented 1 space.
PA1	This ID Code begins a new paragraph with the first line indented 1 space and all subsequent lines indented 2 spaces.
PA2	This ID Code begins a new paragraph with the first line indented 2 spaces and all subsequent lines indented 3 spaces.
PA3	This ID Code begins a new paragraph with the first line indented 3 spaces and all subsequent lines indented 4 spaces.
PA4	This ID Code begins a new paragraph with the first line indented 4 spaces and all subsequent lines indented 5 spaces.
PA5	This ID Code begins a new paragraph with the first line indented 5 spaces and all subsequent lines indented 6 spaces.
FNT[1]	This ID Code begins a footnote with all lines justified to the left margin.

---

[1] A footnote in a table will be considered a part of the table (ID Code - TBL or TBL3) and will not have a FNT ID Code.

Appendix A - Definition of Paragraph ID Codes (continued)

ID Code (positions 1-4) of data records)	Definition
TBL	This ID Code identifies the beginning of a table. All data appears within appropriate columns. A hex "0D" character will be present in position 80 of each table record.
TBL3	This ID Code identifies the beginning of a three-column table. A three-column table is a table that is rotated on its side (landscape) in a printed patent document. All rules in Appendix B - The appearance of Text, 1. Data Records will apply to TBL3 tables. Due to the size of a TBL3 table, data does not appear within columns.
EQU	This ID Code identifies the beginning of an in-line equation. An in-line equation is one that can appear on a data line(s and does not have characters or symbols that are drawn above or below a line.

Appendix B - The Appearance of Text

1. Data Records

All text data will be placed in fixed length records formatted as follows:

Positions 1-4	ID Code - (position 4 of the ID Code for data fields will contain a space)
Position 5	Will contain a space in all records
Positions 6-80	Text Data

The ID Code (Positions 1-4) will identify the type of text. Example: TTL for Title of Invention, PAR begins a new paragraph. All possible ID Codes are defined throughout this technical reference.

The text data will appear in positions 6-80 of each record. If a series of text data requires more than one record (75 characters) continuation record(s) will be used. The ID Code (Positions 1-4) of continuation records will contain spaces.

Words in text data will not be hyphenated between records. If a word cannot be completed in one record the entire word will be placed in a continuation record.

The exception to hyphenations appearing in text data is when a hypensation appeared in the printed patent document.

Trailing spaces in text data records will be ignored, leading spaces are significant and will be retained. Therefore, position 6 of continuation record will contain a space.[1]

Examples of the appearance of text data records are in Appendix D - Patent Documents as they appear in machine-readable form on the Patent Full-Text/APS File.

2. Table Data Records[2]

All table text data will be placed in fixed length records formatted as follows:

Positions 1-4	ID Code
Position 5	Will contain a space in all records
Positions 6-79	Will contain table text data.
Position 80	Will contain a Hex "0D" in each table data record.

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[1] This applies to all continuation records, bibliographic data and text data. This does not apply to table text data records.

[2] Applies to TBL tables only. TBL3 tables follow rules as defined in 1. Data Records.

The ID Code (positions 1-4) will contain "TBL " in the first record. This field will contain spaces in all subsequent records of the table.

The table text data will appear in appropriate columns (positions 6-79) of each record.

Columns will be separated by a minimium of 1 space. Therefore, if data from a column runs into another column, the data from the second or subsequent columns will appear in the appropriate column on the next record (line).

Words in table text data will not be hyphenated between records. If a word cannot be completed in one record (line), the entire word will be placed in the appropriate column on the next record (line).

The exception to hyphenations apparing in tables is when a hyphenation appeared in the printed patent document.

3. Special Characters

Patent documents contain information that, in some cases, do not have a binary representation or for photocomposition purpose must be handled with special consideration. This information appears o the patent full-text/APS file using special characters. Reference Appendix C - Special Characters.

Examples of the appearance of special characters can be found throughout the patents documents in Appendix D.

4. Chemical Structures, Tables and Equations

The location of images (chemical structures, tables and equations) residing in patent documents will be identified by a Call-Out Identifier:

Image Type	Call-Out Identifier
Chemical Structure	##STR$_n$##
Table[1]	##TBL$_n$##
Equation[2]	##EQU$_n$##
Vertical Spacing[3]	##SPC$_n$##

[1] A table call-out will only appear when table data is not present, or the complexity of the table is such that it is not feasible to make it machine-readable.

[2] An equation call-out will be present when the equation contains symbols that are drawn above or below a line.

[3] A vertical spacing call-out will be present to identify where hand inserted material would appear.

NOTE: n in the Call-Out Identifier is a number to identify the image. Each image will be numbered sequentially from the beginning of the document. The first chemical structure would be ##STR1##, the second ##STR2##, etc. Each Image Type within a patent would be numbered beginning with 1.

Appendix C - Special Characters

The following identifies special characters. Column 1 shows the appearance of special characters currently used for photocomposition. Column 2 shows the appearance of special characters on the patent full-text/APS file. A space in column 2 would appear on the file. Missing numbers in column 1 means the number is not used.

Column 1	Column 2	Hex	Description
+1	'	79	Single open quote
+2	'	79	Single close quote
+3	'	7D	Apostrophe
+4	.varies.		Varies as
+5	.ident.		Identical
+6	.notident.		Not identical
+7	.differential.		Differential
+8	[	4A	Open bracket
+9	]	5A	Close bracket
+10			Em space
+11			En space
+12			Thin space
+13	--	6060	Em dash
+14	-	60	En dash
+15	.		En leader
+16	.noteq.		Not equal symbol
+17	.intg.		Integral symbol
+18	.about.		Difference symbol
+19	.multidot.		Multiplication dot
+20	.degree.		degree symbol
+21	<		Less than symbol
+22	>		Greater than symbol
+23	.ltoreq.		Less than or equal to symbol
+24	.gtoreq.		Greater than or equal to symbol
+25	.congruent.		Congruent symbol
+26	.apprxeq.		Approx. equal symbol
+27	.cent.		Cent sign
+28	.infin.		Infinity symbol
+29	.sqroot.		Square root symbol
+30	+		Plus sign
+31	-		Minus sign
+32	=		Equal sign
+33	.times.		Multiplication sign
+34	.div.		Division sign
+35	.+-.		Plus or minus sign
+36	.-+.		Minus or plus sign
+37	"		Double open quote
+38	"		Double close quote
+39	.revreaction.		Reversible reaction symbol
+40	'	7D	Prime symbol
+41	"	7F	Double prime symbol
+42	.increment.		Increment symbol
+43	.fwdarw.		Forward arrow (right)
+44	.thrfore.		Therefore symbol
+45	.because.		Because symbol

+46	.music-sharp.		Music sharp symbol
+47	.music-flat.		Music flat symbol
+48	?		Question mark
+49	!	4F	Exclamation point
+50	.dbd.		Double bond symbol
+51	.vertline.		Vertical line symbol
+52	.uparw.		Up arrow
+53	.hoarfrost.		Hoarfrost symbol
+54	.cuberoot.		Cube root symbol
+55	{	C0	Open brace
+56	}	D0	Close brace
+57	.tbd.		Triple bond symbol
+58	.quadrature.		Quadrature symbol
+59	.gradient.		Gradient symbol
+60	.alpha.		Greek alpha symbol
+61	.sym.		Postive earth symbol (symmetry)
+62	.beta.		Greek beta symbol
+63	.crclbar.		Negative earth sym.(circle bar)
+64	.GAMMA.		Greek GAMMA symbol (upper case)
+65	.gamma.		Greek gamma symbol (lower case)
+66	.DELTA.		Greek DELTA symbol (upper case)
+67	.delta.		Greek delta symbol (lower case)
+68	.epsilon.		Greek epsilon sym. (lower case)
+69	.EPSILON.		Greek EPSILON sym. (upper case)
+70	.zeta.		Greek zeta symbol (lower case)
+71	.function.		Function symbol
+72	.eta.		Greek eta symbol
+73	.THETA.		Greek THETA symbol (upper case)
+74	.theta.		Greek theta symbol (lower case)
+75	.dwnarw.		Down arrow
+76	.lota.		Greek lota symbol
+77	.rarw.		reverse arrow - left
+78	.kappa.		Greek kappa symbol (lower case)
+79	.LAMBDA.		Greek LAMBDA symbol (upper case)
+80	.lambda.		Greek lambda symbol (lower case)
+81	.parallel.		Parallel symbol
+82	.mu.		Greek mu symbol
+83	.sup..parallel.		Superscripted parallel symbol
+84	.nu.		Greek nu symbol
+85	.XI.		Greek XI symbol (upper case)
+86	.xi.		Greek xi symbol (lower case)
+87	.sub..parallel.		Subcripted parallel symbol
+88	.omicron.		Greek omicron symbol
+89	.sub..fwdarw.		Superscripted forward arrow
+90	.pi.		Greek pi symbol (lower case)
+91	.sub..fwdarw.		subscripted forward arrow
+92	.rho.		Greek rho symbol
+93	.SIGMA.		Greek SIGMA symbol (upper case)
+94	.sigma.		Greek sigma symbol (lower case)
+95	.sup..rarw.		Superscripted reverse arrow
+96	.tau.		Greek tau symbol
+97	.UPSILON.		Greek UPSILON symbol (upper ca)
+98	.upsilon.		Greek upsilon symbol (lower c
+99	.sub..rarw.		Subcripted reverse arrow
+100	.phi.		Greek phi symbol (lower case)

+101	.PHI.	Greek PHI symbol (upper case)
+102	.chi.	Greek chi symbol
+104	.psi.	Greek psi symbol (lower case)
+105	.PSI.	Greek PSI symbol (upper case)
+106	.OMEGA.	Greek OMEGA symbol (upper case)
+107	.omega.	Greek omega symbol (lower case)
+108	.cndot.	Solid dot - center
+109	.andgate.	And gate symbol
+110	.angle.	Angle symbol
+111	.sup.[	
+112	.sup.]	
+113	.sub.[	
+114	.sub.]	
+115	.sup.+	
+116	.sup.-	
+117	.sub.+	
+118	.sub.-	
+119	.sup.+-	
+120	.sup.-+	
+121	.sub.+-	
+122	.sub.-+	
+123	.sup.*	
+124	.sub.*	
+125	.sup.=	
+126	.sub.=	
+127	.sup.-	
+128	.sub.-	
+129	.permill.	Per mill symbol (salinity)
+130	.sup.1/8	
+131	.sub.1/8	
+132	.sup.3/8	
+133	.sub.3/8	
+134	.sup.5/8	
+135	.sub.5/8	
+136	.sup.7/8	
+137	.sub.7/8	
+138	.sup.1/3	
+139	.sub.1/3	
+140	.sup.2/3	
+141	.sub.2/3	
+142	.sup.1/4	
+143	.sub.1/4	
+144	.sup.1/2	
+145	.sub.1/2	
+146	.sup.3/4	
+147	.sub.3/4	
+148	.sup..lmtoreq.	Superscripted less than or equal
+149	.sub..lmtoreq.	Subscripted less than or equal
+150	1/8	
+151	.sup..gtoreq.	Supercripted greater to or equal
+152	1/8	
+153	.sub..gtoreq	Subscripted greater to or equal
+154	3/8	
+155	.lmtorsim.	less than or approx. equal to
+156	3/8	

NOTE: Column 1 numbers 111 thru 184 represent special characters as previous defined but appearing either subscripted or superscripted.

+157	.gtorsim.		greater than or approx. equal
+158	5/8		
+159	.sup..lmtorsim.		
+160	5/8		
+161	.sup..gtorsim.		
+162	7/8		
+163	.sub..lmtorsim.		
+164	7/8		
+165	.sub..gtorsim.		
+166	1/3		
+167	.perspectiveto.		Perspective to symbol
+168	1/3		
+170	2/3		
+171	.[.		Open bold bracket (reissue)
+172	2/3		
+173	.].		Close bold bracket (reissue)
+174	1/4		
+176	1/4		
+178	1/2		
+180	1/2		
+182	3/4		
+183	3/4		
+184	3/4		
+185	.quadbond.		Quadbond symbol
+186	.sup..crclbar		Superscripted neg. earth symbol
+187	.sub..crclbar.		Subscripted negative earth symbol
+188	.sup..sym.		Superscripted pos. earth symbol
+189	.sub..sym.		Subscripted position earth symbol
+190	#	7B	Number sign
+191	.notlessthan.		not less than symbol
+192	.notgreaterthan.		not greater than symbol
+193	.music-natural.		Music natural sign
+194	.apprch.		Approaches symbol
+195	.perp.		Perpendicular symbol
+196	.fourthroot.		Fourth root symbol
+198	.TM.		Trademark symbol
+199	.SM.		Service mark symbol
+200	.RTM.		Registered trademark symbol
+201	.COPYRG.		Copyright symbol
+202	.sup.'		Superscripted apostrophe
+203	.sub.'		Subscripted apostrophe
+204	.sup."		Superscripted double prime
+205	.sub."		Subscripted double prime
+206	.sup.'		Superscripted prime
+207	.sub.'		Subscripted prime
+208	.sup..degree.		Superscripted degree symbol
+209	.sub..degree.		Subscripted degree symbol
+210	.sup.-		Superscripted en dash
+211	.sup.--		Superscripted em dash
+212	.sub.-		Subscripted en dash
+213	.sub.--		Subscripted em dash
+214	.sup..div.		Supercripted division sign
+215	.sub..div.		Subscripted division sign
+216	.sup..infin.		Superscripted infinity symbol
+217	.sub..infin.		Subscripted infinity symbol

+218	.sup.'	Superscripted single open quote
+219	.sup.'	Superscripted single close quote
+220	.sup..dblquote.	Superscripted double open quote
+221	.sup..dblquote.	Subscripted double close quote
+222	.sub.'	Subscripted open single quote
+223	.sub.'	Subscripted close single quote
+224	.sub.dblquote.	Subscripted double open quote
+225	.sub.dblquote.	Subscripted double close quote
+226	.sup.l	Superscripted script l
+227	.sub.l	Subscripted script l
+228	.sub.#	
+229	.sup.#	
+230	.sub.<	
+231	.sup.<	
+232	.sub.>	
+233	.sup.>	
+234	.sub..vertline.	
+235	.sup..vertline.	
+236	.sup..not <.	
+237	.sub..not <.	
+238	.sup..not >.	
+239	.sub..not >.	
+240	.sup..noteq.	
+241	.sub..noteq.	
+242	.sup.	
+243	.sub.	
+244	.sup.	
+245	.sub.	
+246	.sup..sqroot.	
+247	.sub..sqroot.	
+248	.sup..cuberoot.	
+249	.sub..cuberoot.	
+250	.sup..function.	
+251	.sub..function.	
+252	.sup..4th root.	
+253	.sub..4th root.	
+261	A	
+262	B	
+263	C	
+264	D	
+265	E	
+266	F	
+267	G	
+268	H	
+269	I	
+270	J	
+271	K	
+272	L	
+273	M	
+274	N	
+275	O	
+276	P	
+277	Q	
+278	R	
+279	S	

NOTE: Column 1 numbers 228 thru 253 represent special characters as previous defined but appearing either subscripted or superscripted

NOTE: Column 1 numbers 261 thru 286 represent the alphabe in "small caps". They wi appear on APS as normal c

+280	T
+281	U
+282	V
+283	W
+284	X
+285	Y
+286	Z
+290	.sbsb.0
+291	.sbsb.1
+292	.sbsb.2
+293	.sbsb.3
+294	.sbsb.4
+295	.sbsb.5
+296	.sbsb.6
+297	.sbsb.7
+298	.sbsb.8
+299	.sbsb.9
+300	.sup..alpha.
+301	.sub..alpha.
+302	.sup..omega.
+303	.sub..omega.
+304	.sup..theta.
+305	.sub..theta.
+306	.sup..lambda.
+307	.sub..lambda.
+308	.sup..eta.
+309	.sub..eta.
+310	.sup..mu.
+311	.sub..mu.
+312	.sup..delta.
+313	.sub..delta.
+314	.sup..pi.
+315	.sub..pi.
+316	.sup..gamma.
+317	.sub..gamma.
+318	.sup..SIGMA.
+319	.sub..SIGMA.
+320	.sup..epsilon.
+321	.sub..epsilon.
+322	.sup..phi.
+323	.sub..phi.
+324	.sup..sigma.
+325	.sub..sigma.
+326	.sup..nu.
+327	.sub..nu.
+328	.sup..tau.
+329	.sub..tau.
+330	.sup..beta.
+331	.sub..beta.
+332	.sup..upsilon.
+333	.sub..upsilon.
+334	.sup..psi.
+335	.sub..psi.
+336	.sup..rho.
+337	.sub..rho.

NOTE: Column 1 numbers 290 thru 299 represent numberic values 1 - 9 as being a subscript of a subscript.

NOTE: Column 1 numbers 300 thru 337 represent special characters as previous defined but appearing either subscripted or super scripted.

+338	.sbsb.a
+339	.sbsb.b
+340	.sbsb.c
+341	.sbsb.d
+342	.sbsb.e
+343	.sbsb.f
+344	.sbsb.g
+345	.sbsb.h
+346	.sbsb.i
+347	.sbsb.j
+348	.sbsb.k
+349	.sbsb.l
+350	.sbsb.m
+351	.sbsb.n
+352	.sbsb.o
+353	.sbsb.p
+354	.sbsb.q
+355	.sbsb.r
+356	.sbsb.s
+357	.sbsb.t
+358	.sbsb.u
+359	.sbsb.v
+360	.sbsb.w
+361	.sbsb.x
+362	.sbsb.y
+363	.sbsb.z
+364	.sbsp.a
+365	.sbsp.b
+366	.sbsp.c
+367	.sbsp.d
+368	.sbsp.e
+369	.sbsp.f
+370	.sbsp.g
+371	.sbsp.h
+372	.sbsp.i
+373	.sbsp.j
+374	.sbsp.k
+375	.sbsp.l
+376	.sbsp.m
+377	.sbsp.n
+378	.sbsp.o
+379	.sbsp.p
+380	.sbsp.q
+381	.sbsp.r
+382	.sbsp.s
+383	.sbsp.t
+384	.sbsp.u
+385	.sbsp.v
+386	.sbsp.w
+387	.sbsp.x
+388	.sbsp.y
+389	.sbsp.z
+390	.spsp.0
+391	.spsp.1
+392	.spsp.2
+393	.spsp.3

NOTE: Column 1 numbers 338 thru 363 represent lower case letters that appear as a subscript of a subscript.

NOTE: Column 1 numbers 364 thru 389 represent lower case letters that appear as a subscript to a superscrip

NOTE: Column 1 numbers 390 thru 399 represent numeric val 1 - 9 as being a superscr of a supercript.

+394	.spsp.4
+395	.spsp.5
+396	.spsp.6
+397	.spsp.7
+398	.spsp.8
+399	.spsp.9
+400	.sbsp.0
+401	.sbsp.1
+402	.sbsp.2
+403	.sbsp.3
+404	.sbsp.4
+405	.sbsp.5
+406	.sbsp.6
+407	.sbsp.7
+408	.sbsp.8
+409	.sbsp.9
+410	.spsb.0
+411	.spsb.1
+412	.spsb.2
+413	.spsb.3
+414	.spsb.4
+415	.spsb.5
+416	.spsb.6
+417	.spsb.7
+418	.spsb.8
+419	.spsb.9
+438	.spsp.a
+439	.spsp.b
+440	.spsp.c
+441	.spsp.d
+442	.spsp.e
+443	.spsp.f
+444	.spsp.g
+445	.spsp.h
+446	.spsp.i
+447	.spsp.j
+448	.spsp.k
+449	.spsp.l
+450	.spsp.m
+451	.spsp.n
+452	.spsp.o
+453	.spsp.p
+454	.spsp.q
+455	.spsp.r
+456	.spsp.s
+457	.spsp.t
+458	.spsp.u
+459	.spsp.v
+460	.spsp.w
+461	.spsp.x
+462	.spsp.y
+463	.spsp.z
+464	.spsb.a
+465	.spsb.b
+466	.spsb.c

NOTE: Column 1 numbers 400 thru 409 represent numeric valu 1 - 9 as being a subscript of a superscript.

NOTE: Column 1 numbers 410 thru 419 represent numeric valu 1 - 9 as being a superscri of a subscript.

NOTE: Column 1 numbers 438 th 463 represent lower case letters that appear as superscript of a superscri

NOTE: Column 1 numbers 464 thru 489 represent lower case letters that appear as superscript of a subscript.

+467	.spsb.d	
+468	.spsb.e	
+469	.spsb.f	
+470	.spsb.g	
+471	.spsb.h	
+472	.spsb.i	
+473	.spsb.j	
+474	.spsb.k	
+475	.spsb.l	
+476	.spsb.m	
+477	.spsb.n	
+478	.spsb.o	
+479	.spsb.p	
+480	.spsb.q	
+481	.spsb.r	
+482	.spsb.s	
+483	.spsb.t	
+484	.spsb.u	
+485	.spsb.v	
+486	.spsb.w	
+487	.spsb.x	
+488	.spsb.y	
+489	.spsb.z	
+500	.cndot.	Center Dot (Solid Dot)
+501	.circle.	Large Circle
+502	.circleincircle.	Circle in a large circle
+503	.lhalfcircle.	Left-half circle
+504	.rhalfcircle.	Right-half circle
+505	.dottedcircle.	Dotted circle
+506	.THorizBrace.	Top horizonal brace
+507	.BHorizBrace.	Bottom horizonal brace
+508	.dotlhalfcircle	Dotted left-half circle
+509	.dotrhalfcircle	Dotted right-half circle
+510	.dotthalfcircle.	Dotted top-half circle
+511	.dotbhalcircle.	Dotted bottom-half circle
+512	.solthalfcircle.	Solid top-half circle
+513	.solbhalfcircle.	Solid bottom-half circle
+515	.male.	Male symbol
+516	.female.	Female symbol
+517	.sctn.	Section symbol
+518	.0.	Slashed zero (light print)
+519	.0.	Slashed zero (bold print)
+520	.orgate.	or gate symbol
+521	.ANG.	Angstrom (upper case)
+522	.ang.	Asgstrom (lower case)
+601	.smallcircle	Small circle
+701	.largecircle.	Large circle

The following special characters precede data on the patent full-text/APS file:

Column 2	Description
.sub.	- Subscript -
.sup.	- Superscript -
.sbsb.	- Subcript of a Subscript -
.spsp.	- superscript of a superscript-
.sbsp.	- subcript of a superscript-
.spsb.	- superscript of a subscript-

Subcripted and supercripted data will be terminated by a space, a comma (,), a period (.), a right parenthesis ()) or another subscript .sub. or superscript .sup..

NOTE 1 - The following defines the appearance of original and added data in a Reissue Patent on the Patent Full-Text APS File.

Original data, that forms no part of the reissue patent, will begin with .[. and end with .]. New data (appears Italicized on the printed document) will begin with .Iadd. and end with .Iaddend.

NOTE 2 - The following defines the appearance of original and added data in a Reissue of a Reissue Patent on the Patent APS file.

Original data of the first reissue patent, that forms no part of the current reissue patent, will begin with .[. .[. and end with .]. .]. New data of the first reissue patent (appears in BOLD print on the current printed document) will begin with .Badd. and end with .Baddend.

NOTE 1 above applies to the appearance of original and added data on the current Reissue Patent.

APPENDIX D

Patent Documents as they appear in machine-readable form on the patent full-text/APS file.

The following patents contain chemical structures, tables and equations that are identified by a call-out identifer.

The following patents contain tables and in-line equations where the data is present. Chemical structures and those equations requiring characters or symbols above or below a line will be identified by a call-out identifier.

NOTE: Patent documents appearing in this appendix are the same document numbers that appear in printed version in Appendix E.

```
PATN
WKU  D02647354
SRC  6
APN  1402307
APT  4
ART  292
APD  19800414
TTL  Novelty binoculars
ISD  19820601
NCL  1
ECL  1
EXP  Rademaker; Charles A.
NDR  1
NFG  4
TRM  14
INVT
NAM  Ocker; Anna M.
STR  1857 Santa Gertrudis Dr.
CTY  Bismarck
STA  ND
ZIP  58501
CLAS
OCL  D21 59
XCL  D21109
ICL  D2101
FSC  D16
FSS  133
FSC  D21
FSS  59;60;240;109;241
FSC  D 9
FSS  307
FSC  272
FSS  1 R;8 R;8 N
FSC   46
FSS  1 R
UREF
PNO  D14423
ISD  18831100
NAM  Bradley
OCL  D 9307
UREF
PNO  D116921
ISD  19391000
NAM  Sierad
OCL  D 9307
UREF
PNO  D123103
ISD  19401000
NAM  Murray
OCL  D 9341
UREF
PNO  D238304
ISD  19751200
NAM  Hengst et al.
OCL  D16133
LREP
FRM  Kinney, Lange, Braddock, Westman and Fairbairn
DRWD
PAL  FIG. 1 is a perspective view of novelty binoculars, showing my new design;
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PAL  FIG. 3 is a top view thereof; and,
PAL  FIG. 4 is a bottom plan view thereof.
DCLM
PAR  The ornamental design for novelty binoculars, as shown.
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PATN
WKU  H00000400
SRC  6
APN  6320638
APT  7
ART  222
APD  19840718
TTL  Field shields for Schottky barrier devices
ISD  19860401
NCL  13
ECL  1
EXA  Wallace; Linda J.
EXP  Buczinski; S. C.
NDR  5
NFG  8
INVT
NAM  Buchanan, Jr.; William L.
CTY  Reading
STA  PA
INVT
NAM  Kohl; James E.
CTY  Wyomissing
STA  PA
INVT
NAM  Scott; Robert S.
CTY  Spring Township, Berks County
STA  PA
INVT
NAM  Wong; Yiu-Huen
CTY  Berkeley Heights
STA  NJ
ASSG
NAM  AT&T Bell Laboratories
COD  02
CLAS
OCL  357 15
XCL  357 53
XCL  357 20
XCL  357 52
EDF  4
ICL  H01L 2948
ICL  H01L 2906
FSC  357
FSS  15
UREF
PNO  3541403
ISD  19701100
NAM  Lepselter et al.
OCL  317204
UREF
PNO  3616380
ISD  19711000
NAM  Lepselter et al.
OCL  204164
UREF
PNO  4119446
ISD  19781000
NAM  Mastroianni
OCL  148  1.5
```

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PNO  4134123
ISD  19790100
NAM  Shannon
OCL  357 15
FREF
PNO  5224465
ISD  19770200
CNT  JPX
OCL  357 15M
OREF
PAL  "Silicon Schottky Barrier Diode. . .", Bell System Technical Journal, vol.
      47, No. 2, Feb. 1968 , pp. 195-208, Lepselter et al.
PAL  Reverse Current-Voltage Characteristics. . .", Solid-State Electronics,
      vol. 13, pp. 1011-1023, J. M. Andrews et al.
PAL  Optimum Doping Profile. . .", IEEE Transactions on Electron Devices, vol.
      Ed-26, No. 3, Mar. 1979, pp. 243-244, C. Hu.
PAL  Schottky-Barrier Diodes. . .", Electronic Components and Applications, vol.
      4, No. 4, Aug. 1982, pp. 201-205, Hafemeister.
PAL  High-Voltage Power Schottky. . .", IBM Technical Disclosure Bulletin, vol.
      25, No. 5, Oct. 1982, pp. 2331-2333, Jambotkar.
PAL  Electric-Field-Shielding Layers. . .", Electronics Letters, vol. 19, No.
      15, Jul. 21, 1983, pp. 568-570, S. Nakashima et al.
LREP
FR2  Koba; Wendy W.
ABST
PAL  The present invention relates to an improved Schottky barrier device
      wherein the leakage current present in the reverse bias mode attributed to
      the presence of an electric field at the Schottky barrier (18) is
      significantly reduced by the inclusion of one or more field shields (22),
      P.sup.+ -type diffusions located under the metal anode (16) of the
      Schottky barrier device at the Schottky barrier (18). The P.sup.+ -type
      field shields, which are disposed in a pattern on the surface of the
      Schottky barrier, reduce the surface electric field present, thereby
      significantly reducing the leakage current related thereto.
BSUM
PAC  BACKGROUND OF THE INVENTION
PAR  1. Field of the Invention
PAR  The present invention relates to the inclusion of field shields in Schottky
      barrier devices, and more particularly, to the inclusion of one or more
      field shield diffusions at the metal-semiconductor interface to reduce the
      surface electric field along the interface, thereby decreasing the reverse
      bias leakage current of Schottky barrier devices.
PAR  2. Description of the Prior Art
PAR  Schottky barrier (metal-semiconductor) devices, in particular, diodes, are
      often used in circuits because they have a low forward voltage drop and a
      very fast reverse recovery time. These properties make Schottky diodes
      very useful in applications such as high-speed switching power supply
      rectifiers. However, compared with conventional p-n junction diodes,
      Schottky barrier diodes exhibit poor reverse bias characteristics
      manifested in an increased leakage, particularly at voltages approaching
      breakdown voltage.
PAR  In the past, the reverse characteristics of Schottky barrier diodes were
      improved by increasing the breakdown voltage of the device, utilizing
      p-type guard rings diffused into the n-type semiconductor material, as
      disclosed in U.S. Pat. No. 3,541,403 issued to M. P. Lepselter et al on
      Nov. 17, 1970. As disclosed, the guard ring is located in the substrate
      under the insulator-metal interface and functions to reduce the edge
      breakdown effects existing at the intersection of this interface and the
      semiconductor surface. The same guard ring structure is discussed in an
      article entitled "Silicon Schottky Barrier Diode with Near-Ideal I-V
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Characteristics" by M. P. Lepselter et al appearing in Bell System Technical Journal, Vol. 47, No. 2, pp. 195-208.

PAR An improved method for forming guard rings in Schottky barrier diodes is disclosed in U.S. Pat. No. 4,119,446 issued to S. T. Mastroianni on Oct. 10, 1978. Here, the metal-semiconductor structure is formed first and the metal is then used in conjunction with another mask to form a guard ring self-aligned with the periphery of the metal.

PAR Although the use of guard rings will improve the reverse characteristics of Schottky barrier diodes by reducing the edge breakdown effects, relatively large leakage current in the reverse blocking mode will still exist, due to the presence of a high surface electric field along the planar metal-semiconductor interface away from the edge of the interface. This leakage current generally increases very rapidly as the reverse potential is increased and may be several orders of magnitude larger than the leakage current of a diffused junction diode when the electric field approaches the silicon avalanche limit.

PAR In order to reduce the Schottky barrier diode reverse leakage current, a Schottky metal (or metal silicide) which has a high barrier potential can be utilized. Although this will improve the reverse characteristics, the high barrier potential results in a higher forward voltage drop and, therefore, greater power dissipation than desired. In an alternative method, the electric field is reduced at the Schottky barrier when the device is under reverse bias, which results in reducing the leakage current. In particular, the electric field is reduced by increasing the resistivity and depth of the N-type silicon cathode (for the case of a metal-N silicon diode). However, this method of decreasing the leakage current will result in an increased series resistance between the anode and the cathode and thus will again result in an increased forward voltage drop. Further, this method is not very desirable in high-voltage integrated circuit technology since the N-type cathode material may also be used as collectors or drains of bipolar or MOS transistors, respectively, and the increased resistivity will adversely affect the characteristics of these devices.

PAR There remains to be solved the problem of eliminating the leakage current present in Schottky barrier devices related to the presence of a surface electric field without unnecessarily increasing the forward voltage drop of the device.

PAC SUMMARY OF THE INVENTION

PAR The above-described problem is addressed by the present invention which relates to the inclusion of field shields in Schottky barrier devices and, more particularly, to the inclusion of one or more field shield diffusions at the metal-semiconductor interface to reduce the surface electric field along the interface, thereby decreasing the reverse bias leakage current of Schottky barrier devices without appreciably increasing the forward bias voltage drop.

PAR It is an aspect of the present invention to diffuse a plurality of closely-spaced P-type regions, referred to as field shields, into an N-type semiconductor substrate (or to diffuse N-type regions into a P-type substrate). The field shields function to modify and thus reduce the surface electric field at the metal-semiconductor interface (Schottky barrier), thereby reducing the reverse leakage current and only moderately increasing the series resistance, without increasing the Schottky barrier height or the cathode material resistivity.

PAR Another aspect of the present invention is to utilize a single P-type diffusion region to reduce the surface electric field, where the single diffusion forms a continuous pattern, for example, a spiral or snake pattern, on the Schottky barrier surface.

PAR Yet another aspect of the present invention is the design of the spacing between the field shields as well as the overall pattern of the diffusions

DRWD

PAC BRIEF DESCRIPTION OF THE DRAWINGS

PAR Referring now to the drawings,

PAR FIG. 1 illustrates a cross-sectional view of a prior art Schottky barrier diode, including a guard ring structure which increases the breakdown voltage related to edge breakdown effects;

PAR FIG. 2 illustrates a cross-sectional view of a Schottky barrier diode formed in accordance with the present invention which includes a plurality of field shields to reduce the leakage current associated with the surface electric field;

PAR FIG. 3 illustrates a top view of an exemplary Schottky barrier diode formed in accordance with the present invention, where the field shields are distributed in a hexagonal array pattern;

PAR FIG. 4 illustrates a top view of an alternative Schottky barrier diode formed in accordance with the present invention, where the field shield comprises a single diffusion disposed in a spiral pattern;

PAR FIGS. 5 and 6 illustrate the calculated electric field contours associated with a prior art Schottky barrier diode (FIG. 5) and a Schottky barrier diode formed in accordance with the present invention (FIG. 6);

PAR FIG. 7 illustrates the reverse bias current-voltage I-V characteristics for a prior art Schottky barrier diode and a plurality of Schottky barrier diodes formed in accordance with the present invention; and

PAR FIG. 8 illustrates the forward I-V characteristics for a prior art Schottky barrier diode and a plurality of Schottky barrier diodes formed in accordance with the present invention.

DETD

PAC DETAILED DESCRIPTION

PAR In order to aid in the understanding of the present invention, the properties of a prior art Schottky barrier diode will be briefly explained with reference to FIG. 1. As shown, an exemplary prior art Schottky barrier diode comprises an N.sup.+ -type cathode layer 10 upon which is deposited an N.sup.- -type substrate region 12. An insulating layer 14 is subsequently deposited on N.sup.- substrate region 12, where a central portion of insulating layer 14 is then etched away, exposing N.sup.- substrate region 12. A metallic layer 16, which forms the anode of the prior art Schottky barrier device, is deposited into the opening created by the etchant and possibly overlaps a portion of insulating layer 14, as illustrated in FIG. 1. Many different metals and alloys may be used as layer 16, where nickel silicide is considered to be one alternative. It is to be understood that a Schottky barrier diode may also be formed with a P-type substrate region and the use of an N-type region throughout the present discussion is considered to be exemplary only.

PAR As is well known, a Schottky barrier diode differs from a conventional diffused p-n junction diode in that Schottky barrier diodes are metal-semiconductor junction devices, where Schottky-barrier 18 is illustrated in FIG. 1. As previously discussed, prior art Schottky barrier diodes attempted to improve the reverse operating characteristics by increasing the reverse breakdown voltage which is related to edge breakdown effects. This was accomplished by the inclusion of an annular guard ring, illustrated in FIG. 1 (in a cross-sectional view) as P-type diffusion 20, where the edges which produce the breakdown effect are indicated at points A and B. As discussed in the above-cited prior art references, guard ring 20 forms a "protection" p-n diode in parallel with the Schottky barrier diode, thus increasing the reverse breakdown voltage of the device. The leakage current related to the electric field along the planar region of Schottky barrier 18 far from guard ring 20, however, is not reduced or eliminated by the inclusion of guard ring 20 in the Schottky barrier diode.

PAR A Schottky barrier diode formed in accordance with the present invention, capable of significantly reducing the surface electric field, which in turn functions to reduce the reverse bias leakage current, is illustrated in FIG. 2. As can be seen, this device differs from the prior art arrangement of FIG. 1 by the addition of a plurality of field shields 22, P.sup.+ -type diffusions disposed in a predetermined geometric pattern inside guard ring 20, where the individual diffusions are separated from one another by predetermined distances. Although the cross-sectional view of FIG. 2 shows only three field shield diffusions, in the actual practice of the present invention, a large plurality of field shields, for example, hundreds or even thousands, may be diffused into substrate region 12 in the opening created by annular guard ring 20. Alternatively, field shield 22 could be formed using a single P.sup.+ -type diffusion in the form of a spiral, or any other type of continuous pattern, over the planar surface of Schottky barrier 18.

PAR In accordance with the present invention, the illustrated distance d separating the plurality of field shields 22, for an embodiment utilizing a plurality of field shields, must be small enough such that their respective depletion regions merge together at reverse potentials well below the avalanche breakdown of the Schottky barrier diode in order to significantly reduce the surface electric field. In the case of a single field shield diffusion, the distance separating adjacent portions of the diffusion must also be small enough to allow the depletion region of the adjacent portions to merge in a similar fashion. Further, the deeper the plurality field shields 22 are diffused into N.sup.- -type substrate 12, and the closer they are spaced, the larger the two-dimensional field-lowering effect will be.

PAR As stated before, the layout of field shields 22 may comprise one of many different geometrical patterns, where the chosen pattern affects the reduction of the surface electric field along the planar region of Schottky barrier 18 located between field shields 22, thus also affecting the resultant decrease in reverse bias leakage current. One exemplary pattern of field shields 22 is shown in FIG. 3, which illustrates a top view of an exemplary Schottky barrier diode with the plurality of field shields 22 disposed in a hexagonal array arrangement. In the hexagonal arrangement, the distance, d separating adjacent field shield diffusions will be constant. Alternatively, the layout pattern may be a set of concentric rings, where the separation between adjacent rings is designed to provide the desired reduction in reverse bias leakage while not greatly increasing the forward bias voltage drop. A single diffusion, as stated above, may also be utilized to reduce the surface electric field. For example, a continuous snake or spiral diffusion pattern over the surface of Schottky barrier 18 can be used to reduce this surface electric field. FIG. 4 illustrates one exemplary embodiment of the present invention where a spiral diffusion pattern is utilized. Other geometric patterns which may be utilized include a rectangular array, or a set of long, parallel stripes, where these patterns are illustrative only and many other patterns may be utilized in accordance with the present invention to provide sufficient improvement in reducing reverse bias leakage current without seriously degrading the forawrd bias voltage drop.

PAR Referring now to FIGS. 5 and 6, the effect on the surface electric field related to the inclusion of the plurality of field shields 22 is demonstrated. FIG. 5 illustrates the calculated electric field contours associated with a prior art Schottky barrier diode, as discussed hereinabove in association with FIG. 1, and FIG. 6 illustrates the electric field contours associated with a Schottky barrier diode formed in accordance with the present invention at the same reverse bias potential as associated with FIG. 5. The illustrated electrical field contours correspond to the electric field present in N.sup.- substrate region 12 as measured in the X (width) and Z (depth) directions, between vertical lines 30 and 32 shown in FIGS. 1 and 2. As can be seen, the inclusion of field barrier junction 18, thereby reducing the leakage current associated therewith.

PAR FIG. 7 contains a semi-log graph illustrating the reverse I-V characteristics of both a prior art Schottky barrier diode and a plurality of Schottky barrier diodes formed in accordance with the present invention, illustrated as a function of the spacing, W, between the windows in the diffusion pattern used to create field shields 22. As stated above, and demonstrated in FIG. 7, the closer together the plurality of field shields 22 are spaced, the lower the reverse bias leakage current becomes.

PAR For example, if the reverse bias voltage, V.sub.r, applied to the particular conventional prior art Schottky barrier diode used in association with FIG. 7 is, approximately, 140 volts, the reverse bias leakage current, I.sub.r, is approximately equal to 0.2 mA. By including a plurality of field shields, in accordance with the present invention, which are diffused using a diffusion window spacing W=24 microns, the reverse bias current I.sub.r decreases from 0.2 mA to approximately 0.04 mA. Using a smaller spacing of W=22 microns current I.sub.r to an approximate value of 9 .mu.A. As shown in FIG. 7, a further spacing reduction to W=20 microns yields a current I.sub.r of approximately 2.5 .mu.A and W=18 microns results in I.sub.r approximately equal to 1.5 .mu.A.

PAR An advantage of the present invention, as stated above, is that the reverse bias leakage current can be reduced without greatly affecting the forward-bias characteristics of the device. FIG. 8 contains a semi-log current-voltage (I-V) plot of the forward-bias characteristics related to a conventional prior art Schottky barrier diode and a plurality of Schottky barrier diodes formed in accordance with the present invention. Assuming a forward bias current I.sub.f of approximately 100 mA, the conventional Schottky barrier diode will exhibit a forward voltage, V.sub.f, of approximately 0.32 volts. Utilizing a Schottky barrier diode formed in accordance with the present invention which uses a diffusion window spacing W=24 microns forward voltage V.sub.f increases only 0.025 volts to approximately 0.345 volts. A spacing of W=22 .mu.m, as seen by reference to FIG. 8, does not greatly change forward voltage V.sub.f. Decreasing the spacing to W=20 .mu.m results in increasing forward voltage V.sub.f to 0.365 volts, where a further reduction in spacing to W=18 microns increase V.sub.f to approximately 0.385 volts. Thus, as seen by reference to FIG. 8, the use of field shields in accordance with the present invention does not greatly affect the overall I-V curve of the forward biased Schottky barrier diode, but merely increases the forward voltage V.sub.f somewhat over the entire forward voltage range.

CLMS

STM What is claimed is:

NUM 1.

PAR 1. A semiconductor device which comprises a

PA1 semiconductor layer of a first conductivity type;

PA1 an insulating layer disposed on a surface of said semiconductor layer and having an aperture therein exposing a portion of said semiconductor layer;

PA1 a metal layer disposed in said aperture and possibly onto a portion of the insulating layer, forming a Schottky barrier with said semiconductor layer therebelow; and

PA1 a plurality of semiconductor regions of a second conductivity type in physical contact with both said semiconductor layer and said metal layer, each semiconductor region of said plurality of semiconductor regions being separated from one another.

NUM 2.

PAR 2. A semiconductor device formed in accordance with claim 1 wherein at least one of the plurality of semiconductor regions of the second conductivity type forms an annular guard ring surrounding the remaining

```
     semiconductor regions of said plurality of semiconductor regions, said
     annular guard ring disposed in physical contact with both the metal layer
     and the insulating layer, completely underlying the edge of the interface
     between said semiconductor layer and said metal layer.
NUM  3.
PAR  3. A semiconductor device formed in accordance with claims 1 or 2 wherein
PA1  the plurality of semiconductor regions of the second conductivity type are
     arranged in a geometric pattern with the separation between adjacent
     regions determined by the desired reverse bias leakage current and the
     desired forward bias voltage drop.
NUM  4.
PAR  4. A semiconductor device formed in accordance with claim 3 wherein the
     geometrical pattern is a regular array.
NUM  5.
PAR  5. A semiconductor device formed in accordance with claim 4 wherein the
     regular array is a rectangular lattice.
NUM  6.
PAR  6. A semiconductor device formed in accordance with claim 4 wherein the
     regular array is a hexagonal lattice.
NUM  7.
PAR  7. A semiconductor device formed in accordance with claim 4 wherein the
     regular array is a set of long parallel stripes.
NUM  8.
PAR  8. A semiconductor device formed in accordance with claim 4 wherein the
     regular array is a set of concentric rings.
NUM  9.
PAR  9. A semiconductor device formed in accordance with claims 1 or 2 wherein
     the plurality of semiconductor regions of the second conductivity type
     comprises a plurality of diffused regions.
NUM  10.
PAR  10. A semiconductor device which comprises
PA1  a semiconductor layer of a first conductivity type;
PA1  an insulating layer disposed on a surface of said semiconductor layer and
     having an aperture therein exposing a portion of said semiconductor layer;
PA1  a metal layer disposed in said aperture and possibly onto a portion of the
     insulating layer, forming a Schottky barrier with said semiconductor layer
     therebelow; and
PA1  a semiconductor region of a second conductivity type in physical contact
     with both said semiconductor layer and said metal layer, said
     semiconductor region disposed to form a continuous pattern adjoining said
     Schottky barrier and extending away from the Schottky barrier edge into a
     central portion of the semiconductor device.
NUM  11.
PAR  11. A semiconductor device formed in accordance with claim 10 wherein the
     semiconductor region of the second conductivity type comprises a diffused
     region.
NUM  12.
PAR  12. A semiconductor device formed in accordance with claims 1, 2, or 10
     wherein the semiconductor layer is silicon and the insulating layer is
     silicon dioxide.
NUM  13.
PAR  13. A semiconductor device formed in accordance with claims 1, 2 or 10
     wherein the metal layer is nickel silicide.
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D-10 is a blank page and is not used in this technical reference.

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PATN
WKU  PP0048534
SRC  6
APN  1852493
APT  6
ART  337
APD  19800908
TTL  Rose plant
ISD  19820601
NCL  1
ECL  1
EXP  Feyrer; James R.
NDR  1
NFG  1
INVT
NAM  Bailey; Dorothy J. S.
CTY  Bakersfield
STA  CA
ASSG
NAM  San Joaquin Rose Co.
CTY  McFarland
STA  CA
COD  02
CLAS
OCL  Plt 11
EDF  3
ICL  A01H  500
FSC  Plt
FSS   11
LREP
FR2  Gioia; Vincent G.
ABST
PAL  A new hybrid tea rose variety of exhibition form and orange red and cadmium
      yellow.
BSUM
PAR  The present invention relates to a new and distinct variety of rose plant
      of the hybrid tea rose class, which was originated by my crossing as seed
      parent the rose known as "Kordes Perfecta" and the rose known as "Mr.
      Lincoln" as pollen parent.
PAR  Among the novel characteristics possessed by this new variety which
      distinguish it from its parents and all other varieties of which I am
      aware are its excellent exhibition form and unusual cadmium yellow and
      orange red coloring at the bottom and top petal edge surfaces,
      respectively. The flowers are borne primarily singly on a plant with
      abundant foliage and superior disease resistance. Asexual reproduction by
      budding of the new variety as performed in Kern County, Calif., shows that
      the foregoing and other distinguishing characteristics come true to form
      and are established and transmitted through succeeding propagations.
PAR  The new and improved rose variety which I have developed is a fine hybrid
      tea rose with unusual coloring, of high centered, excellent hybrid-tea
      form displayed on a vigorous, free branching plant with abundant disease
      resistant foliage. The flowers are of heavy petalage and have a slight
      fragrance.
DRWD
PAR  The accompanying drawing shows typical specimens of the vegetative growth
      and flowers of the new variety in different stages of development and as
      depicted in color as nearly true as it is reasonably possible to make the
      same in a color illustration of this character.
DETD
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terminology in accordance with the Royal Horticultural Society Color Chart (RHSCC). The terminology used in color description herein refers to plate numbers in the aforementioned color chart, e.g., "23D" is plate 23D of the Royal Horticultural Society Color Chart.
PAO Parentage: Seedling.
PA2 Seed parent.--"Kordes Perfecta".
PA2 Pollen parent.--"Mr. Lincoln".
PAO Class: Hybrid tea.
PAR The following observations are made of specimens grown outdoors in Kern County, Calif., during the month of October.
PAC 1. FLOWER
PAO Blooming habit: Recurrent.
PAO A. Bud:
PA2 (1) Size.--Large.
PA2 (2) Form.--Long pointed.
PA2 (3) Color.--First row of petals in bud after sepals fall show petal undersurface color cadmium orange 23D, slightly darker at petal point of attachment. At under surface petal edge, color is between 34D and 37A with color intensity greatest at the lateral edges.
PA2 (4) Sepals.--Simple, about same length as bud.
PA2 (5) Peduncle.--Length -- about 4 inches. Aspect -- straight, smooth. Strength -- erect, strong. Color -- near 146B with purplish red cast.
PAO B. Bloom:
PA2 (1) Size.--Average size when fully expanded -- about 41/2 to 5 inches.
PA2 (2) Borne.--Primarily singly.
PA2 (3) Form.--High centered, petals recurve, maintain high centered exhibition form with circular outline.
PA2 (4) Petalage.--Number of petals under normal conditions -- about 48 to 50.
PA2 (5) Color.--As flowers open petal undersurface color 23D remains about the same and orange red coloring (between 34D and 37A) at petal edges on top surface becomes more prominent but dual coloring of individual petals is also evident on the top petal surface. The washing of the darker orange red coloring at the edging into the cadmium orange, which also appears to lighten on inner petals, makes the petal veining more visible. In the open bloom there is varied orange red to red (39A) coloring most visible on the petal edges and highlights of 39C and 39D may be seen.
PAO C. Petals:
PA2 (1) Texture.--Thick, good substance.
PA2 (2) Appearance.--Velvety to satiny.
PA2 (3) Form.--Rounded.
PA2 (4) Arrangement.--Regularly arranged.
PA2 (5) Petaloids in center.--Few.
PA2 (6) Persistence.--Drop off cleanly.
PA2 (7) Fragrance.--Slight.
PA2 (8) Lasting quality.--Long lasting on plant and as cut flower.
PAC 2. REPRODUCTIVE ORGANS
PAO A. Stamens, filaments and anthers:
PA2 (1) Arrangement.--Regularly arranged about styles.
PA2 (2) Color.--26B.
PAO B. Pollen:
PA2 Color.--23B.
PAO C. Styles: Uniform and long.
PAO D. Stigmas:
PA2 Color.--31B.
PAO E. Hips:
PA2 Shape.--Globular.
PA2 Size.--Large.
PA2 Color.--25A.
PA2 Do seeds protrude?--Slightly.
PAC 3. PLANT

```
PAO  A. Form: Upright.
PAO  B. Growth: Vigorous.
PA2  Height attained.--About 41/2 feet first season.
PAO  C. Foliage: Compound 5 to 7 leaflets.
PA2  (1) Size.--Large.
PA2  (2) Quantity.--Abundant.
PA2  (3) Color.--New foliage: upper side -- purplish red; under side -- greenish
       red. Old foliage: upper side -- near 136A to 136B; under side -- near
       191A.
PA2  (4) Shape.--Oval.
PA2  (5) Texture.--Upper side is leathery and under side is dull.
PA2  (6) Edge.--Serrated.
PA2  (7) Serration.--Simple.
PA2  (8) Leaf stem.--Color -- near to 146B. Under side -- near 147C.
PA2  (9) Stipules.--Long, slightly bearded.
PA2  (10) Resistance to disease.--Blackspot -- excellent. Mildew -- excellent.
PAO  D. Wood:
PA2  (1) New wood.--Color -- near 146B with red tones. Bark -- smooth.
PA2  (2) Old wood.--Color -- near 146A. Bark -- smooth.
PAO  E. Thorns:
PA2  (1) Thorns.--Quantity (main stalk) -- few. On laterals from stalk -- very
       few. Form -- ovoid. Length -- large. Color -- near 146C. Position
       -- regular.
PA2  (2) Prickles.--None.
PAO  F. Winter hardiness: Good winter hardiness.
CLMS
STM  I claim:
NUM  1.
PAR  1. A new and distinct variety of rose plant of the hybrid tea class,
       substantially as shown and described, characterized particularly by high
       centered, flowers of good exhibition form and cadmium yellow petals with
       orange red petal edges borne primarily singly to a stem.
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PATN
WKU  RE0309540
SRC  6
APN  0726419
APT  2
PBL  E
ART  355
APD  19790905
TTL  Wheelchairs
ISD  19820601
NCL  10
ECL  6
EXP  Zugel; Francis K.
NDR  3
NFG  7
INVT
NAM  Smith; Royal
STR  4646 Dover St., NE.
CTY  St. Petersburg
STA  FL
ZIP  33703
INVT
NAM  Carson; Edward H. D.
STR  200 Country Club Dr.
CTY  Largo
STA  FL
ZIP  33540
REIS
COD  50
APN  707203
APD  19760721
PNO  04046418
ISD  19770906
CLAS
OCL  297118
XCL  297 81
XCL  297DIG4
EDF  3
ICL  A47C 1300
ICL  A47C  1036
FSC  297
FSS  90;DIG. 4;322;323;80;81;83;119;118
FSC    5
FSS  67
UREF
PNO  416906
ISD  18891200
NAM  Flowers
OCL  297 81
UREF
PNO  611049
ISD  18980900
NAM  Allen
OCL  297 90
UREF
PNO  1553689
ISD  19250900
NAM  Hill
OCL  297 90
UREF
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PNO  1748784
ISD  19300200
NAM  Mierley
OCL  297 90
UREF
PNO  2375151
ISD  19450500
NAM  Troxell
OCL  297 83
UREF
PNO  2857954
ISD  19581000
NAM  Voelker et al.
OCL  297 83
UREF
PNO  3132897
ISD  19640500
NAM  Linden
OCL  297322
UREF
PNO  3147039
ISD  19640900
NAM  Smith et al.
OCL  297 90
UREF
PNO  3489459
ISD  19700100
NAM  Katan, Sr. et al.
OCL  297316
FREF
PNO  163976
ISD  19550300
CNT  AUX
OCL    5 67
LREP
FRM  Brady, O'Boyle & Gates
ABST
PAL  A wheelchair is disclosed which is convertible into a wheeled stretcher,
      wherein the chair seat will assume a comfortable angle with respect to the
      horizontal when the chair is in the seating position and will assume a
      horizontal position coplanar with the back of the chair when the chair is
      in the stretcher position. The chair seat and back may be locked into any
      relative position between a fully erect seated position and a fully
      reclined stretcher position. Leg support members which are connected to
      the chair may assume any angular position with respect to the horizontal
      without regard for the relative positions of the seat and back of the
      chair. The leg support members may have their lengths independently
      adjusted.
BSUM
PAC  FIELD OF THE INVENTION
PAR  The invention disclosed relates to wheelchairs and more particularly
      relates to wheelchairs which are convertible into wheeled stretchers.
PAC  BACKGROUND OF THE INVENTION
PAR  Hospital equipment and invalid home care equipment has become quite
      expensive, so that it becomes economic to combine the functions of several
      pieces of hospital apparatus to enable a single, combined function
      apparatus to have a higher frequency of utilization and therefore a
      greater return on investment. Following this philosphy, wheelchairs have
      been made, in the prior art, which are convertible into wheeled
      stretchers, thereby combining the function of a conventional wheelchair
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for transporting a patient in a seated position, with the function of a wheeled stretcher for transporting a patient in a lying position. Prior art convertible wheelchairs however, have suffered from several deficiencies. One deficiency is that in order that the seat of the prior art convertible wheelchair can assume a coplanar position with respect to the back of the chair when it is in the stretcher position, the seat must remain horizontal when the chair is in the erect seated position. A horizontal seat for a chair is uncomfortable for the patient who must remain seated thereon for long periods of time. Designers of conventional chairs have recognized that a seat which assumes a slight angle with respect to the horizontal, toward the back of the chair, is much more comfortable to sit in for long periods of time. However, prior art convertible wheelchairs have suffered from this source of discomfort to the patient. A second deficiency of prior art wheelchairs is that the leg support member which supports the patient's leg is not angularly adjustable with respect to the horizontal in a manner independent of the relative positions of the seat and the back of the chair. Thus the flexibility of the chair to accommodating various patient ailments requiring the special positioning of the patient's limbs, has not been available in prior art convertible wheelchairs. Still a third deficiency of prior art convertible wheelchairs is that the length of the leg support members for the chair have been fixed, causing the chair to be incapable of accommodating a variety of leg lengths.

PAC OBJECTS OF THE INVENTION

PAR It is therefore an object of the invention to provide a convertible wheelchair having a seat which will assume a comfortable angle with respect to the horizontal when the chair is in a seating position and will assume a horizontal position coplanar with the back of the chair when the chair is in a stretcher position.

PAR It is still another object of the invention to provide a convertible wheelchair wherein the chair seat and back may be locked in any relative position between a fully erect seated position and a fully reclined stretcher position.

PAR It is still a further object of the invention to provide a convertible wheelchair having leg support members which can assume any angular position with respect to the horizontal with no regard for the relative position of the seat and back of the chair.

PAR It is still a further object of the invention to provide a convertible wheelchair having leg support members whose lengths may be independently adjusted.

PAC SUMMARY OF THE INVENTION

PAR These and other objects, features and advantages of the invention are accomplished by the convertible wheelchair invention disclosed herein. The convertible wheelchair has a seat supported by a pair of extendable seat supports, which assume a comfortable angle with respect to the horizontal when the chair is in a seating position and will assume a horizontal position coplanar with the back of the chair when the chair is in a stretcher position. A pair of wheeled support frame members are horizontally spaced from one another and have a corresponding rearwardly positioned first pivot and a forwardly positioned second pivot at substantially the same elevation. A pair of first levers, each having a first length, are pivotally mounted on respective ones of the first pivots. A chair back support having two lateral sides, each proximate to a respective one of the support frame members, is rigidly mounted to the free end of the corresponding one of the first levers. A pair of second levers, each having substantially the first length, are pivotally mounted on respective ones of the second pivots. A pair of front arms are each rigidly mounted at an intermediate point to the free end of a respective one of the second levers. A pair of linkages connect the upper end of each respective arm to the corresponding lateral side of the chair back support. The pair of extendable chair seat supports each comprise a first and second portions which slidably engage one another with the free end of the first portion pivotally connected to the corresponding one of the lateral sides of the back support at a given length below the mounting point for the corresponding one of the first levers, and the free end of the second portion is pivotally connected to the corresponding one of the front arms at a shorter length below the intermediate point on the arm. With this mechanism, the chair seat which is supported by the pair of extendable seat supports, will assume a comfortable angle with respect to the horizontal when the chair is in a seating position and will assume a horizontal position coplanar with the back of the chair in the stretcher position.

DRWD

PAC DESCRIPTION OF THE FIGURES

PAR These and other objects, features and advantages of the invention will be more particularly appreciated with reference to the accompanying figures.

PAR FIG. 1 is a three dimensional overall view of the convertible wheelchair invention.

PAR FIG. 2 is a more detailed breakaway view of the chair seat mechanism.

PAR FIG. 3a illustrates the relative position of the elements for the chair seat mechanism when the chair is in a fully erect seating position.

PAR FIG. 3b illustrates the chair of FIG. 3a, at a position intermediate between the fully erect seated position and a fully reclining stretcher position.

PAR FIG. 3c illustrates the chair of FIG. 3a, in the fully reclining stretcher position.

PAR FIG. 4 further illustrates the leg support mechanism of the chair.

PAR FIG. 5 is a detailed illustration of the locking mechanism for the seat of the chair.

DETD

PAC DISCUSSION OF THE PREFERRED EMBODIMENT

PAR The convertible wheelchair invention is shown in an overall three dimensional view in FIG. 1. There is seen that a pair of wheeled support frame members 2, each have larger rear wheels 8 and smaller forward wheels 10 attached thereto. The wheeled support frame members 2 are horizontally spaced from one another by means of the struts 4 and 6 and the forward portion of each support frame member is connected to the rearward portion by an additional strut 7. Each wheeled support frame member 2 has a corresponding rearwardly positioned first pivot 12 and a forwardly positioned second pivot 14 at substantially the same elevation above the ground.

PAR As shown in FIG. 2 and 3a, a pair of first levers 16 each have a first length x and are pivotally mounted on a respective one of the first pivots 12. The chair back 18 is supported by the back support 20 which has lateral sides 22 and 22', each proximate to a respective one of the support frame members 2. Each of the lateral sides 22 and 22' is rigidly mounted at 15 to the free end of a corresponding one of the first levers 16.

PAR A pair of second levers 24 each have substantially the first length x and are pivotally mounted on a respective one of the second pivots 14. A pair of front arms 26 are each rigidly mounted at an intermediate point 28 to the free end of the respective one of the second levers 24.

PAR A pair of linkages 30 each have a first end pivotally connected at 31 to a respective one of the front arms 26 at a point a second length w above the intermediate point 28. The linkages 30 have a second end pivotally connected at 33 to a corresponding one of the lateral sides 22 of the back support 20 at substantially the second length w above the mounting point 15 for the corresponding one of the first levers 16. The linkages 30 can serve as arm rests for the chair.

PAR The chair seat 32 is supported by a pair of extendable chair seat supports

34. Each chair seat support 34 is proximate to a respective one of the support frame members 2. Each extendable chair seat support 34 comprises a first portion 36 and the second portion 38 which slidably engage one another. The free end of the first portion 36 is pivotally connected at 40 by means of the cross member 42 to a corresponding one of the lateral sides 22 of the back support 20 at a third length Y below the mounting point 15 for the corresponding one of the first levers 16. The free end of the second portion 38 is pivotally connected at 44 by means of the cross member 46 to a corresponding one of the front arms 26 at a fourth length y below the intermediate point 28. The third length Y is greater than the fourth length y so that the extendable seat support 34 will assume a comfortable angle .theta. with respect to the horizontal when the chair is in a seating position as is shown to better advantage in FIG. 3a and will assume a horizontal position coplanar with the back 18 of the chair when the chair is in the stretcher position, shown to better advantage in FIG. 3c.

PAR The chair seat 32 and back 18 may be locked in any relative position between a fully erect seated position as is shown in FIG. 3a and a fully reclined stretcher position as is shown in FIG. 3c by means of the seat locking means such as the set screw 51 shown in FIGS. 3a-3c or the locking shoe 82 shown in FIG. 5. A cross member 49 is rigidly connected to the struts 7 on both of the wheeled support frame members 2. A first tube 74 is pivotally mounted by means of the pivot mount 73 to the cross member 49. A second tube 50 is mounted in sliding engagement with the first tube 74, with its free end pivotally connected to the cross member 46 which, in turn, is connected to the pair of extendable seat supports 34. A locking means mounted to the first tube 74 comprises the extensions 76 having a first end rigidly mounted to the tube 74 and a second end which forms a pivot point 78 for the arms 80. Pivotally attached to the arms 80 is a locking shoe 82 which can selectively frictionally engage the second tube 50. Locking arms 80 are loaded by the tension spring 84 so as to normally cause the engagement of the locking shoe with the tube 50. Control cable 86 connected to the arms 80, permits the selective engagement of the locking shoe with respect to the tube 50, by actuating knob 88.

PAR FIG. 4 illustrates the leg support member 52 which can assume any angular position with respect to the horizontal without regard for the relative position of the seat 32 and back 18 of the chair. The leg support member 52 is pivotally mounted on the cross member 46. The cross member 46 connects to the second portions 38 of each of the pair of extendable seat supports 34. A first tube 62 is pivotally mounted by means of the pivot 54 on the second portion 38 of one of the pair of extendable seat supports 34 in a position rearward of the mounting point at the cross member 46 for the leg support member 52. A second tube 60 is mounted in sliding engagement with the first tube 62, with its free end pivotally connected at pivot 56 to the leg support member 52. A locking means 64 which may be a set screw for example, is mounted on the first tube 62 and may be placed in selective frictional engagement with the second tube 60. In this manner, the leg support member 52 can assume any angular position with respect to the horizontal without regard for the relative position of the seat 32 and back 18 of the chair. There are two leg support members 52 and 52' and each has the corresponding elements described above and are capable of independent adjustment of their relative position.

PAR Each leg support member 52 and 52' may have its length adjusted to accommodate varying leg sizes. The leg support member comprises a first and second outer tubes 66, each pivotally mounted on the cross member 46. The cross member 46 is, in turn, mounted to the second portion 38 of each of the pair of extendable seat supports 34. A first and second inner tubes 68 are each mounted in sliding engagement with a respective one of the outer tubes 66. A foot rest means 72 which may be, for example, a folding foot rest of conventional design, is mounted on the free ends of the inner tubes 68. A locking means 70 which may be for example, a set screw, is mounted on one of the outer tubes 66 and may be placed in selective frictional engagement with the corresponding one of the inner tubes 68. In this manner, each leg support member 52 and 52' may have its length independently adjusted.

PAR Although the invention has been described with some specificity, it is understood that the present disclosure is made only by way of example and that many changes in the details of construction and the combination and the arrangement of the elements may be made without departing from the spirit and the scope of the invention.

CLMS

STM We claim:

NUM 1.

PAR 1. A wheelchair convertible into a wheeled stretcher, comprising:

PA1 a pair of wheeled support frame members horizontally spaced from one another, each having a corresponding rearwardly positioned first pivot and a forwardly positioned second pivot at substantially the same elevation;

PA1 a pair of first levers, each having a first length and pivotally mounted on a respective one of said first pivots;

PA1 a chair back support having two lateral sides each proximate to a respective one of said support frame members, each rigidly mounted to the free end of a corresponding one of said first levers;

PA1 a pair of second levers, each having substantially said first length and pivotally mounted on a respective one of said second pivots;

PA1 a pair of front arms, each rigidly mounted at an intermediate point to the free end of a respective one of said second levers;

PA1 a pair of linkages, each having a first end pivotally connected to a respective one of said front arms at a point a second length above said intermediate point and a second end pivotally connected to a corresponding one of said lateral sides of said back support at substantially said second length above said mounting point for the corresponding one of said first levers;

PA1 a pair of extendable chair seat supports, each proximate to a respective one of said support frame members, each comprising a first and second portions which slideably engage one another with the free end of said first portion pivotally connected to a corresponding one of said lateral sides of said back support at a third length below said mounting point for the corresponding one of said first levers and with the free end of said second portion pivotally connected to a corresponding one of said front arms at a fourth length below said intermediate point, said third length being greater than said fourth length;

PA1 whereby a chair seat supported by said pair of extendable seat supports, will assume a comfortable angle with respect to the horizontal when the chair is in a seating position, and will assume a horizontal position coplanar with the back of the chair when the chair is in a stretcher position.

NUM 2.

PAR 2. The apparatus of claim 1, which further comprises:

PA1 a first tube pivotally mounted to said pair of support frame members;

PA1 a second tube mounted in sliding engagement with said first tube, with its free end pivotally connected to said second portions of said pair of extendable seat supports;

PA1 locking means mounted on said first tube and in selective frictional engagement with said second tube;

PA1 whereby said chair seat and back may be locked in any relative position between a fully erect seated position and a fully reclined stretcher position.

NUM 3.

PAR 3. The apparatus of claim 1, which further comprises:

```
      of extendable seat supports;
PA1  a first tube pivotally mounted on said second portion of one of said pair
      of extendable seat supports, rearwardly of the mounting point for said leg
      support member;
PA1  a second tube mounted in sliding engagement with said first tube, with its
      free end pivotally connected to said leg support member;
PA1  locking means mounted on said first tube and in selective frictional
      engagement with said second tube;
PA1  whereby said leg support member can assume any angular position with
      respect to the horizontal without regard for the relative positions of
      said seat and back of the chair.
NUM  4.
PAR  4. The apparatus of claim 3, wherein said leg support member further
      comprises:
PA1  a first and second outer tubes, each pivotally mounted on said second
      portions of said pair of extendable seat supports;
PA1  a first and second inner tubes, each mounted in sliding engagement with a
      respective one of said outer tubes;
PA1  a foot rest means mounted on the free ends of said inner tubes;
PA1  a locking means mounted on one of said outer tubes and in selective
      frictional engagement with the corresponding one of said inner tubes;
PA1  whereby said leg support member may have its length adjusted.
NUM  5.
PAR  5. The apparatus of claim 4, which further comprises two of said leg
      support members being so mounted on the chair, capable of independent
      adjustment of their relative positions. .Iadd.
NUM  6.
PAR  6. A wheelchair convertible into a wheeled stretcher, comprising:
PA1  a pair of wheeled support frame members, horizontally spaced from one
      another, each having a corresponding rearwardly positioned first pivot,
      and a forwardly positioned second pivot at substantially the same
      elevation;
PA1  a pair of first lever means, each having a first length and pivotally
      mounted on a respective one of said first pivots;
PA1  a chair back support having two lateral sides, each proximate to a
      respective one of said support frame members and each rigidly mounted to
      the free end of a corresponding one of said first lever means;
PA1  a pair of second lever means, each having substantially said first length
      and pivotally mounted on a respective one of said second pivots;
PA1  a pair of front arm members, each rigidly mounted at an intermediate point
      to the free end of a respective one of said second lever means;
PA1  a pair of linkages, each having a first and pivotally connected to one of
      said front arm members at a point a second length above said intermediate
      point and a second end pivotally connected to a corresponding one of said
      lateral sides of said back support at substantially said second length
      above said mounting point for the corresponding one of said first lever
      means;
PA1  a pair of seat support members, pivot means connecting one end of said pair
      of seat support members to said chair back support at a third length below
      said mounting point for the corresponding one of said first lever means,
      the opposite end of said pair of seat support members being supported by
      the lower portion of said front arm members at a fourth length below said
      intermediate point, said third length being greater than said fourth
      length to thereby position said seat support at an angle .theta. to the
      horizontal; and lost motion means operatively connected between said
      opposite end of said seat support members and the lower portion of said
      front arm members; the chair back support, the front arm members, the
      linkages and associated pivot points to said front arm members and said
      back support, the seat support members and associated pivot means on said
      chair back and lost motion means on said front arm members, all being
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       substantially horizontally coplanar when the chair is folded to a
       stretcher position,
PA1   whereby a chair seat supported by said pair of seat support members will
       assume a comfortable angle with respect to the horizontal when the chair
       is in a seating position, and will assume a horizontal position coplanar
       with the back of the chair when the chair is in a stretcher position.
       .Iaddend. .Iadd.
NUM   7.
PAR   7. The apparatus of claim 6 which further comprises a pair of leg support
       members operatively supported by said chair and being capable of
       independent adjustment of their relative positions. .Iaddend. .Iadd.
NUM   8.
PAR   8. The apparatus of claim 6 which further comprises:
PA1   a first tube pivotally mounted to said pair of support frame members;
PA1   a second tube mounted in sliding engagement with said first tube, with its
       free end pivotally connected to said pair of seat support members;
PA1   locking means mounted on said first tube and in selective frictional
       engagement with said second tube;
PA1   whereby said chair seat back may be locked in any relative position between
       a fully erect seated position and a fully reclined stretcher position.
       .Iaddend. .Iadd.
NUM   9.
PAR   9. The apparatus of claim 6 which further comprises:
PA1   leg support means pivotally mounted on said pair of seat supports;
PA1   a first tube pivotally mounted on said pair of seat supports rearwardly of
       the mounting point for said leg support means;
PA1   a second tube mounted in sliding engagement with said first tube, with its
       free end pivotally connected to said leg support means; and
PA1   locking means mounted on said first tube and in selective frictional
       engagement with said second tube; whereby said leg support means can
       assume any angular position with respect to the horizontal without regard
       for the relative positions of said seat and back of the chair.
       .Iaddend..Iadd.
NUM   10.
PAR   10. The apparatus of claim 9 wherein said leg support means further
       comprises:
PA1   first and second outer tubes each pivotally mounted on said pair of seat
       supports;
PA1   first and second inner tubes, each mounted in sliding engagement with a
       respective one of said outer tubes;
PA1   foot rest means mounted on the free ends of said inner tubes; and
PA1   locking means mounted on one of said outer tubes and in selective
       fricitional engagement with the corresponding one of said inner tubes;
PA1   whereby said leg support means may have its length adjusted. .Iaddend.
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PATN
WKU  T01019015
SRC  6
APN  2852136
APT  5
PBL  H
ART  173
APD  19810720
TTL  Ammonium polyphosphate sulfate fertilizers from wet-process phosphoric acid
ISD  19820601
NCL  6
NDR  2
NPS  29
INVT
NAM  Achorn; Frank P.
STR  Box 176
CTY  Killen
STA  AL
ZIP  35645
INVT
NAM  McGill; Kenneth E.
STR  Rte. 1, Box 163
CTY  Virginia Shores, Sheffield
STA  AL
ZIP  35660
CLAS
OCL   71 36
XCL   71 40
XCL   71 6410
EDF  3
ICL  C05B  700
ABST
PAR  A process for the production of fluid fertilizers (suspensions and/or
      solution type) made from merchant-grade phosphoric acid (50-58 percent
      P.sub.2 O.sub.5), sulfuric acid, liquid anhydrous ammonia, and water,
      wherein liquid ammonia is heated in heat exchange means juxtaposed hot
      fertilizer product to form gaseous ammonia, which gaseous ammonia, along
      with phosphoric acid and sulfuric acid, is fed to a pipe-cross reactor
      wherein a melt of ammonium polyphosphate sulfate is formed, which melt is
      subsequently mixed with cooled recycled product to produce a fluid
      fertilizer with N:P.sub.2 O.sub.5 weight ratios ranging from about 0.3 to
      1, which contains from about 10 to 60 percent of its P.sub.2 O.sub.5
      values in the form of polyphosphates and 3 to 8 percent by weight sulfur.
      About 45 percent of the P.sub.2 O.sub.5 as polyphosphate is easily
      attainable in the product with ambient acid feed temperatures, i.e., about
      50.degree. F. to 100.degree. F., versus prior-art teachings of only about
      15 percent poly formation with preheat of the feed acids. It is a solution
      when it is produced, and when diluted with 10 percent by weight water, it
      can be stored at 40.degree. F. without the formation of troublesome
      crystals. When gelling clay is added, it stores well as a suspension and
      remains fluid at temperatures as low as -25.degree. F.
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PATN
WKU  043322352
SRC  6
APN  1332104
APT  1
ART  345
APD  19800324
TTL  Rotating air draft fireplace
ISD  19820601
NCL  7
ECL  1
EXA  Green; Randall L.
EXP  Scott; Samuel
NDR  1
NFG  4
INVT
NAM  Hannebaum; Harold W.
STR  P.O. Box H
CTY  Shoshone
STA  ID
ZIP  83352
RLAP
COD  72
APN  943842
APD  19780919
PSC  01
PNO  4273096
RLAP
COD  82
APN  843827
APD  19771020
PSC  01
PNO  4181117
RLAP
COD  82
APN  762014
APD  19770124
PSC  03
CLAS
OCL  126120
XCL  126146
XCL  126164
EDF  3
ICL  F24B  118
FSC  126
FSS  120;121;123;126;298;164;165;146
FSC  D23
FSS  96;97
FSC  D 7
FSS  207;211
FSC  211
FSS  60 R
FSC  108
FSS  91
UREF
PNO  237750
ISD  18810200
NAM  Johnston
OCL  126164
UREF
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PNO  3339540
ISD  19670900
NAM  Kreider
XCL  126164
UREF
PNO  3499432
ISD  19700300
NAM  Hannebaum
OCL  126120
UREF
PNO  4156418
ISD  19790500
NAM  Berg
OCL  126120
UREF
PNO  4176652
ISD  19791200
NAM  Berg
XCL  126120
LREP
FR2  Podell; Howard I.
ABST
PAL  An enclosed fireplace of circular cross-section mounted on a pedestal in
      which air is drawn into the fire chamber from spaced vertical air intake
      tubes mounted about the periphery of the fire chamber. A free standing
      wood holder rests on the center of the fire chamber and is formed of
      spaced horizontal concentric rings joined to a plurality of vertical legs,
      each leg being in the shape of a flat vane. The legs are oriented so that
      each of the vanes extend in a common circular direction away from the
      external perimeter of the rings, at an angle to the radius of the rings at
      the juncture of the vanes to the rings so as to impart a rotational torque
      to draft air passing by said vanes into the interior of the rings. The
      rings are of a size to contain one or more pieces of firewood with each
      piece preferably oriented along its vertical axis. The air intake tubes
      are preferably joined to a common air intake that enters through the
      bottom of the fireplace pedestal.
PARN
PAR  This invention is a continuation-in-part of co-pending application Ser. No.
      943,842, now U.S. Pat. No. 4,273,096 filed on Sept. 19, 1978, which
      application is a continuation-in-part of application Ser. No. 843,827, now
      U.S. Pat. No. 4,181,117 filed on Oct. 20, 1977, which is a
      continuation-in-part of abandoned application Ser. No. 762,014 filed on
      Jan. 24, 1977. Application Ser. No. 843,827 has been issued as U.S. Pat.
      No. 4,181,117.
BSUM
PAC  BACKGROUND OF THE INVENTION
PAR  Circular enclosed fireplaces have been known in the art. U.S. Pat. No.
      3,499,432 describes such a fireplace which I invented and discloses means
      to impart a rotational motion to intake air to produce a beautiful
      lighting effect, while at the same time keeping the external windows of
      the enclosure free of soot. Other circular fireplaces are disclosed in
      U.S. Pat. Nos. 3,515,122; 3,809,058; 3,768,457; 4,156,418; 3,910,251; and
      4,112,913; and 3,260,256. U.S. Pat. No. 4,131,108 discloses an andiron for
      standing logs in a fire chamber.
PAC  SUMMARY OF THE INVENTION
PAR  My invention is an enclosed fireplace of circular cross-section mounted on
      a pedestal in which air is drawn into the fire chamber from spaced
      vertical air inake tubes mounted about the periphery of the fire chamber.
      A free standing wood holder rests on the center of the fire chamber and is
      formed of spaced horizontal concentric rings joined to a plurality of
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vertical legs, each leg being in the shape of a flat vane. The legs are oriented so that each of the vanes extend in a common circular direction away from the external perimeter of the rings, at an angle to the radius of the rings, at the juncture of the vanes to the rings, so as to impart a rotational torque to draft air passing by said vanes into the interior of the rings. The rings are of a size to contain one or more pieces of firewood with each piece preferably oriented along its vertical axis. The air intake tubes are preferably joined to a common air intake that enters through the bottom of the fireplace pedestal.

PAR This invention improves on the advantages of my previous fireplace inventions by imparting a rotational torque to the intake air as it directly approaches the center of the fire chamber, so as to evenly feed the flames of vertically stacked firewood. This rotational torque is imparted to the intake air by the vanes of the shaped wood holder, with the spaced rings of the wood holder serving to maintain the firewood along a vertical axis so as to distribute the bulk of the radiant heat from the flaming firewood through the transparent walls of the enclosure of the fire chamber.

PAR The vertical air intake tubes, by being joined to a common central intake duct, permit intake air to be drawn into the fireplace from below the floor of the fireplace or from a duct that extends through a side wall of the room in which the fireplace is mounted.

DRWD

PAC BRIEF DESCRIPTION OF THE DRAWINGS

PAR The objects and features of the invention may be understood with reference to the following detailed description of an illustrative embodiment of the invention, taken together with the accompanying drawings in which:

PAR FIG. 1 is a perspective view of the wood holder of the invention;

PAR FIG. 2 is a detail perspective view of an air intake tube;

PAR FIG. 3 is a detail perspective view of an alternative embodiment of the fire chamber and pedestal with the wood holder removed; and

PAR FIG. 4 is a perspective view of the invention.

DETD

PAC DESCRIPTION OF THE PREFERRED EMBODIMENT

PAR Turning now descriptively to the drawings, in which similar reference characters denote similar elements throughout the several views, FIG. 4 illustrates the fireplace 10 which is formed with a conical metal hood 12 connected to a flue pipe 14, and resting on the top of transparent vertical side walls 16. Side walls 16 form a polygon in plan view being joined at their common vertical edges with sealing material or sealing strips. An upturned conical base 18 supports the side walls 16 and is mounted on a hollow pedestal section 20 that rests on a floor 22.

PAR At spaced intervals about the interior of the side walls 16, and preferably at the vertical juncture of two such walls, vertical hollow air intake tubes 24 extend the height of the side walls. Each tube 24 is joined at its bottom end to a draft tube 26 that extends within the base 18 to the interior 28 of the pedestal. The base is filled with cemented refractory material 30 to form a floor for the fire chamber on which wood holder 40 rests.

PAR Wood holder 40 is formed of a plurality of spaced concentric horizontal rings 42, all welded at their periphery to a plurality of vane-shaped legs 44. Each leg 44 is preferably in the form of a thin flat strip, with the exterior face surfaces 46 of the strip, each extending along a plane that extends, when seen from above, at an angle to a radial line 50 drawn from the juncture of the vane and the ring, with all face surfaces similarly oriented so as to direct air approaching from the exterior of the wood holder into a rotary path within the wood holder in a common circular direction.

PAR The size of rings 42 is such as to permit a plurality of pieces of firewood rings, each of a diameter of twelve inches and fixed to vane legs so as to extend a height of twelve inches is satisfactory for common sizes of split firewood. The wood holder may be fixed to the refractory floor of the fire chamber. However, the vane legs which extend from the periphery of the rings furnishes excellent stability to a free standing wood holder, which may be lifted above the refractory floor for cleaning purposes.

PAR Vertical air intake tubes 24 are each formed with an exterior open slit 62 along a trailing edge of the tube, as seen from above, with all slits oriented so as to impart a rotary motion in a common direction to air exiting from the slits, which direction is in the same circular direction as that to which the vane legs of the wood holder are oriented.

PAR The interior 28 of the pedestal may be joined to an opening 67 under the floor, with an air intake duct 66 joined to opening 67 or alternatively a horizontal intake tube 68 may extend from the interior of the pedestal to exit through an exterior wall adjacent the fireplace.

PAR Preferably the side walls may extend sixteen inches between base and hood, with opposed walls approximately thirty-two inches apart.

PAR As shown in FIG. 3, alternatively the refractory section 30 at the base of the fire chamber may be suspended within the pedestal housing so as to provide an air intake chamber 70 between the refractory section 30 and the housing walls of the pedestal. Preferably, as shown in FIG. 4, the refractory section 30 extends to the housing walls of the pedestal, with air draft tubes 26 embedded in the refractory section 30.

PAR Since obvious changes may be made in the specific embodiment of the invention described herein, such modifications being within the spirit and scope of the invention claimed, it is indicated that all matter contained herein is intended as illustrative and not as limiting in scope.

CLMS

STM Having thus described the invention, what I claim as new and desire to secure by Letters Patent of the United States is:

NUM 1.

PAR 1. An enclosed fireplace in which a fire chamber, fitted with means to introduce intake air into said chamber, is formed by vertical walls fitted with first non-moveable means to impart a rotational movement in the fire chamber, to intake air entering the fire chamber, with said fireplace fitted with second non-moveable means to impart a further rotational movement, in the same direction, to the air already in the fire chamber that approaches a central location of the fire chamber in which a supply of fuel may be located, so as to cause a rotating draft of intake air about burning fuel located in said central location of the fire chamber,

PA1 in which the first said non-moveable means comprise a plurality of vertical tubes mounted in the fire chamber adjacent to the vertical walls of the chamber, with each tube joined at its base to a duct leading to a supply of intake air, and with a vertical exit slit extending substantially the length of each tube and located so as orient air exiting from said slit in a common circular direction in the fire chamber.

NUM 2.

PAR 2. The combination as recited in claim 1, in which the second said means is in the form of a plurality of spaced joined vertical legs, locatable about the center of the fire chamber with each leg in the shape of a flat fin, and each located so as to orient air passing the legs in a common circular direction about the center of the fire chamber.

NUM 3.

PAR 3. The combination as recited in claim 2 in which the vertical flat fins are joined together by a plurality of spaced circumferentially oriented means, which bars serve to both fix the fins in position and to form an enclosure that serves as retaining means for maintaining stacked firewood in a vertical position in the interior of the said second means.

NUM 4.

PAR 4. The combination as recited in claim 3 in which the said means are in the

```
     form of circumferential rings.
NUM  5.
PAR  5. The combination as recited in claim 3 in which the said means are fixed
     to the fins so that the fins extend substantially outwards of the
     enclosure bound by the bars.
NUM  6.
PAR  6. The combination as recited in claim 3 in which the said means extend
     substantially in the horizontal direction, when the fins are aligned along
     their normal vertical axis.
NUM  7.
PAR  7. An enclosed fireplace in which a fire chamber, fitted with means to
     introduce intake air into said chamber, is enclosed by vertical walls
     fitted with non-moveable means to impart a rotational movement, in the
     fire chamber, to intake air entering the fire chamber, so as to cause a
     rotating draft of intake air about burning fuel located in a central
     location of the fire chamber, in which the said means comprise a plurality
     of vertical tubes mounted in the fire chamber adjacent to the vertical
     walls of the chamber, with each tube joined at its base to a duct leading
     to a supply of intake air, and with a vertical exit slit extending
     substantially the length of each tube and located so as orient air exiting
     from said slit in a common circular direction in the fire chamber.
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PATN
WKU  043327249
SRC  5
APN  8519927
APT  1
ART  126
APD  19771116
TTL  Process for preparing 4,5,6,7-tetrahydro-7-oxobenzo[b]thiophenes and
      1,2,3,4-tetrahydro-4-oxonaphthalenes
ISD  19820601
NCL  25
ECL  1
EXP  Siegel; Alan
INVT
NAM  Bentley; Terence J.
CTY  Cranbury
STA  NJ
INVT
NAM  Gastrock; William H.
CTY  Hightstown
STA  NJ
INVT
NAM  Asato; Goro
CTY  Titusville
STA  NJ
ASSG
NAM  American Cyanamid Co.
CTY  Stamford
STA  CT
COD  02
RLAP
COD  71
APN  713768
APD  19760812
PSC  03
GLAS
OCL  260326S
XCL  549 51
XCL  560 28
XCL  564 45
XCL  564 44
XCL  564 48
XCL  564161
XCL  564166
XCL  564176
XCL  564215
XCL  548465
XCL  548473
XCL  548527
XCL  548545
XCL  548548
EDF  3
ICL  C07D20934
ICL  C07D20724
ICL  C07D33324
ICL  C07C12506
FSC  260
FSS  332.2 R;332.3 P;586 P;590 C;326 S;326.5 SA;326.5 C;326 A;326 R
FSC  549
FSS  51
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FSC  560
FSS  28
FSC  564
FSS  45;44;48;161;166;176;215
UREF
PNO  3546303
ISD  19701200
NAM  Hornberger
OCL  260586
UREF
PNO  3994924
ISD  19761100
NAM  Asato
OREF
PAL  House "Modern Synthesis Reactions", 2nd ed. (1972), p. 278.
LREP
FR2  Jackson; H. G.
ABST
PAL  There is provided a process for the preparation of an amido or an ureido
      derivative of certain 4,5,6,7-tetrahydro-7-oxobenzo[b]thiophenes or
      certain 1,2,3,4-tetrahydro-4-oxonaphthalenes which can be employed as an
      animal growth regulant. The process comprises: oxidizing in the presence
      of a cobalt catalyst a compound having the formula:
      ##STR1##
      wherein R.sub.1 and R.sub.2 are each a substituent selected from the group
      consisting of alkanoyl C.sub.1 -C.sub.7, halogen-substituted alkanoyl
      C.sub.1 -C.sub.7, carboalkoxy C.sub.1 -C.sub.4,
      ##STR2##
      and
      ##STR3##
      R.sub.3 is selected from the group consisting of hydrogen and alkyl
      C.sub.1 -C.sub.4 ; R.sub.4 is selected from the group consisting of hydr
      ogen, alkyl C.sub.1 -C.sub.8, alkanoyl C.sub.2 -C.sub.4,
      halogen-substituted alkanoyl (C.sub.2 -C.sub.4), and
      ##STR4##
      and when the
      ##STR5##
      moiety is cyclized each represents a moiety selected from the group
      consisting of succinimido, maleimido and phthalimido; X and Y are each a
      radical selected from the group consisting of hydrogen, fluorine,
      chlorine, bromine, iodine, nitro, alkyl C.sub.1 -C.sub.4 ; the racemic
      mixtures and the optical isomers thereof.
PARN
PAR  This is a continuation, of application Ser. No. 713,768 filed Aug. 12,
      1976, now abandoned.
BSUM
PAR  The present invention relates to a novel process for the preparation of
      amido and ureido derivatives of 4,5,6,7-tetrahydro-7-oxobenzo[b]thiophene
      and 1,2,3,4-tetrahydro-4-oxo-naphthalene which are useful as animal growth
      regulants. More particularly, it relates to the oxidation of amido or
      ureido derivatives of 4,5,6,7-tetrahydro-benzo[b]thiophenes or
      1,2,3,4-tetrahydro-4-oxo-naphthalenes. Still more particularly, it is
      concerned with a process for the preparation of an amido or an ureido
      derivative of certain 4,5,6,7-tetrahydro-7-oxobenzo[b]thiophenes or
      certain 1,2,3,4-tetrahydro-4-oxonaphthalenes which comprises oxidizing in
      the presence of a cobalt catalyst a compound having the formula:
      ##STR6##
      wherein R.sub.1 and R.sub.2 are each a substituent selected from the group
      consisting of alkanoyl C.sub.1 -C.sub.7, halogen-substituted alkanoyl
      C.sub.1 -C.sub.7, carboalkoxy C.sub.1 -C.sub.4
```

##STR7##

and

##STR8##

R.sub.3 is a radical selected from the group consisting of hydrogen and alkyl C.sub.1 -C.sub.4 ; R.sub.4 is a radical selected from the group consisting of hydrogen, alkyl C.sub.1 -C.sub.8, and alkanoyl (C.sub.2 -C.sub.4) halogen-substituted alkanoyl (C.sub.2 -C.sub.4) and

##STR9##

and when the

##STR10##

moiety is cyclized, each represents a moiety selected from the group consisting of succinimido, maleimido and phthalimido; X and Y are each a radical selected from the group consisting of hydrogen, fluorine, chlorine, bromine, iodine, nitro, alkyl C.sub.1 -C.sub.4 ; the racemic mixtures and the optical isomers thereof.

PAR The above-identified tetrahydro-oxobenzo[b]thienylureas are useful as animal growth promoting agents as disclosed in German Offenlegungschrift No. 2,501,788, published on July 7, 1975, and in an application for U.S. Pat., Ser. No. 532,449, filed Dec. 13, 1974. Further, the above-identified tetrahydro-oxonaphthylureas and their use as animal growth promoting agents are disclosed in an application of G. Asato, for U.S. Pat., Ser. No. 582,559, filed on May 30, 1975. Since there is an ever increasing demand for greater food production, animal growth-promoting agents are of considerable interest. Consequently, it is of prime importance to find processes suitable for large-scale manufacturing of said animal growth-promoting compounds in satisfactory yields.

PAR In accordance with the process of the invention, it has been found that one of the alpha-methylene groups of a cycloalkanoheterocycle of formula (I) or benzocycloalkane of formula (II) set forth hereinbelow can be oxidized, albeit the presence of a nitrogen containing functional group, such as an amido or ureido group attached to the carbon atom of the second alpha-methylene group, so as to obtain in good yields the corresponding oxo compounds of formula (III) or (IV), respectively, as graphically illustrated:

##STR11##

where R.sub.1 and R.sub.2 are each as defined above.

PAR A preferred group of compounds represented by formula (I) or (II) above is that wherein R.sub.1 and R.sub.2 are each a radical selected from the group consisting of alkanoyl C.sub.1 -C.sub.7, halogen-substituted alkanoyl C.sub.2 -C.sub.4, benzoyl and

##STR12##

R.sub.3 is a radical selected from the group consisting of hydrogen and alkyl C.sub.1 -C.sub.4 ; R.sub.4 is a radical selected from the group consisting of hydrogen and alkyl C.sub.1 -C.sub.8, acetyl, trichloroacetyl and benzoyl; and where the

##STR13##

moiety is cyclized, each represents phthalimido; the racemic mixtures and the optical isomers thereof are oxidized in accordance with the process of the invention to the corresponding formula (III) of (IV), above.

PAR Another preferred group of compounds represented by formula (I) or (II) above is that wherein R.sub.1 and R.sub.2 are each a radical selected from the group consisting of formyl, acetyl,

##STR14##

benzoyl and

##STR15##

R.sub.3 is a radical selected from the group consisting of hydrogen, methyl and iso-propyl; R.sub.4 is a radical selected from hydrogen, methyl, n-octyl and benzoyl; and when the

##STR16##

moiety is cyclized, each represents phthalimido; the racemic mixtures and the optical isomers thereof are oxidized by the process of the invention to the corresponding formula (III) or (IV), above.

PAR As hereinabove indicated, the 4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-ylurea compounds of formula (III) and the 1,2,3,4-tetrahydro-4-oxo-1-naphthylurea compounds of formula (IV) are valuable and useful growth promoting agents for poultry, fur-bearing animals and farm animals.

PAR In general, a compound represented by formula (I) or (II) above is oxidized with an oxygen-containing gas, such as oxygen, air or a mixture of oxygen and an inert gas, such as helium at atmospheric or superatmospheric pressure in the presence of a cobaltous or cobaltic salt catalyst in an organic solvent such as (a) a lower alkanoic acid or the anhydride thereof (b) a mixture of a lower alkanoic acid and an aliphatic or cycloaliphatic ketone, or (c) an aliphatic aldehyde other than formaldehyde, at a temperature range of 20.degree. C. to 150.degree. C. and, preferably, at from 25.degree. C. to 120.degree. C. The aforementioned reaction can be graphically illustrated as follows:

##STR17##

wherein R.sub.1 and R.sub.2 are each as defined above.

PAR In the process above described, a compound of formula (I) or formula (II) is oxidized in a straightforward manner with oxygen, or with oxygen admixed with an inert gas such as nitrogen, helium, argon, neon, xenon and krypton, or with air and, preferably, with oxygen, oxygen-nitrogen mixtures and air, at pressures ranging from atmospheric to superatmospheric pressures usually up to 200 psig and, preferably, from 25 to 100 psig in the presence of a cobalt salt catalyst, such as CoBr.sub.2 and Co(OAc).sub.2. However, the preferred catalyst is cobaltous acetate bromide (CAB), prepared by mixing approximately equimolar amounts of cobaltous acetate (or its tetrahydrate) and cobaltous bromide (or its tetrahydrate) with an appropriate amount of water in a C.sub.2 -C.sub.6 alkanoic acid. Alternatively, it can be prepared from cobaltous acetate tetrahydrate and a solution of hydrogen bromide in acetic acid and in a C.sub.2 -C.sub.6 alkanoic acid, or from cobaltous acetate tetrahydrate and aqueous hydrogen bromide in a mixture of a C.sub.2 -C.sub.6 alkanoic acid and a C.sub.2 -C.sub.6 alkanoic acid anhydride. The molar ratio of substrate to catalyst ranges from about 1:1 to 15:1 and, preferably, from about 1.5:1 to 6:1.

PAR In general, the above reaction is carried out in an organic solvent selected from the group consisting of

PAR (a) a C.sub.2 -C.sub.6 alkanoic acid, such as propionic or isobutyric acid, or the corresponding anhydride thereof,

PAR (b) a mixture of C.sub.2 -C.sub.6 alkanoic acid, preferably acetic acid or isobutyric acid with an aliphatic ketone, such as acetone, methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, methyl isoamyl ketone and a cycloaliphatic ketone, such as cyclohexanone, or an aliphatic aldehyde other than formaldehyde, and

PAR (c) a mixture of a C.sub.2 -C.sub.6 alkanoic acid, preferably, acetic acid or isobutyric acid, with t-butyl alcohol or acetonitrile

PAL at a temperature in the range of 20.degree. C. to 150.degree. C. and, preferably, from 25.degree. C. to 120.degree. C., at atmospheric pressure. When the reaction is carried out at a superatmospheric pressure, ambient temperature usually is sufficient, but the rate of the reaction can be increased by heating said reaction mixture. It has also been found that when the oxidation reaction of said novel process is carried out at near ambient temperature, then the rate of the reaction can be increased by introducing into the reaction mixture catalytic amounts of free radical initiators, such as azobisisobutyronitrile, hydrogen peroxide, t-butyl peroxide, dibenzoyl peroxide or peracids, such as peracetic acid and perbenzoic acid.

conveniently followed by an oxygen analyzer, as well as by measuring the flow rates of oxygen entering and leaving the reaction mixture. The reaction is substantially complete when the oxygen uptake is no longer measureable. In addition, standard analytical procedures, such as gas chromatographic or high pressure liquid chromatographic analysis, can be used to check the completeness of the oxidation.

PAR Thus, when R.sub.2 is

##STR18##

and R.sub.3 and R.sub.4 are as hereinabove defined, the oxo compounds obtained by the above process are usually the desired animal growth promoting ureas, namely, 4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-ylureas of formula (VII) and 1,2,3,4-tetrahydro-4-oxo-1-naphthylureas of formula (VIII) as graphically illustrated below:

##STR19##

wherein R.sub.3 is selected from the group consisting of hydrogen, and alkyl C.sub.1 -C.sub.4 ; R.sub.4 is hydrogen, alkyl C.sub.1 -C.sub.4, alkanoyl C.sub.2 -C.sub.4, halogen-substituted alkanoyl C.sub.2 -C.sub.4 and

##STR20##

X and Y are selected from the group consisting of hydrogen, halogen, nitro and alkoxy C.sub.1 -C.sub.4 ; the word "halogen" is used above to represent bromine, chlorine, fluorine and iodine; and said compounds are the racemic mixtures and the optical isomers thereof.

PAR When R.sub.4 is defined as alkanoyl C.sub.2 -C.sub.4, halogen-substituted alkanoyl C.sub.2 -C.sub.4 or

##STR21##

X and Y are as defined above, alkaline hydrolysis of these ureas affords ureas of formulae (VII) and (VIII) wherein R.sub.4 is hydrogen.

PAR However, when R.sub.2 is not

##STR22##

then the oxo compounds obtained by the above process are the corresponding formulae (III) and (IV) amides and imides, where

##STR23##

is each cyclized to form a moiety selected from the group of cyclic imides consisting of succinimido, maleimido and phthalimido. These amides and imides can be converted in a straightforward manner to the desired formula (VII) or (VIII) urea compound as follows: As amide (or imide) of formula (III) or formula (IV) is hydrolyzed with dilute acid or alkali, preferably an acid, e.g. hydrochloric acid to the corresponding formula (V) or formula (VI) amine (or a salt thereof) as hereinbelow graphically illustrated:

##STR24##

wherein R.sub.1 and R.sub.2 are each a radical selected from the group consisting of alkanoyl C.sub.1 -C.sub.6, halogen-substituted alkanoyl C.sub.1 -C.sub.6, carboalkoxy C.sub.1 -C.sub.4,

##STR25##

and and when H-N-R.sub.1 or H-N-R.sub.2 is each cyclized, each represents a moiety selected from the group consisting of succinimido, maleimido and phthalimido; X and Y are selected from the group consisting of hydrogen, halogen, nitro and alkoxy C.sub.1 -C.sub.4 ; said "halogen" denoting bromide, chlorine, fluorine and iodine and said compounds are the racemic mixtures and the optical isomers thereof.

PAR Formula (VII) above, namely, 4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-ylurea compounds and formula (VIII) above, namely, 1,2,3,4-tetrahydro-4-oxo-1-naphthylurea compounds, wherein R.sub.3 and R.sub.4 are hydrogen can be advantageously prepared from the above-identified formula (V) or (VI) amines or acid salts thereof, by reacting said amines with an approximately equimolar amounts of sodium or potassium cyanate. However, it is generally preferable to employ from about 5% to about 50% excess of a suitable cyanate. The reaction can be conducted at atmospheric or superatmospheric pressure at a temperature in the range of 0.degree. C. to 100.degree. C., but is preferably conducted at atmospheric pressure at 0.degree. C. to 70.degree. C. in the presence of a solvent, such as water, C.sub.1 -C.sub.3 aliphatic alcohol, tetrahydrofuran, dioxane, ethylene glycol dimethyl ether, acetone, methyl ethyl ketone, and mixtures thereof in the pH range of from 5 to 7 and, preferably, at pH 6. The above reaction may be graphically illustrated as follows:

##STR26##

PAR Substituted ureas of formula (VII) or (VIII) can be prepared advantageously by treating the above-identified amines of formulae (V) or (VI) with an appropriately substituted alkyl isocyanate of formula: R.sub.3 -NCO or with a carbamoyl halide of the formula

##STR27##

halide, wherein R.sub.3 and R.sub.4 are alkyl as hereinabove defined and the halide is chloro or bromo. The free bases of formula (V) or (VI) or the acid addition salts thereof, preferably the hydrochloride, can be employed in the presence of an acid acceptor. Illustrative acid acceptors are pyridine, triethylamine or any suitable tertiary amine, alkali metal carbonates, such as potassium carbonate and sodium carbonate, strong basic ion-exchange resins, and aqueous alkali. The reaction may be run from about 0.degree. C. to 100.degree. C. and, preferably, at 0.degree. C. to 70.degree. C. until the desired reaction is complete. The isocyanate or carbamoyl halide is generally employed in equimolar amounts, but it may be used in excess.

PAR Exemplary organic solvents for the above reactions include: aprotic aromatic solvents, such as benzene, toluene and xylene; chlorinated hydrocarbon solvents, such as methylene chloride, chloroform and dichloroethane; ethers such as tetrahydrofuran, diethyl ether, dimethoxyethane, diethylene glycol dimethyl ether and dioxane; ketones such as acetone, methyl ethyl ketone, methyl butyl ketone, methyl isobutyl ketone; or mixtures of said solvents. The above reactions may be graphically illustrated as follows:

##STR28##

wherein R.sub.3 and R.sub.4 are as hereinabove defined.

PAR All of the hereinbefore described preparations of 4,5,6,7-tetrahydro-7-oxobenzo[b]thiophene-, and 1,2,3,4-tetrahydro-4-oxonaphthalene derivatives yield racemic (dl) mixtures. The optically active isomers of the above compounds can be obtained by the resolution of the racemic (dl) formula (I) or (II) where R.sub.2 is hydrogen, e.g. with (R)-(+)- and (S)-(-)-N-benzoylglutamic acids respectively, in sequence, and employing the thus obtained optically active isomers in subsequent reactions.

PAR As stated above, formulae (VII) and (VIII) compounds are useful as growth promoting agents for animals, such as poultry, fur-bearing and farm animals, and the use of said compounds for this purpose provides the added advantage of improving feed conversion for said animals. The term "feed conversion" means the ratio of unit weight of feed per unit weight of gain and the improvement in feed conversion means increased weight gain from a given unit of feed consumed.

PAR A growth-promoting amount of a formula (VII) or a formula (VIII) compound or an optically active isomer thereof is administered to a host animal in, or with, the animal's feed. Said compound may also be administered as a subcutaneous implant under the skin of said animal or as a parenteral injection. When administered in the feed of said animals, usually from about 0.0001% to about 0.08% by weight, and, preferably, from 0.001% to 0.04% by weight of formula (VII) or formula (VIII) urea, is effective for increasing growth rate and improving feed conversion. When administered as a parenteral injection or subcutaneous implant, usually in amounts that per kg of body weight per day of the active compound, it will produce the desired improvement in weight gain and will enhance feed conversion.

PAR The practice of the present invention is further illustrated by the non-limiting examples set forth below.

DETD

PAC EXAMPLE 1

PAC Preparation of N-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl) acetamide

PAR A mixture of N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)-acetamide (2.0 g; 10.25 m mole), cobaltous acetate (0.49 g; 2.77 m mole), cobaltous bromide tetrahydrate (0.635 g; 2.18 m mole), water (0.4 ml), acetic acid (5.0 ml) and methyl isobutyl ketone (35.0 ml) in suitable flask fitted with a reflux condenser, a gas dispersion tube and a thermometer is stirred vigorously. Air is introduced through the dispersion tube into the turbid blue solution at room temperature for 45 minutes, and then the mixture is heated. After 25 minutes, the solution turns greenish blue (temperature: 45.degree. C.) and in 15 minutes green (temperature: 55.degree. C.). The reaction is run overnight with periodic additions of methyl isobutyl ketone. The greyish green reaction mixture containing some suspended dark gray solid is then diluted with water (40.0 ml) and saturated with sodium chloride. The upper organic phase is separated and the aqueous phase extracted with chloroform (2.times.100 ml). The organic phase and the chloroform extracts are combined, washed with brine (50 ml) and water (25 ml), respectively. The water wash is counter-extracted with chloroform (50 ml) and the chloroform extract added to the above organic phase. The combined organic phase is evaporated in vacuo to afford a gum, which contains the desired compound. The latter is hydrolyzed without further purification and the resultant amine hydrochloride is converted to 4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-ylurea.

PAC EXAMPLE 2

PAC Preparation of 4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-ylurea

PAR The crude material from Example 1 is stirred in a mixture of water (10.0 ml) and concentrated hydrochloric acid (10.0 ml) and heated at reflux for 4.3 hours. The reaction mixture is cooled, the solution decanted from the brown semisolid, which is then further washed with water (2.times.10 ml). The combined aqueous solutions are evaporated to afford brown crystals.

PAR The above crystals are dissolved in water (10 ml), a solution of potassium cyanate (1.55 g; 19 m mole) in water (4 ml) added and the reaction mixture stirred overnight. The reaction mixture is then filtered, the solid collected is washed with water (70 ml) and methanol (10 ml) to attain 1.06 g of title compound, m.p. 234.degree. C. to 236.degree. C.

PAC EXAMPLE 3

PAC Preparation of N-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl)-acetamide

PAR Oxygen is passed into a mixture of N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)acetamide (1.0 g; 5.13 m mole), cobaltous acetate (0.25 g; 1.4 m mole), cobaltous bromide tetrahydrate (0.32 g; 1.1 m mole), isobutyric acid (20 ml) and water (0.2 ml) in a sintered glass funnel fitted with a condenser and thermometer, via the stem of the funnel. The dark brown mixture is oxygenated for 100 minutes at room temperature, then heated briefly to 48.degree. C. After 2 hours and 10 minutes, the mixture is reheated to 50.degree. C. and the flow of oxygen is terminated 2 hours later. The mixture is then worked up as described in Example 1 to attain a 37% yield of the title compound.

PAC EXAMPLE 4

PAC Preparation of 4,5,6,7-Tetrahydro-7-oxobenzo[b]thien-4-ylurea

PAR A mixture of 4,5,6,7-tetrahydrobenzo[b]thien-4-ylurea (2.0 g), cobaltous acetate tetrahydrate (1.12 g), methyl isobutyl ketone (20 ml), acetic acid (20 ml) and a 30.2% solution of hydrobromic acid in acetic acid (0.9 ml) is shaken in a pressure bottle with 51 psig of oxygen. After 21.5 hours, the excess oxygen (33.2 psig) is vented and water (40 ml) added. The mixture is then saturated with sodium chloride and the organic phase is separated and washed well with brine. The organic phase is evaporated to dryness in vacuo to afford 2.62 g of oily solid. This material is stirred well with methanol (15 ml) and filtered to give 0.433 g of the title compound, m.p. 219.degree. C. to 220.degree. C.

PAC EXAMPLE 5

PAC Preparation of 4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-ylurea

PAR A mixture of 4,5,6,7-tetrahydrobenzo[b]thien-4-ylurea (2.0 g), cobaltous acetate (0.49 g), cobaltous bromide tetrahydrate (0.635 g), water (0.4 ml), acetic acid (5 ml) and methyl isobutyl ketone (35 ml) is stirred and air is introduced via a capillary gas dispersion tube. The mixture is gradually heated to 45.degree. C. and a deep green mixture is obtained. After heating overnight, the air flow is terminated and water (15 ml) added to the mixture. The mixture is saturated with sodium chloride and extracted with a 1:4 acetic acid: ethyl acetate mixture (3.times.50 ml). The combined extracts are washed once with water and evaporated to dryness in vacuo to afford 3.37 g of dark solid, which contains 15.8% of the title compound by high pressure liquid chromatographic analysis.

PAC EXAMPLE 6

PAC Preparation of N-(1,2,3,4-tetrahydro-4-oxo-1-naphthyl)formamide

PAR A mixture of N-(1,2,3,4-tetrahydro-1-naphthyl)-formamide (2.0 g), cobaltous acetate tetrahydrate (0.95 g), a 30% solution of hydrobromic acid in acetic acid (0.925 g) and a 1:1 mixture of acetic acid: methyl isobutyl ketone (40 ml) is stirred and oxygen introduced via a capillary gas delivery tube. The blue reaction mixture is gradually heated to 76.degree. C. in 42 minutes during which time the color changes to purple. The reaction mixture is then allowed to cool to room temperature. Water (40 ml) is added and the mixture saturated with sodium chloride. The mixture is extracted with chloroform (3.times.20 ml), the combined extracts are washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate and evaporated to dryness in vacuo. The residual red oil is triturated with ether and after cooling the title compound (0.4 g) collected. Further work-up of the mother liquor affords an additional 0.6 g of title compound.

PAC EXAMPLE 7

PAC Preparation of N-(1,2,3,4-tetrahydro-4-oxo-1-naphthyl)acetamide

PAR A mixture of N-(1,2,3,4-tetrahydro-1-naphthyl)-acetamide (30 g), cobaltous acetate tetrahydrate (13.12 g), 30% hydrobromic acid in acetic acid (4.28 g), methyl isobutyl ketone (400 ml) and acetic acid (100 ml) is stirred and oxygen is introduced via a capillary gas dispersion tube. The mixture is heated gradually to 62.degree. C. and the reaction is run 17 hours at 62.degree. C. The reaction mixture is then cooled, the oxygen flow terminated and water (500 ml) is added. The mixture is extracted with chloroform (500 ml and 2.times.300 ml), the chloroform extracts are combined, washed with saturated sodium chloride solution and evaporated to dryness in vacuo. Benzene (200 ml) is added to the residue, the solution is filtered and the filtrate evaporated to dryness in vacuo to afford 40.3 g (damp) of the title compound.

PAC EXAMPLE 8

PAC Preparation of 1,2,3,4-Tetrahydro-4-oxo-1-naphthylurea

PAR A mixture of crude N-(1,2,3,4-tetrahydro-4-oxo-1-naphthyl)acetamide (41.4 g), concentrated hydrochloric acid (300 ml) and water (250 ml) is heated at reflux overnight. The mixture is decanted, filtered and the cooled filtrate extracted with chloroform (300 ml). The aqueous solution is evaporated to dryness in vacuo and the residue dissolved in water (250 ml). A solution of potassium cyanate (21.8 g) in water (75 ml) is added dropwise to the aqueous solution and the reaction mixture stirred at room temperature for 72 hours. The title product is collected and dried to afford 21.45 g, m.p. 225.degree. C. dec.

PAC EXAMPLE 9

PAC Preparation of 1,2,3,4-Tetrahydro-4-oxo-1-naphthylurea

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PAR  A mixture of 1,2,3,4-tetrahydro-1-naphthylurea (1.9 g), cobaltous acetate
      tetrahydrate (1.08 g), 30% hydrobromic acid in acetic acid (0.9 ml) and a
      1:1 mixture of methyl ethyl ketone: acetic acid (30 ml) is shaken in a
      pressure vessel under 31 psig of oxygen for 7.5 hours. The vessel is then
      vented, the contents are mixed with an equal volume of water and extracted
      with chloroform (2.times.25 ml). The combined chloroform extracts are
      dried over anhydrous magnesium sulfate and evaporated to dryness in vacuo
      to afford 2.34 g solid. The solid is washed with cold methanol (30 ml) to
      afford 0.75 g of title compound, m.p. 210.degree. C. to 214.degree. C.
PAC  EXAMPLES 10 TO 21
PAC  Preparation of N-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl) acetamide
PAR  By following the procedure of Example 1 in every detail except that
      reaction parameters are varied in the following reactions which are
      summarized in Table I, below.
      ##TBL1##
PAC  EXAMPLES 22 TO 48
PAC  Preparation of Various Ketoamides from the Corresponding Amides
PAR  By the procedure of Example 4, the following amides are oxidized to the
      ketoamides as summarized in Table (II) below:
      ##STR29##
      where R.sub.1 and R.sub.2 are each as hereinbelow defined. The starting
      materials (I) and (II) are prepared by allowing the corresponding amines
      of (I) and (II), respectively, to react with R.sub.2 acid anhydrides or
      R.sub.2 acid chlorides/Et.sub.3 N in benzene.
      ##TBL2##
PAC  EXAMPLE 49
PAC  Preparation of N-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl) acetamide
PAR  A mixture of N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)-acetamide (2.0 g),
      cobaltous acetate tetrahydrate (1.12 g), azo-bis-isobutyronitrile (0.05
      g), a 30% solution of hydrobromic acid in acetic acid (0.9 ml) and
      isobutyric acid (40 ml) is stirred and oxygen bubbled through via a gas
      dispersion tube. The dark blue mixture gradually turns green and the
      temperature rises from 25.degree. C. to 28.degree. C. After 6.3 hours, the
      flow of oxygen is terminated and water (40 ml) added to the reaction
      mixture. The mixture is then saturated with sodium chloride, the organic
      phase is separated, the aqueous phase is extracted with chloroform
      (3.times.80 ml) and the chloroform extracts combined with the organic
      phase. The combined organic phase is washed with saturated sodium chloride
      solution and then evaporated to dryness. The residue is dissolved in
      chloroform, the solution is washed with saturated sodium carbonate
      solution (10 ml) and then evaporated to dryness in vacuo to afford 2.46 g
      of solid, which on analysis by high pressure liquid chromatography (HPLC)
      is shown to contain the title compound amounting to a yield of 51.3%.
PAR  Similarly, use of air instead of pure oxygen in the above reaction affords
      the title compound in 49.6% yield as determined by HPLC.
PAC  EXAMPLE 50
PAC  Preparation of N-(1,2,3,4-tetrahydro-4-oxo-1-naphthyl)acetamide
PAR  A solution of N-(1,2,3,4-tetrahydro-1-naphthyl) acetamide (189.3 g) in
      methyl isobutyl ketone (2.54 l) and acetic acid (635 ml) is mixed with
      cobaltous acetate tetrahydrate (83 g) and a solution of 30% hydrobromic
      acid in acetic acid (65 ml). The blue reaction mixture is stirred and
      heated and oxygen bubbled through at the rate of 453.3 ml/min and nitrogen
      is passed over the reaction mixture as a blanket and to dilute the
      outflowing oxygen. The effluent gas contains 15.5% oxygen as measured by
      an oxygen analyzer. After 30 minutes, as the mixture is heated the oxygen
      consumption becomes noticeable at about 48.degree. C. and the blue mixture
      begins to turn green. The flow rate of oxygen is then increased until the
      oxygen uptake stops in about 0.5 hours. The temperature is allowed to rise
      to 93.degree. C. After oxygen is no longer consumed, the mixture is
      cooled, diluted with water (3 l), and the organic phase separated. The
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aqueous phase is extracted with chloroform (1000 ml and 2.times.500 ml) and the extracts combined with the organic phase. The combined organic solutions are washed with saturated sodium chloride solution (2 l) and dried over anhydrous magnesium sulfate. The organic solution is then evaporated to dryness in vacuo to afford 219 g of solid, which contains 68.2% of the title compound by HPLC assay.

PAC EXAMPLE 51

PAR The following compounds of formula "A" are prepared by acylating 4,5,6,7-tetrahydrobenzo[b]thiophen-4-amine with the respective acid chlorides or anhydrides in the presence of pyridine or triethylamine. Subsequently, the thus obtained compounds of formula "A" are oxidized by the procedure of Example 1 to afford compounds of formula "B" as summarized in Table III, below.

##TBL3##

PAC EXAMPLE 52

PAC Mouse Growth Regulant Tests

PAR CFI female mice from Carworth Farm are received when they are six weeks old. They are housed ten to a cage in air-conditioned rooms (72.degree.-76.degree. F.) with automatically controlled lights, 14 hours on and 10 hours off. The basal diet used in these studies is Purina Laboratory Chow (see description below), which is supplied ad libitum. Water is also allowed ad libitum.

PAR Thirteen days after arrival, the mice are weighed in groups of ten and assigned at random to the different treatments. The concentration of the different compounds in the diet is indicated in the following Tables. Twelve days later the mice are weighed again and the experiment terminated. At least three cages (30 mice) of untreated controls are included in each test. Test data are provided in Table IV below, wherein data are reported as percent weight gain over controls. The following is a description of the diet to which the growth-promoting compounds are added.

##TBL4##

##TBL5##

PAR Similarly in the same growth promotion test, at 200 ppm in the diet, 4,5,6,7-tetrahydrobenzo[b]thien-4-ylurea, 4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-ylurea, and 1,2,3,4-tetrahydro-1-naphthylurea, respectively, give 132.2%, 117% and 66.8% weight gain over controls.

PAC EXAMPLE 53

PAR The following compounds of formula "A" are prepared by acylating 1,2,3,4,-tetrahydro-1-naphthylamine with the respective acid chlorides or anhydrides in the presence of pyridine or triethylamine. Subsequently, the compounds are oxidized by the procedure of Example 1 to afford compounds of formula "B" as summarized in Table V.

##TBL6##

PAC EXAMPLE 54

PAC Preparation of N-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl) acetamide

PAR A mixture of N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl acetamide (2.0 g), cobaltous acetate tetrahydrate (1.12 g), methyl isobutyl ketone (20 ml), acetic acid (20 ml) and a 30.2% solution of hydrobromic acid in acetic acid (0.95 ml) is shaken in a pressure bottle with 79.2 psig of oxygen. After 16 hours, the excess oxygen (70.1 psig) is vented and water (40 ml) added. The mixture is extracted with chloroform (3.times.40 ml) and the combined extracts are washed with brine and evaporated to dryness in vacuo to afford 2.98 g of an oil. HPLC analysis shows the title compound is present amounting to a 57.3% yield.

PAR Similarly, use of cobaltous acetate recovered from the above chloroform extracted aqueous solution via evaporation gives a 51.5% yield of the title compound by HPLC analysis.

PAR By the above procedure N-(1,2,3,4-tetrahydro-1-naphthyl)acetamide affords a 64.5% yield of N-(1,2,3,4-tetrahydro-4-oxo-1-naphthyl)acetamide.

```
PAC  EXAMPLE 55
PAC  Preparation of Substituted-4,5,6,7-tetrahydro-7-oxobenzo[b]-thien-4-ylureas
PAR  By the method described in Example 4, following compounds are prepared.
      ##TBL7##
PAC  EXAMPLE 56
PAC  Preparation of (-)-N-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl)acetamide
PAR  In the manner described in Example 7,
      (-)-N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)acetamide is oxidized to give
      the title compound.
PAR  Similarly, (-)-4,5,6,7-tetrahydrobenzo[b]thien-4-yl-urea is oxidized to
      afford (-)-4,5,6,7-tetrahydro-7-oxobenzo[b]-thien-4-yl urea, m.p.
      247.degree.-249.5.degree. C. (dec.).
PAC  EXAMPLE 57
PAC  Preparation of (-)-1,2,3,4-tetrahydro-4-oxo-1-naphthylurea
PAR  In the manner described in Example 9, (-)-1,2,3,4-tetrahydro-1-naphthylurea
      is oxidized to afford the title compound, mp.p 237.degree.-240.degree. C.
PAR  Similarly, (-)-N-(1,2,3,4-tetrahydro-1-naphthyl)-acetamide is oxidized to
      afford (-)-N-(1,2,3,4-tetrahydro-4-oxo-1-naphthyl)acetamide, melting point
      147.degree. C. to 157.degree. C.
PAC  EXAMPLE 58
PAC  Preparation of
      1-Benzoyl-3-(4,5,6,7-tetrahydro-7-oxobenzo[b]-thien-4-yl)urea
PAR  In the manner described in Example 4,
      1-benzoyl-3-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)urea, m.p.
      187.degree. C. to 190.degree. C., is oxidized to afford the title
      compound, m.p. 204.degree.-207.degree. C.
PAR  Similarly, the following compounds are prepared:
      ##STR30##
      where R is defined as: CH.sub.3 CO,Cl.sub.3 C--CO, F.sub.3 C--CO,
      4--Cl--C.sub.6 H.sub.4 CO, 4--O.sub.2 N--C.sub.6 H.sub.4 CO,
      2--CH.sub.3 O--C.sub.6 H.sub.4 CO, 2--CH.sub.3 O--C.sub.6 H.sub.4 CO,
      4--CH.sub.3 O--C.sub.6 H.sub.4 CO, 2--ClC.sub.6 H.sub.4 CO,
      3--Cl--C.sub.6 H.sub.4 CO--, 2--O.sub.2 N--C.sub.6 H.sub.4 CO,
      3--O.sub.2 N--C.sub.6 H.sub.4 CO, or 2--C.sub.3 H.sub.7 CO.
PAR  The starting materials are prepared by allowing
      4,5,6,7-tetrahydrobenzo[b]thiophen-4-amine to react with the requisite
      isocyanate or by allowing 4,5,6,7-tetrahydrobenzo[b]thien-4-yl isocyanate
      to react with the requisite amide.
PAR  Alkaline hydrolysis of these ketoureas affords
      4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-ylurea.
PAC  EXAMPLE 59
PAR  By following the procedure of Example 4 the following carbamates are
      oxidized to the ketocarbamates:
      ##STR31##
      where aryl is phenyl, 2- or 3- or 4-isomers of chlorophenyl, nitrophenyl,
      tolyl, methoxyphenyl, 2,4-dichlorophenyl, alpha- or beta-naphthyl or
      2,4-dinitrophenyl.
PAR  The starting materials are readily prepared by the addition of the
      requisite phenols to 4,5,6,7-tetrahydrobenzo-[b]thien-4-yl isocyanate.
PAC  EXAMPLE 60
PAC  Preparation of 4,5,6,7-Tetrahydro-7-oxobenzo[b]thien-4-ylurea and
      1,2,3,4,-tetrahydro-4-oxo-1-naphthylurea
PAR  A 3 g sample of
      1-benzoyl-3-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl)urea is stirred in
      10 ml of 1 N NaOH and the mixture is heated at reflux for 6 hr. An
      additional 5 ml of 1 N NaOH is then added and the mixture is heated for
      another hour. The mixture is cooled to room temperature and the title
      compound is collected by filtration and washed well with H.sub.2 O. The
      title compound is dried to afford 1.71 g, m.p. 241.degree. C. to
      244.degree. C.
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PAR  Substitution of
      1-benzoyl-3-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl)urea with
      1-acetyl- or
      1-trichloroacetyl-3-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl)urea in
      the above hydrolysis also affords the title compound.
PAR  In the same manner, 1-benzoyl-3-(1,2,3,4-tetrahydro-4-oxo-1-naphthyl)urea
      is hydrolyzed to afford 1,2,3,4-tetrahydro 4-oxo-1-naphthylurea, m.p.
      241.degree. C. to 244.degree. C.
PAC  EXAMPLE 61
PAC  Preparation of 1-Benzoyl-3-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)urea and
      1-benzoyl-3-(1,2,3,4-tetrahydro-1-naphthyl)urea
PAR  A 2.94 g sample of benzoyl isocyanate in 5 ml of CH.sub.2 Cl.sub.2 is added
      to 3.04 g pf 4,5,6,7-tetrahydrobenzo[b]thiophen-4-amine in 50 ml of
      CH.sub.2 Cl.sub.2 under N.sub.2 atmosphere. After stirring overnight at
      room temperature, the reaction mixture is evaporated to dryness in vacuo.
      The residue is then stirred in 100 ml of Et.sub.2 O and filtered to afford
      1-benzoyl-3-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)urea, m.p.
      189.degree. C. to 194.degree. C. Substitution of trichloroacetyl
      isocyanate for benzoyl isocyanate affords
      1-trichloroacetyl-3-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)urea. Use of
      4,5,6,7-tetrahydrobenzo[b]thien-4-ylisocyanate and acetamide in the above
      manner affords 1-acetyl-3-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)urea.
PAR  In the same manner, substitution of 1,2,3,4-tetrabydro-1-naphthylamine for
      4,5,6,7-tetrahydrobenzo[b]thiophen-4-amine affords 1-benzoyl-, and
      1-trichloroacetyl-3-(1,2,3,4-tetrahydro-1-naphthyl)urea when benzoyl
      isocyanate and trichloroacetyl isocyanate are used. Use of
      1,2,3,4-tetrahydro-1-naphthylisocyanate and acetamide in the same manner
      affords 1-acetyl-3-(1,2,3,4-tetrahydro-1-naphthyl)urea.
PAC  EXAMPLE 62
PAC  Preparation of 4,5,6,7-Tetrahydrobenzo[b]thien-4-ylurea and
      1,2,3,4-tetrahydro-1-naphthylurea
PAR  In the manner described in Example 60,
      1-benzoyl-3-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)urea and
      1-benzoyl-3-(1,2,3,4-tetrahydro-1-naphthyl)urea are hydrolyzed to afford
      4,5,6,7-tetrahydrobenzo[b]thien-4-ylurea, m.p. 204.5.degree. C. to
      208.5.degree. C., and 1,2,3,4-tetrahydro-1-naphthylurea, m.p.
      212.degree. C. to 214.degree. C.
PAC  EXAMPLE 63
PAC  Preparation of N-(1,2,3,4-Tetrahydro-4-oxo-1-naphthyl)acetamide
PAR  In 40 ml of HOAc and 6 ml of acetaldehyde, 3.78 g of
      N-(1,2,3,4-tetrahydro-1-naphthyl)acetamide; 2.24 g of Co(OAc).sub.2.4
      H.sub.2 O, and 1.76 ml of 30% HBr in HOAc are shaken in a glass pressure
      vessel on a Paar apparatus under 38 psig of O.sub.2. The mixture is heated
      to 86.degree. C. over a 0.5 hr. period and gradually allowed to cool. The
      mixture is then shaken at room temperature for 18.5 hr and 50 ml of
      H.sub.2 O is added after the O.sub.2 is vented. The mixture is extracted
      with CHCl.sub.3  (3.times.50 ml) and the combined organic phases are dried
      over MgSO.sub.4 and evaporated to dryness in vacuo. The residue is then
      triturated with 100 ml of Et.sub.2 O, stirred for 18 hours and the crude
      title compound is collected by filtration. This gives 2.12 g of the title
      compound, m.p. 104.degree. C. to 115.degree. C.
PAR  Substitution of acetaldehyde in the above reaction with propionaldehyde,
      butyraldehyde, isobutyraldehyde or octyladehyde also affords the title
      compound. Similarly, substitution of
      N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)acetamide for
      N-(1,2,3,4-tetrahydro-1-naphthyl)acetamide in the above-mentioned
      procedure affords N-(4,5,6,7-tetrahydro-7-oxobenzo[b]thien-4-yl)acetamide.
CLMS
STM  We claim:
NUM  1.
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PAR   1. A process for the preparation of a compound of the formula:
      ##STR32##
      wherein R.sub.1 and R.sub.2 are each a substituent selected from the group
      consisting of alkanoyl C.sub.1 -C.sub.7, halogen-substituted alkanoyl
      C.sub.1 -C.sub.7, carboalkoxy C.sub.1 -C.sub.4,
      ##STR33##
      R.sub.3 is a radical selected from the group consisting of hydrogen and
      alkyl C.sub.1 -C.sub.4, R.sub.4 is a substituent selected from the group
      consisting of hydrogen, alkyl C.sub.1 -C.sub.8, alkanoyl
      (C.sub.2 -C.sub.4), halogen-substituted alkanoyl (C.sub.2 -C.sub.4),
      halogen-substituted alkanoyl (C.sub.2 -C.sub.4) and
      ##STR34##
      and when the
      ##STR35##
      moiety is cyclized, each represents a moiety selected from the group
      consisting of succinimido, maleimido and phthalimido, X and Y are each a
      radical selected from the group consisting of hydrogen, fluorine,
      chlorine, bromine iodine, nitro, alkyl C.sub.1 -C.sub.4 ; the racemic
      mixtures and the optical isomers thereof; comprising the steps of:
      subjecting a compound of the formula:
      ##STR36##
      wherein R.sub.1 and R.sub.2 are each a radical selected from the group
      consisting of alkanoyl C.sub.1 -C.sub.7, halogen-substituted alkanoyl
      C.sub.1 -C.sub.7, carboalkoxy C.sub.1 -C.sub.7,
      ##STR37##
       R.sub.3 is selected from the group consisting of hydrogen and alkyl
      (C.sub.1 -C.sub.4); R.sub.4 is selected from the group consisting of
      hydrogen, alkyl (C.sub.1 -C.sub.8), alkanoyl (C.sub.2 -C.sub.4), and
      halogen-substituted alkanoyl (C.sub.2 -C.sub.4), and
      ##STR38##
      is each cyclized, each represents a moiety selected from the group
      consisting of succinimido, maleimido and phthalimido; X and Y are selected
      from the group consisting of hydrogen, halogen, nitro, alkyl
      C.sub.1 -C.sub.4 and alkoxy (C.sub.1 -C.sub.4); the racemic mixtures and
      the optical isomers thereof; to the action of an oxygen containing gas at
      positive pressures up to about 100 psig and at a temperature ranging from
      about 20.degree. C. to about 150.degree. C. in the presence of a cobalt
      catalyst selected from the group consisting of a cobaltous salt and a
      cobaltic salt, said catalyst being present in a solvent-substrate mixture,
      wherein said catalyst is present in said mixture in a molar ratio of 1:1
      to 15:1, and said solvent being selected from the group consisting of a
      (C.sub.2 -C.sub.6) alkanoic acid, a mixture of a (C.sub.2 -C.sub.6)
      alkanoic acid and a (C.sub.2 -C.sub.6) alkanoic acid anhydride, a mixture
      of a (C.sub.2 -C.sub.6) alkanoic acid and an aliphatic ketone, a mixture
      of a (C.sub.2 -C.sub.6) alkanoic acid and a cycloaliphatic ketone, a
      mixture of a (C.sub.2 -C.sub.6) alkanoic acid and an aliphatic aldehyde
      other than formaldehyde, a mixture of a (C.sub.2 -C.sub.6) alkanoic acid
      and t-butyl alcohol and a mixture of a (C.sub. 2 -C.sub.6) alkanoic acid
      and acetonitrile, for a period of time sufficient to essentially complete
      the reaction, and thereafter recovering said resultant oxidized product.
NUM   2.
PAR   2. The process according to claim 1, wherein R.sub.1 and R.sub.2 are each
      selected from the group consisting of alkanoyl C.sub.1 -C.sub.6,
      halogen-substituted alkanoyl C.sub.2 -C.sub.3, carboalkoxy
      C.sub.1 -C.sub.4,
      ##STR39##
      R.sub.3 is selected from the group consisting of hydrogen and alkyl
      C.sub.1 -C.sub.2 ; R.sub.4 is selected from the group consisting of
      hydrogen, alkyl C.sub.1 -C.sub.4, alkanoyl (C.sub.2 -C.sub.4),
      halogen-substituted alkanoyl (C.sub.2 -C.sub.4) and
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     ##STR40##
     is cyclized, each represents a moiety selected from the group consisting
     of succinimido, maleimido and phthalimido; X and Y are selected from
     hydrogen, chlorine, nitro, methyl and methoxy; the racemic mixtures and
     the optical isomers thereof; the oxidizing agent is oxygen,
     oxygen-nitrogen mixtures or air; the pressure ranges from atmospheric
     pressure 100 psig; the catalyst is cobaltous acetate bromide, said
     catalyst being present in a solvent substrate:catalyst molar ratio of
     1.5:1 to 6:1; the alkanoic acid is a C.sub.2 -C.sub.4 alkanoic acid; the
     anhydride is a C.sub.2 -C.sub.4 alkanoic acid anhydride; the aliphatic
     ketone is methyl ethyl ketone and methyl iso-butyl ketone.
NUM  3.
PAR  3. The process according to claim 1, wherein R.sub.1 and R.sub.2 are each
     selected from the group consisting of alkanoyl C.sub.1 -C.sub.7,
     halogen-substituted alkanoyl C.sub.2 -C.sub.4 ; benzoyl and
     ##STR41##
     R.sub.3 is selected from hydrogen and alkyl C.sub.1 -C.sub.4  R.sub.4 is
     selected from hydrogen, alkyl C.sub.1 -C.sub.8, alkanoyl
     (C.sub.2 -C.sub.4), and benzoyl; and when
     ##STR42##
     is cyclized, each are taken together with nitrogen represents phthalimido;
     the racemic mixtures and the optical isomers thereof; the oxidizing agent
     is oxygen, oxygen-nitrogen mixtures or air; the pressure ranges from
     atmospheric pressure to 100 psig; the catalyst is cobaltous acetate
     bromide, said catalyst being present in a solvent substrate:catalyst molar
     ratio of 1.5:1 to 6:1; the alkanoic acid is a C.sub.2 -C.sub.4 alkanoic
     acid; the anhydride is a C.sub.2 -C.sub.4 alkanoic acid anhydride; the
     aliphatic ketone is methyl ethyl ketone and methyl iso-butyl ketone.
NUM  4.
PAR  4. The process according to claim 1, wherein R.sub.1 and R.sub.2 each is
     selected from the group consisting of formyl, acetyl,
     ##STR43##
     R.sub.3 is selected from the group consisting of hydrogen, methyl and
     iso-propyl; and R.sub.4 is selected from the group consisting of hydrogen,
     methyl, n-octyl, acetyl, trichloroacetyl and benzoyl.
NUM  5.
PAR  5. The process according to claim 1, wherein the solvent is selected from
     the group consisting of acetic acid, propionic acid, butyric acid and
     isobutyric acid.
NUM  6.
PAR  6. The process according to claim 1, wherein the solvent is a mixture of
     acetic acid and tertiary butyl alcohol.
NUM  7.
PAR  7. The process according to claim 1, wherein the solvent is a mixture of
     acetic acid and acetonitrile.
NUM  8.
PAR  8. The process according to claim 1, wherein the solvent is a mixture of
     acetic acid and diethyl ketone.
NUM  9.
PAR  9. The process according to claim 1, wherein the solvent is a mixture of
     acetic acid and methyl isobutyl ketone.
NUM  10.
PAR  10. The process according to claim 1, wherein the solvent is a mixture of
     acetic acid and methyl isoamyl ketone.
NUM  11.
PAR  11. The process according to claim 1 wherein a compound of the formula:
     ##STR44##
     wherein R.sub.1 and R.sub.2 are each selected from the group consisting of
     hydrogen, methyl, ethyl, propyl, isopropyl, t-butyl and phenyl; is
     subjected to oxidation in the presence of a cobalt catalyst to obtain a
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      compound of the formula:
      ##STR45##
NUM  12.
PAR  12. The process according to claim 1, wherein the compound to be oxidized
      is N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)-acetamide.
NUM  13.
PAR  13. The process according to claim 1, wherein the compound to be oxidized
      is (-)-N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)acetamide.
NUM  14.
PAR  14. The process according to claim 1, wherein the compound to be oxidized
      is 4,5,6,7-tetrahydrobenzo[b]thien-4-ylurea.
NUM  15.
PAR  15. The process according to claim 1, wherein the compound to be oxidized
      is (-)-4,5,6,7-tetrahydrobenzo[b]thien-4-ylurea.
NUM  16.
PAR  16. The process according to claim 1, wherein the compound to be oxidized
      is N-(1,2,3,4-tetrahydro-1-naphthyl)-acetamide.
NUM  17.
PAR  17. The process according to claim 1, wherein the compound to be oxidized
      is (-)-N-(1,2,3,4-tetrahydro-1-naphthyl) acetamide.
NUM  18.
PAR  18. The process according to claim 1, wherein the compound to be oxidized
      is 1,2,3,4-tetrahydro-1-naphthylurea.
NUM  19.
PAR  19. The process according to claim 1, wherein the compound to be oxidized
      is (-)-1,2,3,4-tetrahydro-1-naphthylurea.
NUM  20.
PAR  20. The process according to claim 1, wherein the compound to be oxidized
      is N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)-phthalimide.
NUM  21.
PAR  21. The process according to claim 1, wherein the compound to be oxidized
      is N-(1,2,3,4-tetrahydro-1-naphthyl)-phthalimide.
NUM  22.
PAR  22. The process according to claim 1, wherein the compound to be oxidized
      is N-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl-formamide.
NUM  23.
PAR  23. The process according to claim 1, wherein the compound to be oxidized
      is N-(1,2,3,4-tetrahydro-1-naphthyl)-formamide.
NUM  24.
PAR  24. The process according to claim 1, wherein the compound to be oxidized
      is 1-benzoyl-3-(4,5,6,7-tetrahydrobenzo[b]thien-4-yl)urea.
NUM  25.
PAR  25. The process according to claim 1, wherein the compound to be oxidized
      is 1-benzoyl-3-(1,2,3,4-tetrahydro-1-naphthyl)urea.
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PATN
WKU  043330975
SRC  6
APN  1864246
APT  1
ART  234
APD  19800912
TTL  Visual display terminal without finger repositioning
ISD  19820601
NCL  2
ECL  1
EXP  Trafton; David L.
NDR  4
NFG  7
INVT
NAM  Buric; Milorad R.
CTY  Chatham
STA  NJ
INVT
NAM  Maxemchuk; Nicholas F.
CTY  Mountainside
STA  NJ
ASSG
NAM  Bell Telephone Laboratories, Incorporated
CTY  Murray Hill
STA  NJ
COD  02
CLAS
OCL  340711
XCL  340365R
XCL  340721
EDF  3
ICL  G09G  100
FSC  340
FSS  365 R;721;711;712
UREF
PNO  2040248
ISD  19360500
NAM  Dvorak et al.
UREF
PNO  3381276
ISD  19680400
NAM  James
UREF
PNO  3428747
ISD  19690200
NAM  Alferieff
OCL  340365R
UREF
PNO  3526892
ISD  19700900
NAM  Bartlett et al.
UREF
PNO  3633724
ISD  19720700
NAM  Samuel
UREF
PNO  3675513
ISD  19720700
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UREF
PNO  3833765
ISD  19740900
NAM  Hilborn et al.
UREF
PNO  3879722
ISD  19750400
NAM  Knowlton
UREF
PNO  3967273
ISD  19760600
NAM  Knowlton
UREF
PNO  4005388
ISD  19770100
NAM  Morley et al.
OCL  340365R
UREF
PNO  4067431
ISD  19780100
NAM  Whitaker
OCL  340365R
UREF
PNO  4185282
ISD  19800100
NAM  Pick
XCL  340721
UREF
PNO  4193119
ISD  19800300
NAM  Arase et al.
XCL  340712
UREF
PNO  4200913
ISD  19800400
NAM  Kuhar et al.
OREF
PAL  Norman Abramson; Information Theory and Coding, 1963, McGraw-Hill, pp. 34,
      35.
PAL  Robert Parkinson; "The Dvorak Simplified Keyboard: Forty Years of
      Frustration," Computers and Automation, Nov. 1972, pp. 18-25.
PAL  Rochester, Bequaekt and Sharp, "The Chord Keyboard", Computer; (IEEE) vol.
      11, No. 12, Dec. 1978, pp. 57-63.
LREP
FR2  Roddy; Richard J.
ABST
PAL  The subject terminal includes a keyboard (20) having a plurality of keys
      (30-1 through 30-10), each key adapted to accommodate a respective finger
      of the typist, and apparatus (100, 150) responsive to the depression of
      one of the keys for generating and displaying a symbol upon a cathode ray
      tube. Also displayed on the cathode ray tube is a replica (300, 701) of
      the keyboard and a plurality of symbols (310-1, 510-1, 610-1, et seq)
      representing different functions for each of the plurality of keys. By
      altering (702, 703, 704, 705, 706) the label in a key location on the
      replica, the function associated with that key, for example, the symbol
      displayed responsive to its depression, may be altered. Thereby the
      operator need not reposition his fingers among the keys.
BSUM
PAC  TECHNICAL FIELD
PAR  This invention relates to terminals and, more particularly, to visual
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display terminals including keyboards for generating or for displaying a greater plurality of symbols using a lesser plurality of keys.

PAC BACKGROUND OF THE INVENTION

PAR U.S. Pat. No. 3,967,273; issued June 29, 1976 and entitled "Method and Apparatus for Using Pushbutton Telephone Keys for Generation of Alpha-Numeric Information"; discloses a four column, three row pushbutton telephone keyboard by way of which a desired alpha-numeric symbol may be generated. The symbol is generated responsive to a two step finger repositioning process: (1) the operator locates and pushes a first button on which the desired symbol is labeled, each of the twelve buttons being labeled with at most a three-by-three array of symbols, and (2) the operator locates and pushes a second button, which second button is identified by the position of the desired symbol in the array labeled on the first button. The alpha-numeric symbols are arranged similar in layout to a standard typewriter keyboard thereby making it likely that anyone, who is familiar with the location of symbols on a typewriter keyboard, can quickly reposition his fingers to the desired symbol on the telephone keyboard. It is, however, no secret that the layout of symbols on the standard typewriter keyboard is an inefficient layout.

PAR The typewriter originated as a purely mechanical device. Because of the crudity of its initial mechanical linkages, the symbols on the keys of early typewriters were intentionally positioned, or laid out, so as to slow the typist down to a speed compatible with the capabilities of the mechanical device. As a result, an awkward layout pattern is obtained. Unfortunately, the original awkward typewriter keyboard layout has persisted to the present time. A more efficient keyboard layout is disclosed in U.S. Pat. No. 2,040,248; issued May 12, 1936 to A. Dvorak et al. and entitled "Typewriter Keyboard." The Dvorak keyboard includes the letters being arranged in three rows. The upper row contains consecutively the letters p, y, f, g, c, r and l. The home row contains the letters a, o, e, u, i, d, h, t, n and s. The lower row contains the letters z, q, j, k, x, b, m, w and v. With that keyboard layout, Dvorak sought to produce an arrangement of the keys (having in mind the letter sequences found in the most commonly used words of a language) such that the automatic rhythm of the operator, in moving from one key to another key while typing a continuous flow of word-wholes and phrases-wholes, would better fit the mechanical rhythm of the typewriter.

PAR Of course, other keyboard layouts are possible. For example, U.S. Pat. No. 3,879,722; issued Apr. 22, 1975 and entitled "Interactive Input-Output Computer Terminal with Automatic Relabeling of Keyboard"; discloses an arrangement for transferring symbols by optical means from a television screen display to a telephone keyboard having twelve pushbuttons. The disclosed optical means is a semitransparent mirror, which is interposed between the television screen and the pushbutton keyboard and which is oriented in such a manner that the operator of the terminal sees a virtual image of the television screen image overlaying the keyboard. By altering the symbols on the television screen, the keyboard layout may be dynamically adjusted. As a result, a lesser plurality of keys may be automatically relabeled by dynamically adjusting and by optically transferring a greater plurality of computer generated graphical or alpha-numeric symbols from the television screen to the telephone keyboard. Unfortunately, it appears that the operator must pre-learn sequences of displays to effectively use the U.S. Pat. No. 3,879,722 keyboard. That is, what a next-in-time display should be is not evident from the current-in-time display. Also, such pushbutton telephone or typewriter keyboards require repositioning of the operator's fingers in the use of the keyboard. Frequent repositioning of fingers consumes time and leads to an inefficiently operated keyboard.

PAR To mitigate repositioning the operator's fingers among the keys, U.S. Pat. No. 3,633,724; issued Jan. 11, 1972 and entitled "Electric Typewriter Key

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        and Keyboard Arrangement"; discloses a keyboard including eight keys, each
        key for generating five symbols and the keyboard for generating the 40
        symbols common to a standard typewriter. Each key is arranged to be moved
        both axially and pivotally on the arcuate upper edges of a support member
        for selecting a respective one of the five symbols generated by depressing
        the key. Unfortunately, such a keyboard is not easy to use, for example,
        by an operator who is not skilled with the keyboard or by one who requires
        more than an occasional glance at the key labels to determine the symbol
        to be generated, e.g., the so-called hunt-and-peck typist. Also, while a
        finger need not be moved among the keys as with a standard keyboard, a
        finger is moved on a key for axially and/or pivotally moving the key. Such
        moving of the finger on a key tends toward an awkward relationship among
        the fingers as different keys are moved in different directions.
PAC   SUMMARY OF THE INVENTION
PAR   These and other problems are solved in accord with the principles of our
        invention with an improved terminal including a keyboard having a
        plurality of keys and including apparatus responsive to the operation of
        one of the keys for generating and extending a symbol signal to visual
        display apparatus. Responsive to the symbol signal, the generated symbol
        is displayed upon the visual display apparatus. The terminal also includes
        an arrangement for producing a replica of the keyboard upon the visual
        display as well as for displaying a plurality of keyboard layout patterns
        thereon. Also, the plurality of keys are adapted for the various fingers
        of the operator so that the finger need not be repositioned. Rather, the
        function of a key may be altered as the label appearing on the replica of
        the keyboard pattern is altered.
DRWD
PAC   BRIEF DESCRIPTION OF THE DRAWING
PAR   The various features of the present invention will be readily understood
        from the following detailed description when taken in conjunction with the
        drawing in which:
PAR   FIG. 1 illustrates a visual display terminal including a cathode ray tube
        (CRT) and a keyboard in accord with the principles of our invention;
PAR   FIG. 2 illustrates in more specific schematic form the apparatuses and an
        interconnective relationship among the apparatuses illustrated in FIG. 1;
PAR   FIG. 3 illustrates a replica of the keyboard in FIG. 1 being displayed on
        the CRT as well as the labels of a lower case keyboard layout pattern
        thereupon in accord with the principles of our invention;
PAR   FIG. 4, which illustrates a downshift alteration of the labels on the
        replica shown in FIG. 3, is useful in describing the dynamic adjustment of
        the function of the keys of an illustrative embodiment in accord with the
        principles of our invention;
PAR   FIG. 5 illustrates a replica of the keyboard in FIG. 1 being displayed on
        the CRT as well as the labels of an upper case keyboard layout pattern
        thereupon in accord with the principles of our invention;
PAR   FIG. 6 illustrates a replica of the keyboard in FIG. 1 being displayed on
        the CRT as well as the labels of a special character keyboard layout
        pattern thereupon in accord with the principles of our invention; and
PAR   FIG. 7 illustrates some typical tasks, which may be embodied in the
        illustrative housing of FIG. 2.
DETD
PAC   DETAILED DESCRIPTION
PAR   FIG. 1 depicts an illustrative terminal for generating symbols and for
        displaying the symbols in accord with the principles of our invention. The
        terminal can be constructed using standard visual display terminal 10
        having standard cathode ray tube (CRT) 15 for displaying the generated
        symbols. Housing 100, the illustrative details of which are depicted
        schematically in FIG. 2, includes keyboard 20, which, in turn, comprises a
        plurality of keys 30-1 through 30-10. The respective keys may be aligned
        in a row on the keyboard or, as here illustrated, staggered and adapted
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for readily accommodating the respective fingers and thumbs, herein called fingers unless otherwise noted, of the operator. For example, keyboard 20 may be a reconfiguration of a digital keyboard or of a standard multifrequency pushbutton telephone keyboard such as a TOUCH-TONE.RTM. dialing telephone set with keys 30-1 to 30-4 being adapted for operation by the four left hand fingers, with keys 30-5 to 30-8 being adapted for operation by the four right hand fingers and with keys 30-9 and 30-10 being adapted for operation by the left and right thumbs, respectively. While the keys of keyboard 20 may be adapted for the fingers of the operator, the face plate of keyboard 20 may be adapted for resting the palms of the operator's hands.

PAR Functionally, one of the ten keys of keyboard 20 may be operated, e.g., by being depressed, for generating a symbol signal(s) representative of the one or more symbols to be displayed. Responsive thereto, as schematically illustrated in FIG. 2, a digital symbol signal may be extended from keyboard 20 through keyboard interface unit 40 to an input of microcomputer 50. Responsive to the digital signal, microcomputer 50 may extend a signal or a signal sequence representing the symbol or symbols including replica to be displayed through visual display interface unit 60 over cable 150 to an input of visual display 10 for displaying the one or more symbols on CRT 15.

PAR While at first glance the aforedescribed configuration may appear known, some interesting aspects thereof mark our departure over the prior art.

PAR According to one aspect of our invention, the symbols to be generated and to be displayed may be arranged according to a keyboard layout pattern that may be dynamically adjusted and yet need not require the operator to pre-learn the sequence of displays and need not require the operator to reposition his fingers. For example, unlike a standard typewriter keyboard or pushbutton telephone keyboard, which usually have symbols labeled directly thereon for identifying the symbol to be generated by each respective key, our keyboard 20 need not be labeled direct thereon. Rather, the operator's fingers remain on the respective keys while a graphical replica of keys 30-1 through 30-10, here replica 300 in FIG. 3 includes ten generally rectangular polygons, may be displayed on the lower part of CRT 15. Replica 300 may be generated using standard graphical display techniques to provide replica producing task 701, which operates in cooperation with microcomputer 50 and interface units 40 and 60 for displaying rectangular polygons on CRT 15. Further, the label of the function of each respective key may be displayed in a respective polygon of replica 300. For example, in FIG. 3, the labels in row 310-3 i.e., spec, U.CASE, a, t, down, up, space, e, o, delete, are displayed in the respective polygons of replica 300. Still further, as the function of a key changes, its label on replica 300 also changes. For example, we start with a default layout pattern, e.g., here we start with a default pattern including the labels of row 310-3 being displayed on replica 300 as shown in FIG. 3. Then, responsive to a depression of key 30-9, here labeled down, the labels in row 310-2 move down one row replacing the labels in row 310-3 as shown in FIG. 4, i.e., here the labels on replica 300 are replaced with p, m, d, h, down, up, l, s, c, y. Thereby the operator of our improved keyboard 20 need not reposition his fingers on the keyboard. Instead, a change of the labels on the replica, and concomitantly a change of the functions of the keys, may occur. For example, the specific labels to be displayed on replica 300 may be generated using standard graphical display techniques to provide key function altering task 702, which operates in cooperation with various keyboard layout tasks such as lower case layout task 703, upper case layout task 704, and special symbol layout task 705 as well as with microcomputer 50 and interface units 40 and 60 for displaying the label of the function of each respective key in a respective polygon of replica 300. Still, even further, rather than have the operator reposition his fingers among rows of keys to accomplish different functions, each key may have a plurality of functions which are dynamically adjusted and involve no repositioning of the operator's fingers. Also, the sequence of displays is displayed on CRT 15 to obviate the need for the operator to pre-learn the sequences.

PAR More specifically, the screen of CRT 15 may be divided into an upper part and a lower part. The generated symbols may be displayed in the upper part of the screen, the next symbol being displayed wherever generally rectangular cursor 16 may be situated. Concurrently, replica 300 of our keyboard, as illustrated in FIG. 3, may be displayed in the lower part of the screen. It may be observed that FIG. 3 includes several rows of labels 310-1 through 310-5, which may be generated through lower case keyboard layout task 703. Initially the keys of our keyboard 20 have the functions illustrated by the labels in row 310-3, here called the default layout pattern. Notwithstanding, two or more rows, here five rows, may be displayed on the screen. Thereafter, it being noted that the letter a is shown in the replica polygon location of key 30-3, responsive to a depression of key 30-3, the letter a is generated through lower case task 703 and displayed in the upper part of the screen at a location specified by the location of cursor 16. Cursor 16 is then moved through cursor movement task 706 to a location where the next symbol is to be displayed and the default layout pattern of FIG. 3 remains displayed. Other symbols may be subsequently generated and displayed following a tree-like process. To illustrate, depression of left thumb key 30-9, here labeled down, leads to a downshift of the respective label rows such that, for example, the labels in row 310-2 appear on replica 300 as illustrated in FIG. 4 while the labels of label row 310-5 disappear off the bottom of the screen. Thereafter, the functions associated with the respective keys of our keyboard 20 are as labeled on replica 300 in FIG. 4. For example, it being noted that the letter d is shown in the replica polygon location of key 30-3, responsive to a depression of key 30-3, the letter d is generated through lower case task 703 and displayed in the upper part of the screen at a location specified by the location of cursor. Thereafter, the lower case default layout of FIG. 3 reappears in the lower part of the screen. In parallel fashion, two consecutive depressions of key 30-10, here labeled up, leads to a double upshift of the respective label rows such that, for example, the labels in row 310-5 appear on replica 300 while label rows 310-1 and 310-2 disappear off the top of the screen. Thereafter, it being noted that the number 3 is shown in the replica polygon location of key 30-3, responsive to a depression of key 30-3, the number 3 is generated through lower case task 703 and displayed in the upper part of CRT 15.

PAR Hence, our keyboard 20 may require two or more depressions, or strokes, of the keys to generate a particular symbol. Also, after the symbol is generated and usually displayed, the lower case default keyboard layout pattern of FIG. 3 reappears on CRT 15. Thusly, the default layout pattern is a layout pattern to which the key functions return after a symbol is generated. As a result, the operator begins typing each symbol with the default pattern of FIG. 3 on the lower part of the screen and need not remember how he got to the pattern presently displayed on the lower part of the screen. Notwithstanding, as later described, a lock feature may override the described default pattern.

PAR According to a second aspect of our invention, our keyboard layout pattern allows for more efficient use of the keyboard. For example, unlike the awkward standard typewriter keyboard layout, our improved keyboard layout obtains after due consideration as to the relative frequency of the symbols to be generated and as to the relative strength of the various fingers of the typical operator. Studies have been made as to determining the relative frequency of symbols common to the English language. According to one study, the following tabulates the frequency of symbols common in the English language:

##TBL1##

Studies have also been made as to determining the relative strengths of the eight fingers usually used in typing. According to one study, the following recites, from strongest to weakest, the rank order of the relative strengths of the eight typing fingers:

PA1 1. Right index finger;
PA1 2. Right middle finger;
PA1 3. Left index finger;
PA1 4. Left middle finger;
PA1 5. Right ring finger;
PA1 6. Left ring finger;
PA1 7. Right little finger; and
PA1 8. Left little finger.

PAL Our improved keyboard layout pattern, as illustrated in FIG. 3, obtains from balancing the relative frequency of symbols common in the English language with the relative strengths of the operator's fingers. For example, it may be noted that, when comparing the aforecited frequencies of symbols with the default keyboard layout of FIG. 3, the symbols in label row 310-3 include the higher frequency symbols. As a result, the higher frequency symbols require a lesser number of strokes for generating the symbol. In parallel fashion, label rows 310-2 and 310-4 include symbols with correspondingly lower frequencies than the symbols in label row 310-3 and yet include symbols with correspondingly higher frequencies than the symbols in label rows 310-1 and 310-5. Also, with our improved keyboard layout pattern and for representative English text, the relative frequency of using the aforedescribed eight fingers is about 0.3140, 0.2050, 0.1597, 0.1187, 0.1058, 0.0373, 0.0316, and 0.0279, respectively, clearly consistent with the rank order of the relative strengths of the eight typing fingers.

PAR As aforedescribed, because of the upshift or downshift of the rows of labels, two or more key strokes may be required to generate and have displayed a particular symbol when using our keyboard. English text studies with our improved keyboard 20 indicate that, on average, the keyboard layout pattern of FIG. 3 requires about 1.5 strokes per symbol. Importantly however, our keyboard does not require repositioning of the fingers on the keyboard. Further, our keyboard layout pattern obtains after due consideration as to the relative frequency of the symbols to be generated and as to the relative strengths of the operator's fingers. Hence, our keyboard allows for more efficient use.

PAR According to a third aspect of our invention, still other symbols may be generated and displayed on visual display terminal 10. For example, FIG. 5 illustrates an upper case keyboard layout pattern similar to the lower case keyboard pattern illustrated in FIG. 3. The upper case symbols shown in label rows 510-1 through 510-5 of FIG. 5 parallel the lower case symbols shown in label rows 310-1 through 310-5 of FIG. 3. The upper case labels may be generated using standard graphical display techniques to provide upper case layout task 705. Thereafter, the keyboard layout pattern of FIG. 5 is displayed on CRT 15 responsive to a depression of key 30-2 when replica 300 includes label row 310-3, that is, when replica key 30-2 is labeled U.CASE. On the other hand, keyboard layout pattern of FIG. 3 is displayed on CRT 15 responsive to a depression of key 30-2 while replica 300 includes label row 510-3, that is, when replica key 30-2 is labeled 1.case. In our illustrative embodiment, the upper case layout pattern of FIG. 5 may be locked on the display responsive to a depression of key 30-1 when same is labeled lock. That is, the aforedescribed lower case default pattern of FIG. 3 is replaced, or locked out, by the upper case pattern of FIG. 5, row 510-3 of which becomes a new default pattern. Otherwise, after an upper case symbol has been generated and displayed, the default keyboard layout pattern of FIG. 3 may be displayed on CRT 15. Also, for example, as illustrated in FIG. 6, a special character keyboard

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      layout pattern for generating and displaying various special characters
      through special symbol layout task 705 may be displayed for defining
      certain special functions of the ten keys. Specifically, the keyboard
      layout pattern of FIG. 6 may be displayed on CRT 15 responsive to a
      depression of key 30-1 when replica 300 includes label row 300-3, that is,
      when replica key 30-1 is labeled spec. Thereafter, keys 30-1 through 30-10
      are altered to provide the functions implicit in the FIG. 6 keyboard
      layout pattern.
PAR  Although our invention has been described and illustrated in detail, it is
      to be understood that the same is by way of illustration only. Various
      modifications will occur to those skilled in the art. For example, not all
      the self-evident functions labeled in the drawing have been described nor
      have all possible functions been illustrated. It should be clear that
      other functions, for example, editing functions, may be assignable to the
      various keys of our terminal. It should also be clear that more or less
      than five rows of symbols may be displayed on the lower part of the
      screen. It should further be clear that, while the description of our
      improved terminal is as though the terminal were a stand-alone terminal,
      our terminal may be readily interconnected to a communication path for
      transmission of generated symbols to another terminal or to a computer and
      for reception of signals generated therefrom. Accordingly, the spirit and
      scope of our invention will be limited only by the appended claims.
CLMS
STM  We claim:
NUM  1.
PAR  1. A terminal including
PA1  a keyboard having a plurality of keys,
PA1  means for producing a replica of said keyboard upon visual display
      apparatus,
PA1  a first set of labels for identifying a first keyboard layout pattern, said
      first set being displayed on said replica, a label comprising a symbol,
      said symbol for identifying a function of a key associated with said
      label, a respective first symbol for identifying a first function of a
      respective one of said keys and
PA1  characterized in that said terminal further comprises
PA1  a second set of labels for identifying a second keyboard layout pattern,
PA1  said second set being displayed in a position juxtaposed to said replica,
PA1  said second set including an alternative second symbol for identifying a
      second function of said respective one of said keys;
PA1  said first set and said second set being concurrently displayed on said
      visual display apparatus,
PA1  means coupled to said replica producing means for altering the function of
      a key, said key function altering means including
PA1  means for moving said alternative second symbol from said juxtaposed
      position and for displaying said alternative second symbol on said replica
      in place of said respective first symbol, and
PA1  means responsive to the operation of the key associated with said first and
      said second symbols for replacing said first function with said second
      function;
PA1  each key being adapted for operation by a respective finger of an operator
      of said terminal and
PA1  each key being adapted for avoiding the repositioning of said fingers
      during the operation thereof and
PA1  there being no more keys than there are fingers of an operator.
NUM  2.
PAR  2. The terminal defined in claim 1 wherein said key function altering means
      further comprises:
PA1  means responsive to the operation of said key associated with said first
      and second symbols for restoring said keyboard layout to a default
      keyboard layout pattern.
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PATN
WKU  PP0052272
SRC  6
APN  4136012
APT  6
ART  331
APD  19820831
TTL  Chrysanthemum plant named Favor
ISD  19840501
NCL  1
ECL  1
EXP  Feyrer; James R.
NDR  3
NFG  3
INVT
NAM  Duffett; William E.
CTY  Salinas
STA  CA
ASSG
NAM  Yoder Brothers, Inc.
CTY  Barberton
STA  OH
COD  02
CLAS
OCL  Plt 82
EDF  3
ICL  A01H  500
FSC  Plt
FSS   82
LREP
FRM  Schwartz, Jeffery, Schwaab, Mack, Blumenthal & Koch
ABST
PAL  A chrysanthemum plant named Favor characterized by the combined
       characteristics of flat capitulum form; decorative capitulum type; bronze
       red ray floret color; diameter acrosss face of capitulum ranging from 80
       to 120 mm. at maturity; uniform nine (9) week photoperiodic flowering
       response to short days; medium plant height when grown as a pinched,
       disbudded pot mum and spreading branching pattern.
BSUM
PAR  The present invention comprises a new and distinct cultivar of
       Chrysanthemum morifolium, Ramat., hereinafter referred to by the cultivar
       name Favor.
PAR  Favor is a product of a planned breeding program which had the objective of
       creating new chrysanthemum cultivars for pinched, disbud and spray pot mum
       programs having decorative capitulum type, bronze floret color, 8 to 9
       week flowering response and having the ability to produce commercially
       acceptable quality in year round programs. Such traits in combination
       required improvements in previously available commercial cultivars.
PAR  Favor was originated from a cross planned and executed in a controlled
       breeding program by William E. Duffett in Salinas, Calif. in 1978. The
       female parent of Favor was Tempo (U.S. Plant Pat. No. 4,505), a lavender
       decorative originated by the present inventor from a hybridization of two
       unnamed seedlings. Both were lavender decoratives. The male parent of
       Favor was an unnamed bronze daisy seedling originated from a cross between
       two unnamed seedlings. All were products of the originator's breeding
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PAR  Favor was discovered and selected as one flowering plant within the progeny
      of the stated cross by William E. Duffett on Sept. 9, 1979 in a controlled
      environment in Salinas, Calif.
PAR  The first act of asexual reproduction of Favor was accomplished when
      vegetative cuttings were taken from the initial selection in December,
      1979 in a controlled environment in Salinas, Calif. by a technician
      working under formulations established and supervised by William E.
      Duffett. Horticultural examination of selected units initiated in 1980 has
      demonstrated that the combination of characteristics as herein disclosed
      for Favor are firmly fixed and are retained through successive generations
      of asexual reproduction.
PAR  Favor has not been observed under all possible environmental conditions.
      The phenotype may vary significantly with variations in environment such
      as temperature, light intensity and day length. The observations,
      measurements and comparisons describe plants grown in Salinas, Calif.
      under greenhouse conditions which approximate those generally used in
      commercial practice.
PAR  The following traits have been repeatedly observed and are determined to be
      basic characteristics of Favor which in combination distinguish this
      chrysanthemum as a new and distinct cultivar:
PAR  1. flat capitulum form;
PAR  2. decorative capitulum type;
PAR  3. bronze red ray floret color;
PAR  4. diameter across face of capitulum ranging from 80 to 120 mm. at
      maturity;
PAR  5. uniform nine (9) week photoperiodic flowering response to short days;
PAR  6. medium plant height requiring 1-2 long day weeks prior to pinch and
      short days, and 1-2 applications 2500 ppm B-9 SP 14 to 21 days after the
      beginning of short days to attain a flowered plant height of 25 to 35 cm.;
      and
PAR  7. spreading branching pattern.
DRWD
PAR  The accompanying sheets depict typical foliage and inflorescence
      characteristics of Favor. Sheet 1 is a color photograph of a plant of
      Favor grown as a pinched, disbudded pot mum, with colors being as accurate
      as possible with renditions of this type. Sheet 2 is a black and white
      photograph of three views of the inflorescence of Favor. Sheet 3 shows the
      top and bottom leaves of Favor in three stages of growth (mature,
      intermediate, immature).
DETD
PAR  Of the many commercial cultivars known to the present inventor, the most
      similar in comparison to Favor is Torch (not patented). Reference is made
      to attached Chart A which compares certain characteristics of Favor to
      those same characteristics of Torch.
PAR  In comparison to Torch, Favor has a more intense bronze red ray floret
      color, larger diameter across the face of the capitulum by approximately
      20 mm., a more spreading, branching pattern, and a medium versus a short
      plant height. The capitulum form, capitulum type and flowering response to
      controlled photoperiods are similar to the same characteristics of Torch.
PAR  In the following description, color references are made to the Royal
      Horticultural Society Color Chart. The color values were determined
      between 10:30 and 11:00 A.M. on June 1, 1982 under 150 foot-candle light
      intensity at Salinas, Calif.
PAC  CLASSIFICATION
PAO  Botanical: Chrysanthamum morifolium, Ramat., cv Favor.
PAO  Commercial: Pinched disbud and spray pot mum.
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PAC  INFLORESCENCE
PAO  A. Capitulum:
PA2  Form.--Flat.
PA2  Type.--Decorative.
PA2  Diameter across face.--80 to 120 mm.
PAO  B. Corolla of ray florets:
PA2  Color (general tonality from a distance of three meters).--Red Bronze.
PA2  Color (abaxial).--42B and 42C at base to 44A at tip.
PA2  Color (adaxial).--28C to 28D.
PA2  Shape.--Flat. Very small corolla tube.
PAO  C. Corolla of disc florets:
PA2  Color (mature).--1A.
PA2  Color (immature).--154A.
PAO  D. Reproductive organs:
PA2  Androecium.--Present disc florets only; scant pollen.
PA2  Gynoecium.--Present both ray and disc florets.
PAC  PLANT
PAO  A. General appearance:
PA2  Height.--Medium; 25 to 35 cm. given 2 long day weeks before pinch and
      lights out, and 1-2 applications 2500 B-9 SP after lights out.
PA2  Branching pattern.--Spreading.
PAO  B. Foliage:
PA2  Color (abaxial).--147A.
PA2  Color (adaxial).--147B.
PA2  Shape.--Serrate and moderately lobed.
TBL               CHART A
     ___________________________________________
     COMPARISON OF FAVOR AND TORCH
     ___________________________________________
                          CAPITULUM
              RAY FLORET  FORM         BRANCHING
     CULTIVAR COLOR       AND TYPE     PATTERN
     ___________________________________________
     FAVOR    BRONZE      FLAT         SPREADING
              RED         DECORATIVE
     TORCH    BRONZE      FLAT         UPRIGHT
                          DECORATIVE
     ___________________________________________
              DIAMETER                 FLOWERING
              ACROSS FACE   PLANT      RESPONSE
     CULTIVAR OF CAPITULUM  HEIGHT     PERIOD
     ___________________________________________
     FAVOR    80 to 120 mm. MEDIUM     9 week
                            25 to 35
                            cm.
     TORCH    75 to 100 mm. SHORT      9 week
                            20 to 30
                            cm.
     ___________________________________________
     COMPARISONS MADE OF PLANTS GROWN AS PINCHED
     AND DISBUDDED POT MUMS IN SALINAS, CALIFORNIA
CLMS
STM  I claim:
NUM  1.
PAR  1. A new and distinct cultivar of Chrysanthemum morifolium, Ramat., plant
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particularly characterized as to uniqueness by the combined characteristics of flat capitulum form; decorative capitulum type; bronze red ray floret color; diameter across face of capitulum ranging from 80 to 120 mm. at maturity; uniform nine (9) week flowering response; medium plant height and spreading branching pattern.

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PATN
WKU  RE0315699
SRC  6
APN  3328023
APT  2
PBL  E
ART  321
APD  19811221
TTL  Tension control of fasteners
ISD  19840501
NCL  55
ECL  51
EXP  Combs; Ervin M.
NOR  9
NFG  16
INVT
NAM  Eshghy; Siavash
CTY  Pittsburgh
STA  PA
ASSG
NAM  Rockwell International Corporation
CTY  Pittsburgh
STA  PA
COD  02
REIS
COD  50
APN  912151
APD  19780602
PNO  04179786
ISD  19791225
RLAP
COD  72
APN  712554
APD  19760809
PSC  03
RLAP
COD  75
APN  766429
APD  19770207
PSC  01
PNO  4106570
CLAS
OCL   29407
XCL   29240
XCL  173 12
EDF  3
ICL  B23P 1906
FSC   29
FSS  240;407
FSC   73
FSS  761;862.21-862.24
FSC   81
FSS  467;469
FSC  173
FSS  1;12
FSC  364
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FSS  505;508
UREF
PNO  2600549
ISD  19520600
NAM  Ledbetter
XCL   73761
UREF
PNO  2740507
ISD  19560400
NAM  Shaff
OCL  173 12
UREF
PNO  2740508
ISD  19560400
NAM  Shaff
OCL  173 12
UREF
PNO  3316782
ISD  19670500
NAM  Tullis
OCL   81470
UREF
PNO  3693726
ISD  19720900
NAM  Hornig et al.
OCL  173 12
UREF
PNO  3827506
ISD  19740800
NAM  Himmelstein et al.
OCL  173 12
UREF
PNO  3939920
ISD  19760200
NAM  Hardiman et al.
OCL  173  1
UREF
PNO  3962910
ISD  19760600
NAM  Spyridakis et al.
OCL   73761
UREF
PNO  3965778
ISD  19760600
NAM  Aspers et al.
XCL  173 12
UREF
PNO  3973434
ISD  19760800
NAM  Smith
OCL   73862.24
UREF
PNO  3974685
ISD  19760800
NAM  Walker
XCL  173 12
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UREF
PNO  3974883
ISD  19760800
NAM  Sigmund
OCL  173 12
UREF
PNO  3975954
ISD  19760800
NAM  Barnich
OCL   73862.23
UREF
PNO  3982419
ISD  19760900
NAM  Boys
OCL   73862.24
UREF
PNO  4000782
ISD  19770100
NAM  Finkelston
OCL  173 12
UREF
PNO  4008772
ISD  19770200
NAM  Boys
OCL  173 12
UREF
PNO  4008773
ISD  19770200
NAM  Wallace et al.
OCL  173 12
UREF
PNO  4013895
ISD  19770300
NAM  Akiyoshi et al.
XCL   73761
UREF
PNO  4016938
ISD  19770400
NAM  Rice
OCL  173  1
UREF
PNO  4023406
ISD  19770500
NAM  Benz
OCL   73862.24
UREF
PNO  4026369
ISD  19770600
NAM  Vliet
OCL  173 12
UREF
PNO  4027530
ISD  19770600
NAM  Tambini et al.
XCL  173 12
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```
PNO  4074772
ISD  19780200
NAM  Jonsson
OCL  173 12
UREF
PNO  4081037
ISD  19780300
NAM  Jonsson
OCL  173  1
UREF
PNO  4091451
ISD  19780500
NAM  Weineret al.
XCL  173 12
UREF
PNO  4104778
ISD  19780800
NAM  Vliet
OCL   29407
UREF
PNO  4104779
ISD  19780800
NAM  Sigmund
OCL   29407
UREF
PNO  4104780
ISD  19780800
NAM  Sigmund
OCL   29407
UREF
PNO  4106176
ISD  19780800
NAM  Rice et al.
OCL   29407
UREF
PNO  4106570
ISD  19780800
NAM  Eshghy et al.
OCL  173 12
UREF
PNO. 4110829
ISD  19780800
NAM  Boys
XCL  173 12
UREF
PNO  4142266
ISD  19790300
NAM  Dahl
XCL   29407
UREF
PNO  4142591
ISD  19790300
NAM  Himmelstein
OCL  173 12
UREF
PNO  4161220
```

ISD 19790700
NAM Carlin et al.
OCL 173 1
ABST

PAL There is disclosed a technique for tightening threaded fasteners in which values of offset torque, initial tension rate relative to angle, final tension rate relative to angle and other joint related factors are empirically determined by instrumenting a plurality of fasteners of the type ultimately to be tightened. In one embodiment, torque and angle are monitored during tightening. Calculations are conducted, while tightening, to determine the tension prevailing in the bolt at a particular angle of advance. By using the calculated tension value and the particular angle of advance, an instantaneous position of threading advance on the tension-angle curve of the fastener is established. From this instantaneous position, it is determined how much greater angle of advance or how much torque is required to tighten the fasteners to a final desired tension value. The same technique may also be used merely to monitor tightening which is terminated by a different tightening strategy. A number of quality control procedures are conducted to determine if the fastener and the tightening tool are performing normally. In another embodiment, analog devices are utilized to convert sensed values of torque and the rate of threading advance into parameters which control tool shut off.

PARN

PAR This application is a continuation-in-part of abandoned application Ser. No. 712,554, filed Aug. 9, 1976 and is a continuation-in-part of application Ser. No. 766,429, filed Feb. 7, 1977, U.S. Pat. No. 4,106,570.

BSUM

PAR This invention relates to a technique for tightening threaded fasteners. The function of threaded fasteners is, of course, to unite two or more pieces into a typically rigid part called a joint. For purposes of convenience, the term fastener pair may be used to designate male and female threaded members, e.g. a nut and bolt, bolt and internally threaded hole of a joint part, threaded stud and nut, and the like. The connected pieces of a joint should be so tightened as to remain in contact during vibration, static and/or dynamic loading of the part, and the like. In many applications where several threaded fasteners are used, it may be of substantial importance to assure that the contact pressure between the pieces created by the fasteners is uniform since nonuniform deflection of the pieces may create unacceptable joint conditions. Proper assembly should produce uniform contact pressures from joint to joint in accordance with design requirements. This can be achieved only by assembly procedures that produce uniform joint preload or clamping load. Although it is conceivable to determine joint preload or clamping load in terms of compression of a nut, it is more practical to deal in terms of bolt tension. There is, unfortunately, no direct technique for measuring bolt load externally without instrumenting the bolt or using a load washer which is either impractical or uneconomic for assembly line production. Accordingly, all practical techniques of bolt tension control in production quantities are inferential.

PAR There are a number of well known techniques for tightening threaded fasteners based on information available from external instruments such as torque and angles sensors as contrasted to specially designed fasteners or load washers. Included in these techniques are torque control, turn-of-the-nut method, the yield point method, acoustic measuring, overrunning schemes and torque rate methods

PAR One of the present techniques in wide use is torque control in which a constant final torque is applied to all fasteners. Final torque is typically produced by a stall air tool and the degree of torque control depends on the uniformity of air pressure, motor performance and the hardness of the joint. The intention is to achieve tension scatters in the range of .+-.10-20% about the mean. The actual scatter limits can be verified by instrumenting the bolts in a laboratory environment. Opinions vary on what tension scatters are actually present in large quantities of fasteners tightening with torque control methods. It would not be surprising to learn that total tension scatter in production quantities is on the order of .+-.100% of mean which can be caused by a .+-.41% scatter in friction alone.

PAR Torque is, of course, related to tension but the relationship is subject to large uncertanties resulting from a first order dependence on thread and head friction. In the simplest theoretical consideration, the following equation describes the relation of torque and tension:

EQU T=(f.sub.h r.sub.h +f.sub.th r.sub.th)F (1)

PAL where T is torque, f.sub.h is the coefficient of friction between the fastener head and the abutting piece, r.sub.h is the effective radius of head friction, f.sub.th is the coefficient of friction between the threads of the fastener, r.sub.th is the effective radius of thread friction and F is bolt tension. Although the mean value of the coefficients of friction can be substantially reduced by lubricants and coatings, the relative scatter about the mean value cannot be substantially affected. Combining the friction uncertainties with the variations in applied torque, the tension control actually achieved in practice is quite poor. Accordingly, in order to minimize fastener failure during assembly, the mean torque must be designed at unreasonably low levels as compared with the strength of the bolt. Even with unreasonably low mean torque values, a significant proportion of the fasteners are woefully understressed while many have been stressed past the elastic limit.

PAR Discussions of torque control methods of tightening threaded fasteners are found in Assembly Engineering, October 1966, pages 24-29; Hydrocarbon Processing, January 1973, pages 89-91; Machine Design, Mar. 6, 1975, pages 78-82; The Engineer, London, May 26, 1967, pages 770-71; Iron Age, Feb. 24, 1966, page 66; Machine Design, Feb. 13, 1964, pages 180-85; Power Engineering, October 1963, page 58; and U.S. Pat. Nos. 3,555,938 and 3,851,386.

PAR Another widely used technique for tightening threaded fasteners in production quantities is called the turn-of-the-nut method which makes use of the applied torque as well as the angle of threading advance. In its simplest form, the technique is to advance the fasteners until a predetermined torque value is reached, for example snug torque, and then turn each nut an additional constant predetermined angle. The concept is that the relation of the turn of the fastener to the strain of the bolt will eliminate the influence of friction on the final desired tension value. If the clamped pieces were purely elastic and contact between them were immediate and perfect, one would expect the bolt tension to increase linearly with unit angle of advance starting with the value of zero at the onset of contact. In theory, tension control would be as accurate as the uniformity of the joint tension rate which is the slope of the curve obtained by plotting tension against angle of advance.

PAR In practice, the tension rate is not exactly a constant from joint to joint nor is it uniform as a function of angle for any single joint. The reasons are related to microplasticity which is the yield of surface irregularities in the moving fastener components, lubricant squeeze film and the fact that contact is gradual rather than immediate. The turn-of-the-nut method is customarily considered to be substantially superior to the torque control technique although data developed during the investigation of this invention suggests that this method is substantially overrated, at least at low to moderate tension values. The turn-of-the-nut method does have the disadvantage of partly relying on torque which is subject to the large uncertainties previously discussed. The selection of the threshold torque is a critical decision. If threshold torque is too high, the theoretical advantage over the torque control method is substantially reduced. If threshold torque is too low, final bolt tension will fluctuate greatly from joint to joint, since at low torque values, both the torque-angle and the tension angle curves have varying curvature. The combination of uncertain tension at the threshold torque and nonuniformity of tension rate in a large angle span will more than offset the theoretical advantage gained. The turn-of-the-nut method, being essentially a strain approach to tightening, has the advantage of reducing substantially the rate of bolt failure during assembly because very large strains can be sustained by the bolt material in the plastic zone. During the investigation of this invention it has been learned that the difference between low torque rate fasteners and high torque rate fasteners from the same sample can develop a scatter in the final desired tension value of .+-.50% at tension values in the range of 3000 pounds for a 5/16"-24, grade 8 bolt using the turn-of-the-nut method. As the final tension value increases, the scatter reduces as a percentage of final tension.

PAR Another difficulty with turn-of-the-nut methods is that recalibration is required when the final desired tension value is changed. This is in contrast to this invention where the final desired tension value can be changed at will so long as this value is in the second tension rate range and is sufficiently far from the break in the tension curve so that the tool will not run past the desired value because of tool overrun.

PAR Discussion of turn-of-the-nut methods of tightening threaded fasteners are found in Hydrocarbon Processing, January 1973, pages 89-91; Machine Design, Mar. 6, 1975, pages 78-82; Journal of the Structural Division, Proceedings of the American Society of Civil Engineers, April 1966, pages 20-40; Machine Design, Feb. 13, 1964, pages 180-85; and U.S. Pat. No. 3,891,386.

PAR As pointed out in some detail in U.S. Pat. Nos. 3,643,501; 3,963,726; 3,965,778; 3,973,434; 3,974,883; 3,982,419; 4,000,782; and 4,008,772; and Design Engineering (London), January 1975, pages 21-23, 25, 27, 29, another approach for tightening threaded fasteners is known as the yield point method. In this approach, an attempt is made during tightening to sense the onset of plastic elongation of the bolt and terminate tightening in response thereto. The yield point, which is the boundary between the elastic and plastic deformation zones of a metal in a uniaxial state of stress, is quite difficult to determine precisely. Accordingly, the yield point is often defined in terms of an offset strain, typically 0.1-0.2%, which is arbitrarily chosen.

PAR It is apparent that a joint is made up of the clamped pieces as well as the fasteners. The design is usually such that yielding occurs in the bolt shank although it could conceivably occur in the bolt head or nut. The bolt is also subject to shear as a result of torsion created by the turning moment or torque. Accordingly, a bolt is in a combined state of stress. Thus, at high torque values, the stress in the bolt is due to both torque and tension and can substantially alter the tensile strength of a bolt tension control due to natural scatters in the material yield point. Other errors involved in yield point methods are the result of noise in the torque signal and other uncertainties in consistently sensing the yield point. The main objection to the yield point method is the concern over the fatigue strength and reusability of the bolt. Although the matter is subject to some controversy, it appears clear that one time application and release of an external load will cause relaxation of the joint and accordingly reduce the clamping force applied by the bolt below the original clamping force. In extreme cases, the bolt may lose all tension and be loose.

PAR Other techniques related to yield point methods are found in U.S. Pat. Nos. 3,939,920 and 3,974,685. In the former, the technique basically is to measure a tightening parameter, e.g. torque, at the yield point, conduct certain calculations and back off the nut until the final desired axial stress is achieved and terminate tightening. In the latter, the technique is to provide a washer which yields at a known stress value below the yield point of the bolt. When the washer yields, a torque value is obtained and noted at a known stress value. Extrapolations are made to obtain a calculated torque value at a desired elevated stress value in the bolt. Tightening is terminated in response to the calculated torque value.

PAR An overrunning approach which may be used to detect galled threads or cross threaded members is disclosed in U.S. Pat. Nos. 3,368,396 and 3,745,820. In this technique, a warning signal is generated when a predetermined torque is developed before a given number of turns has been effected which may be indicative of galled threads. A different warning signal is generated when a larger number of turns are effected before the development of a desired higher torque is obtained which is suggestive of cross threading. It will be apparent that these approaches are not designed to control bolt tension.

PAR Another approach for controlling bolt tension involves acoustic devices which attempt to measure the elongation in a bolt caused by tension. Such devices are discussed and illustrated in U.S. Pat. Nos. 3,306,100; 3,307,393; 3,650,016; 3,759,090 and 3,822,587.

PAR Another group of prior art techniques which has been suggested involve a consideration of the rate of torque increase relative to the angle of threading advance as disclosed in Assembly Engineering, September 1974, pages 42-45; Design Engineering (London), January 1975, pages 21-23, 25, 27, 29; Iron Age, Apr. 28, 1975, page 44; and Machine Design, Volume 47, Jan. 23, 1975, page 44. These techniques monitor the torque-angle curve during tightening in order to terminate tightening in response to conclusions derived from the torque-angle relationship. In the Design Engineering disclosure, tightening is terminated upon sensing a significant drop in the torque rate, which occurs at the yield point. In the remaining articles, tightening is apparently terminated when a predetermined torque range is attained within a fairly narrow angle range. These disclosures are thus similar to the overrunning schemes mentioned above.

PAR The goal of inferential tightening techniques is not merely to achieve a predetermined clamping load on one set of fasteners, since this can be readily done in the laboratory by instrumenting the bolt. The goal is to achieve consistent and reproducible clamping loads or final tension values in large lots of fasteners at a low cost per fastener. Thus, the major fallacy in prior art inferential tightening techniques has been to select a fixed tightening parameter, such as torque or angle in the torque control and turn-of-the-nut methods respectively, or a fixed range of a particular tightening parameter and terminate tightening in response to the attainment of the fixed tightening parameter or range thereof. This broad approach of the prior art has several major difficulties. First, the critical item in tightening is clamping load as may be measured by final bolt tension. With the possible exception of some of the acoustic methods, no one has apparently heretofore been able to inferentially determine final bolt tension in production operations. Second, because of the selection of some parameter other than tension, there is introduced such widely variable factors as friction coefficients, speed related losses, and the like which grossly affect the relationship between the fixed tightening parameter or the fixed range thereof and the only important result in tightening, which is clamping load or bolt tension.

PAR In one aspect, this invention contemplates the determination, during tightening, of the value of a tightening parameter which is sufficient to tighten each fastener pair to a final desired tension value, which parameter varies from one fastener pair to the next. Tightening of the fastener pair is then terminated in response to the variable value of the determined tightening parameter. By this approach, the variation in friction from one fastener pair to the next is largely eliminated. The technique of this invention produces typical tension scatters on the order of less than .+-.10% in production quantities whereas scatters with turn-of-the-nut techniques are at least 2-3 times higher and scatter with torque control techniques are at least 5-6 times higher. It is accordingly apparent that this invention produces substantially more consistent tightening results than do the significantly inaccurate techniques of the prior art.

PAR In another aspect, an important part of this invention constitutes the quality control procedures that are conducted as a consequence of the acquisition of torque and angle data of each fastener tightened. Most of the quality control procedures are done well prior to the termination of tightening and include procedures for determining whether the prevailing torque of the fastener is too high, determining whether the torque rate of the fastener is linear or arcuate, determining whether the torque rate of the fastener is too low, determining whether the tool is performing normally and determining whether the fastener has exhibited significant nonlinear strain. Any of the fastener related quality control checks are used to prematurely terminate tightening in the event indications are that the fastener or its mating engagement with the clamped pieces is defective. The tool related quality control checks provide a warning so that maintenance attention can be given to the tool.

PAR It is accordingly an object of this invention to provide a technique for tightening threaded fasteners which produces substantially more consistent results than the prior art.

PAR Another object of the invention is to provide a tightening technique which provides sufficient data to conduct a number of quality control procedures during tightening.

PAR Another object of this invention is to provide an improved technique for tightening threaded fasteners incorporating monitoring the torque-angle curve, calculating the tension in the fastener being tightened and instructing a tool to tighten the fasteners to a final desired tension value.

PAR Another object of this invention is to provide an improved technique for tightening threaded fasteners incorporating the monitoring of the torque-angle relationship, calculating during tightening the tension appearing in the fastener being tightened and instructing the wrench to continue tightening until a predetermined value of torque or angle is

PAR Other aspects, objects and advantages of this invention will become apparent as the description proceeds.

DRWD

PAC IN THE DRAWINGS

PAR FIG. 1 is an illustration of typical torque-angle and tension-angle curves generated during the continuous tightening of a fastener pair far beyond the elastic limit;

PAR FIG. 2 is an enlarged illustration of the low end of a typical torque-angle curve illustrating very early torque-angle relationships;

PAR FIG. 3 is an enlarged illustration of a typical torque-angle curve constituting a continuation of FIG. 2;

PAR FIG. 4 is an illustration of a typical torque-speed relationship of an air powered tool;

PAR FIG. 5 is a torque-angle diagram illustrating the determination of non-linear strain in the fastener at the mid-point stop;

PAR FIG. 6 is an illustration of a typical tension-angle curve representing the relaxation of a joint at the termination of continuous tightening;

PAR FIG. 7 is an illustration of a typical tension-angle curve representing the relaxation of the joint at the mid-point stop during tightening to a higher tension value;

PAR FIG. 8 is a torque-angle diagram illustrating the determination of non-linear strain in the fastener during tightening toward a final tightening parameter;

PAR FIG. 9 is an enlarged illustration of torque-angle and tension-angle curves graphically explaining another facet of the invention;

PAR FIG. 10 is a schematic view of the mechanism of this invention;

PAR FIG. 11 is a side view of a component of the mechanism of FIG. 10;

PAR FIGS. 12A and 12B are circuit diagrams of another component of the device of FIG. 10;

PAR FIG. 13 is a front view of a typical operator's console;

PAR FIG. 14 is a graph illustrating the relative effectiveness of this invention compared to prior art techniques; and

PAR FIG. 15 is a block diagram illustrating another mechanism of this invention .

DETD

PAR Referring to FIG. 1, there is illustrated a typical torque-angle curve 10 and its corresponding tension-angle curve 12 which are developed during the continuous threading of a fastener pair to a point far beyond the elastic limit of the bolt, as may be measured in the laboratory by suitable equipment. In the torque curve 10, there is typically a free running region or period 14 where only a small torque is required to advance the nut and no appreciable bolt tension exists. This is followed by a region or period 16 of incipient clamp up where the joint parts are being brought toward engagement. This is followed by an engagement period or region 18 where the contact between the surfaces of the fastener and the clamped pieces are being established while the rate of angle advance is gradually being reduced in accordance with the torque-speed characteristics of the tool employed. The tension rate FR.sub.1 in the region 18 is typically less than the ultimate tension rate FR.sub.2 but is rather well defined. The engagement period 18 appears to cover an approximate tension range of about ten percent to about fifty percent of the elastic limit of the bolt. Above the engagement region 18 is a final tensioning region or period 20 which normally exhibits an increased tension rate FR.sub.2. Fortunately, FR.sub.1, FR.sub.2 and the location of the bend therebetween are normally well defined and reproducible properties of the joint and are not related to friction or other variable factors which may develop in the course of tightening.

PAR The torque rate is essentially zero in the free running region 14 and begins to rise substantially during the incipient clamp up period 16. The torque rate TR in the engagement period 18 approaches linearity. Due to the existence of speed-dependent losses such as lubricant squeeze film and microplasticity of the surface irregularities between the fastener parts and clamped pieces, a linear approximation of the torque curve 10 in the region 18 does not intersect the angle axis at the point of origin of the tension curve 12. An offset angle .alpha..sub.os exists which is proportional to such speed dependent losses. .alpha..sub.os describes the angular separation between the origin of the average torque slope TR and the origin of the average tension slope FR.sub.1. Because of the torque-speed curve of the tool employed, it can be shown that .alpha..sub.os is torque rate dependent so that the offset torque T.sub.os is the appropriate joint property and T.sub.os is the product of the offset angle .alpha..sub.os and the torque rate TR.

PAR The elastic limit 22 occurs at a point beyond which strain is not receivable upon unloading and appears toward the upper end of the final tightening region 20 as is well known in classical mechanics. Somewhere in the yield region 24, the bolt commences to deform plastically rather than elastically. As alluded to previously, the normal definition of the yield point is in range of 0.1-0.2% strain which is somewhat arbitrary. The proportional limit occurs substantially below the yield point 22 and occurs where the stress/strain ratio is no longer constant.

PAR In order to implement the hereinafter disclosed method of tension control, one needs to determine FR.sub.1, FR.sub.2, T.sub.os and other parameters as discussed more fully hereinafter. This is conveniently accomplished by selecting a reasonably large sample of the fasteners that ultimately will be tightened by the technique of this invention and empirically determining the values in the laboratory. It will normally be experienced that scatters in FR.sub.1 and either FR.sub.2 or r, the ratio of FR.sub.2 /FR.sub.1, will be quite small. In new bolts, FR.sub.2 is normally 5-15% higher than FR.sub.1. In fasteners that have previously been tightened, FR.sub.2 is normally quite close to FR.sub.1. The conclusion is that the difference between FR.sub.1 and FR.sub.2 is related to the microplasticity of surface irregularities between the mating faces of the joint. As is true in all torque measurements, T.sub.os will have much larger scatters. Fortunately, the offset torque correction is normally quite small so that its lack of consistency has a quite minimal effect of the final tension values. One exception is in the use of so-called "prevailing torque" fasteners which usually comprise a bolt or nut having the threads intentionally deformed for various reasons. Another exception involves the use of a bolt or nut in which the threads are unintentionally deformed. In such situations, the normal value of T.sub.os should be increased by the addition of the measured "free running" or prevailing torque or this effect compensated for as more fully explained hereinafter.

PAR Broadly, the technique of this invention is to periodically or continuously sense the torque applied to the fastener pair and the angle of advance corresponding to the sensed torque, determine the tension appearing at least at one point 26, calculate a value of a tightening parameter sufficient to achieve a final desired tension value F.sub.D and instruct a tool to advance the fastener pair until the attainment of the tightening parameter.

PAR During a study of torque-tension-angle relationships, it was discovered that the inverse of the rate with respect to angle of the logarithm of

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     friction. Defining,
EQU  P.ident.(d/d.alpha.) log T                                  (2)
EQU  F.varies.(1/P). .alpha.>.alpha..sub.q                       ( 3)
PAL  where .alpha..sub.q is the angle where P achieves a maximum value and
      conceivably could be used as the origin for the turn-of-the-nut method
      thereby totally eliminating the influence of joint friction. In practice,
      it is difficult to detect a single meaningful peak which can be labeled
      .alpha..sub.q because of the noise inherent in the actual torque-angle
      signal. Although the concept expressed in equation (2) is valid, it
      requires a different procedure for processing the torque-angle data to
      achieve a practical solution. As will be apparent to those skilled in the
      art, the solution may be analog or digital. The theoretical basis for
      equation (2) can be derived from equation (1). Differentiating equation
      (1) relative to angle,
      ##EQU1##
      Dividing equation (4) by equation (1),
EQU  (dT/d.alpha.)/T=(dF/d.alpha.)/F.                            (5)
PAL  Since dT/T is the definition of d log T,
EQU  (dF/d.alpha.)/F=(d/d.alpha.) log T,                         (6)
PAL  If dF/d.alpha., the joint tension rate, is a constant, then:
      ##EQU2##
PAR  Equation (7) shows that the constant of proportionality in equation (3) is
      the tension rate FR.
PAR  Several assumptions have been made in the above derivation:
PA1  (1) The tension rate is a constant. This is not precisely true throughout
      the tightening range. The more precise assumption would have been that
      tension at any angle of advance after the angle of origin, where the
      tension rate commences, is a unique function of the joint and therefore
      that the tension rate at any angle after the angle of origin is a unique
      function of the joint.
PA1  (2) Torque is not a function of the turning speed. This is not strictly
      true and for accurate application, it should be accounted for.
PA1  (3) Joint friction (f.sub.h, f.sub.th) is not load dependent for any one
      sample. This is a good assumption except when non-metallic (molybdenum
      disulfide, Teflon, etc.) coatings are utilized. Even in the case of
      non-metallic coatings, any changes in a finite tension range should be
      small.
PAR  For purposes of convenience, the tightening technique of this invention may
      be referred to as the logarithmic rate method.
PAR  The importance of equations (5) and (7) should now be appreciated. It has
      been demonstrated in the laboratory that the value of tension rate
      dF/d.alpha. is a function of the joint having small scatter and is
      independent of friction. The torque rate dT/d.alpha. can be determined
      from torque and angle measurements taken during the tightening of each
      fastener pair by suitable torque and angle sensors on the tightening tool.
      The torque value T is, of course, measured by same torque transducer. It
      will accordingly be apparent that the friction dependent parameters, i.e.
      torque rate and torque, are determined for each fastener during
      tightening, which is here defined as the time frame commencing with the
      onset of threading and stopping at the termination of tightening. Since
      tension rate dF/d.alpha. is a function of the joint which is determined
      empirically prior to the tightening of production fasteners, it is a
      simple matter to solve equation (5) for tension.
PAR  While theoretically correct, several adjustments should be made to
      equations (5) or (7) in order to enhance accuracy and reliability. First,
      the effect of prevailing torque T.sub.pv should be taken into account.
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Prevailing torque is that torque necessary to overcome the thread-to-thread resistance to fastener advance which does not contribute to the inducement of bolt tension and which may be sensed during the threading advance of the fasteners in the region 14. Second, the effect of offset torque T.sub.os should likewise be taken into account. Offset torque is that torque necessary, at zero prevailing torque, to advance the fastener to an angle location corresponding to the origin of tension. These accomodations may be expressed mathematically as: ##EQU3##

PAR The importance of equations (8) and (9) should now be appreciated.

PAR Referring to FIG. 1, it may be assumed that the fasteners are threaded together with measurements being taken of both torque and angle with tightening being advanced to the point 26. The average torque rate TR is calculated, as by the use of the least squares method. Since the tension rate FR.sub.1 is known from empirical measurements of the joint in question, the tension in the joint can be calculated at the point 26 from equation (5) or (9). Graphically, the angle required to advance the fasteners from the tension value calculated at the point 26 to the final desired tension value F.sub.D can be easily done since the tension rate FR.sub.2 has likewise been determined empirically. After determining the additional angle .alpha..sub.final, the tool may be instructed to so advance the fasteners thereby attaining the desired final tension value F.sub.D. In a similar fashion, the additional torque .DELTA.T or the final desired torque T.sub.D can be calculated.

PAR There are substantial difficulties in applying these principles to production line operations. It will be apparent that the calculations being made are being done while tightening. It will be apparent that the duration of tightening should be minimized so far as practicable commensurate with the attainment of consistent results. In any event, it will be apparent that long tightening times, for example two minutes, would render the technique unsuitable for many production line operations although some suitability may remain for special purpose applications such as in the fabrication of reactor vessels, aircraft and the like where precision is paramount. It is accordingly evident that the use of electronic computation techniques is highly desirable for processing the data obtained from measurements taken during tightening. Even with the use of electronic computation techniques, it is desirable to advance the fasteners for some initial distance, suspend tightening momentarily and then resume tightening to the final desired tension value. The momentary stop allows time to complete lengthly calculations and has the additional benefit of allowing the joint to relax at this point rather than at the final tension value attained. As will be more fully apparent hereinafter, many of the calculations are being done while the tool is running as well as when the tool is momentarily stopped. It will, however, be evident that simplified computations may be utilized thereby eliminating the necessity for a momentary pause in the tightening operation.

PAR More specifically, the following steps may be taken to attain a consistent bolt tension utilizing an instructable tool equipped to measure torque and angle information only, after the acquisition of certain empirical information:

PAR 1. Engage the fasteners, start the tool and record torque at predetermined angle increments.

PAR 2. Shut the tool off in a tension range of 0.4-0.75 of elastic limit. Although a turn-of-the-nut approach or torque control strategy may be used to estimate the initial tool shut off, a simplified logarithmic rate

PAR 3. Calculate the torque rate from the torque and angle measurements by a suitable smoothing technique, e.g. least squares. Calculate the torque at the mid-point of the range from which the torque rate was calculated, by averaging the torque value along this range. The intersection of the average torque rate with the axis represented by (T.sub.pv +T.sub.os) is accordingly established. Since the offset torque T.sub.os is largely a function of the joint, the intersection of the tension curve with the angle axis is established.

PAR 4. The tension curve is then a straight line emerging from the origin or intersection determined in 3. above with the initial slope FR.sub.1. This is typically valid up to about 0.5 elastic limit at which point the tension curve has a slope of FR.sub.2. The location of the bend in the tension-angle curve is determined empirically when determining the values of FR.sub.1, FR.sub.2 and T.sub.os.

PAR 5. Calculate the tension value appearing in the fasteners at some location, for example, point 26. Given the tension value at point 26, calculate the additional angle .alpha..sub.final or the additional torque .DELTA.T necessary to tighten the fasteners to the final desired tension value F.sub.D.

PAR 6. Instruct the tool to resume tightening and advance the fasteners through the angle .alpha..sub.final or for the increased torque .DELTA.T.

PAR As disclosed in applicant's copending application Ser. No. 766,429, the disclosure of which is incorporated herein by reference, the angle of advance measured by an angle encoder is not the true angle through which the fastener turns because of torsional twist in the tightening tool and because of torsional twist in the bolt. To achieve maximum accuracy, it is necessary to compensate the measured angle of advance for the torsional twist of the tool and bolt. In addition, it is necessary to take into account the torsional twist of the laboratory equipment utilized to acquire values for the tension rates FR.sub.1 and FR.sub.2.

PAR For purposes of discussion, the implementation of the technique of this invention may be broken down into six generally chronological segments: (1) quality control procedures in the regions 14, 16; (2) reaching the mid-point stop and conducting torque rate determinations and quality control procedures; (3) procedures determining the final shut off parameters; (4) procedures involving restarting the tool; (5) procedures determining the occurrence of non-linear strain during tightening toward the final shut off point; and (6) quality control procedures conducted at the termination of tightening.

PAC QUALITY CONTROL PROCEDURES IN THE REGIONS 14, 16

PAR It has been learned that considerable information can be acquired about the quality of the fasteners during the free running region 14. Specifically, deductions can be made about cross threading, grossly imperfect threads, bolt bottoming, and whether the bolt is already tight. Because the joint has not clamped up, it is evident that the information so acquired concerns the fasteners only and is not affected by other joint properties. It has also been learned that deductions can be made during the incipient clamp up region 16 concerning the tool. Specifically, it can be determined whether the tool has engaged the fastener, whether a fastener is in place, the bolt is broken, one of the threaded members has no threads, or one of the threaded fasteners is the wrong size.

PAC Prevailing Torque

PAR Although the region 14 is referred to as the "free running" region, a small amount of torque is necessary to advance the fasteners because of friction between the mating threads. Some types of fasteners, known as prevailing torque fasteners, include intentionally imperfect threads which require more than a minimum amount of torque in order to threadably advance. Other fasteners which are unintentionally imperfect also require more than a minimum torque to effect threadable advance. For all practical purposes these types of fasteners may be treated identically with one caveat. Any batch of fasteners which are not intended to be prevailing torque fasteners will include some fasteners which have substantially perfect threads thereby requiring only a minimum torque and will also include some fasteners having imperfect threads which require more than a minimum torque for threadable advance. Thus, any technique which is intended to be universal or which is intended to be used with non-prevailing torque fasteners must have the capability of accomodating fasteners which vary from substantially perfect to grossly imperfect.

PAR Broadly, one goal of this procedure is to detect, during tightening in the free running region 14, those fasteners which exhibit instantaneous prevailing torque values T.sub.pvi which exceed a maximum expected prevailing torque (T.sub.pv).sub.max. The value of (T.sub.pv).sub.max may be acquired in any suitable manner, as by relying on the published information of fastener manufacturers, by measuring the prevailing torque on a significant number of fasteners, or by adding an incremental percentage, for example 10-20%, to either published information or acquired values. Similarly, it may be desired to detect those fasteners which exhibit instantaneous prevailing torque values T.sub.pvi which are less than a minimum prevailing torque (T.sub.pv).sub.min, as when using prevailing torque fasteners and assurance is required that the fasteners are up to specifications.

PAR Another goal of this procedure is to acquire sufficient information to provide a reasonably accurate value for average prevailing torque T.sub.pv. This may prove to be of value in correcting a final shut off parameter for the effect of prevailing torque.

PAR Several precautions are desirably taken for the measuring of prevailing torque to assure that the data is reliable. First, it is essential that the acquisition of data occur before the commencement of clamp up of the joint parts. Otherwise, the normal torque required to begin tightening up the joint will be confused or erroneously deduced as abnormal prevailing torque. This error in data acquisition is fatal to proper results because applied torque rapidly increases during joint clamp up as is evident from the showing in region 16 is FIG. 1. Second, the acquisition of data should be delayed until the fastener parts are rotating or other steps should be taken to avoid spurious torque readings from the static friction exhibited between the fastener parts at rest or due to the transition from static to dynamic friction effects.

PAR With the criteria outlined above, it is evident that there is considerable leeway in designing a system for acquiring prevailing torque data for a particular application. Because the need in a particular application may be to reject defective parts, to acquire values for average prevailing torque T.sub.pv, or both, the design selections are subject to change.

PAR In the system disclosed, utilizing the fasteners described immediately preceding Table II, it is desired to take prevailing torque data to reject fasteners at an early stage of tightening and to acquire an average prevailing torque value T.sub.pv to compensate the final shut off parameter. Referring to FIG. 2, there is illustrated a typical torque-angle plot 28 of an acceptable fastener exhibiting an initial torque peak 30 caused by static friction between the fastener components and the change over from static to dynamic friction. After the initial torque peak 30, the curve 28 levels out to a reasonably constant value maximum expected prevailing torque (T.sub.pv).sub.max. Although the curve 28 is illustrated as a continuously recorded value, in digital systems it is highly desirable to take torque sensings only at selected locations spaced apart by a predetermined angle increment .DELTA..theta..

PAR In operation, the tool is turned on to commence rotation of the fastener component and a delay of one .DELTA..theta. angle increment is allowed before a first torque sensing 32 is taken. Thereafter, a torque sensing is taken at every angle increment .DELTA..theta., indicated by the data points 34, until the expected rundown angle .theta..sub.rd is reached. During the expected rundown angle .theta..sub.rd, the instantaneous torque sensing T.sub.pvi at each of the data points 32, 34 is compared with (T.sub.pv).sub.max. If the instantaneous prevailing torque T.sub.pvi exceeds (T.sub.pv).sub.max more than once, a shut off command to the tool is issued, an indication is made that the joint is unacceptable and the system is reset for the next tightening cycle. Although it is normally desirable to have the tool operator intervene following the rejection of a joint and although the typical air powered tools used to tighten fasteners are not reversible, it may be desired in some applications to automatically back off the nut by providing a reversible tool and instructing the tool to back the nut off prior to reset for the next tightening cycle. In connection with the fasteners exhibiting the curve 28, it is apparent that no shut off command is issued.

PAR With the system designed in this manner, decisions need to be made about the size of the angle increments .DELTA..theta., the size of the rundown angle .theta..sub.rd, and the size of a sampling region .theta..sub.s. The value of .DELTA..theta. is selected so that the transient effect of the static-to-dynamic peak 30 and any other transient effect will be sensed only once if at all. It has been found that the transient torque effects in the free running region 14 are of quite short angular duration. Although the value of .DELTA..theta. is susceptible to considerable compromise, a selection of 22.degree. has proved satisfactory. The value of the rundown angle .theta..sub.rd is selected to assure that both the rundown angle .theta..sub.rd and the period of data acquisition .theta..sub.s immediately following .theta..sub.rd are completed substantially before the incipient clamp up region 16 commences. The value of .theta..sub.rd accordingly depends on the duration of the sampling period .theta..sub.s, the length of the threaded fastener compared to the size of the parts to be clamped up and the like. The selection of .theta..sub.rd and .theta..sub.s should be conservative to provide assurance that these angular periods are completed prior to the incipient clamp up region 16. The value of .theta..sub.rd may thus vary widely and in one embodiment of the invention is five complete revolutions of the fastener or torque appling tool.

PAR Similarly, the duration of the sampling region .theta..sub.s may also vary widely. It is not essential to take an enormous number of torque readings to establish a reasonably reliable value for average prevailing torque T.sub.pv for the following reasons. It will be shortly apparent that the value of T.sub.pv is relatively small when compared to the torque readings T from which T.sub.pv will be subtracted. Accordingly, any difference between the true average prevailing torque and the calculated value will be smaller still. It is accordingly quite satisfactory to obtain an average value from a fairly modest number of data points, e.g. 5-30. Although the duration of the sampling period .theta..sub.s is susceptible to considerable compromise, a sampling duration on the order of one revolution has proved satisfactory. Since prevailing torque T.sub.pv iscreated by circumferential asymmetry of the nut and bolt, a selection of one revolution for the sampling region .theta..sub.s is a natural one. The sampling interval between the data points 36 in the region .theta..sub.s may conveniently continue to be 22.degree.. Accordingly, approximately sixteen data points 36 are used.

PAR In calculating the average prevailing torque T.sub.pv in the sampling region .theta..sub.s, there are a number of conceivable approaches. First, one may merely add the values of the torque sensings T.sub.pvi and divide by the number of data points. In the alternative, one may elect to use a smoothing technique such as least squares. Furthermore, one could conceivably average the torque sensings after disregarding any value above (T.sub.pv).sub.max and either arithematically averaging or smoothing the remaining data. For reasons mentioned previously, any reasonably accurate averaging technique will suffice because the difference between the calculated average and the true average will be a very small value.

PAR It will be seen that by delaying the first data point 32 by the angle increment .DELTA..theta. from the onset of rotation, the existence of the static-to-dynamic peak 30 will likely be masked. By separating the data points 32, 34, 36 by the angle increment .DELTA..theta., any transient torque effect will be sensed only once if at all. By delaying the sampling period .theta..sub.s until after the rundown angle .theta..sub.rd, one is reasonably assured that sampling for averaging purposes avoids any spurious sensings related to the onset of tightening.

PAR As will be more fully pointed out hereinafter, a reasonably reliable value for T.sub.pv is desirable to compensate a final shut off parameter for the effect of prevailing torque. In this regard, it will be evident that the amount of torque applied to a fastener during the free running region 14 has nothing whatsoever to do with the attainment of tension in the bolt at the termination of tightening. The compensation made for the tightening strategy of this invention will be discussed more fully hereinafter. In a torque control strategy, however, the running torque sensed by the torque encoder in the final tightening region 18 should be adjusted by the amount of the noted prevailing torque to obtain a torque value which can be compared to the desired torque shut off parameter. For example, if empirical data suggests that the fastener needs to advance 30 ft-lbs above an average prevailing torque of 3 ft-lbs and the fastener being tightened exhibits a prevailing torque of 5 ft-lbs, the tool should be instructed either: (1) to advance the fastener to 35 ft-lbs, or (2) to advance the fastener 30 ft-lbs beyond the noted prevailing torque of 5 ft-lbs, or (3) to advance the fastener until the difference between the sensed torque and the noted prevailing torque equals 30 ft-lbs. In a turn-of-nut strategy, the torque sensings used in reaching the angle location known as snug torque should be similarly adjusted by the amount of the noted prevailing torque.

PAR Also shown in FIG. 2 is a torque-angle curve 38 which clearly indicates an undesirable fastener pair. The curve 38 exhibits a torque peak 40 caused by the change over from static to dynamic friction and then levels out to a running value above (T.sub.pv).sub.max. A preferred technique for determining when a fastener pair is unacceptable is the occurrence of two torque sensings T.sub.pvi above (T.sub.pv).sub.max. The torque sensing at the first data point 32 is above (T.sub.pv).sub.max so that when the second data point 34 is likewise above this value, the tool shuts off, the joint is indicated as being unacceptable and the system is reset for the commencement of a new tightening cycle.

PAR It is evident that any system which rejects fasteners having excessive prevailing torque sensings will reject the fastener pair exhibiting the are, however, a number of fasteners which exhibit a torque-angle curve 42 which is distinctly different than either of the curves 28, 38. The curve 42 includes a static-to-dynamic peak 44 and then levels out initially to a value below (T.sub.pv).sub.max. The curve 42 also exhibits a transient peak 46 which is above (T.sub.pv).sub.max which is detected at the subsequent data point 34. Thereafter, the curve 42 levels out below (T.sub.pv).sub.max. It is highly desirable not to reject the fasteners exhibiting the curve 42 because the transient torque peak 46 does not repeat or is not sensed more than once. Accordingly, the conclusion is that the transient peak 46 is not indicative of a serious thread imperfection.

PAR A somewhat different situation is evidenced by a torque-angle curve 48 which exhibits a static-to-dynamic peak 50 and at least a pair of subsequent transient torque peaks 52, 54. In this situation, there are at least two instances where data taken at the points 34 indicate that the instantaneous prevailing torque T.sub.pvi exceeds (T.sub.pv).sub.max. Although it is within the bounds of judgment to accept fasteners exhibiting several transient peaks, such as illustrated by the curve 48, it is preferred to reject these fasteners.

PAR It will accordingly be seen that there is provided a technique for rejecting threaded fasteners at an early stage of the tightening cycle in response to a torque sensing indicative of serious fastener imperfections.

PAR If fasteners are often rejected because of high T.sub.pvi sensings, it may be concluded that the batch of fasteners is suspect. Accordingly, a running average of rejections to fasteners run is conducted. If

EQU R.sub.pv /N.gtoreq.E (10)

PAL where R.sub.pv is the number of fasteners rejected, N is the sample size and E is a fractional value acceptable to the user, such as 0.15, a signal is displayed at the operator's station to indicate a parts defect. The value of N is preferably not the cumulative number of joints tightened but is a running value, as by storing, on a first-in, first-out basis, a finite number of joints tightened, such as 30.

PAR In the event that prevailing torque fasteners are being tightened and it is desired to determine that the fasteners do exhibit prevailing torque, it appears that the check to be made is to compare average prevailing torque T.sub.pv with (T.sub.pv).sub.min. In the event that T.sub.pv is less than (T.sub.pv).sub.min, the fasteners should be rejected.

PAC Is Tool Advancing Fastener?

PAR Another quality control procedure conducted early in the tightening cycle is to determine whether the fastener is threadably advancing. This is accomplished by measuring the time elapsed between the instant the tool is turned on until the torque encoder senses a predetermined minimum torque T.sub.sth which is the threshold torque stored by the data processor after the preliminary data points 32, 34, 36. To establish T.sub.sth, a torque value T.sub.1 is empirically determined and is the first torque value utilized to calculate a preliminary torque rate as discussed hereinafter. T.sub.1 is on the order of about 20-30% of the average final torque value obtained in running the same to empirically determine FR.sub.1, FR.sub.2 and T.sub.os. When the storing threshold torque T.sub.sth is sensed to be

EQU T.sub.sth =0.25(T.sub.1 +T.sub.pv) (11)

PAL the data processor begins to store torque values sensed by the torque encoder. If the data processor does not commence to store torque values within a very short period, on the order of 3-10 seconds, of the onset of tool turn-on, the conclusion is that no bolt is present, the tool socket has not engaged the bolt head, the bolt is broken, one of the threaded members has no threads, or one of the threaded members is the wrong size.

In this event, a signal is generated by the data processor to turn off the tool, signal that one of these conditions exists and reset the tool for the next tightening cycle.

PAC REACHING THE MID-POINT STOP, TORQUE RATE PROCEDURES, AND QUALITY CONTROL PROCEDURES

PAC Reaching the Midpoint

PAR The intent at the mid-point stop is for the joint to be tightened to an angular location corresponding to the break in the tension-angle curve for reasons more fully pointed out hereinafter. Although a torque control or turn-of-the-nut method can be used to determine the mid-point stop, it is preferred to use a simplified logarithmic rate method in accordance with this invention. Referring to FIG. 3, which is a continuation of the normal torque-angle curve 28 of FIG. 2, the tool continues to turn the fasteners with torque values being recorded and stored at fairly small equal angle increments which may be, for example, in the range of 0.2.degree.-3.degree..

PAR The angle encoder may conveniently be of the digital type to deliver a pulse at small, equal angle increments. The unit of angle used for calculation purposes is .DELTA..alpha. which is one or more multiples of the angle pulse. The value for .DELTA..alpha. depends on the elastic properties of the joint and typically are in the range of 0.5.degree.-6.degree. although a wider range is acceptable in some circumstances. With fasteners of the type studied, a selection in the range of 2.degree.-3.degree. seems preferable. In getting to the mid-point, torque and angle measurements obtained in the region 16 are used.

PAR Referring to FIG. 3, when running torque is first sensed to be equal to or greater than T.sub.1, such as at the location 56, the angular position of the location 56 is noted and stored. When the tool passes the point 58 which is one .alpha..sub.k degrees beyond the location 56, the torque value T.sub.2 is sensed and stored. The value of .alpha..sub.k is preferably large enough to give a rough approximation for a preliminary torque rate, which is calculated as (T.sub.2 -T.sub.1)/.alpha..sub.k. If .alpha..sub.k were very large, the tool would not be stopped until late, leaving little or no additional room to resume tightening. If .alpha..sub.k were very small, the value of torque rate calculated from (T.sub.2 -T.sub.1)/.alpha..sub.k would be so influenced by noise in the torque sensings that it would be unreliable. The actual value of .alpha..sub.k depends on the elastic properties of the joint. A compromise of 9.degree. for .alpha..sub.k has proved acceptable for the particular joint described preceeding Table II although other compromises are obviously acceptable.

PAR The data processor then calculates .alpha..sub.1, in accordance with the following equations:

EQU .alpha..sub.1 =c+a(T.sub.2 -T.sub.pv) (12)
##EQU4##
.alpha..sub.d is the desired angle from tension origin to mid-point and is F.sub.M /FR.sub.1 or slightly greater where F.sub.M is the tension value at the junction of the two tension regions indicated by FR.sub.1 and FR.sub.2, .alpha..sub.or is the tool overrun at idle due to actuation delay, T.sub.o is the stall torque of the tool, K.sub.o is a typical torque rate for the particular fasteners involved and is determined empirically, and N.sub.1 and N.sub.2 are correction factors necessitated by the inaccurate algebraic expansion of more precise equations, which expansion substantially reduces calculation time compared to the exact

involving the same size bolts and the same size tools, every value in these equations, except T.sub.2 and T.sub.pv can be reduced to numbers before starting. Thus, the computations are actually easier and quicker than appears.

PAR It might be questioned why the value of .alpha..sub.k is of any importance since neither equation (12), (13) or (14) appears to contain a value for preliminary torque rate. Equations (12), (13) and (14) constitute one application of the logarithmic rate method to achieve a mid-point tension value of FR.sub.1 .alpha..sub.d with provisions made for tool overrun due solely to the time delay between the shut off command and exhaustion of air from the tool. The mathematical complexities have, by design, been transferred from equation (12) to equations (13) and (14) so that computation of equation (12) during tightening requires the least possible elapsed time. Equations (13) and (14) can be computed manually either prior to system installation or computed by the microprocessor when in a dormant portion of the tightening cycle, for example, prior to the initiation of tightening. Although the preliminary torque rate (T.sub.2 -T.sub.1)/.alpha.k does not appear in equations (12), (13) or (14) as written, if one were to substitute the equations for a and c into equation (12), one would find that the preliminary torque rate appears. Accordingly, the reasons why .alpha..sub.k should not be too large or too small are as previously discussed.

PAR As will be recognized by those skilled in the art, equations (13) and (14) do not include a tool overrun prediction due solely to the inertia of the rotating parts of the tool. For moderate and high torque rate bolts, the amount of angular overrun due solely to inertia is rather insignificant. The reason, of course, is that the tool is not rotating very fast. With low torque rate bolts, which the tool is able to turn faster, the amount of overrun due solely to inertia is still modest. For applications where maximum accuracy is desirable, equations (13) and/or (14) may be modified to incorporate a measure of overrun prediction based on inertia.

PAR The determination of the mid-point stop is of some importance as may be visualized from an appreciation of FIG. 1. It will be recollected that it is desired to calculate the average torque rate TR. If the mid-point stop occurs, for example, in the lower part of the region 18, the average torque rate will be substantially too low. If the mid-point stop is too late and well into the region 20, two difficulties are presented: (1) the calculated torque rate TR may be substantially too high although some calculations can be done to disregard some of the later data in order to shift the range where torque rate calculations are actually being conducted, and (2) there may be little or no additional room available to resume tightening to the final desired tension value considering allowance for tool overrun.

PAR Referring to FIG. 3, the tool is commanded to shut off at a point 60 which is .alpha..sub.1 degrees beyond point 56 which was where the torque value T.sub.1 was first equalled or exceeded. Because of the time delay in the tool from the shut off command until the tool actually stops, which is represented by the point 62, the tool has overrun by an angle .delta..alpha.. The mid-point stop 62 typically falls in the range of about 0.4-0.75 of the elastic limit. For any given application, the empirically determined values act to establish the mid-point stop 62 at a given fraction of the elastic limit which is not changed until new empirical data is developed which, as for example, may occur when a different type fastener is selected.

PAC Torque Rate Procedures

PAR In order to calculate the average torque rate TR, a decision must be made of which torque and angle measurements are to be used. It has been learned that the torque sensings approaching the stopping point 62 are somewhat unreliable because of speed dependent variables. Accordingly, in the computations conducted to determine average torque rate TR, those sensings which are affected by the act of stopping are disregarded. Although more than one torque sensing may be discarded in order to provide greater assurance, it is assumed for purposes of simplicity that only the last torque value is ignored. Accordingly, the highest torque value used in the torque rate calculations is at a location 64 which is one .DELTA..alpha. backward from the point 62. The torque value at the point 64 is T.sub.3. The total number of values used in torque rate calculations, designated n for more general purposes, may vary widely and is subject to considerable compromise. A total of fourteen consecutive data points has proved quite acceptable. The mean torque T.sub.m and the average torque rate TR are then calculated using the following summations where i is a designation for each point selected for the torque rate calculations and T.sub.i is the torque value there sensed:

##EQU5##

Equation (15) will be recognized as merely adding the torque values occuring at each of the points i and dividing this sum by the total number of data points n. Equation (16) will be recognized as a least squares fit for the data points i.

PAR It is desirable to assure that the mean torque T.sub.m and the average torque rate TR are taken over substantially the same tension range during the tightening of each fastener pair. This may be accomplished by checking to determine how close the angular position of the stopping point 62 is to the break in the tension-angle curve 12. The angular position of the mean torque T.sub.m along an abcissa T.sub.os +T.sub.pv may be calculated from the equation:

EQU .alpha..sub.F =(T.sub.m -T.sub.os -T.sub.pv)/TR where .alpha..sub.F >0. (17)

PAL The angular distance from the point of origin of the tension curve 12 to the stopping point 62 may be calculated from actual data derived from the fastener being tightened from the equation:

EQU .alpha..sub.origin =-1/2(n+1).DELTA..alpha.-.alpha..sub.F where .alpha..sub.origin <0. (18)

PAL For calculation purposes, it is desirable that .alpha..sub.origin be a negative value. From empirically determined information done prior to the tightening of production fasteners, the start of the second tension region may be calculated from the equation:

EQU .alpha..sub.FM =(F.sub.M /FR.sub.1) where .alpha..sub.FM >0 (19)

PAL where F.sub.M is the tension value at the break. The difference between .alpha..sub.origin and .alpha..sub.FM may be obtained from the equation:

EQU X=-.alpha..sub.origin -.alpha..sub.FM. (20)

PAL It will be remembered that .alpha..sub.origin is a negative value.

PAR If X.gtoreq.O, this means that the mid-point stop 62 is too late and consequently that the largest torque value T.sub.3 in the torque rate calculations is too large. Without revising the value for TR, TR will tend to be too high as previously discussed. Accordingly, one needs to shift the range of torque rate calculations downwardly on the torque-angle curve illustrated in FIG. 3. Thus,

EQU n.sub.H =.dwnarw.(X/.DELTA..alpha.)+1; and (21)

EQU n.sub.1 =n. (22)

PAL From the stopping point 62, one moves dcwnwardly along the torque-angle curve by n.sub.H angle increments of .DELTA..alpha. to define a new point calculated. The symbol .dwnarw. means that any fractional value is dropped so that the number used is the next lowest integer from the calculated value. The total number of data points n remains the same.

PAR If X.ltoreq.0, this means that the stopping point 62 occured too soon which would tend to give a value for torque rate that is too low. Since one cannot move upwardly on the torque-angle curve to obtain an additional area of measurement, the practical solution is to accept fewer data points for torque rate calculations thereby, in effect, lopping off the lower end of the range. Accordingly,

EQU n.sub.H1 =1; and (23)

##EQU6##

where n.sub.H1 indicates that the point or location where the largest torque value used in the torque rate calculations occurs. Since the largest torque value will remain the same, n.sub.H1 =1 so that the torque T.sub.3, being .DELTA..alpha. removed from the stopping point 62, is the largest torque value used. The new value for n.sub.1, which is the total number of data points used, is based on the assumption that the tension rate in the first region is substantially linear above a minimum tension value F.sub.L, determined empirically, and that the tension F.sub.o in the joint at the stopping point 62 lies in the first tension range. The symbol .DELTA.F is the additional tension in the first range per angle increment .DELTA..alpha. and may be expressed mathematically as:

EQU .DELTA.F=FR.sub.1 .DELTA..alpha. (25)

PAL The tension F.sub.o in the joint at the stopping point 62 is

EQU F.sub.o =-FR.sub.1 .alpha..sub.origin where X.ltoreq.0, or (26)

EQU F.sub.o =F.sub.M +rFR.sub.1 X where X>0 (27)

PAL where F.sub.M is the empirically determined tension value at the break in the tension curve 12 and r is the ratio of FR.sub.2 /FR.sub.1.

PAR It is conceivable that n.sub.1 may be too small, e.g. two or three points, to give good results with the least squares equation (16). Accordingly, a check is made to determine if n.sub.1 is less than one half of n. In this event,

##EQU7##

and n.sub.2 is used as the total number of data points.

PAR Accordingly, a new summation is performed for mean torque T.sub.m and torque rate TR in accordance with equations (15) and (16) utilizing the new starting place in the event that X.gtoreq.0 or starting with the same highest torque value but using fewer number of data points in the event that X<0.

PAR With revised values for mean torque T.sub.m and torque rate TR, a revised value may be obtained for the angle of origin of the torque-angle curve using equation (17) and a revised value and for the origin of the tension-angle curve using equation (18). A calculation is again made to determine whether the tool has overshot or undershot the break in the tension curve in accordance with equations (19) and (20). Calculations are again made for the tension value F.sub.o at the stopping point 62. It will be apparent that the values of mean torque T.sub.m, torque rate TR, .alpha..sub.F, .alpha..sub.origin, F.sub.o and the like may be revised as many times as desirable. It is also conceivable not to conduct the second pass under some circumstances.

PAC Quality Control Procedures--Torque Rate Curvature

PAR One of the defects in the technique heretofore described is the assumption that the empirically determined tension rate FR.sub.1 correctly describes the elastic properties of the joint actually being tightened. For good quality joints, the tension rate FR.sub.1 does not vary widely. There are, however, a number of relatively common situations, e.g. galled threads, misaligned fasteners, poor contact surfaces, dirt or other foreign particles between the contact surfaces, and the like, where the actual tension rate for the joint being tightened is significantly below the empirically determined tension rate FR.sub.1. In such poor quality joints, the actual final tension value will be significantly below the desired tension value F.sub.D and significantly below the final calculated tension value F.sub.final. To determine the significance of such poor quality joints, two 5/16"-24, SAE grade 8 nuts and bolts were tightened with a shim, 0.015 inches in thickness, inserted from one end under the bolt in order to simulate poor contact due to misalignment. The final desired tension value F.sub.D was 5500 pounds. The actual measured final tension value was 2400 pounds and 1700 pounds for the two fasteners, a percentage variation of -56% and -69% from desired. It will accordingly be apparent that the occurrence of such poor quality joints can have a major effect on the scatter seen in fasteners tightened by the technique of this invention. It will also be evident, upon reflection, that such poor quality joints will have a like effect on the scatter in fasteners tightened by a turn-of-the-nut method.

PAR It has been learned that poor quality joints of the type exhibiting abnormally low tension rates can readily be detected by the data encoded and stored during the course of tightening a fastener pair with this invention. In such poor quality joints, the torque rate is not constant in the upper part of the region 18 where the average torque rate TR is calculated, as contrasted to the showing of FIG. 3. Instead, the torque-angle plot is arcuate and, if plotted, is upwardly concave. Thus, it is a relatively simple matter to measure or calculate and then directly compare the average torque rates in the upper and lower parts of the range where the torque rate TR is calculated. For example, in a situation where thirteen data points are being used to calculate TR, with the point 64 being the highest torque value used, the torque rate TR.sub.a over an angle of six .DELTA..alpha. increments backward from the point 64 would be calculated. The calculations may, of course, be a two point or a least squares technique. Next, the torque rate TR.sub.b over an angle commencing with six .DELTA..alpha. increments backward from the point 64 and ending twelve increments backward from the point 64 is calculated by a two point or least squares technique. Then, the ratio of TR.sub. a /TR.sub.b is computed. If the ratio of TR.sub.a /TR.sub.b is near unity, e.g. 1.+-.0.10, the conclusion is that the joint has an acceptable tension rate. If the ratio of TR.sub.a /TR.sub.b diverges significantly from unity, e.g. TR.sub.a /TR.sub.b >1.10, the conclusion is that the joint has an abnormally low tension rate FR.sub.1 and, if tightened by the technique of this invention or by a turn-of-the-nut method, will result in a fastener stressed substantially below the desired tension value F.sub.D. A suitable signal may be displayed at the operator's station, the joint rejected and the parts replaced.

PAR Rather than directly checking the curvature of the torque-angle plot, indirect methods are available. One approach is to compare the values of the calculated mid-point tension F.sub.o in the first pass with that in the second pass. This is, in effect, calculating a first tension value at a predetermined location using a torque rate in a first area, calculating a second tension value at the same location using a torque rate in a second area and then comparing the first and second tension values. If the two values deviate by more than about 13%, joint problems are highly likely. The figure 13% is, of course, somewhat arbitrary. It is based on the expectation of tension control of .+-.10% within three standard deviations, a mean shift of 2% plus 1% for other uncertainties. The selection of 13% rarely produces false signals when parts have reasonable quality. If a better number is available, it should be used.

PAC Quality Control--Torque Rate Too Low

PAR As will be appreciated, the torque rate calculations are conducted on each successive fastener in the same tension range, i.e. F.sub.L -F.sub.H, the values of which are determined empirically. If the torque rate TR is unusually high, the conclusion is that the fastener pair exhibits very high friction. In the practice of this invention, there is nothing wrong with high friction rates and consequently no upper limit on the torque rate TR is specified. Unusually low values of TR are, however, cause for concern. First, the theoretical minimum torque rate TR.degree. is not zero because the tool does reversible work on the joint in the absence of friction by producing tensile stress in the bolt and compressive stress in the clamped pieces and nut. When friction is zero, it can be shown that

EQU TR.degree.=(w/2.pi.)FR>0 (29)

PAL where TR.degree. is the theoretical minimum torque rate and w is the pitch of the threads. Accordingly, TR.degree. is positive and its value depends on thread pitch and the joint tension rate. The observed torque rate TR is made up of TR.degree. and TR.sub.f which is the friction component. If it is assumed that friction can change at most .+-.60% from its expected value, represented by the typical torque rate TR.sub.o, then the minimum expected torque rate TR.sub.min under normal conditions can be expressed by:

EQU TR.sub.min =0.6TR.degree.+(1-0.6)TR.sub.o, (30)

PAL The factor 0.6, representing a 60% change in friction coefficient, is somewhat arbitrary. If a better estimate is available, it should be used. Whenever a torque rate less than TR.sub.min is observed, it indicates a joint problem. This could mean wrong parts, poor contact between the parts, or poor data processing, e.g. if the mid-point tension F.sub.o is far too low. In any event, when the calculated torque rate TR is less than TR.sub.min, a signal is given to indicate that the joint is rejected. Because this calculation is conducted during the mid-point pause, the tool is already off. Accordingly, the tool is reset for a new tightening cycle. It will be appreciated that this approach is a direct technique for assuring that TR exceeds TR.sub.min for acceptable joints.

PAR There are, however, techniques for indirectly detecting very low torque rates. A first indirect technique involves the second pass or second calculations for TR. The second pass requires a value of n.sub.H greater than one. When TR is abnormally low, the first estimate of F.sub.o is very large leading to a value of n.sub.H so great that the location of F.sub.L lies outside the stored data, i.e. F.sub.L appears to lie below the torque storing threshold T.sub.sth. Another indirect approach is to compare the calculated tension F.sub.o at the mid-point with the final desired tension F.sub.D. If they are too close, the observed torque rate TR must be unusually low.

PAC Quality Control--Tool Performance

PAR One of the advantages of the mid-point stop is that one obtains a measurement of the actual amount of tool overrun .delta..alpha. occuring between the angular locations 60, 62 corresponding to the torque values T.sub.4 and T.sub.d. This allows for a check of tool performance. Although the tool overrun at the termination of tightening may be used to determine tool malfunction, this operation is more conveniently and accurately monitored during overrun adjacent the mid-point stop 62.

PAR When the tool is instructed to stop, it takes some time for all motion to cease. For any given tool speed at the time of the shut off command, there exis given angle of rotation that occurs before all motion ses.

There are two phenomena that affect tool overrun: (1) the time lapse between the issuance of the shut off command and the complete closing of the air control valve, and (2) the rotational inertia of the relevant parts. By selecting appropriately designed rotors, the overrun due to inertia is noticeable only when idling. For purposes of simplicity, tool overrun due to inertia may be neglected.

PAR There are accordingly two assumptions in tool overrun calculations: (1) overrun is due solely to time delay and the motor stops immediately after the air supply valve is completely shut off; and (2) the tool has a linear torque-speed curve as shown in FIG. 4 which can be characterized by two parameters, the stall torque T.sub.o and the idle angular speed .omega..sub.o such that:

EQU (T/T.sub.o)=1-(.omega./.omega..sub.o) (31)

PAL where T is the sensed torque at any location and .omega. is the angular speed at that location. On this basis, it can be shown that:

##EQU8##

with only a small error where .delta..alpha..sub.a is the anticipated angular overrun at the time applied torque is T.sub.a, .alpha..sub.or is the angular overrun at idle and the tool speed is .omega..sub.a when the applied torque is T.sub.a.

PAR In an unregulated pneumatic vane motor, the stall torque T.sub.o varies approximately with .DELTA.p which is the difference between the absolute air pressure upstream of the tool and atmospheric pressure which is, of course, the equivalent of the gauge pressure upstream of the tool. The speed of the tool varies with .DELTA.p.sup.1/2. As shown in application Ser. No. 766,429, filed Feb. 7, 1977, a typical tightening tool used with this invention incorporates an air supply valve which is biased toward the closed position by inlet air pressure and moved toward the open position by a solenoid operator. In this situation, the time required to close the valve after energization of the solenoid decreases as gauge pressure increases. This relationship is approximately .DELTA.p.sup.-1/2. If the line pressure changes, .alpha..sub.or remains substantially constant while the stall torque T.sub.o varies linearly. On this basis, the actual tool overrun .delta..alpha. at the mid-point 62 is a measure of the actual stall torque. If:

EQU T.sub.s =T.sub.o (1+.epsilon.) (33)

PAL where T.sub.s is the actual stall torque in any particular tightening cycle and .epsilon. is the relative change observed in stall torque. It can be shown that:

EQU .epsilon.=y/(1-z)-1 (34)

PAL where

EQU y=T.sub.a /T.sub.o ; (35)

EQU z=.delta..alpha./.alpha..sub.or. (36)

PAL T.sub.a and .delta..alpha. are measured and are accordingly known at the mid-point 62. .alpha..sub.or and T.sub.o are fixed input values. If .epsilon. is negative, the tool is underperforming and, if positive, the tool is overperforming.

PAR Although equation (31) is set up on the basis of line pressure changes, it remains meaningful if changes in stall torque are related to lack of lubrication, blade abnormalities or impending bearing failure. The micro-processor will in each case calculate .epsilon. and, if it is less than a prescribed negative such as -0.25, then a signal is generated to indicate at the operator's station that the tool has underperformed. If tool underperformance occurs too frequently, as pointed out more fully hereinafter, this may also be displayed indicating the existance of a

```
PAR  In the alternative, let
EQU  y.sub.1 =(T.sub.1 +.alpha..sub.1 TR)/T.sub.o ;              (37)
EQU  z.sub.1 =.delta..alpha./2.alpha..sub.or ; and               (38)
      ##EQU9##
      where .alpha..sub.1 is the angular distance (FIG. 3) from T.sub.1 to the
      shut off point 60. It will be apparent that y.sub.1 is a dimensionless
      number and basically is the ratio of T.sub.4 /T.sub.o. As shown in FIG. 3,
      T.sub.4 is the existing torque value at the mid-point shut off location 60
      while T.sub.o is the normal stall torque. It will be seen from FIG. 4 that
      Y.sub.1 is an inverse function of tool speed. If the time delay between
      the giving of the shut off command and the closing of the valve remains
      constant, y.sub.1 is a prediction of tool overrun. Since .delta..alpha. is
      the measured tool overrun, it will be seen that z.sub.1 is a function of
      measured tool overrun while .alpha..sub.or is the normal angular overrun
      of the tool under no torque conditions. .epsilon..sub.1 will be recognized
      as a percentage change in tool and control performance.
PAR  If .epsilon..sub.1 is low, for example, .1toreq.-10%, the deduction is that
      actual stall torque has decreased significantly, such as from a loss or
      decline in air pressure, lack of lubrication, worn or broken parts, or the
      like. In such an event, a signal may be displayed at the tool location to
      indicate that the tool requires inspection, maintenance, repair or
      replacement. It is conceivable, but quite unlikely, that a significant
      decrease in .epsilon..sub.1 could be caused by a decrease in time delay
      between the shut off command and the air valve closing.
PAR  If .epsilon..sub.1 is positive, i.e. greater than zero, complications
      arise. It appears that z.sub.1 which is a simplification of a more complex
      equation, loses accuracy. The more complex equation indicates that if
      .epsilon..sub.1 is positive, z.sub.1 should be reevaluated as:
EQU  z.sub.2 =.delta..alpha./.alpha..sub.or.                      (40)
PAL  Accordingly, .epsilon. should be reevaluated for greater accuracy, when,
      positive, as:
      ##EQU10##
      If .epsilon..sub.2 is high, for example .gtoreq.+10%, the deduction is
      that the time delay between the shut off command and the air valve closing
      has decreased significantly or that air pressure supplied to the tool has
      increased. This normally indicates that the valve control solenoid is
      beginning to stick or that air pressure is too high. In such event, a
      signal may be displayed at the tool location to indicate that the air
      control system requires inspection, maintenance, repair or replacement. It
      is conceivable, but quite unlikely, that a significant increase in
      .epsilon..sub.2 could be caused by increased tool efficiency.
PAR  As will be apparent to those skilled in the art, the prediction of tool
      overrun embodied in equation (37) does not include a measure of overrun
      based on inertia, but instead based solely on time delay. As mentioned
      previously, inertial overrun is rather insignificant with moderate to high
      torque rate fasteners although accuracy can be improved somewhat for low
      torque rate fasteners by including an inertial overrun provision. In the
      event that it is desirable, a measure of inertial overrun can be
      incorporated into equation (39) through one or both of equations (37) or
      (38).
PAR  It is apparent that a single indication of tool malfunction is probably not
      significant but that an abnormal frequency of tool malfunction is
      significant. Thus, a running ratio of
EQU  C.sub.TL /C.sub.J .gtoreq.C                                  (42)
PAL  is maintained where C.sub.TL is the number of times that
      .epsilon..1toreq.-10%, C.sub.J is the number of joints tigh[illegible]ned and C is
```

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     a fraction acceptable to the user. The ratio C.sub.TL /C.sub.J is
     preferably a running ratio, as by storing on a first-in, first-out basis,
     rather than a cumulative ratio. From present information, it appears that
     C should be in the range of 0.1-0.2, for example 0.15.
PAR  Similarly, a running ratio of
EQU  C.sub.TC /C.sub.J .gtoreq.D                                   (43)
PAL  is maintained where C.sub.TC is the number of times that
     .epsilon..gtoreq.+10% and D is a fraction acceptable to the user, for
     example, 0.15.
PAR  Another approach for predicting tool overrun and thereby detecting tool
     malfunction is pointed out by:
     ##EQU11##
     where .alpha..sub.p is the predicted tool overrun from the shut off
     command point 60 where the torque value T.sub.4 appears. The measured
     value of overrun .delta..alpha. from the point 60 can be compared against
     .alpha..sub.p, as follows:
EQU  H.ltoreq..delta..alpha./.alpha..sub.p .gtoreq.G                (45)
PAL  where H and G are values acceptable to the user, such as 0.85 and 1.15
     respectively. When measured overrun .delta..alpha. is too small, this
     indicates a motor malfunction while if .delta..alpha. is too large, it
     indicates a control system malfunction.
PAC  Quality Control--Non-Linear Strain
PAR  Another quality control procedure employed at the mid-point stop 62 is the
     detection of non-linear strain, whether elastic or plastic. If non-linear
     strain occurs before the mid-point stop, it could be detected by any of
     the following indirect techniques. First, if the joint is deeply within
     the plastic zone, the torque rate calculations will be askew so that an
     attempt will be made to search for torque data outside the memory. This
     indirect method is similar to indirectly determining whether the torque
     rate TR is abnormally low and will cause the joint to be rejected. Second,
     the joint might be rejected because the observed torque rate TR is less
     than the minimum expected torque rate TR.sub.min. Third, it is possible
     that the joint will be rejected because the torque-angle plot is not
     linear but is instead demonstratably arcuate. In addition to or in lieu of
     relying on indirect techniques for detecting excessive non-linear strain,
     it is desirable to directly determine if it has been experienced by the
     fastener.
PAR  To this end, a classic yield point determination is made. Referring to FIG.
     5, there is illustrated a torque-angle curve 68 which is intended to
     represent a simplification of the showing of FIG. 3. The curve 68
     terminates at the mid-point stop 62 and describes, in the region 70, a
     torque rate TR. Ideally, and in accordance with classic yield point
     determinations, an imaginary line 72 is spaced from the location of mean
     torque T.sub.m and accordingly from the linear region 74 of the curve 68
     by an offset angle or offset strain .alpha..sub.y. Although the value of
     .alpha..sub.y may vary as pointed out more fully hereinafter, a typical
     value to the particular fasteners disclosed immediately preceding Table II
     is 12.degree..
PAR  The angular location of T.sub.m, which is .alpha..sub.F, is known as shown
     in FIG. 3 and as calculated from equation (17). The angular location of
     the mid-point stop 62 along an abcissa T.sub.os +T.sub.pv is, of course,
     the absolute value of .alpha..sub.origin.
PAR  Thus, a torque value T.sub.t on the imaginary line 72 which is used to
     compare with the torque reading at the mid-point stop 62 is:
PAL  T.sub.t =T.sub.m +(-.alpha..sub.origin -.alpha..sub.F -.alpha..sub.y)TR
```

PAL In the event that T.sub.t is less than T.sub.d, the conclusion is that the joint has not experienced significant non-linear strain. It will be apparent that the value of T.sub.d is suppressed by the act of stopping rotation. Accordingly, if T.sub.t is less than T.sub.d, there is great assurance that the joint has experienced no significant non-linear strain. In the event that T.sub.t is equal or greater than T.sub.d, the conclusion is that the joint has experienced significant non-linear strain and the joint is rejected. A portion 76 of the torque-angle curve of an unacceptable joint is illustrated as crossing the imaginary line 72 at a torque value below T.sub.t.

PAR The actual digital logic for conducting a non-linear strain determination in the region surrounding the mid-point and a determination in the region adjacent the termination of tightening is somewhat complex. Accordingly, a more generalized version may be used which can accomodate both the mid-point and the final determinations.

PAC FINAL SHUT OFF PARAMETER PROCEDURES

PAR It will now be appreciated that the location 62 of calculated tension F.sub.o appearing in the joint corresponds to the point 26 illustrated in the more general showing of FIG. 1. The determination yet to be made is the additional angle .alpha..sub.final or the additional torque .DELTA.T required to achieve the final desired tension value F.sub.D. Compared to the manipulations used to assure consistently reliable values for torque rate TR and the angle of tension origin .alpha..sub.origin, these calculations are relatively straight forward.

PAC Angle Option

PAR One tightening parameter that may be selected to attain the final desired tension value F.sub.D is the additional angle .alpha..sub.final.

##EQU12##

F.sub.o is, of course, obtained from equations (26) or (27) while F.sub.M is the tension value at the break in the tension-angle curve and is determined empirically.

PAR It will be appreciated that the tool overran an angle .delta..alpha. when stopping at the mid-point 62. It is equally apparent that some amount of tool overrun will occur approaching the final desired tension value F.sub.D. A typical torque-speed curve for an air powered tool is shown in FIG. 4. Since the tool will be slowing down during tightening, it will be apparent that the tool overrun approaching the final desired tension value F.sub.D will be less than the overrun approaching the point 62. Defining,

EQU .alpha..sub..alpha. .ident.(T.sub.o -T.sub.4)/TR-.delta..alpha.(49)

PAL where T.sub.4 is the torque value at the point 60 where the initial shut off command was given prior to reaching the stopping point 62, T.sub.o is the stall torque of the tool, TR is the calculated torque rate and .delta..alpha. is the measured angle overrun approaching the point 62. The expected tool overrun d.alpha. approaching the final desired tension value F.sub.D is:

##EQU13##

PAR In the alternative, it can be shown that:

##EQU14##

where T'.sub.4 is the applied torque at the moment of final tool shut off. The overrun .delta..alpha. at the mid-point stop 62 is measured by the angle encoder while its theoretical value is:

##EQU15##

where T.sub.4 is the torque value at the shut off at the point 60 preceding the mid-point stop 62. Dividing equation (51) by equation (52), a relationship can be found between the two overruns which is independent of alpha..sub.or. Accordingly, one can use a semiempirical roach to

```
     estimate d.alpha.. In order to do so, an estimate of the final torque
      T.sub.D must be provided.
EQU  if X.gtoreq.0, T.sub.D =T.sub.sp +u.alpha..sub.final       ( 53)
EQU  if X>0, T.sub.D =T.sub.sp +u.alpha..sub.final +X(u-TR)     (54)
PAL  where
EQU  u=rRTR                                                     (55)
PAL  and R is defined as TR.sub.2 /rTR. Consequently, equation (55) reduces to
      the proposition that u=TR.sub.2.
PAR  It can be shown that the semiempirical relationship between final and
      mid-point overruns is:
      ##EQU16##
PAR  Regardless of how the amount of final overrun d.alpha. is determined, the
      shut off command to the tool is given at an angle location
      .alpha..sub.final --d.alpha.. Overrun of the tool causes the fastener to
      move to the final angle location .alpha..sub.final. The next problem is
      where to commence the measurement of the angle increment .alpha..sub.final
      --d.alpha.. The problem has two components: the effect of joint relaxation
      and the effect of a transient rise in torque during restarting.
PAR  It has become apparent that a typical joint will relax, i.e. lose tension
      without unthreading of the fasteners, at the mid-point stop 62 and/or at
      the termination of tightening. If the fasteners were continuously
      tightened, i.e. without a mid-point stop, the relaxation at termination of
      tightening can be rather significant while, with a mid-point stop, the
      relaxation at termination of tightening is quite modest. By stopping at
      the mid-point 62, the bulk of joint relaxation occurs prior to the
      resumption of tightening. Thus, the stopping at the mid-point 62 provides
      greater consistency in final joint tension although this phenomenon
      complicates the determination of the final shut off parameter, or more
      correctly, complicates the determination of where to commence measuring
      the final angle of advance.
PAR  If the joint did not relax at the mid-point stop 62, the tool would be
      instructed to go an additional angle .alpha..sub.final --d.alpha. beyond
      the mid-point stop 62 where the final shut off command would be given. As
      shown in FIG. 1, the final shut off command would occur at about the point
      78 whereby the tool overruns to tighten the fastener pair through an angle
      d.alpha. until stopping at the final desired tension value F.sub.D.
PAR  The phenomenon of joint relaxation is illustrated in FIG. 6 where the curve
      80 represents the tension-angle relationship during continuous tightening
      to a location 82 below the elastic limit of the fastener. When tightening
      stops, the joint relaxes as suggested by the tailing off of tension along
      a constant angle line 84. The final tension appearing in the fastener is
      accordingly at the point 86. A typical value for joint relaxation along
      the line 84 is 7% of joint tension within twenty-one hours.
PAR  Referring to FIG. 7, the curve 88 represents the tension-angle relationship
      during tightening to the mid-point stop 62. Because the joint relaxes,
      tension in the fastener tails off along a constant angle line 90 to a
      tension value at the point 92.
PAR  One technique for accomodating joint relaxation is, instead of instructing
      the tool to go an additional angle .alpha..sub.final --d.alpha. from the
      mid-point stop 62, the instruction is to advance the fasteners an
      additional angle .alpha..sub.final --d.alpha. after the running torque
      equals or exceeds T.sub.sp where
EQU  T.sub.sp =T.sub.3 +TR(.DELTA..alpha.) in the event that X.ltoreq.0, or (57)
EQU  T.sub.sp =T.sub.3 +u(.DELTA..alpha.)in the event that X>0. (58)
PAL  T.sub.sp will be recognized as the calculated torque value which would be
```

recollected that the torque value T.sub.3 is located at the point 64, which is one .DELTA..alpha. backward from the mid-point stop 62. By advancing the tool until running torque equals or exceeds T.sub.sp, the torque and tension values at the mid-point stop 62, before relaxation occurs, are essentially reproduced. This is indicated in FIG. 7 where the point 94 designates the location where running torque is equal to or greater than T.sub.sp. Tightening will then be done correctly, regardless of prevailing tension in the bolt at the time the tool resumes tightening. As shown in FIG. 7, the final shut off command occurs at the point 96 whereby the tool overruns to tighten the fastener pair through an angle d.alpha. until stopping at the final desired tension value F.sub.D. In order to shift the bulk of joint relaxation from the final stopping point to the mid-point stop 62, the mid-point stop is at least 0.4 of yield strength and conveniently is in the range of 0.4-0.75 yield strength. With the mid-point stop 62 so located, typical joint relaxation at the final stopping point is on the order of 1/2-2% of final bolt tension within one hour. It should be clear that this amount of joint relaxation is the relaxation of a good quality joint rather than a joint suffering from misaligned parts, compressed gaskets and the like.

PAR Although measuring the angle of advance from T.sub.sp provides better results than merely measuring the advance from the mid-point stop 62, the results can be further improved upon. Accordingly, a preferred technique for accommodating joint relaxation, accommodating a transient torque rise immediately on restart and to take up any gear-socket backlash is to advance the fasteners the additional angle .alpha..sub.final --d.alpha. after the running torque equals or exceeds a value slightly greater than T.sub.sp. This transient torque rise is caused by static friction and/or the change over from static to dynamic in much the same manner that the torque peak 30 is generated at the onset of tightening as shown in FIG. 2. The amount that T.sub.sp should be increased is subject to compromise and is somewhat arbitrary. In the absence of joint relaxation, the transient torque rise has been observed to lie between 0-15% above the expected torque. Accordingly, a compromise adjustment of 8% is preferred so that the measurement of the angle .alpha..sub.final --d.alpha. is preferably measured from 1.08T.sub.sp. In the absence of joint relaxation, the transient torque rise is so fast that essentially only the backlash in the tightening tool is taken up, regardless of any compensating factor in the range of 0.9-1.1. In other words, in the absence of joint relaxation, essentially no angle error is created in restarting the tool and measuring the angle of advance from T.sub.sp. When joint relaxation occurs, however, the compensating factor is material.

PAC Torque Option

PAR Another tightening parameter that may be selected to attain the final desired tension value F.sub.D is the additional torque .DELTA.T or the final torque T.sub.D (FIG. 1). The final torque T.sub.D is preferred since the joint may relax at the mid-point stop 62. Because the tool instruction is to achieve an absolute torque value T.sub.D, any relaxation in the joint is automatically accomodated. In using a torque governed shut off parameter, even a possible tightening of the joint at the mid-point stop will also be automatically compensated for.

PAR In using a torque governed shut off, an interesting phenomenon has been noted for which no simple explanation appears. Referring to FIG. 1, it will be noted, as previously mentioned, that the tension rate FR.sub.2 is greater than the tension rate FR.sub.1, typically by 5-15% depending mainly on the value selected for F.sub.M. This would lead one to believe that the torque rate in the region 20 would be greater by a similar amount

```
     than the torque rate in the region 18. Laboratory investigations indicate
     that the torque rate in the region 20 typically exhibits a slightly
     smaller increase over the torque rate in the region 18. Fortunately, the
     ratio of the torque rates in the regions 18, 20 to the ratio of the
     tension rates FR.sub.1, FR.sub.2 is more nearly constant for a single type
     fastener pair. In calculations for a final torque shut off command, this
     factor is taken into account, as follows:
     ##EQU17##
     where T.sub.MC is a calculated value for the torque at the break in the
     tension curve, R is defined as TR.sub.2 /rTR, TR.sub.2 is the torque rate
     in the region 20, TR is the torque rate in the region 18, and r is the
     ratio of FR.sub.2 /FR.sub.1.
PAR As is the case in the angle governed final shut off calculations, the tool
     will overrun after the final shut off command. Defining,
EQU .delta.T=TR.sub.2 (d.alpha.)                                   (61)
EQU T.sub.a 32 T.sub.o -T.sub.4 -.delta.T                          (62)
     ##EQU18##
     where d.alpha. is a calculated value for angle overrun from equation (50),
     (51) or (56). In the alternative,
EQU T.sub.b =T.sub.D -TR.sub.2 d.alpha.                            (64)
PAL where T.sub.b is the torque value at shut off.
PAR After tightening is resumed, the final shut off command is given either
     when running torque T.gtoreq.T.sub.b or T.sub.D --dT. As shown in FIG. 1,
     the final shut off command will occur at about the point 78 whereby the
     tool overrun continues to tighten the fastener pair for an additional
     torque value dT until stopping at the final desired tension value F.sub.D.
PAR It is apparent that tightening of the fastener pair can be terminated in
     response to calculated tension which is derived by the techniques of this
     invention. Upon analysis, it will be evident that terminating tightening
     in response to calculated tension is in reality the same as terminating
     tightening in response to either angle or torque, depending on how the
     calculations of tension are conducted.
PAC Torque--Angle Option
PAR It will be apparent that tightening may be terminated in response to a
     combination of torque and angle, for example, a linear combination of
     torque and angle. Assuming that one wished to equally weigh the calculated
     advance derived from the torque and angle computations, the appropriate
     equation is generically:
     ##EQU19##
     where F.sub.o is the calculated tension value at the mid-point stop 62 as
     may be calculated from equation (26) or (27) depending on whether
     X.ltoreq.O or X>O, and T.sub.sp is the calculated torque value at the
     mid-point stop 62 as may be calculated from equation (57) or (58)
     depending on whether X.ltoreq.O or X>O. The calculations for
     .alpha..sub.final will depend on whether X.gtoreq.O or X>O as pointed out
     in equations (47) and (48). Calculations for T.sub.D are made using
     equations (53) and (54).
PAR As with the use of other tightening parameters, it is desirable to provide
     an overrun correction. It is apparent that the angle overrun correction of
     equation (50) may be incorporated as an overrun prediction, as follows:
EQU F.sub.or =r(FR.sub.1)d.alpha.                                  (66)
PAL where F.sub.or is the increase in tension due to overrun. It may also be
     desirable to use an equally weighted linear combination of torque and
     angle in determining the predicted tool overrun. The tension produced in
     the bolt during overrun may be calculated as:
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PAR  It will be apparent that one cannot merely instruct the tool to proceed an
      additional angle or until a desired torque level is reached in order to
      stress the bolt to the desired tension value F.sub.D when using a mixed
      parameter of torque and angle. Instead, one may calculate the tension
      appearing at any angular position .alpha..sub.3 beyond the point 62 as
      ##EQU21##
      where T.sub..alpha.3 is the sensed torque value at the angular position
      .alpha..sub.3, T.sub.sp is the calculated torque value at the mid-point
      stop 62, and T.sub.MC is the calculated torque value at the location of
      F.sub.M according to equation (59).
PAR  The calculated tension value at the point of shut off is:
EQU  F.sub.so =F.sub.D -F.sub.or                                    ( 70)
PAL  where F.sub.D is from equation (65) and F.sub.or is from equation (67). By
      comparing the value of F.sub..alpha.3 at angle increments, such as
      .DELTA..alpha., 1.degree. or the like, with F.sub.so, as soon as
      F.sub..alpha.3 .gtoreq.F.sub.so, the shut off command is given. In this
      fashion, tightening may be terminated in response to a linear combination
      of torque and angle.
PAC  PROCEDURES INVOLVING RESTARTING OF THE TOOL
PAC  Decision to Advance
PAR  It is evident that the tension achieved in the fastener at the mid-point 62
      may be substantially less than F.sub.D, equal to or very close to F.sub.D
      or greater than F.sub.D. If the tension F.sub.o achieved at the mid-point
      62 is greater than or equal to F.sub.D, the tool is not restarted but is
      instead reset to commence the tightening of the next fastener. In this
      circumstance, it may be desirable to provide an indication that the joint
      is satisfactorily tightened provided that the previously conducted quality
      control operations indicate that the joint is acceptable.
PAR  Accordingly, the question is whether to restart the tool when the mid-point
      tension F.sub.o is less than F.sub.D. Using, for purposes of illustration,
      the angle option technqiue for advancing the tool, if
EQU  .alpha..sub.final -d.alpha.>0                                   (71)
PAL  the tool is instructed to advance the angle increment .alpha..sub.final
      -d.alpha. after either T.sub.sp or 1.08T.sub.sp, depending on the election
      on how to handle joint relaxation. If .alpha..sub.final -d.alpha.=0, the
      tool is instructed to commence turning and the shut off command is given
      immediately upon observing T.sub.sp or 1.08T.sub.sp. If, however,
      .alpha..sub.final -d.alpha.<0, two decisions are possible. The value of
      d.alpha. is normally greater than zero. Accordingly, if
EQU  d.alpha.>2.alpha..sub.final                                     ( 72)
PAL  then the tool is instructed to open the air supply valve and issue a shut
      off command upon observing either T.sub.sp or 1.08T.sub.sp. Otherwise, the
      best available final tension is the mid-point value F.sub.o.
PAC  Torque Signal Filtering
PAR  There are many tools, for example the tool illustrated in copending
      application Ser. No. 766,429, that do not exhibit any substantial internal
      chattering which is reflected as noise in the torque signal. There are,
      however, a number of tools in which internal chattering produces
      undesirable noise in the torque signal. One such tool is of the type
      having the tool output angularly disposed relative to the motor shaft. In
      tools of this type, a set of meshing gear teeth effect the inclination of
      the output drive. In this situation, the meshing gear teeth apparently
      produce the noise that is reflected in the torque signal. It is desirable
      to filter the torque signal to reduce this noise. The difficulty is that a
      filter which will remove noise caused by internal chatter tends to slow
      the  me response of the torque signal during startup for th  nal
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advance and causes response time problems near the termination of tightening.

PAR To overcome these difficulties, there is preferably employed a pair of filters which are placed in circuit with the torque sensor by a switch controlled by the microprocessor. The first filter, which is conveniently of the resistance-capacitance type, has a substantial capacitance and accordingly acts to substantially filter the torque signal. The processor controls the switch to place the first filter in circuit with the torque sensor during the initial part of the tightening cycle, usually up to and including the mid-point stop 62. At the mid-point, the first filter is switched out of circuit with the torque sensor and a second filter is placed in circuit therewith. The second filter may also be of the resistance-capacitance type and has a much lower capacitance. The second stage filtering merely eliminates any very high frequency noise.

PAR The difficulty with this approach is that the initial heavy filtering will cause a predictable torque-angle distortion that fortunately can be compensated for during the joint set up procedure. The other problem with filtering the torque signal is that deterioration or failure of the filter would cause tension errors.

PAC NON-LINEAR STRAIN PROCEDURES DURING THE FINAL ADVANCE

PAR Referring to FIG. 8, another feature of the invention is illustrated. When tightening to the final desired tension value, it is highly desirable to assure that the yield point is not reached or is at least not substantially exceeded. This may be done graphically as shown in FIG. 8 by drawing a line 98 parallel to the torque curve 10 in the region 20 or parallel to the tension curve 12 and spaced therefrom by an angle .alpha..sub.y in accordance with the classic offset strain technique. The value of .alpha..sub.y can be correlated with an acceptable amount of strain in the bolt since the amount of nut rotation in this region of the torque curve can be calculated into a percentage of bolt elongation because of the known pitch of the threads. When the running torque value T intersects the line 98 at the point 100, the tool is given a shut off command and ultimately comes to rest at a point 102 because of tool overrun.

PAR In order to implement this technique, the torque value sensed by the tool is monitored after the tool is turned on again after the mid-point stop 62. One difficulty arises since the restarting torque applied to the fastener in order to resume tightening typically is relatively substantially larger than the running torque immediately prior to the mid-point stop 62 as is caused by the difference between the static and dynamic coefficients of friction and complicated dynamic factors. When the sensed value of running torque T first equals or exceeds the value of T.sub.M where:

EQU T.sub.M =T.sub.3 +TR(.DELTA..alpha.-X) (73)

PAL this location is marked and two .DELTA..alpha. increments beyond this location, which is location 104, the running torque T is sensed and stored as T.sub.5. T.sub.M will be recognized as a calculated torque value which appears at the location on the torque-angle curve corresponding to the break in the tension curve.

PAR As is apparent from FIG. 8, the calculations being done to detect the yield point or, in the alternative, an amount of non-linear strain below the yield point, occur in the region 20 where the torque rate is somewhat lower than the torque rate value calculated in the region 18. The torque rate in the region 20 can be expressed in accordance with equation (55).

PAR Yield or non-linear strain calculations can be conducted periodically

Although the calculations can be done at every angle increment .DELTA..alpha., results are quite satisfactory if done every other angle increment .DELTA..alpha.. Accordingly,

EQU .DELTA.T.sub.1 =2u(.DELTA..alpha.) (74)

EQU .DELTA.T.sub.y =u.alpha..sub.y (75)

PAL where .alpha..sub.y is the angle corresponding to a desired strain level which can either be elastic but non-linear or plastic, .DELTA.T.sub.1 is the incremental torque over the incremental angle 2.DELTA..alpha. and .DELTA.T.sub.y is the incremental torque over the incremental angle .alpha..sub.y. By selecting small values for .alpha..sub.y, the shut off command will tend to be in the elastic but non-linear range below the yield point. If .alpha..sub.y is selected to be a large value, the shut off point will appear in the plastic range above the yield point. It is thus apparent that the detection of non-linear strain can encompass both elastic and plastic strain. The only difficulty is selecting very small values for .alpha..sub.y is that noise in the torque curve 10 in the range 20 might create a premature and false yield signal. At a point 106, which is two .DELTA..alpha. degrees after the occurrence of T.sub.5, the value of running torque T is compared with

EQU T.sub.y1 =T.sub.5 +.DELTA.T.sub.y +.DELTA.T.sub.1 (76)

PAL It is apparent that T.sub.y1 is a torque value on the line 98 at the point 108. If T>T.sub.y1, tightening continues. At a point 110, which is two .DELTA..alpha. degrees beyond the point 106, the value of running torque T is compared with
##EQU22##
If T>T.sub.y2, tightening continues. This procedure continues by adding an additional torque valve .DELTA.T.sub.1 to the preceding value of T.sub.y at angle increments of two .DELTA..alpha.. In the event that T.ltoreq.T.sub.y before the occurrence of the shut off command derived from the normal tightening parameter of torque or angle, a shut off command is given to the tool. It will be apparent that the actual shut off command from detection of non-linear strain or the actual detection of non-linear strain will not occur at exactly the point 100 since comparisons are being made every two .DELTA..alpha.. Thus, the actual yield detection will probably occur later, e.g. at the point 112 as shown in FIG. 8.

PAR Thus, tightening is normally terminated in response to a torque governed, an angle governed or a mixed shut off command, but in the case of yield point detection or, in the alternative, detection of non-linear strain below the yield point, a premature shut off command is given. It will accordingly be apparent that the upper end of the scatter band is eliminated by a secondary yield point shut off. Thus, the total scatter will be reduced. It will also be apparent that the detection of non-linear strain may be conducted as disclosed in U.S. Pat. Nos. 3,643,501 or 3,693,726, although the technique herein disclosed in deemed preferable.

PAR It will be appreciated that the non-linear strain detection conducted at the mid-point stop 62 is conceptually the same as the determination made during tightening toward the final desired tension value. The details of the determination as here disclosed are somewhat different. In order to simplify the program, it may be desirable to utilize a common approach.

PAR It has been discovered that tightening can be consistently terminated in response to non-linear strain in the elastic region provided that certain precautions are taken. It is essential that a reliable value be obtained for the average torque rate of the fastener being tightened. Necessary to obtaining a reliable torque rate is conducting the calculations over an angle increment of significant size relative to the angular distance between the origin of stress and the proof load of the fastener. Typically, the minimum angle increment over which torque rate calculations are conducted should be in the range of 10-20% of this angular distance. Torque rate determinations made over smaller angle increments tend to be unduly influenced by noise in the torque signal. Another desirable feature is avoiding a two point torque rate calculation and instead using an averaging technique using at least 5 and preferably 10 different data points in order to minimize the effect of a single unusual torque sensing on the calculated torque rate. The approach of this invention is particularly suited to terminating tightening in response to non-linear strain in the elastic zone because of the pains taken to obtain a consistently reliable average torque rate. It will be appreciated that this feature is of considerable importance because of the desire of joint designers to achieve high tension stresses in the bolts without advancing threading into the zone of plastic deformation.

PAC PROCEDURES AT TERMINATION

PAC Frequency of Shut Off Due to Non-linear Strain

PAR It is preferred that the selection of F.sub.D will be low enough so that the cutoff due to detection of non-linear strain will be rare, e.g. 0.1%. In the event that the percentage of premature tightening termination due to non-linear strain detection rises substantially during a production run, this indicates that the fasteners, i.e. bolts and/or threaded parts, employed do not meet design specifications. Accordingly, a high percentage of non-linear strain detections is a signal that quality control investigations need to be conducted on the fasteners employed. For example, if the normal occurrence of non-linear strain is on the order of 0.1%, and a running average of non-linear strain detections is 10%, it is likely that the fasteners being run do not meet specifications.

PAR To identify batches of fasteners which do not meet specifications, a running count of the number of joints tightened is maintained and a running count of the number of joints exhibiting non-linear strain is maintained. A frequency determination is accordingly made, as follows:

EQU (C.sub.Y /C.sub.J).gtoreq.A (79)

PAL where C.sub.J is the number of joints tightened, C.sub.Y is the number of joints experiencing non-linear strain and A is some fraction acceptable to the user. From present information, it appears that the value of A should be in the range of 0.10-0.20, e.g. 0.15. The ratio of C.sub.Y /C.sub.J is preferably a running ratio, rather than a cumulative ratio, as by storing, on a first-in, first-out basis, a finite number of joints tightened C.sub.J, e.g. 30, and any instances of non-linear strain detection C.sub.Y. When the running ratio of C.sub.Y /C.sub.J equals or exceeds the selected value A, a suitable signal may be provided indicating that the frequency of non-linear strain is much too high. The investigations to be conducted normally include analysis of the strength and material composition of the fasteners, a technique well known in the art.

PAC When to Conduct Extensive Quality Control Procedures

PAR It will be appreciated that termination of tightening may occur normally, i.e. in response to the final shut off parameter, may occur in response to the detection of non-linear strain during tightening toward the final shut off parameter, may occur because the mid-point tension F.sub.o is too close to the final desired tension value F.sub.D or may occur in response to one of the quality control procedures done at the mid-point 62. If tightening is terminated because the mid-point tension F.sub.o is too close to F.sub.D so that the tool cannot be restarted, one of two conclusions can be reached: (1) the joint has an unusually low value for provided that F.sub.o passes the final tension check discussed hereinafter. The decision depends on the other quality control procedures conducted at the mid-point 62 and the decision of the system designer. In the circumstance where tightening is terminated because the joint is rejected by one of the quality control procedures, nothing further needs to be done. Accordingly, there are two situations where extensive quality control procedures are desirable, i.e. when tightening is terminated normally and when tightening is terminated in response to the detection of non-linear strain occurring after the mid-point stop 62.

PAC Final Tension Determination in the Elastic Zone

PAR It is desirable to calculate and store the final tension appearing in a fastener, the tightening of which is terminated normally, i.e. in response to torque and/or angle rather than non-linear strain. When using a torque approach, equation (87) gives a value for F.sub.final regardless of whether yield has occurred or not. When using an angle approach, the final achieved tension value may be calculated from:

EQU F.sub.final =F.sub.D -rFR.sub.1 (.alpha..sub.final -.alpha..sub.actual) (80)

PAL where .alpha..sub.actual is the actual measured angle increment between the T.sub.sp or 1.08T.sub.sp and the final stopping point.

PAC Final Tension at Tool Stall

PAR It is also desirable to calculate and store final tension appearing in a fastener in other circumstances, such as when the tool stalls. Tool stall may occur before the mid-point stop 62 or after. Before the mid-point stop 62.

EQU F.sub.final =F.sub.o (81)

PAR After the mid-point stop 62, the final desired tension value F.sub.final may be calculated using a torque approach as:
##EQU23##
where T.sub.sp is the calculated torque at the mid-point stop by equation (57) and T.sub.final is the last highest torque sensing obtained within one or two .DELTA..alpha. increments of the final stopping point.

PAR After the mid-point stop 62, the final desired tension value F.sub.final may alternatively be calculated, using an angle approach, as:

EQU F.sub.final =F.sub.o +rFR.sub.1 .alpha..sub.actual, where X>0 (83)

PAL where .alpha..sub.actual is the actual measured angle from T.sub.sp or 1.08T.sub.sp to the final stopping point.

PAC Non-linear Strain Detection

PAR This is a theoretically redundant check on the possible occurrence of excessive non-linear strain. The joint is rejected or indicated as having experienced excessive non-linear strain in the event that:

EQU T.sub.final .ltoreq.T.sub.m +TR(-.alpha..sub.origin -.alpha..sub.F)+u(.alpha..sub.actual -.alpha..sub.y) (84)

PAL where T.sub.m is the mean torque value at the angle location .alpha..sub.F. It will be recollected that .alpha..sub.origin is a negative value thereby requiring the minus sign. The technique is basically to add a calculated torque value to the mean torque T.sub.m to obtain a calculated torque value at the mid-point stop and then add another calculated torque value representing the additional increase in torque from the mid-point stop to the final stopping place which occurs at the angle sensing .alpha..sub.actual. If this calculated value is equal to or greater than the highest torque sensing T.sub.final obtained within one or two .DELTA..alpha. increments of the final stopping place, the joint is flagged.

PAC Final Tension Determination in the Plastic Zone

PAR It is highly desirable to calculate and store the final tension appearing in a fastener which has been stopped prematurely because of non-linear strain detection. It may be that the final tension value achieved is well within an acceptable range. In the event, it would be disadvantageous to require removal and replacement of the fastener pair if the problems associated with marginally yielded fasteners are not material if the fasteners are sufficiently stressed to assure acceptable joint conditions.

PAR Accordingly, when using an angle approach, the value of final tension may be calculated as follows:

EQU F.sub.final =F.sub.D -rFR.sub.1 (.alpha..sub.actual +.alpha..sub.y -.alpha..sub.2) (85)

PAL where .alpha..sub.2 is the angle from the stopping point 102 to the location where yield detection is sensed. It will be appreciated that any calculated value of F.sub.final is somewhat of an approximation since the tension rate well above the proportional limit is unknown and perhaps unknowable with any degree of accuracy. FIG. 9 graphically illustrates the difficulty. If the final tension value were calculated:

EQU F.sub.final =F.sub.D -rFR.sub.1 (.alpha..sub.final -.alpha..sub.2) (86)

PAL the tension actually being calculated would be at the point 114 which is at the same angular position .alpha..sub.2 from the stopping point 102 as the yield detection point 112. It will be appreciated that the difference in tension values between the points 112, 114 may be significant in some circumstances. Since it is known that the tension rate falls off substantially immediately prior to the point 100, it is safe to calculate the tension value at the point 116 which is spaced downwardly along the slope FR.sub.2 by an angular distance .alpha..sub.y. Thus, the rationale for the equation (86) is apparent. It will be appreciated that the actual final tension appearing in the joint is that at the point 112 which differs from the calculated tension value appearing at the point 116. It will be seen, however, that the tension value at the point 116 is a substantially better estimation of actual final tension than is the tension that would be calculated at the point 114. This is particularly true since the tension rate in the range 118 is known to be quite low. The final tension value F.sub.final along with a notation that the bolt has yielded may be displayed at the tool location, printed or otherwise recorded for further use or analysis.

PAR In the event the torque governed final shut off parameter is being used, when T.ltoreq.T.sub.y, non-linear strain is detected and a shut off command is given the tool. The final tension value may be calculated from a torque approach, as follows:

##EQU24##

where T.sub.final is the highest value of torque sensed within one or two .DELTA..alpha. increments before the final stopping place 102. This is likewise illustrated in FIG. 9. The detection of yield occurs at point 112 on the torque curve 10 which the point 102 being the final stopping point. The torque at the point 102 is unreliable for the same reasons that the torque reading at the mid-point stop 62 is unreliable. Accordingly, the torque value T.sub.final is taken as the peak within one or two .DELTA..alpha. increments backward from the point 102, such as at the point 120. The effect of this, graphically, is shown by the horizontal line 122 terminating on the torque slope TR.sub.2 at the point 124 and the vertical line 126 terminating at the point 128 on the tension slope FR.sub.2. Thus, the final tension value F.sub.final is the calculated tension at the point 128.

PAR In the alternative, the following estimate is fairly accurate:

##EQU25##

```
     T.sub.mm. is T.sub.m +TR(-.alpha..sub.origin -.alpha..sub.F). If T.sub.sp
     <T.sub.mm, then T.sub.mm =TR(-.alpha..sub.origin -.alpha..sub.F).
PAR  In the event the tool continues to run far beyond any reasonable angle of
     advance, the conclusion is that the bolt has failed without yield
     detection, as may occur before the mid-point stop 62. Thus, no appreciable
     tension appears in the bolt and
EQU  F.sub.final =0.                                            (89)
PAC  Final Tension Check
PAR  In any circumstance where F.sub.final is calculated, it may be desirable to
     compare it with the final desired tension value F.sub.D. In this event, if
     ##EQU26##
     where B is a fraction deemed acceptable to the user, a suitable signal may
     be displayed to indicate that calculated tension is substantially below
     desired tension. From present information, it appears that the magnitude
     of B should be greater than the expected scatter from use of this
     invention and preferably should be 3-4 normal deviations. Thus, B should
     be in the range 0.10-0.17.
PAC  Final Tension Consistency Check
PAR  Another approach of this invention is to normally terminate tightening in
     response to one parameter, e.g. torque, and check this shut off parameter
     against another shut off parameter, e.g. angle. If the results compare
     closely, this is an indication that the assumptions made, the empirically
     determined joint parameters and the like are reasonably correct. If the
     comparisons are significantly different, this is an indication that
     something is amiss and that the operation should be stopped or
     investigations instituted to determine the cause. When using torque as the
     tightening parameter, F.sub.D has been placed in the calculations for the
     final torque value T.sub.D by equation (53) or (54) depending on whether
     X.gtoreq.7 0 or X<0. The calculated value of final tension F.sub.final
     using an angle approach at a final angle of advance of .alpha..sub.final
     is:
EQU  F.sub.final =F.sub.D -rFR.sub.1 (.alpha..sub.final -.alpha..sub.actual)
     (91)
PAL  where .alpha..sub.actual is the angle of advance from T.sub.sp or
     1.08T.sub.sp to the final stopping point. If the different between F.sub.D
     and F.sub.final is small, e.g. .+-.5-10%, it is apparent that substantial
     confidence may be placed in the technique. If the difference between
     F.sub.D and F.sub.final is larger, e.g. .+-.20%, it is apparent that
     something is amiss and that the tightening operation should be stopped or
     investigations instituted to determine the cause.
PAC  Final Torque Consistency Check
PAR  Assuming that the final advance of the fastener was determined in terms of
     angle and the joint has not experienced non-linear strain, a check of the
     value of the actual final peak torque T.sub.final against a calculated
     value of the expected final torque T.sub.D provides an independent
     evaluation of the procedures. In order to make this determination,
     preliminary calculations are made. First, the actual attained final
     tension value F.sub.final differs from the expected tension value F.sub.D
     only if the actual amount of tool overrun is different from the estimate
     d.alpha.. The actual attained tension value is
EQU  F.sub.final =F.sub.D +(.alpha..sub.actual -.alpha..sub.final)rFR.sub.1 (
     92)
PAL  where .alpha..sub.actual is the actual observed angle from T.sub.sp or
     1.08T.sub.sp. This calculation will provide a value for actual attained
     tension for F.sub.final. Realizing that the actual attained tension value
     F.sub.final will differ from F.sub.D, a correction is made in the expected
```

value of final torque T.sub.D, as follows:

EQU T.sub.D '=T.sub.D (F.sub.final /F.sub.D) (93)

PAL where T.sub.D ' is the revised value of T.sub.D. The value of T.sub.D ' must be comparable with T.sub.final. A torque-angle consistency factor .eta..sub.T is then defined as

EQU .eta..sub.T =(T.sub.D '-T.sub.final)/T.sub.D ') (94)

PAL Ideally, .eta..sub.T should be zero. It will be appreciated, however, that minor deviations in .eta..sub.T from zero are not indicative of any substantial problem. In good quality joints, it has been found that values of .eta..sub.T on the order of about 0.13 rarely give false indications of defective joints. Accordingly, this value is used. If a better value is available, it should be used instead. Thus, a joint is judged defective in the event that

EQU -0.13.ltoreq..eta..sub.T .gtoreq.0.13. (95)

PAL the tool is reset for the next tightening cycle and a signal is given that the joint has failed. In the event that parts quality is known to be subnormal, the value of .eta..sub.T should be increased somewhat.

PAR This quality control procedure causes the rejections of joints experiencing thread galling, joint where the mid-point analysis, for some reason, is performed in a very low tension range, joints which yield and the non-linear strain procedures do not detect if, joints tightened with faulty torque or angle instrumentation, or joints tightened with incorrect input parameters fed to the microprocessor.

PAC Final Torque Rate Consistency

PAR This quality control procedure is intended to provide additional insurance against a fairly flat torque-angle curve near the termination of tightening which may possibly indicate significant penetration of the plastic zone somehow not detected by other routines. In this procedure, the final torque rate is checked against the empirically determined torque rate u or TR.sub.2 within the angle interval of actual tool overrun. Defining,

EQU FRC.ident.(T.sub.final -T.sub.marker)/u (96)

PAL where T.sub.marker is the torque sensing at the shut off command and T.sub.final is the peak torque value sensed in the last few .DELTA..alpha. increments prior to stopping. If FRC is less than some suitable value, e.g. 0.25, the joint is indicated as failing this procedure. This procedure has its difficulty because the value of T.sub.final, which is the peak value of torque within one or two .DELTA..alpha. increments from the final stopping point, is influenced by the act of stopping rotation for the same reason that the last torque readings prior to the mid-point stop 62 are suspect. Experience indicates that if joints are rejected when FRC<0.25, there is a false indication of joint inacceptability approximating a 1% frequency. This is believed to be caused in large part by the suspect value of T.sub.final. The procedure does, however, have its value in providing considerable assurance against premature yielding if that is of paramount concern to the user.

PAC Frequency of Joint Rejections

PAR It is desirable to indicate a parts integrity problem when the number of joints that have failed at least one of the quality control procedures is too frequent. In other words, the joint failure frequency determinations are desirably merged into one single frequency determination. The difficulty to be avoided is, of course, counting twice a joint which fails two of the quality control procedures. Under normal circumstances, this is not a substantial problem because the quality control procedures are conducted sequentially and not simultaneously. Accordingly, any joint that for the next succeeding tightening cycle. Accordingly, when

EQU (C.sub.FTR +C.sub.TRC +C.sub.TRL +C.sub.NM +C.sub.NLS +C.sub.F +C.sub.NF +C.sub.TC +C.sub.FT)/C.sub.J .gtoreq.J (97)

PAL a signal is generated to energize a parts integrity indicator, where C.sub.FTR is the number of failures of the final torque rate check, C.sub.TRC is the number of failures of the torque rate curvature check, C.sub.TRL is the number of occurrences where the torque rate is too low, C.sub.NM is the number of failures of the non-linear strain determination at the mid-point stop 62. C.sub.NLS is the number of times that tightening is terminated in response to non-linear strain rather than in response to the normal tightening parameter, C.sub.NF is the number of failures of the final non-linear strain determination, C.sub.F is the number of failures of the tension check, C.sub.TC is the number of failures of the tension consistency check, C.sub.FT is the number of failures of the final torque consistency check, C.sub.J is the number of joints tightened and J is a fraction acceptable to the user. It will be apparent, of course, that a number of these quality control procedures may be omitted from any particular application and consequently will have no bearing on this frequency check. It is preferred, as in other frequency checks, that C.sub.J be a finite running number of joints stored on a first in, first out basis. The quantity selected for this finite number should be sufficiently large to avoid statistical aberrations and accordingly is preferably on the order of 50-500. The value of J is inversely related to the selected quantity of C.sub.J in the sense that the higher the value for C.sub.J, the lower may be the selected value of J. From present information, it appears that J should be on the order of about 0.05-0.20 and is preferably about 0.10 to avoid giving false indications of a systematic parts problem when none exists.

PAC Repair of Failed Joints

PAR When a joint is rejected by the tightening technique of this invention, it is highly likely that at least one part constituting the joint is not up to specifications. In such cases, it is highly desirable that defective parts be replaced and the tightening process repeated. However, if the user so wishes, rejected joints can be automatically tightened to a different parameter and the shut off command given. Because of the stored values of torque and angle, it is conceivable that the repair technique could comprise a turn-of-the-nut approach so that the tool could be instructed to advance a predetermined number of degrees beyond a particular torque location. It appears, however, that a turn-of-the-nut approach is not the most desirable for repairing failed joints. Instead, it is preferred that the rejected joints be tightened to a specified minimum torque and the shut off command given. Because of overrun, the final torque achieved would be somewhat greater than the minimum specified. This could, of course, be accomodated by making a simple overrun prediction along the lines of equation (64). It is apparent that this procedure is applicable to joints tightened in accordance with this invention using either the torque or angle option or tightened in accordance with a turn-of-the-nut strategy.

PAC Shear Joint Routine

PAR In joints which are subjected to significant axial loads, i.e. loads parallel to the bolt axis, the only object of tightening is to induce a desired tensile stress in the bolt. This is not precisely true in joints where all or a substantial fraction of the external load is transverse, i.e. in a plane perpendicular to the bolt axis. In shear joints of this type, it is desirable from the standpoint of joint mechanics to assure that a minimum torque value has been applied in addition to assuring that the bolt stress is above a predetermined value. Accordingly, a typical fastener in a shear joint might be tightened to 90% proof and 40 foot pounds. Calculations are conducted in accordance with the previous disclosure to terminate tightening at 90% proof. If the estimated or actual torque value at the termination of threading advance or one or two .DELTA..alpha. increments prior thereto is less than the minimum predetermined torque, the tool is restarted until the minimum torque value is attained. Accordingly, if the final estimated torque T.sub.D or the final peak torque T.sub.final is equal to or greater than the minimum torque T.sub.min, tightening is terminated normally. On the other hand, if the estimated final torque T.sub.D or the peak torque T.sub.final is less than T.sub.min, a value of shut off torque T.sub.sh is calculated as

EQU T.sub.sh =T.sub.min -ud.alpha. (98)

PAL The tool is accordingly restarted and the air supply valve is closed at a location where the running torque value is T.sub.sh. The tool overruns for an angle increment d.alpha. so that the final attained torque value is T.sub.min.

PAC Joint With Multiple Fasteners

PAR When tightening seriatim a multiplicity of fasteners comprising part of a single joint using a conventional technique, it is well known that the first tightened fasteners will lose at least some tension by the time the last fasteners are tightened. This is, of course, related to joint relaxation and alignment of the joint parts. In accordance with this invention, one powered instructable tool as disclosed more fully hereinafter may be used for each fastener and used in the following manner.

PAR The tools are started simultaneously. When all of the tools have stopped at the mid-point 62, all the tools are restarted simultaneously to accomplish the final advance. In this manner, the alignment of all the fasteners and all joint relaxation occurs at the mid-point stop 62. Each tool would then compensate for any relaxation that may have occurred adjacent the fastener coupled thereto. It will be apparent that the control mechanism for the tools would be interconnected electronically in a fashion that will be apparent to those skilled in the art following the more complete description of the tool hereinafter.

PAC EQUIPMENT

PAR Referring to FIG. 10, there is illustrated a schematic showing of a mechanism 126 for performing the previously described technique. The mechanism 126 includes an air tool 128 connected to the air supply 130 and comprising an air valve 132, an air motor 134 having an output 136 coupled to the fastener pair comprising part of the joint 138, a torque transducer 140 and an angle transducer 142. The torque transducer 140 is connected to a signal conditioner 144 of a data processing unit 146 by a suitable electrical lead 148.

PAR The signal conditioner 144 is designed to receive electrical signals from the transducer 140 and modify the voltage and/or amperage thereof into a form acceptable by an analog-to-digital converter 150 through a suitable connecting circuit 152 described more fully hereinafter. The converter 150 changes the analog signal received from the conditioner 144 into digital form for delivery to an interface logic unit 154 through a suitable connection 156. The angle transducer 142 is connected to the interface logic unit 154 by a lead 158.

PAR The connecting circuit 152 provides the torque signal filtering function discussed. To this end, the circuit 152 includes a pair of parallel leads 158, 160 connecting the signal conditioner 144 to the analog to digital converter 150. The lead 158 is connected to a ground 162 by a lead 164

The lead 160 includes a resistor 166. Extending between the leads 158, 160 is a lead 168 having a first capacitor 170 therein. A second lead 172 also extends between the leads 158, 160 and has therein a second capacitor 174 as well as a switch mechanism 176 of a relay 178. The relay 178 may be of any suitable type and is designed, when energized, to close the switch mechanism 176 to place the second capacitor 174 in parallel with the first capacitor 170 in the connecting circuit 152.

PAR In operation with the relay 178 unenergized, the resistance 166 and the first capacitor 170 act as an R-C filter to remove very high frequency noise from the conditioned torque signal passing across the leads 158, 160. When the relay 178 is energized, the second capacitor 174 is placed in parallel with the first capacitor 170. Together, the resistor 166 and the capacitors 170, 174 act to filter the analog torque signal appearing in the leads 158, 160. As mentioned, the circuit 152 is employed with tightening tools which produce a substantial amount of internal chatter. In such tools, the relay 178 is energized during an initial portion of the tightening cycle, usually up to and including the mid-point stop 62. Accordingly, the resistance-capacitance network provided by the resistor 166 and the capacitors 170, 174 act to substantially filter the analog torque signal appearing on the leads 158, 160. At the mid-point stop 62, the energizing signal delivered to the relay 178 is terminated so that the switch mechanism 174 opens to remove the capacitor 176 from the connecting circuit 152.

PAR It will be appreciated that the relative sizes of the resistor 166, first capacitor 170 and second capacitor 174 control the degree of filtering actually accomplished. Although the design of the filtering network is subject to design selections, the following sizings have proved acceptable: the resistance of the resistor 166 is 2000 ohms, the capacitance of the first capacitor 170 is 0.5 microfarads, and the capacitance of the second capacitor 174 is 5 microfarads.

PAR The interface logic unit 154 comprises an interface logic section 180 designed to handle information and is connected through suitable connections 182, 184 to a microprocessor unit 186 which is in turn connected to a data memory unit 188 and an instruction memory and program unit 190 through suitable connections 192, 194, 196, 198. The interface logic section 180 is also designed to receive input parameters such as T.sub.os, FR.sub.1, r, F.sub.D and the like.

PAR The interface logic unit 154 also comprises an amplifier section 200 controlling a solenoid (not shown) in the air valve 132 through a suitable electrical connection 202. The amplifier section 200 also controls a display panel 204 having suitable signal lights through an electrical connection 206 as will be more fully explained hereinafter. The relay 178 is similar energized through a connection 208 from the amplifier section 200.

PAR The air tool 128 may be of any type desired such as a Rockwell model 63W which has been modified to reduce the amount of overrun or such as is shown in copending application Ser. No. 766,429. It has been surprising to learn that the bulk of the tool overrun occurs between the time the shut off command is given through the electrical connection 202 and the time that high pressure air downstream of the valve 132 is exhausted through the motor 134 while the amount of overrun attributable to inertia of the air tool 128 is rather insignificant at high running torque values because tool speed is rather slow.

PAR The data processor 146 is shown in greater detail in FIG. 11 and conveniently comprises a Rockwell microprocessor model PPS8. For a more complete description of the data processor 146, attention is directed to publications of Rockwell International pertaining thereto.

PAR The data processor 146 comprises a chassis 210 having a power source 212 mounted thereon along with the signal conditioner 144, the instruction memory and program unit 190, the data memory unit 188, the microprocessor unit 186, the interface logic section 180, the converter 150 and the logic interface amplifier section 200. The signal conditioner 144, the interface logic section 180, the microprocessor unit 186, and the data memory unit 188 are not modified in order to equip the data processor 146 to handle the calculations heretofore described.

PAR The instruction memory and program unit 190 is physically a part of the data processor 146 and is physically modified to the extent that a suitable program has been placed therein. The initial machine language program developed during the investigation of this invention contains over 7,000 instructions and, on conventional computer output paper, is approximately 150

##SPC1##

pages long. In the interests of brevity, economy and clarity, the following program is a FORTRAN version of the machine language program. This FORTRAN program will be understandable to any programmer skilled in the art and may be reconverted into a machine language program either manually or by the use of a standard language translation program. There are some input-output functions performed in the microprocessor 186 which cannot be converted into FORTRAN. These functions are pointed out in subroutines with comments describing what events should occur and be controlled by the subroutines. The FORTRAN program is as follows:

##SPC2##

##SPC3##

PAR Because of the limitations of the FORTRAN language, all of the abbreviations in lines 30-100 of the program may not be immediately recognizable. The abbreviations that may not be recognizable are:

PAR KA is a in equation (8);

PAR KC is c in equation (8);

PAR RR.sub.1 is r or FR.sub.2 /FR.sub.1 ;

PAR NN is n or the number of data points used in the first calculation of TR;

PAR ALPHOV is the overrun angle under no-torque conditions;

PAR STTHR is T.sub.sth ;

PAR TM1 and TM2 are the mean torque values from equation (15) on the first and second calculations of the torque rate in the region 18;

PAR TR1 and TR2 are the average torque rates from equation (16) on the first and second calculations of the torque rate in the region 18;

PAR ALPHF1 and ALPHF2 are the results of equation (17) on the first and second torque rate calculations;

PAR ALPHO1 and ALPHO2 are the results of equation (18) on the first and second torque rate calculations;

PAR XX1 and XX2 are the values for X from equation (20) on the two torque rate calculations;

PAR FO1 and FO2 are the calculated tension values at the mid-point stop 62 on the two torque rate calculations;

PAR NNN is n.sub.1 in equation (22);

PAR TPV is the prevailing torque;

PAR GDALPHA is actual measured overrun at the mid-point stop 62;

PAR GDT is the result of equation (61);

PAR TSH is the torque value at the shut off command and is T.sub.D --dT;

PAR TMC is T.sub.MC in equation (59);

PAR ALPHAA is the result of equation (49);

PAR IDALPHA is the result of equation (50) and is the calculated tool overrun;

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PAR  ANGSH is the angle at the shut off command;
PAR  TMM is T.sub.sp from equation (57) or (58);
PAR  UU is u from equation (55);
PAR  DELTAT is the result from equation (74);
PAR  DELTTY is the result from equation (75);
PAR  TREST is the torque value upon restarting from the mid-point stop 62;
PAR  ACTANG is the actual angle from the mid-point stop 62 to the final stopping
      point;
PAR  PKTOR is the peak torque value sensed immediately prior to the final
      stopping point; and
PAR  TENSON is the final calculated tension value.
PAR  Since the filing of the parent application, a second generation program has
      been developed. Rather than unduly lengthen this specification, the
      following program instructions will enable anyone of ordinary programming
      skills to prepare a program in any suitable language for any suitable data
      processor.
      ##SPC4##
PAC  Program Instructions
PAR  Fixed input: .theta..sub.rd, (T.sub.pv).sub.max, T.sub.1 (time or loop
      number limit), .alpha..sub.k, a, c, S.sub.T (number of counts from torque
      encoder per ft-lb), S.sub..alpha. (number of pulses from angle encoder per
      degree), .alpha..sub.or, T.sub.o, .OMEGA. (correction for torsional
      flexibility of bolt and tool downstream of angle encoder), F.sub.M,
      FR.sub.1, r, R, T.sub.os, .DELTA..alpha., n, .alpha..sub.y, K.sub.min (in
      these instructions, K=TR), (angle divisor), (special routine flags), and
      F.sub.D.
PAO  1. Reset memory and registers.
PAO  2. .DELTA..theta.=22 degrees.
PAO  3. Convert input values from engineering to internal units (degrees to
      pulses, ft-lb or N-m, etc to counts).
PAO  4. Let one (1) .DELTA..theta. elapse, read torque there and every
      .DELTA..theta. thereafter until:
PA1  (i) T.gtoreq.(T.sub.pv).sub.max twice then call Subroutine (abnormal); or
PA1  (ii) .theta..sub.rd is reached. Over the next revolution find the average
      T.sub.pv and store. Continue to check for condition (i).
PAO  5. T.sub.1 =T.sub.1 +T.sub.pv.
PAO  6. T.sub.sth =0.25 T.sub.1.
PAO  7. Search T.gtoreq.T.sub.sth, if time or loop number.gtoreq.(time or loop
      number limit), call Subroutine (abnormal); otherwise,
PAO  8. Search for T.gtoreq.T.sub.1, if time or loop number.gtoreq.limit, call
      Subroutine (abnormal), otherwise,
PAO  9. Pace ahead .alpha..sub.k pulses in torque memory and wait for appearance
      of data. If time or loop number.gtoreq.limit, call Subroutine (abnormal);
      otherwise, read and store T.sub.2.
PAO  10. .alpha..sub.1 =c+a(T.sub.2 =T.sub.pv).
PAO  11. Pace ahead .alpha..sub.1 pulses from T.sub.1 address in torque memory
      and wait for appearance of data. If time or loop number.gtoreq.limit, call
      Subroutine (abnormal); otherwise,
PAO  12. Read and store T.sub.4, turn tool off.
PAO  13. Verify tool has stopped.
PAO  14. n.sub.H =3. Values of 1 or 2 are acceptable as long as the product
      n.sub.H .DELTA..alpha. is approximately the same.
PAO  15. Call Subroutine (T.sub.m, K).
PAO  16. Call Subroutine (.alpha..sub.orig, X).
PAO  17. If X.gtoreq.O, n.sub.H =.dwnarw.(X/.DELTA..alpha.)+3 and n=n;
PA1  If n.sub.H +n>(T.sub.stop -address)-(T.sub.sth -address), call Subroutine
```

```
     (abnormal);
PA1  If X<O, n.sub.H =3 and n=n+.dwnarw.(X/.DELTA..alpha.).
PAO  18. Call Subroutine (T.sub.m, K).
PAO  19. If K.ltoreq.K.sub.min, call Subroutine (abnormal).
PAO  20. Call Subroutine (.alpha..sub.orig, X).
PAO  21. If X.gtoreq.O, F.sub.o =F.sub.M +rFR.sub.1c X; otherwise, F.sub.o
     =-.alpha..sub.orig FR.sub.1c.
PAO  22. n.sub.H =n.sub.H +.dwnarw.(n/2)+1.
PAO  23. K.sub.a =K.
PAO  24. Call Subroutine (T.sub.m, K).
PAO  25. K.sub.b =K.
PAO  26. If .vertline.(K.sub.a /K.sub.b)-1.vertline..gtoreq.0.13, call
     Subroutine (abnormal).
PAO  27. Call Subroutine (peak torque, T.sub.f).
PAO  28. T.sub.fm =T.sub.f.
PAO  29. K=K.sub.a.
PAO  30. T.sub.mm '=T.sub.m +K(-.alpha..sub.orig -.alpha..sub.F).
PAO  31. u=rRK.
PAO  32. If T.sub.fm .ltoreq.T.sub.mm '-u.alpha..sub.y, call Subroutine
     (abnormal).
PAO  33. .delta..alpha.=(T.sub.stop -address)-(T.sub.4 -address).
PAO  34. y=T.sub.4 /T.sub.o.
PAO  35. z=.delta..alpha./.alpha..sub.or.
PAO  36. .epsilon.=Y/(1-z)-1.
PAO  37. If .epsilon..ltoreq.-0.25, give marginal tool signal, advance counter.
PAO  38. If .epsilon.>0 and
     ##EQU27##
     39. Read torque one (1) .DELTA..alpha. back from T.sub.stop ; store as
     T.sub.3.
PAO  40. Call Subroutine (.alpha..sub.f, T.sub.rst, T.sub.D).
     ##EQU28##
     42. If d.alpha.>2.alpha..sub.f, call Subroutine (end). 43. If T.sub.rst
     .gtoreq.T.sub.mm ', T.sub.mm =T.sub.rst, otherwise, T.sub.mm =T.sub.mm '.
PAO  44. T.sub.6 =1.08 T.sub.rst.
PAO  45. .alpha..sub.sh =.alpha..sub.f -d.alpha..
PAO  46. .DELTA.T=u.DELTA..alpha..
PAO  47. T.sub.y =T.sub.mm +3.DELTA.T-u(.alpha..sub.y -0.25 d.alpha.).
PAO  48. Turn tool on.
PAO  49. Search for T.gtoreq.T.sub.6 until:
PA1  (i) Time or loop number.gtoreq.limit, then call Subroutine (stall).
PA1  (ii) Turn-memory on and proceed.
PAO  50. Pace .alpha..sub.sh pulses adhead of T.sub.6 address, wait until data
     appears. Turn tool off, call Subroutine (end).
PAO  51. Pace three (3) .DELTA..alpha.'s ahead of T.sub.6 address and read
     torque T. If T.ltoreq.T.sub.y, turn tool off; call Subroutine (end).
PAO  52. T.sub.y =T.sub.y +.DELTA.T pace ahead one (1) .DELTA..alpha. and read
     T. If T.ltoreq.T.sub.y, turn tool off; call Subroutine (end). Otherwise,
     proceed repeating T.sub.y and .alpha..sub.sh checks until one or the other
     is satisfied.
PAO  53. End.
PAC  SUBROUTINES
PAC  Subroutine (abnormal)
PAO  1. Turn tool off.
PAO  2. Verify tool has stopped. This is done by waiting for a short time or
     number of loops after the last data point appears.
```

```
PAO  4. If T>T.sub.1, T.sub.1 =T.sub.1 -T.sub.pv, read .alpha..sub.T1
      =(T.sub.stop -address)-(T.sub.1 -address),
PAO  5. Report Joint unacceptable (lights, error symbols, etc.)
PAO  6. Report T.sub.f and .alpha..sub.T1.
PAO  7. Go to Start.
PAO  8. End.
PAC  Subroutine (T.sub.m, K)
PAO  1. For torque array T.sub.i at .DELTA..alpha. angle intervals where i=n is
      n.sub.H spaces back from T.sub.stop and i=1 is (n-1) spaces beyond that.
      ##EQU29##
      4. Return.
PAC  Subroutine (.alpha..sub.orig, X)
PAO  1. .alpha..sub.F =(T.sub.m -T.sub.os -T.sub.pv)/K.
PAO  2. FR.sub.1c =FR.sub.1 (1-.OMEGA.K).
PAO  3. .alpha..sub.orig =-.alpha..sub.F -0.5(n-1+2n.sub.H).DELTA..alpha..
PAO  4. X=-.alpha..sub.orig -(F.sub.M /FR.sub.1c).
PAO  5. Return.
PAC  Subroutine (Peak Torque, T.sub.f)
PAO  1. Inspect torque at each angle pulse within one (1) .DELTA..alpha. from
      the stopping point. Find the highest and store under T.sub.f. If
      .DELTA..alpha.=3, for instance, four (4) locations are sampled, including
      the last data point.
PAO  2. Return.
PAC  Subroutine (.alpha..sub.f, T.sub.rst, T.sub.D)
PAO  1. If X.gtoreq.O, .alpha..sub.f =(F.sub.D -F.sub.o)/rFR.sub.1c T.sub.rst
      =T.sub.3 +u.DELTA..alpha., and T.sub.D =T.sub.rst +u .alpha..sub.f.
      Otherwise, .alpha..sub.f =-X+(F.sub.D -F.sub.M)/rFR.sub.1c.T.sub.rst
      =T.sub.3 +K.DELTA..alpha. and T.sub.D =T.sub.rst +u.alpha..sub.f +X(u-K).
PAO  2. Return.
PAC  Subroutine (end)
PAO  1. Verify tool has stopped.
PAO  2. .alpha..sub.act =(T.sub.stop -address)-(T.sub.6 -address).
PAO  3. Call Subroutine (peak torque, T.sub.f).
PAO  4. T.sub.1 =T.sub.1 -T.sub.pv.
PAO  5. .alpha..sub.T1 =(T.sub.stop -address)-(T.sub.1 -address).
PAO  6. If NLS indicated, go to (A).
PAO  7. If T.sub.f .ltoreq.T.sub.mm +u(.alpha..sub.act -.alpha..sub.y), go to
      (A).
PAO  8. F.sub.f =F.sub.D +(.alpha..sub.act -.alpha..sub.f) rFR.sub.1c. 9.
      T.sub.D '=T.sub.D (F.sub.f /F.sub.D)
PAO  10. .eta..sub.T =(T.sub.D '-T.sub.f)/T.sub.D '.
PAO  11. If .eta..sub.T .gtoreq.0.13, go to (C).
PAO  12. If (F.sub.f -F.sub.D)/F.sub.D .gtoreq.0.13, to go to (C).
PAO  13. Go to (B).
PAC  (A)
PAO  1. F.sub.f =F.sub.D -(T.sub.mm +u.alpha..sub.f -T.sub.f) rFR.sub.1c /u.
      ##EQU30##
PAC  (B)
PAO  1. If NLS indicated, give such output signal (NLS light, symbol, etc.).
PAO  2. Output "joint accepted" (light, symbol).
PAO  3. Output values of T.sub.f, .alpha..sub.T and FF (display and/or print,
      etc.).
PAO  4. Return to Start.
PAC  (C).
PAO  1. Report "joint unacceptable" (lights, error symbols, etc.).
PAO  2. Report T.sub.f and .alpha..sub.T1.
```

PAO 3. Go to Start

PAO 4. END

PAC Subroutine (Stall)

PAO 1. Call Subroutine (peak torque, T.sub.f). If T.sub.f /T.sub.o .ltoreq.0.87, give marginal tool signal, increment the counter.

PAO 2. Call Subroutine (end).

PAO 3. END

PAR The interface logic and amplifier circuits 154, 200, illustrated schematically in FIGS. 12A and 12B, serve to provide interfacing of data and control signals between the microprocessor unit 186, a conventional teletype console (not shown), the torque and angle transducers, 140, 142, and the air valve 132 controlling tool operation.

PAR Interfacing between teh teletype console and the microprocessor 186 is necessitated by the fact that the console receives and transmits data in a serial format while the microprocessor 186 receives and transmits in a parallel format. The interface logic and amplifier circuits 154, 200 include a universal asynchronous receiver transmitter circuit 212 which receives input data, such as a desired tension value F.sub.D, from the teletype console over the lines 214 in a serial or one bit at a time format, temporarily stores the data, and then transmits the data in parallel format over the lines 216 to the microprocessor 186. Thus a teletype console or other suitable means may provide an input 218 (FIG. 10) for variable empirical parameters, desired bolt tension and the like. Likewise, data from the microprocessor 186, which is to be printed out by the teletype console, is converted from the parallel format in which it is received from the microprocessor 186 over the lines 216 into the serial format for reception by the teletype console.

PAR Timing pulses for the control of the universal asynchronous receiver transmitter 212 as well as other components of the interface logic and amplifier circuits are provided from the microprocessor 186 over line 220, the pulse train being supplied to a conventional divider circuit 222 to produce a timing signal on the line 224 which is a pulse train of lesser but proportional rate to that supplied by the processor 186. Timing pulses are also provided to other components of the interface logic and amplifier circuit over the line 226. The microprocessor 186 also provides signals over the lines 228 which signals are generated in response to the program to control the transmission of data to and from the microprocessor 186. Thus, for example, when the microprocessor 186 is in condition to input data, such as the final desired torque value T.sub.D, a signal is transmitted from the microprocessor 186 over the lines 228 to a gating circuit 230 to furnish control inputs at 232, 234 to the universal asynchronous receiver transmitter 212. Control and status indication signals for the teletype console are also provided over the lines 236 and, via signal conditioner circuits 238, over the lines 240.

PAR FIG. 12B schematically illustrates that portion of the circuit which provides interfacing between the microprocessor 186, the torque and angle transducers 140, 142 and the air valve 132. Torque data from the torque transducer 140 (FIG. 10) is converted by the analog to digital converter 150 into twelve digit binary signals transmitted on the line 156. The particular microprocessor employed is, however, only capable of receiving an eight digit input. In order to permit transmission of torque data to the processor, a multiplexing arrangement is provided. Thus, the twelve digit output of the analog to digital converter 150 is supplied, through logic level buffers 242, 244 to a pair of steering gates 246, 248, the first four digits being supplied to the first inputs a of the gate 246 inputs a of the gate 248. The final four digits are supplied to the second inputs b of the gate 246. The corresponding second inputs b of the gate 248 are connected to ground, supplying a constant zero input. The eight line output 250 of the steering gates 246, 248 provides the torque data input to the microprocessor 186. The gates 246, 248 are controlled by signals on the lines 252, 254 to first pass the a input signals, i.e. the first eight bits of the torque signal, to the output lines 250 followed by the b input signals, i.e. the final four bits and four zeros. In addition to being supplied to the steering gates 246, 248, the torque data transmitted on lines 156 is also temporarily stored in the registers 256, 258, 260. These registers normally store the current torque value received from the analog to digital converter 150. A hold signal furnished by the microprocessor 186 over the line 262 actuates a latching circuit 264 to temporarily freeze the registers 256, 258, 260 permitting the torque values stored therein to be read over the lines 266. This arrangement permits reading of the torque data into the microprocessor 186 while updated torque data is being supplied from the analog to digital converter 150 without the danger of inadvertently reading into storage a data value which is a mixture of old and updated values.

PAR The analog to digital converter 150 supplies an end of conversion signal over line 268 which signal is supplied to the latching circuit 264 over the line 270 to reset the circuit 264 when transmission of a torque value has ended permitting updating of the registers 256, 258, 260. It should be noted that the analog to digital converter 150 is under the control of the microprocessor 186. Thus the microprocessor 186 provides an enable signal over the line 272 and a convert signal over the line 274 to a gate 276 which also receives, over a line 278, a tool rotation indicating signal, the origin of which will be described below. It will be understood that the enable and convert signals on lines 272, 274 are generated in response to the program controlling the microprocessor 186. The output of the gate 276 provides a start conversion signal to the analog to digital converter 150 over the line 280.

PAR As mentioned previously, the steering gates 246, 248 receive control signals over the lines 252, 254. These control signals are generated by a pair of gating circuits 282, 284. The gating circuit 282 is responsive to the end of conversion signal from the analog to digital converter 150 on the line 268 and an enable signal on the line 286 which signal is derived from the enable signal supplied by the microprocessor 186 over the line 272. The gating circuit 282 provides an input to the gating circuit 284 which also receives a signal over the line 288 from the microprocessor 186 in the form of a response back signal indicating that the previous data has been loaded into the microprocessor memory. In addition to controlling the steering gates 246, 248, the gating circuit 284 furnishes a data ready signal on the line 290 to the microprocessor 186. A further input 292 is provided for the logic gating circuit 282. The function of this input is to supply an event market to memory.

PAR The circuitry of FIG. 12B also provides interfacing between the angle transducer 142 and the microprocessor 186. The output signals of the angle transducer 142, in the form of sine and cosine signals are supplied over the line 158 to a converting circuit 294 which, in response to the transducer signals, generates an output pulse for each degree of rotation of the tool. This pulse signal on the line 296 provides the tool rotation indicating signal on the line 278 and also provides an input to a gating circuit over a line 298. The gating circuit 300 also receives an input signal from the microprocessor 186 over the line 302. This latter signal is present during the tool on period and goes off simultaneously with the tool off signal. The output 304 of the gating circuit 300 provides an input to the microprocessor 186 in the form of a pulse train with one pulse for each degree of tool rotation. The portion of this signal occurring after the input signal on the line 302 has been removed is a measure of the degree of tool overrun.

PAR Also included in the interface logic and amplifier circuits is a reset circuit 306 connected at 308 to a reset switch and providing output signals on lines 310, 312 which serve to reset various of the circuit components when the system is turned on. Signal conditioner circuits are also provided, with the circuits 314 providing interfacing between the microprocessor 186 and external controls for reset, gain, internal calibration and external calibration while the circuit 316 serves to interface the tool on signal from the microprocessor 186 over the line 318 with a solid state relay controlling the air valve 132, the output signal being provided over the line 320. A further circuit 322 is connected to a single pole double throw external switch 324 serving as an emergency or panic switch. The output 326 of the circuit 322 supplies an interrupt signal to the microprocessor 186.

PAR The components illustrated in FIGS. 12A and 12B are more completely identified in Table I, below:

TBL TABLE I

Identification or Standard Parts No.	Number
SN74LS04	1
SN7474L	3
SN7400L	5
SN7410L	7
SN7402L	9
Resistor Pack, 4.7K ohms	11
Potentiometer, 1K ohms	13
72747, Texas Instruments	15
Diode, 1N914	unmarked
SN7404L, Inverter	unmarked
SN7437L	17
Transistor	unmarked
SN74157L	246, 248
SN7498L	256, 258, 260
SN74161L	21
Resistor Pack, 15K ohm	23
SN7420L	25
SN7442L	27
TR1602	212
Transistor 2N2905	29
Resistors 33, 620 have 1/2 watt rating	unmarked

PAL The number adjacent each resistor is the resistance in ohms. All resistors except 33, 620 have 1/4 watt ratings. The number adjacent each capacitor is the capacitance in microfarads. The symbol "v" is used to designate e.g. of 1000 ohm capacity, to prevent damage to the component. The symbol "POR" is used to designate "power on reset" which means that power stays on about 1/2 second.

PAR Although the computer program and the circuitry of the interface amplifier section 200, previously described, are designed to activate a conventional teletype console in order to enter different values for the empirically determined parameters and to obtain a printed readout of certain calculated values such as the tension at the mid-point stop 62, it is apparent that the details thereof can be adapted to manipulate a display panel 204 as shown in FIG. 13. The display panel 204 is preferably located within view of the tool operator and comprises a base section 332 supported in any suitable fashion having a first group of signal lights 334, 336, 338, 340 indicating features of the joint 138. The signal light 334 indicates that the final desired tension value F.sub.D has been reached or that the final calculated tension value F.sub.final is within an acceptable range. The signal light 336 indicates that the joint has experienced non-linear strain. The signal light 338 indicates that the final calculated tension value F.sub.final is in an unacceptable range. With the lights 334, 336 lit, the deduction is that non-linear strain has occurred but that F.sub.final is acceptable. With the lights 336, 338 lit, the deduction is that non-linear strain has occurred but that F.sub.final is not acceptable. The light 340 is energized when the fastener exhibits a low tension rate as pointed out by the ratio of TR.sub.a /TR.sub.b.

PAR The display 204 also provides another group of lights 342, 344, 346 indicating quality control features. The light 342 is normally energized when the frequency of non-linear strain detection is minimal while the light 344 is energized when the frequency of non-linear strain detection is too high as pointed out in equation (79). The light 346 is energized when the final calculated tension F.sub.final differs significantly from the final desired tension values F.sub.D as pointed out by equation (90). It will be evident that additional lights may be provided to signal that other quality control procedures have indicated that the joint is subnormal. In the alternative, a single light may be used to signal joint abnormality and the microprocessor arranged to deliver a signal to another computer for record keeping purposes.

PAR The display 204 also comprises a third group of lights 348, 350, 352 indicating tool operating features. The light 348 indicates that the tool is functioning normally. The light 350 is energized when the ratio .delta..alpha./.delta..alpha..sub.p is too small or when the frequency of low ratio values becomes significant. Similarly when the ratio of .delta..alpha./.delta..alpha..sub.p is too large, or when the frequency of high ratio values becomes significant, the light 352 is energized.

PAC EXAMPLES

PAR A typical fastener system for use with this invention may comprise 5/16", 24 threads/inch, SAE grade 8 nuts and bolts. With this fastener pair and the modified Rockwell 63W air tool, the following values were found for the empirically determined parameters:

TBL

FR.sub.1 = 47 lb/degree
n = 14 r = 1.12
T.sub.o = 54 ft-lb
F.sub.M = 2900 lb
a = 11.6 degrees/ft-lb
F.sub.L = 1000 lb
c = -52.3 degrees
T.sub.1 = 5 ft-lb

.alpha..sub.d = 68 degrees
N.sub.k = 0.80
R = 0.93
T.sub.os = .4 ft-lb
.alpha..sub.y = 12 degrees
K.sub.o = .21 ft-lb/degrees
.alpha..sub.or = 20 degrees
.alpha..sub.K = 9 degrees
.DELTA..alpha. = 3 degrees

PAL Using these parameters and the described fasteners, which have a grip length of 2.44", and having a cadmium dichromate coating, the following data was developed using part of the technique here disclosed. The stiffness of the load washer used to measure tension directly was a 5.times.10.sup.6 lb/in and the clamped pieces were hardened steel. In running the tests reported in the following table, the angle option was used and execution was within +2 to -1 degrees, which corresponds to +104 to -52 pounds tension. The overall instrumentation repeatability and linearity, including the tension probe and the torque transducer, is estimated at 4%. The tension value reported in the second column was recorded approximately 15 seconds after the tool stopped. This is believed to involve a relaxation in the joint amounting to 1-2% of the recorded tension value.

PAR A statistical analysis of the data gathered on the twenty fasteners reported in Table II shows that the partial technique of this invention acts to control tension to within .+-.11.1% of the desired value in 99 out of 100 cases, or within 2.58 standard deviations. It should be thoroughly understood that the above data was taken with a program which does not include a number of features disclosed herein, including (1) the use of a second calculation for TR and .alpha..sub.origin ; (2) the provision of yield detection and shut off in response thereto; (3) the use of a curvature check of torque rate in the region where TR is calculated in order to identify and reject low tension rate fasteners; (4) the adjustment of the final tightening parameter for the effects of prevailing torque; and (5) the use of the quality control procedures disclosed herein which were not disclosed in copending application Ser. No. 712,554. The effect of these additions to the program is, of course, somewhat speculative. It is believed, however, that the inclusion thereof will reduce scatter still further.

PAR With the same joint and tool, the use of a torque control method would have to produce an average final torque of 22.68 ft-lbs to achieve an average final tension value of 6287 pounds. The observed deviations from average is +43.0 to -45.5%. Thus the torque control method would have produced a tension scatter of .+-.82.3% of the desired value in 99 out of 100 cases, assuming that the bolts would have been capable of accepting any tension. In reality, 10.4% of the bolts would have ruptured, producing no tension at the termination of tightening. Another 14.7% of the bolts

TBL TABLE II

Final Angle From
Exact .alpha..sub.T1
Exact Torque
LRM Set for 6,200
5 ft-lb for 6,200 lb
for 6,200 lb

```
                T.sub.final, ft-lb
                     .alpha..sub.T1, deg
                          Tension
                              Tension Condition
1       6355    28.91  108     105   28.22  As received
2       6179    32.33  109     109   32.44  As received
3       6517    34.00  107     101   32.18  As received
4       6356    27.61  107     104   26.93  As received
5       6274    28.23  105     104   27.90  As received
6       6147    30.65  108     109   30.91  As received
7       6221    28.91  106     106   28.81  As received
8       6205    30.77  108     108   30.75  As received
9       6151    28.85  102     103   29.08  As received
10      6742    31.02  109     99    28.37  As received
11      6377    16.38  90      87    15.93  Lubricated with SAE 10
                                            oil
12      6706    18.05  96      87    17.18  Lubricated with SAE 10
                                            oil
13      6407    16.81  100     96    16.27  Lubricated with SAE 10
                                            oil
14      6103    12.16  70      72    12.35  Lubricated with SAE 10
                                            oil
15      6045    15.14  88      91    15.53  Lubricated with SAE 10
                                            oil
16      6030    16.00  87      90    16.45  Lubricated with SAE 10
                                            oil
17      5634    14.64  84      95    15.59  Lubricated with SAE 10
                                            oil
18      5891    15.20  83      89    15.73  Lubricated with SAE 10
                                            oil
19      6618    17.68  91      83    16.88  Lubricated with SAE 10
                                            oil
20      6381    16.56  91      88    16.09  Lubricated with SAE 10
                                            oil
Average 6267    21.31  97.5    96.3  22.68
Observed
        +7.8    +59.5  +11.9   +13.2 +43.0
deviation from
        -10.1   -42.9  -28.2   -25.2 -45.5
Avg. %
One std.deviation, %
        4.3     --     --
                             ##STR1##
                                 31.9
 of Avg.                     on tension
```

would terminate in the plastic zone, i.e. past the yield point.

PAR With the same joint and tool, the use of a turn-of-the-nut method would have to advance the nut 96.3.degree. from a threshold torque of 5 ft-lbs to achieve a final tension value of 6267 pounds. The observed deviation is +13.2 to -25.2%. Thus, a turn-of-the-nut method would have produced a tension scatter of .+-.21.7% of the desired value in 99 out of 100 cases. It is interesting to note that the selection of 6200 pounds for a bolt having an elastic limit of 695C pounds appears to be optimum because only about 0.6% of these bolts would end up in the plastic zone.

PAR In another test on the same joint, the selected final tension F.sub.D was 90% nominal proof or 6300 pounds. In this test, such refinements as a second pass for the determination of TR and .alpha..sub.origin was used, a non-linear strain procedure and the remaining quality control procedures were available. To obtain independent tension values, a load washer was incorporated into the joint. The load washer was carefully calibrated for mean setting and reading scatters were measured under the same load condition existing in the joint. Table III shows the experimental rasults. The data reported excludes any abnormal joints indicated as unacceptable by the system. Accordingly, any defective joint that would have passed a torque strategy or a turn-of-the-nut strategy is excluded even though conventional systems would not have rejected these fasteners. Thus, the reported data on torque control and turn-of-the-nut strategies are better than would be expected in practice. The reported results are corrected for load washer scatter of approximately 1.8%, one standard deviation.

TBL TABLE III

Tension and Torque Scatter
One Standard Deviation

	Tension Scatter, %	Torque Scatter	
Lube Condition	LRM	T-O-T-N	at 6300 lbs. %
dry	2.2	6.4	18.5
oiled	2.4	5.0	13.8
mixed	2.6	8.2	29.9

PAR Although the data of Table III appears to be substantially different than the data of Table II, the major difference lies in the adjustment in Table III of the load washer error of 1.8%, one standard deviation, whereas this adjustment has not been made in Table II.

PAR It has been learned that torque scatter at constant tension is quite different from tension scatter at constant torque. Whereas torque scatter has a normal distribution, tension scatter at constant torque has a shifted or unsymmetrical distribution. The mixed lubrication condition, which involves the largest variation in friction, has been chosen to show the expectations in achieving tension control with various strategies. Referring to FIG. 14, the probability distributions in finite tension bands are illustrated. It will be apparent that the technique of this invention is substantially superior to the torque control and turn-of-the-nut strategies of the prior art.

PAC ANALOG EMBODIMENT

PAR Referring to FIG. 15, there is illustrated another device 354 for implementing the technique of this invention. The basis of this approach is equation (7) where the value of dF/d.alpha. indicates the tension rate. Rewriting equation (7),

##EQU31##

If d/d.alpha. log T can in some fashion be determined, F in equation (99) can become the final desired tension value F.sub.D or the tension value F.sub.so at the point of shut off command while dF/d.alpha. is an empirically determined tension rate FR.sub.3 which is an appropriate average of FR.sub.1 and FR.sub.2 over the angle interval in question. It will be apparent that

##EQU32##

pickup 356 of any suitable type, such as a tachometer, for continuously sensing a value for d.alpha./dt, which is the speed the fastener is being tightened.

PAR A torque transducer 358 continuously senses the value of running torque T. The transducer 358 may be of the same type as the transducer 140. A logarithmic amplifier 360, such as is available from Analog Devices, Inc., Norwood, Mass., under the designation of Logarithmic Amplifier, Model 755, is connected to the torque transducer 358 by a suitable connection 362. The logarithmic amplifier 360 continuously converts the sensed value of running torque T into a continuous signal representative of log T.

PAR A time differentiating device 364 is connected to the logarithmic amplifier 360 by a suitable lead 366 and continuously differentiates the signal from the logarithmic amplifier with respect to time in order to obtain the differential of the logarithm of running torque d/dt log T. The time differentiating device 364 may be of any suitable type, such as an operational amplifier 368 in parallel with a capacitor 370. A suitable operational amplifier is available from Analog Devices, Inc., Norwood, Mass., under the designation Operational Amplifier, Model 741.

PAR The signal from the time differentiating device 364 is delivered through a lead 372 to a low pass filter 374 which acts to smooth out the signal from the time differentiating device 364 thereby removing some of the noise inherent in the torque signal from the transducer 358.

PAR The angular speed pickup 356 and the low pass filter 374 are connected by suitable leads 376, 378 to an analog divide device 380 such as may be obtained from Analog Devices, Inc., Norwood, Mass. under the designation Divide Module 463B. The leads 376, 378 are connected to the divide device to produce an output signal along a lead 382 consisting of the ratio
##EQU33##
As indicated in equation (100), this signal is representative of d/d.alpha. log T. When the value of

EQU d/d.alpha. log T.ltoreq.FR.sub.3 /F.sub.so, when T.gtoreq.T.sub.1 (101)

PAL where F.sub.so is the tension value in the bolt at the time of shut off, and T.sub.1 is an early predetermined torque value, e.g. about 20-30% of the average final torque, the tool is commanded to shut off. It will be evident that the threshold may be measured in terms of angle, e.g. where .alpha.>.alpha..sub.1, rather than torque.

PAR Because the tool will overrun after shut off, the value of F.sub.so is selected so that average tool overrun advances the fasteners to the final desired tension value F.sub.D. The average tool overrun may be determined empirically or from

EQU .DELTA.F.sub.so =(d.alpha./dt.sub.so)(.DELTA.t)FR.sub.3 (102)

PAL where (d.alpha./dt.sub.so) is the average speed of the tool at shut off, .DELTA.F.sub.so is the average additional tension due to overrun, and .DELTA.t is the time delay between the giving of the shut off command and the closing of the air valve. Thus,

EQU F.sub.so =F.sub.D -.DELTA.F.sub.so. (103)

PAR Because F.sub.so and FR.sub.3 are assumed to be a constant, the ratio of FR.sub.3 /F.sub.so is obviously constant. Thus, a constant signal representative of FR.sub.3 /F.sub.so is placed on a lead 384. The leads 382, 384 are connected to another divide device 386. When the output signal from the divide device 386 on a lead 388 becomes unity, an amplifier 390 is triggered to energize a solenoid catch 392 to allow the solenoid spring (not shown) to close the air valve.

PAR Although the analog device 354 of FIG. 15 is not believed to have the accuracy of the digital device 126, it is apparent that it has the advantage of simplicity, both physical and operational. The analog device

354 operates closer to the theoretical basis of the invention and contains fewer assumptions and simplifications. Some of the disadvantages of a simple analog device, such as the inability to vary the overrun prediction and the noise reduction in the filter 374, are capable of being surmounted by more sophisticated analog techniques as will be apparent to those skilled in the art.

PAR As heretofore disclosed, the analog device 354 is designed to deliver a running torque signal T which is converted into a signal representative of log T which is then differentiated with respect to time to give d/dt log T. As explained previously, it is desirable to adjust the running torque value T by deducting the values of offset torque T.sub.os and prevailing torque T.sub.pv. It will be appreciated that this can be readily accomplished by suitable analog devices placed in the connection 362 between the torque transducer 358 and the log device 360.

PAR As will be apparent to those skilled in the art, the technique of this invention can be used to monitor other tightening strategies thereby determining the accuracy thereof in tightening fasteners to a final desired stress value. This may readily be accomplished by modifying the amplifier section 200 in order not to manipulate the air valve solenoid in response to the tightening parameter.

PAR Although the invention has been described in its preferred forms with a certain degree of particularity, it is understood that the disclosure of the preferred embodiments has been made only by way of example and numerous changes in the details of construction, combination and arrangement of parts, and mode of operation may be resorted to without departing from the spirit and scope of the invention as hereinafter claimed. It is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of patentable novelty exist in the invention disclosed.

CLMS

STM I claim:

NUM 1.

PAR 1. Apparatus for tightening seriatim a multiplicity of substantially identical joints having components including at least one threaded fastener to substantially the same final desired stress value, below the yield point of .[.any component.]. .Iadd.all joint components .Iaddend.that can be correlated with stress, appearing in the fastener, comprising

PA1 a powered instructable tool, capable of terminating tightening in response to an instruction which varies from one fastener to the next, for applying torque to the fastener and tightening the same;

PA1 means for sensing the torque applied to the fastener at various angles of advance;

PA1 means responsive to the torque and angle sensings for determining, while tightening below the yield point of .[.any.]. .Iadd.all .Iaddend.joint .[.component.]. .Iadd.components .Iaddend.that can be correlated with stress, a tightening parameter value, variable from one fastener to the next, sufficient to tighten each fastener to the final desired stress value; and

PA1 means for instructing the tool to terminate tightening of each fastener in response to the determined tightening parameter value.

NUM 2.

PAR 2. The apparatus of claim 1 wherein the determining means comprises means for determining the torque values sufficient to tighten each fastener to the final desired stress value.

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      any joint component that can be correlated with stress from the calculated
      stress; and
PA1  means for instructing the tool to tighten the fastener to the determined
PAR   parameter value..]. 13. The apparatus of claim .[.12.]. .Iadd.52
      .Iaddend.wherein the calculating means and the determining means
      respectively comprises means for calculating the stress and means for
      determining the tightening parameter value in a time period commencing
      with the onset of threading and stopping with the termination of
PAR   tightening. 14. The apparatus of claim 13 wherein the time period is less
      than two minutes.  .[.15. A method of tightening a multiplicity of
      substantially identical joints having components including at least one
      threaded fastener to a final desired stress value below the yield point of
      any joint component that can be correlated with stress, comprising
PA1  tightening the fastener with an instructable powered tool;
PA1  sensing torque at various angles of advance during tightening;
PA1  determining the torque rate of the fastener from the sensed values of
      torque and angle;
PA1  calculating the stress appearing in the fastener at least at least at one
      instant of tightening below the yield point of any joint component that
      can be correlated with stress from the determined torque rate and from
      sensed torque;
PA1  determining the value of a tightening parameter sufficient to tighten the
      fastener to the final desired stress value below the yield point of any
      joint component that can be correlated with stress from the calculated
      stress;
PA1  instructing the tool to tighten the fastener in response to the determined
      parameter; and
PAR  terminating tightening in response to the determined parameter..]. 16. The
      method of claim .[.15.]. .Iadd.53 .Iaddend.further comprising predicting
      the amount of tool overrun and wherein the instructing step comprises
      instructing the tool to tighten each fastener in response to the
      determined parameter and the amount of tool overrun, and the terminating
      step comprises terminating tightening in response to the determined
PAR   parameter and the amount of tool overrun. 17. The method of claim .[.15.].
      .Iadd.53 .Iaddend.comprising the step of empirically determining the value
      of FR.sub.1, FR.sub.2 and T.sub.os where FR.sub.1 is stress rate in a low
      stress range, FR.sub.2 is stress rate in a higher stress range and
      T.sub.os is offset torque, and the calculating step comprises calculating
      the stress from the empirically determined values of FR.sub.1, FR.sub.2
      and T.sub.os as well as from the sensed values of torque and angle.
      .[.18. Apparatus for tightening a multiplicity of substantially identical
      joints having components including at least one threaded fastener to a
      final desired stress value below the yield point of any joint component
      that can be correlated with stress, comprising
PA1  a powered instructable tool for tightening the fastener;
PA1  means for sensing torque at various angles of advance during tightening;
PA1  means for determining the torque rate of the fastener from the sensed
      values of torque and angle;
PA1  means for calculating the stress appearing in the fastener at least at one
      instant of tightening below the yield point of any joint component that
      can be correlated with stress from the determined torque rate and the
      sensed torque;
PA1  means for determining the value of a tightening parameter sufficient to
      tighten the fastener to the final desired stress value below the yield
      point of any joint component that can be correlated with stress; and
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PAR   determined parameter..]. 19. The apparatus of claim .[.18.]. .Iadd.54
      .Iaddend.further comprising means for predicting the amount of tool
      overrun, and wherein the instructing means comprises means for instructing
      the tool to tighten the fastener in response to the determined parameter
PAR   and the amount of tool overrun. 20. The apparatus of claim .[.18.].
      .Iadd.54 .Iaddend.wherein the determining means comprises means for
      determining the torque value sufficient to tighten the fastener to the
PAR   final desired stress value. 21. The apparatus of claim .[.18.]. .Iadd.54
      .Iaddend.wherein the determining means comprises means for determining the
      angle of threading advance sufficient to tighten the fastener to the final
PAR   desired stress value. 22. The apparatus of claim .[.18.]. .Iadd.54
      .Iaddend.wherein the fastener is a bolt and the calculating means
PAR   comprises means for calculating the tension in the bolt. 23. Apparatus for
      tightening a joint having components including at least one threaded
      fastener, comprising
PA1  a powered tool for tightening the fastener;
PA1  means for monitoring stress in the fastener including
PA2  means for sensing torque and angle while tightening; and
PA2  data processor means for calculating stress in the fastener below the yield
      point of .[.any.]. .Iadd.all .Iaddend.joint .[.component.].
      .Iadd.components .Iaddend.that can be correlated with stress from sensed
      values of torque and angle; and
PA1  means for terminating tightening in response to a tightening parameter
PAR   related to monitored stress. 24. The apparatus of claim 23 wherein the
PAR   tightening parameter is torque. 25. The apparatus of claim 23 wherein the
PAR   tightening parameter is angle. 26. The apparatus of claim 23 wherein the
PAR   tightening parameter is a linear combination of torque and angle.
      27. Apparatus for tightening substantially identical threaded fasteners in
      production lots to the same final desired stress value .+-.15%, comprising
PA1  a powered instructable tightening tool having a source of energy, means for
      connecting and disconnecting the tool to the energy source, a torque
      sensor and an angle sensor;
PA1  a data processor connected to the torque and angle sensors including
PA1  means for determining a mid-point stop of the fasteners at least about 0.4
      elastic limit of the weakest joint component from a sensed value of torque
      and angle and means for instructing the tool to halt tightening at the
      mid-point stop;
PA1  means for calculating a torque rate in a region adjacent the mid-point stop
      from sensed values of torque and angle;
PA1  means for calculating the stress appearing in the fastener at a location
      between the onset of tightening and the mid-point stop from a sensed value
      of torque at the location, the calculated torque rate and an empirically
      determined stress rate for the region including 0.1-0.5 elastic limit;
PA1  means for calculating a value of a tightening parameter sufficient to
      tighten the fastener to a final desired stress value from an empirically
      determined stress rate above the region 0.1-0.5 elastic limit;
PA1  means controlled by the data processor for resuming tightening; and
PA1  means responsive to the value of the tightening parameter for terminating
PAR   tightening adjacent the final desired value. 28. The apparatus of claim 27
      further comprising means for calculating the amount of tool overrun
      adjacent the final desired stress value and wherein the tightening
      terminating means comprises means responsive to the value of the
      tightening parameter and the amount of tool overrun for terminating
PAR   tightening adjacent the final desired stress value. 29. The apparatus of
      claim 27 wherein the means for calculating the tightening parameter value
      comprises means for dividing the difference between the final desired
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stress value and the stress calculated at the location by the empirically
PAR determined stress rate above the region 0.1-0.5 elastic limit. 30. The
apparatus of claim 27 wherein the means for calculating the tightening
parameter value comprises means for dividing the difference between the
final desired stress value and the stress at an angular position adjacent
the location by the empirically determined stress rate above the region
PAR 0.1-0.5 elastic limit. 31. The apparatus of claim 27 wherein the
PAR tightening parameter is in units of angle. 32. The apparatus of claim 27
PAR wherein the tightening parameter is in units of torque. 33. The apparatus
of claim 27 wherein the torque rate calculating means includes means for
storing and recalling the sensed values of torque and angle and means for
PAR determining an average torque rate from the sensings. 34. A method of
tightening a joint including a threaded fastener, comprising
PA1 tightening the fastener;
PA1 sensing torque applied to the fastener and the angle of threading advance;
PA1 determining, during tightening, the origin of stress in the fastener from
the sensed values of torque and angle;
PA1 determining a shut off parameter based on the origin of stress; and
PAR terminating tightening in response to the shut off parameter. 35. Apparatus
for tightening a joint including a threaded fastener, comprising
PA1 a powered tool for tightening the fastener;
PA1 means for sensing the torque applied to the fastener and the angle of
threading advance;
PA1 means for determining, during tightening, the origin of stress in the
fastener pair from sensed values of torque and angle;
PA1 means for determining, during tightening, a shut off parameter based on the
origin of stress; and
PA1 means for terminating operation of the powered tool in response to the shut
PAR off parameter. 36. A method of tightening seriatim a multiplicity of
substantially identical production joints including at least one threaded
fastener, comprising
PA1 empirically determining, prior to tightening the production joints, at
least one joint characteristic;
PA1 applying torque to the fastener for tightening the production joint;
PA1 determining, while tightening below the yield point of .[.any.]. .Iadd.all
.Iaddend.joint .[.component.]. .Iadd.components .Iaddend.that can be
correlated with stress, a tightening parameter based on the empirically
determined joint characteristic, which tightening parameter varies from
one joint to the next; and
PAR terminating tightening in response to the tightening parameter. 37. The
method of claim 36 wherein the empirically determined joint characteristic
PAR is the fastener tension rate. 38. The method of claim 36 wherein the
PAR empirically determined joint characteristic is the offset torque.
39. Apparatus for tightening seriatim a multiplicity of substantially
identical production joints including at least one threaded fastener and
having at least one empirically determinable joint characteristic,
comprising
PA1 means for applying torque to the fastener;
PA1 means for determining, while tightening below the yield point of .[.any.].
.Iadd.all .Iaddend.joint .[.component.]. .Iadd.components .Iaddend.that
can be correlated with stress, a tightening parameter based on the
empirically determined joint characteristic, which tightening parameter
varies from one joint to the next, including
PA1 means for delivering a signal to the determining means representative of
the empirically determinable joint characteristic; and

PAR . A method of tightening seriatim a multiplicity of substantially
identical production joints including at least one threaded fastener,
comprising
PA1 determining, prior to tightening the production joints, at least one
tightening tool characteristic;
PA1 applying torque to the fastener with the tightening tool for tightening the
production joint;
PA1 determining, while tightening, a tightening parameter based on the
determined tool characteristic, which tightening parameter varies from one
joint to the next; and
PAR terminating tightening in response to the tightening parameter. 41. The
method of claim 40 wherein the determined tool characteristic is a
PAR function of tool overrun. 42. The method of claim 41 wherein the
PAR tightening tool characteristic is the stall torque of the tool. 43. The
method of claim 41 wherein the tightening tool characteristic is the angle
PAR overrun of the tightening tool under no torque conditions. 44. Apparatus
for tightening seriatim a multiplicity of substantially identical
production joints including at least one threaded fastener, comprising
PA1 a tightening tool for applying torque to the fastener;
PA1 means for determining, while tightening, a tightening parameter based on a
tool characteristic, which tightening parameter varies from one joint to
the next, including
PA1 means for delivering a signal to the determining means representative of
the determined tool characteristic; and
PA1 means for terminating tightening in response to the tightening parameter.
PAR .Iadd.45. The method of claim 57 wherein said joint characteristic is
determined from one or more actual, representative joints. .Iaddend.
.Iadd.46. The method of claim 57 wherein the joint characteristic is
PAR proportional to the joint tension rate. .Iaddend. .Iadd.47. The apparatus
of claim 58 wherein the joint characteristic is proportional to the joint
tension rate. .Iaddend. .Iadd.48. The apparatus of claim 58 further
comprising means for determining, after the onset of tightening, a
parameter proportional to the torque rate of the fastener. .Iaddend.
.Iadd.49. The apparatus of claim 58 wherein the determining means
comprises means for combining the determinable joint characteristic and
the torque rate proportional parameter. .Iaddend. .Iadd.50. The apparatus
of claim 58 wherein the determinable joint characteristic is the joint
tension rate, said apparatus further comprising means for determining,
after the onset of tightening, the torque rate of the fastener and the
determining means comprising means for combining the joint tension rate
PAR and the determined torque rate. .Iaddend. .Iadd.51. A method of
tightening a multiplicity of substantially identical joints having
components including at least one threaded fastener to a final desired
stress value below the yield point of all joint components that can be
correlated with stress, including:
PA1 tightening the fastener with an instructable tool;
PA1 sensing torque at various angles of advance during tightening below the
yield point of all joint components that can be correlated with stress;
PA1 calculating, while tightening below the yield point of all joint components
that can be correlated with stress, the stress appearing in the fastener
at least at one instant of tightening below the yield point of all joint
components that can be correlated with stress from the sensed values of
torque and angle;
PA1 determining the value of a tightening parameter sufficient to tighten the
fastener to the final desired stress value below the yield point of all
joint components that can be correlated with stress from the calculated

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      stress;
PA1  instructing the tool to tighten the fastener to the determined parameter;
      and
PA1  terminating tightening in response to the attainment of the determined
      parameter. .Iaddend. .Iadd.52. Apparatus for tightening seriatim a
      multiplicity of substantially identical joints having components including
      at least one threaded fastener to substantially the same final desired
      stress value below the yield point, comprising:
PA1  a powered instructable tool for tightening the fastener;
PA1  means for sensing torque at various angles of advance during tightening
      below the yield point of all joint components that can be correlated with
      stress;
PA1  means for calculating the stress appearing in the fastener at least at one
      instant of tightening below the yield point of all joint components that
      can be correlated with stress from the sensed values of torque and angle;
PA1  means for determining a tightening parameter value sufficient to tighten
      the fastener to the final desired stress value below the yield point of
      all joint components that can be correlated with stress from the
      calculated stress; and
PA1  means for instructing the tool to tighten the fastener to the determined
      parameter value. .Iaddend. .Iadd.53. A method of tightening a multiplicity
      of substantially identical joints having components including at least one
      threaded fastener to a final desired stress value below the yield point of
      all joint components that can be correlated with stress, comprising:
PA1  tightening the fastener with an instructable powered tool;
PA1  sensing torque at various angles of advance during tightening;
PA1  determining the torque rate of the fastener from the sensed values of
      torque and angle;
PA1  calculating the stress appearing in the fastener at least at one instant of
      tightening below the yield point of all joint components that can be
      correlated with stress from the determined torque rate and from sensed
      torque;
PA1  determining the value of a tightening parameter sufficient to tighten the
      fastener to the final desired stress value below the yield point of all
      joint components that can be correlated with stress from the calculated
      stress;
PA1  instructing the tool to tighten the fastener in response to the determined
      parameter; and
PA1  terminating tightening in response to the determined parameter. .Iaddend.
PAR   .Iadd.54.  Apparatus for tightening a multiplicity of substantially
      identical joints having components including at least one threaded
      fastener to a final desired stress value below the yield point of all
      joint components that can be correlated with stress, comprising:
PA1  a powered instructable tool for tightening the fastener;
PA1  means for sensing torque at various angles of advance during tightening;
PA1  means for determining the torque rate of the fastener from the sensed
      values of torque and angle;
PA1  means for calculating the stress appearing in the fastener at least at one
      instant of tightening below the yield point of all joint components that
      can be correlated with stress from the determined torque rate and the
      sensed torque;
PA1  means for determining the value of a tightening parameter sufficient to
      tighten the fastener to the final desired stress value below the yield
      point of all joint components that can be correlated with stress; and
PA1  means for instructing the tool to tighten the fastener in response to the
PAR   determined parameter. .Iaddend. .Iadd.55.  Apparatus for tightening a
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threaded fastener in a joint including the fastener, the apparatus comprising:

PA1 a tightening tool for imparting input characteristics including torque and rotation to the fastener to tighten the fastener, the tool being capable of terminating the tightening of the fastener in response to an instruction incorporating a directly measurable tightening related parameter which can vary from one to another of ostensibly alike joints in tightening fasteners therein to the same final tension;

PA1 means for sensing at least one of the input characteristics;

PA1 means for determining from the sensed input characteristics, after the onset of tightening and while below the yield point of all joint components that can be correlated with stress, that value of the tightening related parameter which is representative of the amount of tightening required to tighten the fastener to the selected final tension; and

PA1 means for transmitting to the tool an instruction that will cause the tool to terminate the tightening of the fastener in response to the reaching of the determined value of the tightening related parameter. .Iaddend. .Iadd.56. Apparatus for tightening a threaded fastener in a joint including the fastener, comprising:

PA1 a power instructable tool, capable of terminating tightening in response to an instruction which varies from one fastener to the next, for imparting input characteristics including torque and rotation to the fastener;

PA1 means for sensing at least one of the input characteristics;

PA1 means responsive to the sensing means for determining after the onset of tightening and while below the yield point of all joint components that can be correlated with stress, a tightening parameter value, variable from one fastener to the next, sufficient to tighten each fastener to the same final desired stress value; and

PA1 means for terminating tightening of the fastener in response to the determined tightening parameter value. .Iaddend. .Iadd.57. A method of tightening a threaded fastener in a joint including the threaded fastener, comprising:

PA1 determining, prior to tightening the fastener, at least one joint characteristic;

PA1 applying torque to the fastener for tightening the same;

PA1 determining, after the onset of tightening and while below the yield point of all joint components which can be correlated with stress, a tightening parameter based on the determined joint characteristic, which tightening parameter varies from one joint to the next; and

PA1 terminating tightening in response to the tightening parameter. .Iaddend.

PAR .Iadd.58. Apparatus for tightening a threaded fastener in a joint including the fastener and having a determinable joint characteristic, comprising:

PA1 means for applying torque to the fastener;

PA1 means for determining, after the onset of tightening and while below the yield point of all joint components that can be correlated witn stress, a tightening parameter based on the joint characteristic, which tightening parameter varies from one joint to the next; and

PA1 means for terminating tightening in response to the tightening parameter.

PAR .Iaddend. .Iadd.59. Apparatus for tightening seriatim a multiplicity of substantially identical joints having components including at least one threaded fastener to substantially the same final desired stress value, below the yield point of all components that can be correlated with stress, appearing in the fastener, comprising a powered instructable tool, capable of terminating tightening in response to an instruction which varies from one fastener to the next, for applying torque to the fastener and tightening the same; means for sensing the torque applied to the fastener at various angles of advance; means responsive to the torque and angle sensings for determining, while tightening at a value below which any of the aforesaid joint components are alterable in configuration by the application of a load thereto, a tightening parameter value, variable from one fastener to the next, sufficient to tighten each fastener to the final desired stress value; and means for instructing the tool to terminate tightening of each fastener in response to the determined tightening parameter value. .Iaddend.

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PATN
WKU  044455003
SRC  6
APN  4288505
APT  1
ART  164
APD  19820930
TTL  Stroke treatment utilizing extravascular circulation of oxygenated
      synthetic nutrients to treat tissue hypoxic and ischemic disorders
ISD  19840501
NCL  6
ECL  1
EXA  Swisher; Nancy A. B.
EXP  Lesmes; George F.
NDR  10
NFG  13
DCD  20000719
INVT
NAM  Osterholm; Jewell L.
CTY  Radnor Township, Delaware County
STA  PA
ASSG
NAM  Thomas Jefferson University
CTY  Philadelphia
STA  PA
COD  02
RLAP
COD  74
APN  354346
APD  19820303
RLAP
COD  82
APN  275117
APD  19810618
RLAP
COD  89
APN  275116
APD  19810618
PSC  01
PND  4393863
RLAP
COD  90
APN  139886
APD  19800414
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PND  4378797
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RLAP
COD  90
APN  275116
RLAP
COD  92
RLAP
COD  84
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APN  139886
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OCL  128   1R
XCL  424355
XCL  424153
XCL  604 62
EDF  3
ICL  A61K 3100
ICL  A61M  514
FSC  128
FSS  1 R;
FSC  424
FSS  355;153
FSC  604
FSS  52
UREF
PNO  3482575
ISD  19691200
NAM  Claff et al.
OCL  128214
UREF
PNO  3516410
ISD  19700600
NAM  Hakim
OCL  128350
UREF
PNO  3583387
ISD  19710600
NAM  Garner
OCL  128   1
UREF
PNO  3626950
ISD  19711200
NAM  Schulte
OCL  128350
UREF
PNO  3669094
ISD  19720600
NAM  Heyer
OCL  128   2
UREF
PNO  3669116
ISD  19720600
NAM  Heyer
OCL  128350
UREF
PNO  3690323
ISD  19720900
NAM  Wortman et al.
OCL  128350
UREF
PNO  3753865
ISD  19730800
NAM  Belzer
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PNO  3823091
ISD  19740700
NAM  Samejima
OCL  252312
UREF
PNO  3894641
ISD  19750700
NAM  El-Shafei
OCL  128350
UREF
PNO  3941119
ISD  19760300
NAM  Corrales
OCL  128  2
UREF
PNO  3946731
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NAM  Lichtenstein
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ISD  19761100
NAM  Chabert et al.
OCL  424325
UREF
PNO  4110474
ISD  19780800
NAM  Lagow et al.
OCL  424350
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PNO  4148314
ISD  19790400
NAM  Yin
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PNO  4163734
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NAM  Sorensen et al.
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ISD  19791100
NAM  Marx et al.
OCL  128214
UREF
PNO  4173654
ISD  19791100
NAM  Scherer
OCL  424350
OREF
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PAL  Doss et al., Microvascular Research 13, pp. 253-260, (1977).
PAL  Nordstrom et al., Acta Physiol. Scand., (1977).
PAL  Slezyo et al., Adv. Exp. Med. Biol., 78: 261-269, (1977).
PAL  Clark et al., Microvasc. Res., 8:320-340, (1974).
PAL  Abstract No. [85] Pool Rounds.
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PAL Schutz et al., "Brain Mitochondrial Function After Ischemia and Hypoxia", Arch Neurol., vol. 29, pp. 417-419, (Dec. 1973)..
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PAL Mizoi et al., "Experimental Study of New Cerebral Protective Substances

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      Ischemic-Hypoxic Cat", Stroke, vol. 8, No. 3, pp. 371-373, (May-Jun.
      1977).
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      Oedema I. Measurement of Oedema Clearance into Ventricular CSF", Acta
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      with a Perfluorochemical Blood Substitute, Fluosol-DA 20%", Crit. Care
      Med. 8, p. 738, (1980).
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      Lowering in Normocapnic Conditions", J. of Applied Physics, vol. 47, pp.
      369-376, (Jul.-Sep. 1979).
PAL   Abstract No. [85] Pool Rounds, (one p.).
PAL   Booklet, "William Harvey Introduces a New Geometry for Oxygen Performance."
PAL   State of the Art Symposium, "Artificial Blood", National Institutes of
      Health, Apr. 5-6, 1974, Federation Proceedings, vol. 34, No. 6, pp.
      1428-1517, (1975).
PAL   Nordstrom et al., Acta Physiol. Scand., (1977).
PAL   Siezyo et al., Adv. Exp. Med. Biol. 78: 261-269, (1977).
PAL   Clark et al., Microvasc. Res. 8:320-340, (1974).
PAL   S. A. Gould et al., Fed. Proc. 40:2038, (1981).
PAL   Doss et al., Microvascular Research 13, pp. 253-260, (1977).
LREP
FRM   Woodcock, Washburn, Kurtz, Mackiewicz & Norris
ABST
PAL   A novel acute care cerebral support system and method for treating severly
      ischemic brains is disclosed wherein an oxygenated nutrient emulsion is
      circulated through at least a portion of the ventriculo-subarachnoid
      spaces. The nutrient emulsion contains an oxygenatable non-aqueous
      component, an aqueous nutrient component, an emulsification component, and
      other components which render physiologic acceptability to the nutrient
      emulsion. The disclosed system and method have been shown to effectively
      exchange oxygen, carbon dioxide, glucose, and other metabolites in
      severely stroked brains. Significant restoration of oxidative metabolism
      and electrographic activity result from the disclosed treatment. Methods
      for producing the nutrient emulsion and a system for delivering that
      emulsion to the cerebrospinal pathway are also disclosed. Additionally,
      novel diagnostic methods for diagnosing the physiologic state of
      hypoxic-ischmeic and other diseased neurologic tissue during treatment are
      provided.
PARN
PAC   CROSS REFERENCE TO RELATED APPLICATIONS
PAR   The present application is a divisional application of Ser. No. 354,346,
      filed Mar. 3, 1982, which is a continuation-in-part of U.S. patent
      application Ser. No. 139,886, filed Apr. 14, 1980, now U.S. Pat. No.
      4,378,797, entitled "Extravascular Circulation Oxygenated Synthetic
      Nutrients to Treat Tissue Hypoxic and Ischemic Disorders", as well as Ser.
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No. 275,116, filed June 18, 1981, now U.S. Pat. No. 4,393,863 and Ser. No. 275,117, also filed June 18, 1981, which in turn are divisionals of Ser. No. 139,886.

BSUM

PAC BACKGROUND OF THE INVENTION

PAR Cerebrovascular accident, a disease commonly known as "stroke", remains the third leading cause of death, and probably constitutes the single largest category of long term disability in this country. In spite of current medical knowledge and available treatments, a major central nervous system vascular occlusion is quickly attended by irreversible damage to the affected brain region(s). A "completed stroke" is manifest by a fixed and permanent neurological deficit. Millions of dollars have been expended in stroke research and care by Federal and private agencies without a single substantial gain in our present chemotherapeutic abilities for a completed stroke.

PAR On a clinical level, once vascular flow in any portion of the central nervous system has ceased for longer than a few minutes, a permanent "stroke" invariably follows. It is not currently possible to recover substantial neural function with clinical ischemia of 5-7 minutes duration. An exquisite neuronal sensitivity to oxygen deprivation has been blamed for this ultra-short stroke irreversibility. Neurons do indeed have meager metabolic storage and are unable to meet energy needs by anerobic means. Well accepted concepts hold that such permissible cerebral ischemia times are critical and neurons must quickly be resupplied or metabolic infarction will result. While clinically true, recent laboratory investigations have addressed the problems of ischemic vascular and neuronal reactions separately with considerably different results. Recently reported studies indicate neurons are not as sensitive as previously believed. Indeed, it has been suggested that neurons can withstand global ischemia for 1 hour or longer. K. A. Hossman, P. Kleihues, Arch. Neurol. 29, 375-389 (1973). If the clinical and experimental observations are to be reconciled, one hypothesis is that long-term damage results from vascular rather than neuronal sensitivity to oxygen deprivation. It is known that secondary reactive changes appear within the microcirculation after sufficient stagnation. A. Ames III, R. L. Wright, M. Kowada, J. M. Thurston, G. Majno, Am. J. Pathol. 52, 437-448, (1968). J. Ching, M. Kowada, A. Ames III, Am. J. Pathol. 52, 455-476 (1968). E. G. Fischer, Arch Neurol. 29, 361-366, (1973). E. G. Fischer, A. Ames III, E. T. Hedly-Whyte, S. O'Gorman, Stroke 8, 36-39, (1977). Even if blood is represented to the local tree, the small vessels do not completely reopen. Under these circumstances ischemic, though potentially recoverable, neurons may be lethalized because they are not adequately resupplied with blood within their metabolically tolerable limits. This concept shifts the basic fault in stroke from "ultrasensitive" neurons to a protracted blood flood failure. Nonetheless, a long felt need exists to prevent permanent damage and/or reverse neurologic deficits resulting from interrupted vascular flow.

PAR One experimental approach which has been used to investigate the effects of stroke on neurologic tissue is the perfusion of fluids of known composition through ventriculocisternal spaces. For example, E. Fritschka, J. L. Ferguson and J.J. Spitzer have reported increases in free fatty acid turnover in cerebral spinal fluid during hypotension in dogs. According to the Fritschka technique, a "mock" cerebral spinal fluid containing radio-labelled palmitate was perfused from the lateral ventricle to the cisterna magna of conscious dogs. Arteriovenous glucose and fatty acid over a period of 6 hours of perfusion. Estimates of the amount of palmitate recovered from the cisternal effluent and cerebral venous blood lead to the conclusion that a sizeable fraction of free fatty acids may be taken up by tissues "in the vicinity of the CSF space". See Fritschka et al, "Increased Free Fatty Acid Turnover in CSF During Hypotension in Dogs", American Journal of Physiology, 232:H802-H807. In "Bulk Flow and Diffusion in the Cerebral Spinal Fluid System of the Goat", by Heise, Held, and Pappenheimer, a ventriculo cisternal perfusion method was used on chronically prepared, unanaesthized goats. Measurements were made of steady-state rates at which inulin, fructose, creatinine, urea, potassium, sodium, and labelled water were removed from perfusion fluid at various hydrostatic and osmotic pressures. The subject perfusions were carried out on female goats provided with implanted ventricular and cisternal guide tubes or cannulas. Each clearance period involved perfusion of 70-120 mills of fluid through the ventricular cisternal system. Inflow rate was maintained constant in the range of 1.50-2.00 ml-min, and outflow was measured continuously. The data obtained was used to investigate the effects of hydrostatic pressure on inulin clearance, rate of formation of CSF, and the permeability of the ventricular system, particularly as compared with that of the toad bladder. This ventriculo cisternal perfusion method was first reported by Pappenheimer, Heise, Jordan and Downer in "Perfusion of the Cerebral Ventricular in Unanaesthelzed Goats", American Journal of Physiology, Vol. 203, pp. 763-774 (1962). Pappenheimer et al reported that goats are anatomically and tempermentally suited for ventricular cisternal perfusions and can tolerate such perfusions for many hours without showing signs of discomfort. The volume of the ventricular system and rate of production of CSF are at least double corresponding values reported for large dogs, and the thickness of the goat occipital bone and its shape facilitates retrograde placement of cannulas through the occipital bone into or above the cisterna magna without interfering with muscles in the neck. The goat's horns provide natural mechanical protection for the cannulas and "are almost indispensable" for operative procedures. In accordance with the Pappenheimer et al technique, guide tubes are implanted just above the dura over the cisterna magna and just above the ependymal linings of the lateral ventricules. Prior to each perfusion the cisterna and ventricle are punctured with sharp probe needles extending a few millimeters beyond the tips of the guide tubes. Alternatively, cannulas were implanted in the subarachnoid space over the parietal cortex, thus permitting perfusion of the entire ventriculo cisternal-subarachnoid system. Pappenheimer et al followed detailed protocols for implanting the guide tubes, and for preparing sterile, synethetic CSF. The Pappenheimer et al perfusion circuit is reported to comprise a bottle sealed with a rubber cap having two stainless steel tubes extending to the bottom of the bottle. One tube serves as a gas bubbler, the second as a liquid outlet. A third opening connects with atmosphere through a sterile cotton plug. The bottle is mounted on an indicating balance and the reservoir outflow is connected through tubing to a parastalic pump with a variable drive permitting pumping rates in the range of 0.5-5 ml/min. One pump output is lead to a male syringe joint which fits the ventricular probe needles and a second outlet on the joints connects to a strain gauge manometer. A 5 ml empty sterile syringe is placed in parallel with the output to damp pulsations of the pump. The cisternal outflow is connected to an enclosed drop counter and wing flask and the output is recorded cumulatively on a polygraph which also gives a vertical record proportional to outflow rate. Pappenheimer et al reports that perfusion with CSF of normal composition can usually be maintained for 4-8 hours before the animal becomes resistive, and if correctly performed, the animal will show no sign of knowing when the perfusion pump is on or off. No attempt is made to regulate the temperature of fluid entering the ventricular probe, however at flow rates of 1-2 ml/min it is theorized that the fluid reaches temperature equilibrium with the brain before reaching the hypothalmus. At higher flow rates (4-6 ml/min) the animals are reported to start to shiver. In this regard, see also F. H. Sklar and D. M. Long, Neurosurgery 1, 48-56 (1977).

PAR Over the years, many experiments have been conducted with materials possessing high oxygen-dissolving properties, many of which have been incorporated as constituents in "artificial blood". The concept of utilizing materials possessing high oxygen-dissolving properties for the maintenance of tissue respiration was first reported by Rodnight in 1954. See Rodnight, R., Biochemistry Journal, Vol. 57, p. 661. Rodnight capitalized upon the considerable oxygen solubility found in silicone oils, and sustained tissue slices by incubation in these oxygen laden oils. Approximately 12 years later, Clark reported experiments involving the total immersion of small animals in silicone oils and fluorocarbon liquids. Rats totally immersed in oxygenated silicone oil survived for one hour with no apparent ill effects, but died several hours after removal, from unknown causes. Similar experiments using synthetic fluorocarbon liquids, which dissolve about 3 times more oxygen than do the silicone oils, were performed with some success. Under these conditions animals survived immersion in oxygenated synthetic fluorocarbon liquids and thereafter returned to apparent health. See Clark, L. C. Jr. and Gollon F., Science, Vol. 152, p. 1755, (1966); and Gollon, F., Clark, L. C. Jr., Alabama Journal of Medical Science, Vol. 4, p. 336, (1967). While arterial oxygenation was reported as excellent for Clark's studies in rats, coincident impairment of carbon dioxide elimination was also reported, as was pulmonary damage from breathing fluorocarbon liquids. One rat, which was observed for five days following liquid breathing, was described as being in respiratory distress and as succumbing within 15 minutes after the subcutaneous administration of hydrocortisone (50 mg), with copious loss of body fluid from the trachea. In this regard, Clark concluded:

PA1 These organic liquids should prove to be of value in studies of gas exchange in living tissues in animals. Organic liquids, since they can support respiration with oxygen at atmospheric pressure and have other unique qualities, may find use in submarine escape, undersea oxygen support facilities, and medical application. The pulmonary damage caused by the breathing of the organic liquids available at the present time remains a major complication of their use in man. Science, Vol. 152., p. 1756.

PAL See also K. K. Tremper, R. Lapin and E. Levine, Critical Care Medicine 8:738 (1980); S. A. Gould, A. L. Rosen, L. R. Sehgal, Fed. Proc. 40:2038 (1981).

PAR Following these observations, fluorocarbon liquids were used as an incubation medium for isolated rat hearts. See Gollon and Clark, The Physiologist, Vol. 9, p. 191, (1966). In this work, myocardial oxygen requirements were apparently well met, however these hearts did not flourish without intermittent fluorocarbon removal and washing with oxygenated, diluted blood. This phenomenon has been explained in terms of aqueous phase lack in pure fluorocarbons such that necessary ionic exchange is impeded.

PAR More recently, considerable attention has been directed to the use of fluorocarbons as constituents of artificial blood. Sloviter, in order to an emulsion with fluorocarbon and albumin. Sloviter's emulsion sustained the isolated rat brain by a vascular perfusion as well as did an erythrocyte suspension. See Sloviter, H. A. and Kamimoto T., Nature (London), Vol. 216, p. 458 (1967). A better emulsion was later developed comprising a detergent, "Pluronic F 68" (manufactured by the Wyandotte Chemical Corp., Wyandotte, Mich.), and fluorocarbon liquids which were properly emulsified using sonic energy. This improved emulsion permitted the replacement of most of the blood of a rat which was then reported as surviving in an atmosphere of oxygen for five to six hours. See Geyer "Survival of Rats Totally Perfused with a Fluorocarbon-Detergent Preparation", Organ Perfusion and Preservation, edited by V. C. Normen, N.Y.: Appelton-Century-Crofts, pp. 85-96 (1968), Geyer, R. P., Federation Proceedings, Vol. 29, No. 5, September-October, 1970; and Geyer, R. P, Med u Ernohn, Vol. 11, p. 256 (1970).

PAR Experiments have also been reported wherein fluorocarbons have been used to perfuse livers. Ten hours after in vitro fluorocarbon perfusion, the isolated liver ATP; AMP; lactate/pyruvate ratio; and a number of other metabolites were found to be as good or better than livers perfused in vitro with whole blood. See Krone W., Huttner, W. B., Kampf S. C. et al., Biochemika et Biophysica Acta, Vol. 372, pp. 55-71 (1974). These detailed metabolic studies indicated that the organs perfused with 100% fluorocarbon liquid were redeemed "intact"; while only 75% of the whole blood infused organs maintained a similar degree of metabolic integrity. The ability of fluorocarbon perfusion to maintain cellular integrity was confirmed by electron-microscopy studies. The cells had normal mitochondrial ultra structure after ten hours of fluorocarbon support, indicating the persistence of normal or adequate aerobic metabolism. In Brown and Hardison, "Fluorocarbon Sonicated as a Substitute for Erythocytes in Rat Liver Perfusion", Surgery 71, pp. 388-394 (1972) a fluorocarbon perfusate preserved organ function and integrity far better than perfusate with much lower oxygen carrying capacity, but was reported as resulting in a decreased rate of bile secretion which was probably the earliest sign of hepatic damage, tissue edema, and a reproducible rise of portal pressure over a period of 21/2 to 3 hours. Both tissue edema and rising portal pressure with fluorocarbon perfusion were associated with progressive vascular occlusion as determined histogolically. A greatly diminished perfusion of fluorocarbon at the end of experiments was documented by injection of India ink twenty minutes before the end of the perfusion. Brown and Hardison hypothesized that the fluorocarbon perfusate may react with amino acids and proteins, that the oxygen concentration in the fluorocarbon perfusate may affect the perfusion results, and that filtration of the fluorocarbon emulsion through filter paper and differing instrumentation were responsible for the apparently conflicting results in the literature. Brown and Hardison hypothesize that phagocytosis of fluorocarbon particles might completely block reticticuloendothelial cells in liver or that capillary endotheilial damage may be another reason for late fluorocarbon perfusion problems.

PAR Fluorocarbons have also been used in experiments involving cerebral blood circulation. In Rosenblum's studies, mouse hematocrits were reduced to 10-15 by exchanging the animal's blood with a fluorocarbon solution. When the animals were respired with 100% oxygen after intravascular fluorocarbon infusions, the brains remained metabolically sound. These organs were able to reverse rising NADH levels and EEG abnormalities induced by short period nitrogen inhalation. The EEG's of fluorocarbon treated animals could be activated by the central nervous system stimulant me azole. By these criteria, intravascular fluorocarbon doe upport the cerebral microcirculation and provides functions of oxygenation, metabolism and electrical activity which are normally associated with blood transport. Please refer to Rosenblum, W. I., "Fluorocarbon Emulsions and Cerebral Microcirculation", Federation Proceedings, Vol. 34, No. 6, p. 1493 (May 1975). See also S. J. Peerless, R. Ishikawa, I. G. Hunter, and M. J. Peerless, Stroke 12, pp. 558-563 (1981); B. Dirk, J. Creiglstein, H. H. Lind, H. Reiger, H. Schultz, J. of Pharm. Method 4, pp. 95-108 (1980); J. Suzuki, T. Y. Oshomoto, S. Tanaka, K. Moizoi, S. Kagawa, Current Topics 9, pp. 465-470 (1981).

PAR As reported by Kontos et al, the marked vasodilation of small cerebral surface arteries which occurs in response to acute profound hypoxemia may be locally obviated by perfusing oxygen equilibrated fluorocarbon into the space under the cranial window. See Kontos, H. A., et al, "Role of Tissue Hypoxemia in Local Regulation of Cerebral Microcirculation", American Journal of Physiology, Vol. 363, pp. 582-591 (1978). Kontos et al described the effect of perfusions with fluorocarbon with 100% oxygen as resulting from increased supplies of oxygen to the neural cells and consequent partial or complete relief of hypoxia, rather than to a local increase in the oxygen tension in the immediate environment of the vascular smooth muscle of the pial arterioles. Two other potential explanations for the observed action are also suggested in the Kontos et al article.

PAR In 1977, Doss, Kaufman and Bicher reported an experiment wherein a fluorocarbon emulsion was used to partially replace cerebrospinal fluid, with the intention of evaluating its protective effect against acute anoxia. Doss et al, Microvasculer Research 13, pp. 253-260 (1977). According to this experiment, systemic hypoxia was produced through one minute of 100% nitrogen inhalation. A bolus of oxygenated fluorocarbon placed in the cisterna magna immediately prior to nitrogen breathing increased regional cerebrospinal fluid O.sub.2 tension by a factor of 5. During the one minute experimental period, the fluorocarbon emulsion provided twice as much brain tissue oxygen as was found in saline injected controls. Doss et al found the anticipated regional tissue oxygenation decline attending nitrogen inhalation to be halved by the administration of the oxygen bearing fluorocarbon emulsion.

PAR In spite of the above described experiments, there is yet to be reported any practical therapeutic approach to the treatment of ischemic neurologic tissue, and particularly human ischemic central nervous system tissue resulting from stroke, accident or disease.

PAC SUMMARY OF THE INVENTION

PAR The present invention provides a novel nutrient formulation for circulation through cerebrospinal fluid pathways, and systems and methods for using same, to treat central nervous tissue hypoxic-ischemic conditions. Through its use, a new diagnostic methodology is also disclosed.

PAR Applicant has recognized that there is a therapeutic time window through which neuron can be reached and resuscitated. The method of the present invention is designed to bypass obstructed vascular circulation and deliver cerebral metabolic needs through an alternate cerebral spinal fluid (CSF) circulation portal. Since particle size exerts a major influence on brain penetration from CSF, the method of the present invention is hypothesized to permit diffusion of oxygen, glucose, electrolytes and essential amino acids into ischemic neural tissue when presented in abundance in the cerebral spinal pathway. Thus, a rapidly exchanging cerebral spinal fluid perfusion system is provided to amply supply these materials and, at the same time, remove metabolic waste.

permeates brain and spinal cord tissues, constitutes a unique anatomical relationship within the body. Although it has some similarities to systemic lymphatics, its anatomical arrangement differs considerably from that of lymph. Indeed, this system has been named the "third circulation". Due to the extensive area of CSF-tissue contact over the cerebral and cord surfaces, in the miniature Virchow-Robins spaces, and cerebral ventricles, the cerebrospinal fluid system constitutes a vast, complex and intimate therapeutic avenue for access to central nervous tissue. Excepting certain infections and neoplasms where the cerebrospinal fluid is now utilized as a treatment conduit, the cerebrospinal fluid system has not been otherwise widely exploited as an easily accessible therapeutic route and has never been used as a continuous therapeutic diagnostic circulation system in man. The present invention is predicated on the recognition that, when regional cerebral blood flow is interrupted, such as after major stroke, or is otherwise seriously impeded by profound vaso-spastic states, the cerebrospinal fluid pathway actually represents the only practical and viable anatomical route by which these tissues may be readily treated. This results from the fact that the usual vascular delivery system is either occluded or non-functional, and thus tissues within affected territories cannot be properly served.

PAR In accordance with the present invention, essential cellular substrates are delivered to beleaguered ischemic brain regions by utilizing the "back door" cerebrospinal fluid delivery route. Accordingly, the present invention provides a novel nutrient emulsion, circulatory method and system which provide necessary nutrient penetration into regions suffering vascular deprivation.

PAR It has been found that the cerebrospinal fluid to brain relationship is not characterized by the rigid and highly selective barrier mechanism which are present at the blood-brain interface. Thus, the penetration rate of materials from cerebrospinal fluid regions to the brain relate largely to molecular size, that is, small substances penetrate deeply while large molecules move more slowly into brain substance. Although entry rates are generally inversely proportional to molecular weight, penetration is also influenced by lipid solubility and the molecular configuration of the penetrating substance. Accordingly, the present invention provides a nutrient emulsion containing essential brain nutrients including selected electrolytes, having a relatively low molecular size which, in accordance with the methods of the present invention, are caused to relatively freely diffuse from either the ventricular or subarachnoid fluid regions into the brain matter to be treated. Accordingly, the present invention provides a novel nutrient emulsion which has been purified, balanced, and perfected to fall within narrow physiologic limits while nonetheless providing the desired nutritional characteristics referred to above.

PAR In accordance with the preferred embodiment of the present invention, this nutrient emulsion constitutes "synthetic cerebrospinal fluid" comprising preselected electrolytes, glucose, amino acids, at least one oxygen-carrying component, typically a fluorocarbon, and other components which impart to the composition a preselected pH, buffering capability, and osmolarity. This nutrient emulsion is prepared by controlling sonication time and by properly dialyzing the materials to achieve a toxic free emulsion. The resulting solution may be rapidly oxydated to O.sub.2 pressures of 650 mm of mercury by using the herein disclosed modified recirculating pediatric oxygenator. As a result, a novel oxygenated nutrient emulsion is provided which is believed to exhibit exceptional therapeutic properties.

PAR The present invention also provides a novel method and apparatus for circulating the oxygenated nutrient emulsion through cerebrospinal fluid pathways, particularly those pathways which contact brain and spinal cord tissue. According to these methods, treated tissues exhibit a substantially improved ability to resist and/or repair damage which would otherwise result from vascular occlusion. In accordance with the preferred method of the present invention, the novel oxygenated nutrient emulsion is circulated through this cerebrospinal fluid route by injecting it into brain ventricles and withdrawing it from the cisterna magna or the spinal subarachnoid space to nourish and to treat central nervous tissues. In other instances the fluid may be injected into the subarachnoid space and withdrawn from another subarachnoid position. The preferred embodiment oxygenated nutrient emulsion should be circulated to tissues to be treated in amounts sufficient to provide adequate gas exchange. Pure fluorocarbon may contain 50 ml O.sub.2 per 100 ml at one atmosphere oxygen while normal blood contains only 20 ml O.sub.2 /100 ml under the same conditions. The oxygen carrying capability per ml of the final emulsion is considerably less than that of pure fluorocarbon by reason of its content of other constituents for normalizing osmotic pressure, buffering, electrolytes, and other physiologic balancing materials. Thus, the preferred embodiment nutrient emulsion may be charged with oxygen (100% O.sub.2 at one atmosphere) to attain pO.sub.2 tensions of 640-700 mm of mercury and an O.sub.2 content of 20 ml per 100 ml. Under rapid circulation conditions, the integral O.sub.2 exchange (fluorocarbon to tissue) has been found to be about 33%. Thus, an oxygen exchange value of about 6.6 ml O.sub.2 /100 ml nutrient emulsion per minute is provided by the present method.

PAR In accordance with the preferred embodiment of the present invention, sufficient nutrient emulsion should be supplied to counteract oxygen deprivation to the affected tissue. For example, the entire supertentorial adult cat brain weighs 12 grams (.+-.2) and the normal metabolic consumption of oxygen of mammalian brain tissue equals 3-4 ml per 100 grams per minute. This total metabolic need may be met with the circulation rate of 6-8 mls per minute. Metabolic needs necessary to simply sustain and/or salvage tissue may be achieved by perfusion rates of one half or less of this optimum. Within these constraints an easily achieved sustenance flow rate of at least 20-30 ml/minute, optimally 45-60 ml/minute, would be anticipated to salvage 100 gms of human brain tissue. It has been found experimentally that it is possible to supply sufficient oxygen to counteract the deprivation of the affected tissue through circulation of the nutrient emulsion through the cerebrospinal fluid route. In fact, under carefully controlled conditions, it is believed within the scope of the present invention to nourish the entire human brain using the preferred embodiment apparatus, method and substance of the present invention. In this manner, central nervous neurons deprived of major blood supply may be sustained without significant damage.

PAR In accordance with the preferred embodiment of the present invention, a novel system is disclosed for administering and maintaining the oxygenated nutrient emulsion for delivery and circulation through the cerebrospinal route.

PAR The preferred embodiment system of the present invention effectively carries out the circulation and equilibration of the nutrient emulsion during treatment. This system, which is diagrammatically illustrated in FIG. 1, generally comprises a reservoir containing nutrient emulsion; means for delivering the nutrient emulsion at preselected flow rates; an oxygenation means for equilibrating the nutrient emulsion to desired gaseous tension levels; heat exchanger and/or cooling unit means for filtering means for cleansing the nutrient emulsion; and circulation monitoring means for insuring that desired circulation flows and pressures are maintained within the system.

PAR The present invention also provides a method of diagnosing conditions of neurologic tissue in mammals. This novel method generally comprises providing an artificial spinal fluid of known composition, injecting that artificial spinal fluid into at least a first portion of the cerebrospinal pathway of a mammal, withdrawing a diagnostic fluid from a second portion of that pathway to create a circulation of fluid at least through a portion of said pathway, monitoring the composition of said diagnostic fluid, and comparing for at least a selected difference in the compositions of said artificial spinal and diagnostic fluids, whereby the detected differences in those compositions are at least diagnostic of neurologic tissue disposed along said portion of the cerebrospinal pathway. In accordance with the diagnostic methods of the present invention, the diagnostic fluids may be monitored for differences in oxygen content, lactic acid concentration, carbon dioxide concentration, potassium and/or sodium ion concentration, enzyme concentration, pH difference, ammonium concentrations, GABA (gamma-aminobutyric acid) and other amino acid(s) concentrations, microorganism content, bacterial count, myelin fragments, cellular fragments or organelles, malignant cells, and/or poisons.

PAR It is also within the scope of the present invention to provide a novel nutrient liquid and/or diagnostic liquid for treating cerebrospinal tissue containing various novel specified components which is formulated using novel methodology.

PAR It is additionally within the scope of the present invention to provide a novel apparatus for treating patients having ischemic-hypoxic tissues, including novel injection and withdrawal means comprising a novel catheter means which is particularly adapted for injecting oxygenated nutrient liquid into a cerebral ventricle without danger of substantially damaging neurologic tissue in the vicinity of that ventricle.

PAR In addition to the methods described above, it is within the scope of the present invention to provide additional therapeutic agents to the nutrient emulsion, such as antineoplastic agents; antibiotics, and/or other therapeutic agents for use in treating the target tissue(s).

PAR Accordingly, the primary object of the present is the provision of a method, substance, and system for providing early stroke treatment.

PAR Other objects of the present invention are to provide treatments for brain and spinal cord injuries, cerebral hemorrhage, cerebral vasospasm, senility, after general hypoxia and other hypoxic-ischemic related neurological disorders.

PAR It is a further object of the present invention to provide therapeutic treatment which may sustain the life of the brain and central nervous system tissues in case of profound shock and/or temporary cardio-respiratory failure.

PAR It is a further object of the present invention to provide life-sustaining support to the brain and/or spinal cord tissues during the conduct of neurological or cardiovascular surgery.

PAR Other objects of the present invention are the provision of methods which may compliment treatments of central nervous system neoplasms by either external radiation and chemotherapy by providing local tissue hyperoxygenation or drugs which may enhance drug or radiation tumorocidal effects.

PAR Further objects of the present invention include the provision of methods which are useful in treating anoxic states attending birth injury. The present method will also assist in removal of central nervous system poisons.

PAR These and other objects of the present invention will become apparent from the following more detailed description.

DRWD

PAC BRIEF DESCRIPTION OF THE DRAWINGS

PAR FIG. 1 is a diagrammatic view of the preferred embodiment treatment system of the present invention illustrating the circulation of nutrient emulsion from a reservoir, into a cerebral ventricle, such as a lateral ventricle, through a portion of the cerebrospinal fluid pathway for output from the spinal subarachnoid space or from the cisterna magna;

PAR FIG. 2 is a diagrammatic view of a portion of the preferred embodiment treatment system of FIG. 1 illustrating an alternate circulation route wherein oxygenated nutrient emulsion is injected into the spinal subarachnoid space and is collected from the cisterna magna;

PAR FIG. 3 is a diagrammatic view of portion of the preferred embodiment treatment system illustrated in FIG. 1 showing an alternate circulation route wherein oxygenated nutrient emulsion is injected into the cisterna magna for passage through the spinal subarachnoid space for withdrawal from a lumbar region;

PAR FIG. 4 is an EEG power recording from the left and right hemispheres of a cat showing traces from the time of an initial stroke, at the end of the stroke, and four hours after the stroke;

PAR FIG. 5 is an EEG recording of an animal perfused with oxygenated nutrient emulsion having a pO.sub.2 level of 400 and showing a 5% return of EEG at 4 hours;

PAR FIG. 6 is an EEG similar to FIG. 1 for an animal perfused with oxygenated nutrient emulsion having a pO.sub.2 of 645 and showing an 88% return of electrocerebral power within 4 hours;

PAR FIG. 7 is an EEG trace showing the effect on EEG activity of a temporary cessation in oxygenated nutrient emulsion circulation;

PAR FIG. 8 is a graph showing the effect on glucose metabolism (CMRGl), lactate and pyruvate before and after stroke of a perfused animal particularly illustrating the effect of a reduction in perfusion rate to insubstantial levels;

PAR FIG. 9 is a bar graph showing the mean EEG recovery (percent) for groups of cats subjected to strokes resulting in 15 minutes of EEG isoelectricity, and comparing naive animals to those perfused only with artificial cerebral spinal fluid (lumbar) and oxygenated nutrient emulsion through lumbar and cisternal routes;

PAR FIG. 10 is a graph of microequivalents of potassium per minute versus time for two experimental groups of cats subjected to 15 minutes of a stroke induced isoelectric state;

PAR FIG. 11 is a graph similar to FIG. 10 wherein the data in FIG. 10 is represented as a percent of the base line figure;

PAR FIG. 12 is a glucose metabolism (CMRGl) graph plotting milligrams per grams per minute against time for three perfusions using a standard glucose concentration, one perfusion using twice that glucose concentration, and a control using artificial cerebral spinal fluid without fluorocarbon;

PAR FIG. 13 is a diagrammatic view of an alternate embodiment oxygenated nutrient emulsion delivery system for use in performing the methods of the present invention.

DETD

PAC DESCRIPTION OF THE PREFERRED EMBODIMENTS

PAR In the following more detailed description, numerous examples have been embodiments of the present invention. One of ordinary skill in the art will recognize that various changes may be made in the materials and methods disclosed herein without departing from the scope of the present invention, which is defined more particularly in the appended claims.

PAR Referring now to FIG. 1, the preferred system for circulating nutrient emulsion through a cerebrospinal pathway is diagrammatically illustrated. As shown in FIG. 1, a nutrient emulsion reservoir 10 is provided for receiving and retaining nutrient emulsion, the preparation of which will be described more fully hereinafter. In accordance with the preferred system and method of the present invention, the nutrient emulsion is injected into a cerebrospinal pathway following pH adjustment and filtering, temperature adjustment, oxygenation, and adjustment of the pressure and flow rate of the nutrient input stream. In FIG. 1, these steps are illustrated diagrammatically at 12, 14, 16 and 18 respectively. Preferably, the nutrient input stream is delivered to a ventricle of the brain, and more particular to a lateral ventricle 20 of the human brain, designated generally 22. Injection of the nutrient input stream permits the oxygenated nutrient emulsion to come into contact with the subarachnoid spaces, miniature Virchow-Robins spaces, cerebral and cord surfaces, and cerebral ventricles. For the system illustrated in FIG. 1, the nutrient input stream is diagrammatically illustrated as being injected into a lateral ventricle 20. Since the lateral ventricle is in fluid communication with other portions of the cerebrospinal pathway, withdrawal of fluid from a portion of the pathway which is remote from that ventricle will create a circulation of fluid within the cerebrospinal pathway. More particularly circulation of the nutrient input stream though at least a portion of the cerebrospinal pathway may be accomplished by withdrawing fluid from the spinal subarachnoid space, diagrammatically illustrated as 26 in FIG. 1, or alternatively, from the cisterna magna 24.

PAR It is not necessary to conduct steps 10-18 in the sequence illustrated in FIG. 1. In FIG. 13 the presently preferred apparatus for delivering oxygenated nutrient emulsion is diagrammatically illustrated. This apparatus, which may be easily constructed using a pediatric blood oxygenator such as an H-800 Pediatric Oxygenator available from The William Harvey Cardiopulmonary Division of C. R. Bard, Inc., Santa Ana, Calif. 92705, comprises a nutrient emulsion reservoir having oxygenation and temperature adjustment loops for constantly oxygenating and adjusting the temperature of the nutrient emulsion contained within the reservoir. In this manner the flow rates of nutrient emulsion provided from oxygenation by oxygenator 102 or for temperature adjustment 104 may be independently varied through adjusting the flow rate of delivery by variable speed pumps 103 or 105 to optimize the temperature and p0.sub.2 characteristics of the oxygenated nutrient emulsion to be delivered for injection by variable speed delivery pumps 106 and 107. As normally used, pediatric blood oxygenators fail to provide a sufficient oxygen transfer rate to fluid flow rate to accommodate the emulsion of the present invention. The minimum blood flow rate of the H-800 oxygenator, for example, is 0.5 liters per minute, and the oxygen transfer rate (to blood) at this flow rate is less than about 25 ml/min. By routing the output 101 of the oxygenator to the reservoir, the oxygenator output pump 103 may operate at flow rates which easily achieve about 7 liters per minute of oxygen transfer to the fluorocarbon carbon emulsion contained in the 2000 ml reservoir. At the same time, delivery pumps 106 and 107 may provide much lower flow rates of nutrient emulsion to the animal undergoing treatment. In a similar manner, heat exchange may also be optimized. In order to maintain optimal p0.sub.2 values, each conduit of this system should be composed of an oxygen impermeable material to prevent leakage of oxygen from the oxygenated nutrient emulsion during processing and delivery. The filtration and chemical balancing procedures followed in preparing the nutrient emulsion are not presently performed "on line", however it is anticipated that chemical balancing may be performed as a closed loop process, as illustrated in FIG. 13. Filtration 108 is performed on line under pressure from pump 106 using a millipore bacterial filter. Pump 107 establishes the final injection rate. The flow of nutrient emulsion to the chemical balancing system is adjusted using variable speed pump 111. In the embodiment of FIG. 13, pressure monitoring and control is accomplished using an open side arm 114 bearing indicia thereon which correspond to the hydraulic pressure of oxygenated nutrient emulsion within delivery line 19. The height of the side arm is adjusted so that overflow will occur when the maximum desired intracranial pressure has been obtained.

PAR As shown in FIG. 1 the oxygenated nutrient emulsion input stream is carried through input stream conduit 19 to an injection cannula 20a which is coupled thereto by coupling 21. Injection cannula 20a is rigidly attached to skull 22 by fitting 22a which holds the cannula in its proper orientation to permit injection of the oxygenated nutrient emulsion into lateral ventricle 20.

PAR If preferred, a double lumen catheter, such as catheter 120 (FIG. 13), may be utilized in place of input cannula 20a. One of the lumens of this catheter should be connected to a pressure monitoring means for monitoring the intracranial pressure within the lateral ventricle 20. This pressure monitoring means may comprise an open side arm, such as side arm 122 which functions similarly to side arm 114.

PAR The preferred injection means of the present invention comprises a cerebral catheter means for insertion into a brain ventricle. This injection means comprises means for preventing a portion of the catheter located within a brain ventricle from damaging tissues surrounding the ventricle. In the preferred embodiment, an inflatable balloon tip may be provided for this purpose. The actual injection of nutrient emulsion into the brain ventricle is accomplished by providing an arrangement of outlet holes disposed as a series of slits radially spaced around the catheter tip. Both the injection means and withdrawal means also further comprise attachment means for attaching the catheter to the body in the vicinity of the injection or withdrawal sites. Thus the injection catheter may comprise a means for fixing at least a portion thereof with respect to the skull to insure catheter stability. The withdrawal catheter, which may have a tip with multiple perforations disposed therein, further comprises means for attaching at least a portion thereof to tissue in the region of the subarachnoid space. This attachment means may include a staple for attaching a non-collapsible portion of the catheter to a lumbar region of the skin.

PAR In many applications, the oxygenated nutrient emulsion will be delivered under normothermic conditions, that is, at about 37.degree. C. Under these conditions, and under hypothermic or hyperthermic conditions where the delivery temperature of oxygenated nutrient emulsion is higher than ambient temperature, temperature adjustment is easily accomplished by providing a thermostatically controlled heater coupled to a suitable heat exchanger for adjusting the temperature of oxygenated nutrient emulsion recirculated to the nutrient emulsion reservoir.

PAR The circulation route illustrated in FIG. 1 permits the treatment of at least cerebral tissues. It is within the scope of the present invention, alternative points of injection and withdrawal of fluid may be selected by the attending physician. For example, in the case of spinal cord injury, it is anticipated that the point of injection of oxygenated nutrient emulsion may be the lumbar, spinal subaracnnoid space, with the point of withdrawal being the cisterna magna. While the above mentioned cerebrospinal pathway injection and withdrawal points are preferred, it is within the scope of the present invention to utilize other injection and withdrawal locations, provided a substantial circulation of fluid through the area of affected neurologic tissue is established by utilizing the selected loci. Such alternate pathways are illustrated in FIGS. 1-3. In FIG. 1, withdrawal of the nutrient emulsion from the cisterna magna is illustrated via conduit 30 in dotted outline. In FIG. 2 input conduit 19 injects oxygenated nutrient emulsion into the diagrammatically illustrated subarachnoid space 26. Withdrawal from the cisterna magna is via conduit 30b. In FIG. 3 injection into the cisterna magna is accomplished via injection catheter 30a. Withdrawal is from the diagrammatically illustrated spinal subarachnoid space 26 via withdrawal catheter 30c.

PAR The fluid which is withdrawn from the cerebrospinal pathway will not be of identical composition to the oxygenated nutrient emulsion which is injected at the injection point. By taking advantage of differences in composition which are detected in the withdrawn fluid, which may be considered to be a diagnostic fluid, the attending physician may easily monitor the physiologic condition of the neurologic tissue which is being treated. This diagnostic fluid may also be monitored to assure that treatment is proceeding according to plan. Accordingly, fluid which is withdrawn from the cerebrospinal pathway is directed to an output collection means 28 for collecting diagnostic fluid. Preferably, an output monitor 34 will continuously monitor various chemical and physical characteristics of the diagnostic fluid for such properties as flow rate, hydraulic pressure, potassium and sodium ion concentration, temperature, lactic acid concentration, gamma amino butyric acid and other amino acid concentrations, oxygen concentration, carbon dioxide concentration, enzymes, and ammonia concentration. The output of this output monitor will not only provide the attending physician with information concerning the state of the cerebrospinal tissue being treated, but also will be fed back to the monitor, control and alarm systems for at least pressure and flow rate, temperature, oxygen-carbon dioxide and chemical constituency, as described more fully hereinafter. This diagnostic system takes advantage of the fact that ischemic neurologic tissue produces higher concentrations of such materials as Gamma-aminobutyric acid (GABA), lactate ion (lactic acid), enzymes and/or LDH (lactic dehydrogenase), ammonia, and other constituents which have been determined by analyzing cerebrospinal fluid of patients subjected by disease to similar anoxic conditions.* In accordance with the system of the present invention, however, a continuous monitoring of the state of neurologic tissue is possible, since the circulation of oxygenated nutrient emulsion will produce a continuous flushing of the affected tissue regions, and thus will result in diagnostic fluid component variations which are rapidly reflective of the physiologic state of the tissues being treated. Due to the multipoint injection-withdrawal method of the present invention, dangers which are inherent in sampling natural cerebrospinal fluid at a single location are avoided by utilizing a double venting method wherein the cerebrospinal fluid pressure is at all times carefully controlled.

FNT *See for example, "Rapid and Sensitive Ion-Exchange Fluorimetric Measurement of G-Aminobutyric Acid in Physiological Fluids", Hare et al, Ar Biochem. Vol. 101, pp. 349-355 (1980) for a preferred BA measurement method.

PAR It is within the scope of the present invention to sterilize and reconstitute that diagnostic fluid as shown at step 32, whereupon that reconstituted diagnostic fluid may be provided as nutrient emulsion to the nutrient emulsion reservoir 10. As shown in FIG. 1, the output monitor 34 may monitor the diagnostic fluid during the sterilization and reconstitution processes and, if desired, ensure that the reconstituted fluid satisfies the requirements of the nutrient emulsion reservoir. As shown in FIG. 1, in order to ensure that appropriate degrees of oxygenation, filtration and chemical balancing, temperature adjustment, and pressure and flow rate are maintained, the nutrient input stream is monitored by various monitors, controls, and alarms, which are intended to provide a fail-safe nutrient input stream. In particular, a pressure and flow rate monitor, control and alarm 38 is provided for monitoring the pressure and flow rate of the nutrient input stream, for controlling the pressure and flow rate adjustment 18 to establish desired pressures and flow rates, and for sounding an alarm in the event that the nutrient input stream exceeds or falls below preselected pressures or flow rates. If desired, this alarm may additionally disable the pumping mechanism producing flow of the nutrient input stream such that the unit "shuts down" upon detection of unacceptable input stream conditions.

PAR Referring now to the temperature monitor, control and alarm, the temperature characteristics of the nutrient input stream are similarly detected, at least to ensure that hyperthermic states, except when used as therapeutic modality, are avoided. While in most instances, the nutrient input stream will be adjusted to a 37.degree. C. temperature, it may be desired to select hypothermic temperatures in order to establish certain treatment conditions. In either event, the temperature monitor will continuously detect the temperature of the input stream, will control the temperature adjustment 14 to establish a preselected temperature, and will sound an alarm and/or disable the system in the event that a preselected temperature range is not maintained in the nutrient input stream.

PAR Referring now to the chemical monitor, control and alarm 42, the nutrient input stream will be continuously monitored for one or more chemical or physical characteristics of the nutrient input stream, and will control the chemical balancing, filtration, etc. which is performed by the filtration and chemical balancing unit 12. The chemical monitor, control and alarm may, for example, monitor the pH, osmolarity, electrolyte component, carbohydrate component, amino acid component, or other components of the nutrient emulsion to ensure that the nutrient input stream falls within preselected stream characteristics. In the event that these characteristics do not fall within the preselected range, the alarm for unit 42 may sound and/or may disable the system to thereby prevent further injection of nutrient input stream into the cerebrospinal pathway.

PAR Finally, an oxygen/carbon dioxide monitor, control and alarm unit 36 is provided which continuously monitors the oxygen and carbon dioxide contents of the nutrient input stream, which controls the oxygenation unit 16, and which sounds an alarm in the event that the oxygen or carbon dioxide concentrations do not fall within preselected ranges. It is anticipated that each of units 36-42 may provide continuous displays of the information monitored from the nutrient input stream, and may, if desired, enable back-up units which either manually or automatically supplement or replace the functions of units 12-18 in the event that those units are not functioning to produce a nutrient input stream within the desired ranges. For example, it is anticipated that a manual or battery be provided to enable emergency operation of the system, since continual nutrient flow is lifesaving for the devitalized portion of the treated organ.

PAR The preferred nutrient emulsion of the present invention is comprised of carefully formulated components which, to the extent possible while maintaining desired therapeutic activity, mimic the physical and chemical characteristics of natural cerebrospinal fluid. Generally, tissues and cells will not fair well if exposed to large volumes of non-physiologic ionic solutions. Accordingly, it has been recognized that appropriate electrolyte compositions at the tissue level are indispensable when it is considered that the circulatory method of the present invention would otherwise result in the washing and the dilution of electrolytes from the region even after short terms of circulation, to the detriment of cell membrane functions. Accordingly, in accordance with the preferred embodiment of the present invention, sodium, potassium, calcium, magnesium, and chloride ions are carefully balanced in the nutrient emulsion of the present invention to thereby create, to the degree possible, normal extra-cellular compositions. The present invention also provides a non-aqueous oxygen transfer component for selectively combining with oxygen and for transferring oxygen to the tissues to be treated. Numerous compounds are known to the art which are characterized by having a high solvent property for oxygen, carbon dioxide, and other gases. The preferred non-aqueous oxygen transfer component of the preferred nutrient liquid should exhibit when so charged, oxygen vapor pressure ranges of above 400, and preferably 600, Torr. Such oxygen transfer components should similarly not have in themselves high vapor pressures which would boil at body temperatures, nor have viscosities which are difficult if not impossible to emulsify. Generally, the preferred compounds for use as non-aqueous oxygen transfer components are fluorocarbon polymers, such as perfluorocarbons, perfluorinated alkyl polyethers, fluoroethers, fluoramines, etc. While compounds within these groups range in molecular weight from 250 to 7000, their selection for use as non-aqueous transport components are based upon the combination of features of the proper vapor pressure, molecular weight, viscosity, and emulsifiability, emulsion-stability and tissue distribution. One such fluorocarbon which has been found to be particularly suited for the non-aqueous oxygen transport component of the preferred nutrient liquid is a reagent grade perfluorobutyltetrahydrofuran which has been sold by the 3-M Corporation under the trademark "FC-80". FC-80 has an oxygen solubility coefficient ScO.sub.2 of 0.45 of ml O.sub.2 /ml at pO.sub.2 of 760 Torr. See Navari et al., Res. Exp. Med. 170, pp. 169-180 (1977), which paper is specifically incorporated by reference as if fully set forth herein. It should be noted that whole blood under the same circumstances contains 0.23 ml O.sub.2 /ml. The FC-80 ScO.sub.2 is linear from 760 to 200 Torr but declines quite rapidly below the lower level. The high oxygen diffusion coefficient (5.71.times.10.sup.-5 cm.sup.2 /sec per second) indicates more than adequate FC-gas in a physiologic sense. Similar studies concerning CO.sub.2 solubility and diffusion indicate that absorption and release are described by a straight line function. From these observations, metabolic tissue CO.sub.2 accumulations should theoretically be easily removed by fluorocarbon solutions administered through a circulatory method.

PAR Not only do fluorocarbons possess these unique physical gaseous properties but they are for the most part non-toxic. The main acute toxicity has been found to reside in free fluoride ion accumulation which occurs mainly from sonication. See, Clark et al., Fed. Proc. 34, pp. 1468-1477 (1979). The free ion can, however, be removed by repetitive dialysis and the emulsion thereby rendered physiologically acceptable. Accordingly, the preferred embodiment nutrient liquid of the present invention, which has been dialysized and filtered through a millipore filter, has evidenced no toxicity either in short term or long term use during circulation through cerebrospinal pathways of animals. One chief advantage of the CSF circulation route is that most or all the nutrient liquid can be removed by washing at the time of treatment termination. In this way long term cellular retention as previously noted for liver and reticuloendothelial cells in vascular circulations of oxygenating liquids may be avoided.

PAR In the preferred embodiment nutrient liquid of the present invention, an emulsification component is provided for permitting the emulsification of the nutrient component with the oxygen transfer component of that liquid. See Clark et al, Triangle II, pp. 115-122 (1972b); Clark et al, Microvasc. Res. 8, pp. 320-340 (1974). The best currently available material for this purpose is believed to be block polymer polyols, which are known to the art as "pluronics", of which, pluronic F68 has proven to be a most efficient emulsifying agent. As used in a nutrient liquid as described more fully hereinafter, the toxicity from such a pluronic detergent is negligible. At the present time, however, it is anticipated that other emulsification components which will permit the non-aqueous transfer component of the nutrient liquid to become soluble with respect to the aqueous nutrient component of the nutrient liquid may be utilized to provide solutions which have adequate physiologic perimeters. Such other means of solubilizing fluorocarbons includes the formation of micelles, etc.

PAR In the preparation of the preferred nutrient liquid, an important factor in producing an acceptable nutrient liquid is the achievement of an acceptable final osmotic pressure. The osmotic pressure of the nutrient liquid will depend upon the amount of the emulsification component, the particle size of the fluorocarbon, and the ionic composition of the aqueous nutrient component. In accordance with the preferred method of preparing the nutrient liquid of the present invention, toxic emulsification components should be removed by dialysis. Fluorocarbon particle size will be controlled by sonification time and filtering, while the ionic composition of the aqueous nutrient component will be carefully adjusted to produce a nutrient liquid possessing desired osmotic characteristics. If desired, a final osmotic tuning may be accomplished in accordance with the method of the present invention by adding ascorbic acid to the nutrient liquid.

PAR In order to provide fully successful treatment of ischemic tissues, it is desirable to provide nutrient liquid for circulation around those tissues which will compensate for relative or complete deficiencies of blood transport metabolites. In addition to oxygen, other tissue metabolic requirements include glucose, amino acids, ions, hormones, vitamins, etc. While in temporary treatment conditions, it may be suitable to temporarily omit one or more vitamin, hormone, ion, or amino acid, for prolonged treatment and to produce the most desirable results, it is preferred to provide substantially all of the above mentioned metabolites in the preferred nutrient liquid. It is at least desirable to provide in the nutrient liquid all components necessary to support aerobic metabolism which will be available within the medium for use at cellular levels. Glucose deprivation of central nervous system tissue causes a serious cellular metabolic deficiency, as does the same degree of oxygen deficiency. Accordingly, by providing a total and finely adjusted mixture that has all the necessary components for total cell survival, an ideal for circulation through the cerebrospinal pathways.

PAR In order to illustrate the preferred method and composition of such an oxygen-nutrient material, the following example is provided.

PAC EXAMPLE 1

PAR Under conditions of replacing blood borne materials by perfusion all nutrients necessary for aerobic metabolism must be available within the medium for immediate use at cellular levels. As far as the central nervous system is concerned, glucose deprivation causes as serious a cellular metabolic deficiency as does the equivalency of oxygen lack. To achieve the desired ends all known essential nutrients have been added to the FC (fluorocarbon) emulsion. FC itself thereby serves the purpose of a gas transport system while the aqueous emulsion phase contains an array of cellular metabolic essentials. The total and finally adjusted mixture has all the necessary ingredients for total cell survival. The combination material is referred to as an oxygen-nutrient formula (Ox-N), or oxygenated nutrient emulsion.

PAC Method and Composition Preparation of Oxygen-Nutrient Material

PAO 1. Reagents

PA1 (A) 5% Commercial grade Pluronic F68 (Basic Wyandotte).

PA1 (B) 20% W/V FC-80 (3M Corporation)

PA1 (C) Synthetic C.S.F.

TBL

Sodium Chloride	7.3 gm/L
Potassium Chloride	300 mg/L
Calcium Chloride (dehyd)	200 mg/L
Magnesium Sulfate	300 mg/L
Sodium Phosphate (hepta)	200 mg/L
Sodium Bicarbonate	190 mg/L

PA1 Adjust the pH to between 7.380-7.420 with 10% Ascorbic Acid

PA1 (D) Bacitracin Inj. 50,000 U/vial (Pharmacy) reconstitute with 10 ml saline to give a concentration of 5000 U/ml. Use 0.2 ml for each liter of perfusate to obtain a concentration of 1,000 units per liter of perfusate.

PA1 (E) Essential Amino Acids (Pool) (Sigma)

TBL

D-Glutamic Acid	11.8 mg
L-Glutamine	730.0 mg
DL-Serine	26.3 mg
D-Threonine	30.0 mg
D-Lysine	38.8 mg
D-Valine (optional)	19.0 mg
D-Leucine	14.0 mg
DL-Isoleucine	13.0 mg
D-Phenylalanine	15.0 mg
DL-Tyrosine	14.0 mg
D-Methionine	4.5 mg

PA1 Before oxygenating the fluorocarbon emulsion add 9.8*mg. amino acid and 200 mg dextrose for each 100 ml of emulsion.

FNT *Siegel et al., Basic Neurochemistry (2nd edition), Little, Brown and Company, Boston, p. 297.

PA1 (F) Steroid (Methylprednisolone sodium succinate) 125 mgs. (The Upjohn Company). Reconstitute the steroid with 2 ml of diluent to obtain a concentration of 62.5 mg/ml. Add 0.5 ml of this mixture to each liter of emulsion before oxygenation (31.2 mg/L).

PA1 (G) 1 N NaOH

PA0 2. Materials

PA1 (A) Sonifier Cell disrupter (Branson) Model W185D

PA1 (B) Waring Blender for mechanical dispension of Pluronic Acid.

PA1 (C) Dialyzer tubing 7/8 in. (22 mm) (Thomas). It is necessary to dialize the emulsion to remove fluoride ions as well as other low molecular weight contaminants.

PA1 (D) Whatman Filter Paper #1 (46.times.57) (Thomas). The emulsion should be filtered to remove particles originating from disrupted carbon skeletons of fluorocarbon during sonication.

PA1 (E) 0.8 micron filter unit (Thomas). Sterilization is accomplished by filtering the emulsion through a micro filter.

PA1 (F) CO.sub.2 tank (Welders Supply Company). CO.sub.2 is used as a defoaming agent while sonicating.

PA1 (G) 100% O.sub.2 tank (Welders Supply Company). CO.sub.2 is used as a defoaming agent while sonicating.

PA1 (H) 100% O.sub.2 tank (Welders Supply Company) for saturating perfusate.

PA1 (I) Sterile Culture Flasks (Thomas) for storing perfusate.

PA1 (J) Gas Dispersion Tubes (Fisher Scientific Company) for equilibrating the emulsion with O.sub.2.

PA1 (K) Aspiratory Bottle (Thomas)

PA2 a. 250 ml capacity-cut off 21/2" from the neck with a glass cutter in order to accommodate the macrotip for sonification.

PA2 b. 500 ml capacity--for equilibration of the emulsion with 100 ml capacity--100% O.sub.2.

PA1 (L) K50 Extension tubing. Capacity approximately 2.1 ml length 40.7 centimeters (20 in.).

PA1 (M) Circulating Pump

PA1 (N) Sonification Assembly

PA2 a. Fill a container with crushed ice; one that will allow drainage of the water as the ice melts (a fish tank will do).

PA2 b. On the serated outlet near the bottom of the aspiratory bottle connect seven lengths (140 in.) of K50 extension tubing. Place the bottle in the ice bath and connect the tubing to circulating pump.

PA2 c. Place the precooled Pluronic acid in the aspirator bottle. Drape and return extension tubing from the pump over the side of the bottle. Drape the tubes from the CO.sub.2 tank over the side of the bottle and bubble slowly. Carefully lower the macrotip into the solution and start sonification.

PA0 3. Method 20% FC-80 (5% Pluronic (F68)) (w/v)

PA1 (A) Place 25 gms of F68+250 ml of artificial CSF in a Waring blender and blend at a high speed for 2 minutes. The solution will become very foamy. For best results the solution should be refrigerated overnight before using. This allows the head of foam to settle and precools the solution to the proper temperature for sonification.

PA1 (B) Place the precooled Pluronic acid solution in the aspirator bottle. Turn on Sonifier. With a Pasteur pipette add 58.8 mls (100 gm) of FC-80 over a 30 minute period sonifying throughout. Once added allow the mixture to sonicate for 45 minutes. Be sure that the temperature does not exceed 20.degree. C.

PA1 (C) Cut dialyzer tubing that has been presoaked in artificial C.S.F. into 60 inch strips. Fill each strip half full with the mixture. Place strips in containers filled with approximately 1000 ml. of artificial C.S.F. Refrigerate and allow to dialize for 48 hours. The dialyzing solution transferred to additional tubing since the volume is considerably increased during dialysis.

PA1 (D) After dialysis filter the solution through Whatman #1 filter paper, then take the total volume. 25 gm of Pluronic acid and 58 750 ml of emulsion. The former volume represents 20% FC-80 and 5% F68 w/v ratio. The emulsion should be kept in an ice bath while processing.

PA1 (E) Add bacitracin to the emulsion. The pH at this point should be between 6.5 and 6.8.

PA1 (F) It is necessary to adjust the electrolytes at this stage.

TBL

Unadjusted electrolytes:

Na	=	127
K	=	5
Cl	=	126
CO.sub.2	=	1.5
Osmolarity	=	271

PA1 It is necessary to add 696 mg NaCl/L of emulsion in order to normalize the electrolytes.

TBL

Adjusted electrolytes:

Na	=	131
K	=	3.8
Cl	=	130
CO.sub.2	=	3
Osmolarity	=	303

PA1 (G) Using 1.0 N NaOH adjust the pH to between 7.380 and 7.420, then check the osmolarity (Range 298-317).

PA1 (H) Sterilize the emulsion by filtering through 0.8 micron filter. The emulsion can be frozen at -20.degree. C. and is stable for several months.

PA0 4. Immediately Before Using Emulsion

TBL

(A)	Add:	Glucose	0.8-2.5 gm/L
		Amino Acid	0.098 gm/L
		Steroid	31.2 mg/L (optional)

PA1 (B) Warm the emulsion to 37.degree. C. and equilibrate with 100% O.sub.2 using a gas dispersion tube for 30 minutes to obtain a pO.sub.2 of between 580-660.

PA1 (C) A typical batch of FC-80 emulsion shows the following properties:

TBL

Na	=	131	meq/L
K	=	3.8	meq/L
Cl	=	130	meq/L
CO.sub.2	=	3	meq/L
Glucose	=	186	mg. %
Osmolarity	=	311	mOsM

PA1 (D) A typical batch of oxygenated nutrient emulsion contains:

TBL

Fluorocarbon	=	78.6	ml/L
Pluronic Acid	=	213	ml/L
NaCl	=	7.3	gm/L

Potassium Cl = 300 mg/L
Calcium Cl (dehydrated) = 200 mg/L
Mg Sulfate = 300 mg/L
Sodium Phosphate = 200 mg/L
Sodium Bicarbonate = 190 mg/L
Amino Acid Pool = 0.098 gm/L
(added to fluoro-carbon)
Manitol Injection = 50 ml/L
USP 259
Bacitracin = 5000 units/L
Gentamicin = 80 mg/L
Dextrose = 2 gm/L
Ascorbic Acid (10%) = 0.5 ml/L
Sterile Water = remainder per liter

TBL

Gas Characteristics After Oxygen Equilibration

	Unsaturated	Saturated
pH	7.231	7.342
pCO.sub.2	3.7	5.7
pO.sub.2	190	640-5

PAR In order to provide an indication of the efficacy of the preferred treatment methods, the following examples are provided:

PAC EXAMPLE 2

PAR For reasons of simplicity and reproducability a model continually in use in applicant's laboratory has been employed. Osterholm, J. L., Pathophysiology of Spinal Cord Injury, C. C. Thomas, Springfield, Ill. (1978). Extensive experience with spinal cord injury in terms of standardization, quantitative histological studies, regional blood flow and biochemical parameters suggested these procedures. A primary pathophysiologic event in that model has been determined to be discrete regional ischemia. A microcirculatory flow failure within the injured region has been documented by many study techniques including microangiography, distribution of intravascular particulate materials, hydrogen-platinum flow studies, regional istopic techniques and lactate accumulation. Recent C 14 antipyrine microregional blood flow studies conducted in applicant's laboratory have accurately delineated the magnitude of ischemia in the injured cord. Within one hour the regional grey matter flow drops from the control of 44 cc/100 gm/min to only 2 cc/100 gm/min. The white matter is also ischemic. Blood flows in these regions are depressed from 15 cc/100 gm/min to 1-2 cc/100 gm/min.

PAR From these observations, standarized spinal cord injury causes a restricted ischemic lesion which can be easily studied and quantitated. In this rigid system therapeutic treatment effects are readily detected by comparison with our extensive untreated injury data. It should be noted here that the mechanical injury forces used in these experiments are substantially above

PAC Circulation Experiments

PAR Experiments were carried out by continuously injecting either saline or Ox-N emulsion saturated with O.sub.2 at 1 atm into the distal subarachnoid spinal space. The outflow (withdrawal) of the diagnostic fluid was at the cisterna magna. Infusions were begun immediately after severe wounding. An infusion rate of 3 ml/minute was easily achieved, and this rate was maintained for two hours.

PAC Oxygen

PAR Prior to lumbar spinal infusion we were able to develop pO.sub.2 tensions of 535.+-.89 mm O.sub.2 in the Ox-N emulsion by simply bubbling 100% oxygen through the solution. Upon exit at the cisterna magna after traversing the entire spinal subarachnoid space the pO.sub.2 had fallen to 243.+-.63. The oxygen difference between entering and exit was 292.+-.63, or a 55% decline, which is statistically significant at the P<0.001 level. This finding indicates a rapid pO.sub.2 exchange during the thirty seconds or less transit time. For various technical reasons our initial pO.sub.2 was lower than can be achieved under idealized circumstances. More recently it has been possible to regularly attain pO.sub.2 of about 650 Torr. Even better experimental results might have now been obtained under conditions of higher O.sub.2 tension.

PAC Carbon Dioxide

PAR FC-80 is an efficient CO.sub.2 exchange and transport agent, and the emulsion therefore easily extracts tissue CO.sub.2. This is indicated by an initial emulsion pCO.sub.2 of 2.7 Torr which rose to 16.0 Torr after the tissue perfusion contact. This represents a 593% increase in FC-80 CO.sub.2 (P<0.001). The emulsion also removes other acid metabolites since in some experiments the inherent buffering capacities were exceeded as the exit fluid pH exhibited a considerable depression toward the acid side (original pH 7.4, exit pH 7.0). This pH change exceeded any acid contribution by the collected CO.sub.2, and amounted to 0.248 mole lactate/hour.

PAC A. Cross Sectional Area (Edema)

PAR Frozen tissues were sectioned and stained (H & E, and acid phosphatase). The sections were evaluated by projection to 25.times. magnification and preselected lesion parameters measured by means of a compensating polar planimeter. There was considerable increase in the untreated injury cord cross sectional area (1280 mm.sup.2) which was significantly reduced in the Ox-N experiments, (896 mm.sup.2). We have assumed that this substantial cross sectional cord area increase is caused by edema fluid. In the course of other experiments, the degree of edema appearance has been quantified. It was found that net water accumulation at those post injury times ranged from 25% to 40%. The absolute reduction in cross sectional area by the Ox-N treatment is significant at the P=0.001 level.

PAC Lesion Size

PAR Using our standard sampling methodology which includes skip serial sections throughout the injury region, and analysis by quantification techniques, the degree of injury induced hemorrhagic necrosis can be determined. With the perfected injury system the lesion size at any time point can be reliably predicted. The effects of saline and Ox-N circulations upon lesion size were compared to each other and to our established untreated values. The results are summarized in Table I:

TBL TABLE I

LESION SIZE

2 Hour Injuries

% Grey	% White	% Total

Standard 79.5.+-.16% SD
30.1.+-.9% SD
39.5.+-.10% SD
Injury
(No Infusion)
Saline 78.3.+-.15% SD
25.0.+-.14% SD
34.4.+-.12% SD
Circulation
Ox--N 47.4*.+-.17% SD
12.8*.+-.2% SD
19.2*.+-.10% SD
Circulation

Percentages are expressed in terms of total tissue area lesioned by hemmorrhagic necrosis for grey, white or total cord area two hours after servere injury with the various treatments.
(*Statistical Significance P = <0.01. The saline values are not significant).

PAR The data indicates a highly significant degree of protection against injury lesions afforded by the Ox-N circulation treatments. The actual lesions are halved by the treatment and this remarkable stabilizing effect upon the important white matter tracts would be anticipated to substantially improve the final functional result attending severe spinal cord injury.

PAC Anterior Horn Cells

PAR A technique of counting the anterior horn cells which contain visible acid phosphatase histomchemical reaction product has been developed in this laboratory. The procedure has been previously used to assess ischemic cellular effects in terms of cellular survival and/or lysis time.

PAR From Table II it can be seen that untreated injury has a highly lethal effect upon anterior horn neurones. Within the two hour experimental time period, more than 97% of all cells at the injury center undergo cytoplasic lysis. Ox-N infusions stabilized the injured cells as 60% of all neurones were protected from lysis.

TBL TABLE II

ANTERIOR HORN CELLS

Control	34 .+-. 2 (SD)
Injury	2 .+-. 1.73*
Injury + Ox--N circulation	21 .+-. 5.12**

Number of anterior horn cells containing acid phosphatase reaction produc within well defined cytoplasmic borders.
(*statistical difference from control P < 0.001,
**Difference from injury alone P < 0.001).

PAC Spinal Cord Adenosine Triphosphate (ATP)

PAR Biochemical ATP tissue determinations were undertaken to determine the metabolic oxidative state of injured spinal tissues. This metabolite was selected for study since it reflects the progress of normal oxidative metabolism. ATP levels fall very rapidly under sufficient hypoxic-ischemic conditions. Untreated injured cords have a 200% ATP decline in one minute. In the current experiments ATP levels would be expected to reflect (1) the latter aspect is especially important in terms of cellular integrity which was discussed in the preceeding section.

PAR From Table III it can be seen that 2 hour injury causes a four and three fold drop in grey matter and white matter ATP respectively. This information amply supports other observations about the degree of regional cord tissue ischemia after impaction. ATP was found in significantly higher concentration in the Ox-N experiments than noted after saline circulation alone. The high energy compound suffered only a 30% fall from normal in the oxygenated perfusion group which contrasts vividly with the 300-400% loss found with the saline treatments.

TBL TABLE III

ATP LEVELS (.mu.mol/gm) (2 hours post injury)

	Injury & Saline	Injury & Ox--N	Control
Grey Matter	0.46	1.24*	1.88
White Matter	0.40	0.87*	1.23

ATP tissue levels in control, saline and Ox--N injured cords. The difference between saline and Ox--N is significant *(P = 0.05). Although not shown in the Table, the Ox--N treatments also statistically increase ATP in spinal cord regions directly above (P < 0.001) the injury site.

PAL Comparison of the above results to those later reported by R. E. Hanseabout, R. H. C. Van Der Jagt, S. S. Sohal, and J. R. Little, Journal of Neurosurgery 55, pp. 725-732 (1981) is of interest. Hanseabout et al report the use of a commercial oxygenated fluorocarbon artificial blood perfusate to treat experimental spinal cord injuries. Treated dogs are reported as showing improved motor function more rapidly and as having a better final hind limb functional result than did controls. To some extent, this non-prior art report confirms the spinal cord injury findings reported here.

PAC EXAMPLE 3

PAC Cerebrovascular Ischemia

PAR Initial studies have been conducted to determine the efficiency of Ox-N emulsions in protecting the brain against profound ischemia. We employed the cat brain and utilized right hemispheric regional vascular interruption so that the left cerebral hemisphere might serve as an internal control. The middle cerebral artery of cat is accessible through the bony orbit. It lies immediately above the optic nerve after the canal has been opened and can be identified with certainty in that position. Preliminary experiments determined that an inconstant cerebral field was devascularized by occluding the middle cerebral artery. It became apparent that collateral blood flow via the anterior and posterior cerebral arteries supplied some retrograde filling into the experimental region. This phenomenon could be largely prevented by concommittantly reducing the mean systemic blood pressure to 70 mmHg by external bleeding. Hemorrhagic hypotension plus middle cerebral artery occulsion yielded a reasonably constant ischemic cerebral lesion from animal to animal.

PAR In that model either saline or Ox-N were circulated from the right cerebral ventricle to the cisterna magna at a rate of 3 ml/min. Cerebral tissues were harvested one hour after vascular occlusion by immediate immersion in liquid Freon. The tissues were sectioned in the frozen state and reacted with luciferin upon photographic film. A combination of high energy cellular metabolites plus luciferin react to emit visible light, which is recorded upon the film. Tissues removed from saline treated ischemic cerebral regions were uniquely devoid of phospholuminescence, while the opposite hemisphere demonstrated this reaction to a degree similiar to that found in normal animals. Middle cerebral ischemic tissue samples from Ox-N treated animals contained sufficient high energy materials to demonstrate a positive histochemical high energy reaction one hour after vascular arrest.

PAC EXAMPLE 4

PAC Profound Spinal Cord Ischemia

PAR The combined evidence from spinal cord injury and middle cerebral artery occlusion models demonstrate that the preferred oxygenated nutrient emulsion can be circulated to maintain cellular integrity and aerobic metabolism under the stress of profound regional ischemia. A third model was utilized to determine if vascular deprived neurones perfused via cerebrospinal fluid pathways with oxygenated-nutrient would continue to perform a physiologic function. A transthoracic aortic ligation just distal to the left subclavian effectively devascularizes the cervical, thoracic and lumbar cat spinal cord. In some examples the lower brain stem was also found ischemic by regional flow studies. The mid and lower thoracic cord are universally and profoundly blood deprived by this vascular interruption. Animals under light Ketamine anesthesia were treated by circulating from the lumbar subarachnoid space to the cisterna magna with either saline or Ox-N solutions. Respiratory movements were evaluated in these experiments. The lungs were ventilated by positive presence respiration, but the mechanical movements are easily distinguished from neuromuscular respiratory contractions. This is especially so since for the most part the respiration and neuromuscular drive occur at separate times and are largely asynchronous. Following the aorta ligation all physiologic neuromuscular respiratory movements progressively diminished to total cessation after 5-10 minutes in the saline treated cats. The arrest obtains for intercostal muscles as well as diaphragmatic contractions. The Ox-N treated animals, on the other hand, continue to respire in an essentially normal neuromuscular sequence. The respiration, under those conditions, were often of irregular rates, diminished in amplitude, and showed some individual magnitude variations. The singular difference between saline and Ox-N circulations is the universal persistence of respiration in the latter group. It is also true that Ox-N sustained sufficient chest bellow movements so that if the chest were closed the respirations were clinically adequate to support life.

PAC EXAMPLE 5

PAR Experiments have also been conducted to determine the efficacy of the herein disclosed methods on global cerebral ischemia induced in cats.

PAR Although the Ox-N emulsions of the present invention are oxygenatable by bubbling gas through them, perfusate from stroke animals were initially found to have oxygen pressures (p0.sub.2) below those known efficient oxygen exchange values (p0.sub.2 less than 200) for the fluorocarbon component of the material. See Navari et al, supra. Accordingly, the pump oxygenation system described above in connection with FIG. 13 was developed to optimize fluorocarbon 0.sub.2 saturation. As mentioned above, this system comprises a heat exchange-oxygenator which was coupled to recirculating, warming and delivery pumps. This system rapidly oxygenates the emulsion (p0.sub.2 =645[mean] Torr) at 37.degree. C. with oxygen gas delivered at 7 L/min.

induction and nitrous oxide oxygen (70-30%) anesthesia. A double lumen inflow cannula of the type described above was sterotactically placed into a lateral cerebral ventricle while an exit cannula was inserted either into the cisterna magna or lumbar theca. When the conduits are properly installed, the CSF pathways have little resistance and a mean flow perfursion rate of 6.0 cc/min. can be achieved through the animals without intracranial pressure alterations. Entry and exit fluid were collected for metabolic studies. Both gases were normalized by respiratory adjustment. Further experimental manipulations awaited electroencephalograph (EEG) normalization. Cerebral ischemia was produced by the combined insult of hemorrhagic hypotension (mean arterial blood pressure lowered to 30.+-.3 mm Hg) plus simultaneous carotid artery clamping. This method caused a bihemispheric isoelectric EEG within 5-8 minutes. After sustained and total cerebral electro sillence for 15 minutes, the carotid arteries were unclamped and the withdrawn blood reinfused.

PAR A well accepted measure of cerebral function, the EEG, was used to assess both the degree of insult and subsequent discovery. A computer based EEG method, compressed spectral analysis, was used to determine brain activity. A Nicolet Instrument Corporation "MED-80" computer utilizing frequency analysis package "Super C" was used with the following setup parameters:

PA1 2 channels, 1024 SEC. EPOCH, 1024/PTS.EPOCH

PA1 2 sweep average/printout.

PAL The total output is expressed in (microvolts.sup.2) assuming a constant source impedence of 1 ohm. The data presented here is the total cerebral power 0.3-25 Hz in picowatts. Recordings were made from skull electrodes at maximum sensitivity of 1 picowatt. Since a steady state prestroke EEG was obtained, each animal served as its own control.

PAR Ten animals had cannulas placed and the stroke accomplished without perfusion. A second control group of ten animals were treated similarly, but were also perfused through the ventriculo spinal (lumbar) route with nutrient solution without fluorocarbon. There were no apparent differences found for post-stroke electroencephalographic activity in these groups. As a measure of stroke severity, 13 animals (of 20) had persisting electrocerebral sillence. Of the remaining animals, 5 gained only 2% of their base line power while two had 10% power return within the 4 hour experimental period. FIG. 4 is a representative EEG power tracing from the left and right cerebral hemispheres of a cat perfused only with nutrient solution without fluorocarbon and which exhibited persisting electro-cerebral sillence during the 4 hour experimental period. The tracings are read from bottom upwards. Normal activity is seen in the lowest tracing and is totally arrested by the ischemic insult half way through the first grouping. There is electro-cerebral sillence thereafter througout the experimental period.

PAR Thirteen cats underwent the same experimental procedure, but were perfused immediately after ischemia with bubble oxygenated nutrient solution (pO.sub.2 =400). For these cats, the flow rate was 4 ml/min with withdrawal from the umbar theca. Five exhibited continued electro-sillence whereas 8 demonstrated EEG recovery from 5% (6 animals) up to 34% (2 animals). FIG. 5 is a representative EEG tracing of one of the eight animals demonstrating 5% recovery after perfusion with oxygenated nutrient emulsion (pO.sub.2 =400).

PAR A fourth group of 7 cats was perfused with pump oxygenated nutrient solution (pO.sub.2 =645) at 6 ml/min. with withdrawal from the cisterna magna. All cats in this group regained some electrocerebral activity. The final total power which returned ranged from 5 to 88% of the prestroke base line (average 22%; $p<0.01$ compared to all non-oxygen groups). The electroencephalographic activity recovered generally throughout the 4 hour recovery period with the returning total cerebral power exhibiting a first order relationship as a function of time. At the observed recovery rate all animals should achieve completely normal EEG power spectra within 8 hours. An oxygen dependent EEG response is seen when non-oxygenated, bubble oxygenated (p0.sub.2 =400), and pump oxygenated (p0.sub.2 =645) groups are compared as electrocerebral activity recovery greater than 5% was found in 10%, 62% and 100% respectively. FIG. 6 is an EEG tracing of the animal showing 88% return of electrocerebral activity within 4 hours after perfusion with oxygenated nutrient emulsion (p0.sub.2 =645). The asymmetry between hemispheres is an individual variation for this animal.

PAR FIG. 7 is a portion of an EEG tracing showing the recorded effect on electro-cerbral activity of a temporary perfusion failure. This animal, which was perfused using the pump-oxygenated (p0.sub.2 =645) nutrient emulsion described above, experienced an interruption (pt. A) in perfusion for a time period of approximately 1 hour, whereupon perfusion was resumed (pt. B). As seen in this tracing a major deterioration of EEG activity occurred following cessation of perfusion, and resumed thereafter, confirming that the present method in fact sustains EEG activity.

PAR In FIG. 8, the effect of a diminished perfusion flow rate of oxygenated nutrient emulsion is shown on the rate of glucose metabolism, and lactate and pyruvate concentration. In accordance with the above-described ventriculo-lumbar perfusion procedure using bubbled oxygenated (p0.sub.2 =400) nutrient emulsion, flow rate with nutrient emulsion without fluorocarbon was established at about 5.0 ml/min. A base line cerebral metabolic rate of glucose metabolism (CMRGl) was established prior to stroke, which was followed after 15 minutes with the perfusion of the oxygenated nutrient emulsion. CMRGl, which has recovered somewhat after 1 hour, is seen to decline rapidly as the flow rate of perfusate declines. Similarly, lactate levels rise precipitiously with flow rate decay. These results once again confirm that the flow of oxygenated nutrient emulsion through the cerebral spinal pathway should be maintained at acceptable rates in order to sustain neurologic tissue.

PAR In FIG. 9, the mean recovery percent for the four groups of animals discussed above is presented in the form of a bar graph. It is presently preferred to insure that the p0.sub.2 value of oxygenated nutrient emulsion upon input is great enough to insure that efficient oxygen transfer capabilities are maintained at the selected flow rate. For the FC lumbar group, exposure of oxygenated nutrient solution to certain tissue regions when its oxygen exchange value was below the known efficient oxygen exchange value (p0.sub.2 less than 200) for the fluorocarbon component of this material may have occurred. This may be true even though the mean oxygen exchange value of the withdrawn emulsion is above 200. Accordingly, it is presently preferred to maintain the p0.sub.2 value of withdrawn oxygenated nutrient emulsion at twice this minimum, or at above 400, either by raising the input p0.sub.2 value to much higher levels, as with the ventriculo-cisternal animals described above, or by increasing the flow rate of oxygenated nutrient emulsion through the animal to maintain those values. In smaller animals, such as cats, the size of the cerebro spinal pathways creates hydraulic resistance which limits the flow rates which may be achieved at atmospheric pressures using certain pathways. In such animals, higher oxygen exchange values and shorter perfusion routes, such as the ventriculo-cisternal perfusion route, are preferred. In larger animals, such as humans, it is not anticipated that

50% preferably 80+% of the maximum obtainable pO.sub.2) are preferred to minimize the volume of perfusate necessary to perform a given treatment and to provide an additional margin of safety at the selected flow rate.

PAR Samples of the perfusing fluids for the animals of this example were removed at predetermined times from entry and exit perfusion ports for analysis of lactate and pyruvate under a single blind condition. The results are summarzied in Table IV:

TBL TABLE IV

Levels of lactate and pyruvate in cerebral spinal fluid perfusate before (baseline), during (isoelectric) and following (reflow) global ischemia in cats. Data are expressed in mg per 100 ml of perfusate and the values are means .+-. standard error. Six animals were perfused with NS.sup.1 and 7 with OFNS.sup.2 solution. After collecting the perfusate in tubes a 4#C, the samples were stored at -80.degree. C. for analysis. Lactate and Pyruvate were assayed by a Sigma Method (Sigma Technical Bulletin #726, -Oct. 1968 and #862, Oct. 1969) and conducted by Jefferson University Clinical Laboratories.

Experimental Period	Lactate		Pyruvate		Lactate/ Pyruvate Ratio	
	NS	OFNS	NS	OFNS	NS	OFNS
Baseline.sup.+	3.6.+-.1.1*		0.5.+-.0.1		7.2	
Isoelectric.sup.+	8.1.+-.1.9*		0.5.+-.0.1		16.2	
Reflow (5 min)	21.9.+-.11	10.0.+-.1.0	0.5.+-.0.1	1.2.+-.0.6	43.8	8.3.sup.+
Reflow (4 hr)	8.9.+-.3.3	10.4.+-.3.8	0.5.+-.0.1	1.7.+-.0.7	17.8	6.1

*During baseline and isoelectric time periods all cats were perfused with NS.

.sup. + $p < 0.01$ when compared to baseline lactate. $p < 0.025$ when compared to the ratio of reflow (5 min) perfused with NS.

.sup.1 As used herein, NS refers to the nutrient solution of Example 1 without fluorocarbon component.

.sup.2 As used herein, OFNS refers to the preferred oxygenated, fluorocarbon nutrient emulsion of Example 1.

PAL In animals perfused with nutrient solution without fluorocarbon the concentration of lactate during the actual stroke (isoelectro) was of the normal CSF value. The lactate level rose percipitiously, an additional

440%, within 5 minutes of restoring the blood pressure and blood flow through the carotid arteries. Thereafter the level declined during the 4 hour period to 147% of base line. In contrast to the lactate data, the pyruvate concentration remained constant through the perfusion period.

PAR When animals were perfused with oxygenated nutrient emulsion, on the other hand, the percipitious increase in lactate did not occur; instead there was a modest 52% rise during the initial 5 minute period, and the level thereafter remained stable. Significantly, in the oxygenated series the concentration of pyruvate more than doubled during the initial 5 minutes and continued to increase gradually during the remainder of the 4 hour period. The net production of lactate and pyruvate are often used as indictators of anarobic and aerobic glycolysis, respectively. Since these compounds change under different circumstances the expression of lactate/pyruvate (L/P) ratio best illustrates the net metabolic effects. A high L/P ratio indicates that anarobic glycolysis predominates. It is common practice, therefore, to use the L/P ratio as a sensitive indicator of the redox state of cells. Perfusion oxygenation in accordance with the present inventions significantly (p.ltoreq.0.01) lowered the L/P ratio when compared to non-oxygenation (8.3 vs. 43.8). It is further evident that the oxygenated 4 hour L/P ratio is additionally lowered, whereas the non-oxygenated values are still 5 times greater than the control.

PAR Although the oxygenated nutrient perfusate transit time through the brain is only a few seconds, significant oxygen extraction does occur. It was determined by the pO.sub.2 difference between inflow and outflow fluids that oxygenated nutrient emulsion lost pO.sub.2 =210 (mean) during its intracerebral passage. Also unique to the oxygenated nutrient emulsion studies was a rising carbon dioxide presence in the exit fluid which did not occur in non-oxygenated experiments. The pCO.sub.2 rose 5 fold in these fluids over the four hour period (pCO.sub.2 =6.0 vs. 3.0). It is considered that the appearance of carbon dioxide is important since it is a normal product of aerobic metabolism.

PAR In FIGS. 10 and 11 levels of potassium in perfusate before (base line), during (isoelectric) and following (reflow) global cerebral ischemia in cats are represented. Data are expressed in micro equivalents per minute, and the values are means .+-. standard error. Five animals were perfused with nutrient emulsion without fluorocarbon, and six with oxygenated fluorocarbon emulsion. After collecting the perfusate in tubes at 4.degree. C., the samples were stored at -80.degree. C. for analysis. Potassiums were assayed by atomic absorption spectrophotometry. During the base line and isoelectric time periods, all 11 cats were perfused with nutrient emulsion without fluorocarbon. There were no significant differences between isoelectric and base line levels of potassium in the perfusate. As seen from FIGS. 10 and 11, significant differences in the values of potassium were observed beginning almost immediately with perfusion (at time 0) and extending throughout the 4 hour experimental period.

PAR FIG. 12 discloses the effects on glucose metabolism for ventriculo-cisterna perfused animals subjected to the stroke and reperfusion procedure of this example. In accordance with the invention of Dr. John Lewis Alderman, one of these animals was perfused with twice the glucose concentration (372 mg %) of that used for the remaining animals described herein. As seen from FIG. 12, the glucose metabolism of animals provided with oxygenated nutrient emulsion (glucose =186 mg %) is generally superior following reperfusion to the metabolism rate of the control receiving that solution without fluorocarbon. In view of the substantial increase in glucose mg %), it is presently preferred to include at least such elevated glucose concentrations in perfusions performed in accordance with the method of the present invention.

PAR These experimental results demonstrate that extravascular perfusion of oxygenated nutrient emulsion affects a significant reversal of the adverse cerebral metabolic effects induced by the experimental stroke condition. Coincident with the improve metabolic state electrocerebral activity returned. These findings indicate that extravascularly supplied oxygen, glucose and other nutrients were taken up and metabolized in amounts sufficient to restore high energy compounds and thereby reactivate membrane ionic pumps and reinstitute electrocerebral activity.

PAR Oxygenated-fluorocarbon-nutrient-emulsion caused no detrimental effects on vital physiologic functions such as heart rate, blood pressure or electrocerebral (EEG) activity when perfused through the ventricular system for four hours of cats not subjected to the stroke paradigm. These animals exhibited no ill effects after 5-8 months, and were killed for a double blind neuropathologic examination of the brain, spinal cord and subarachnoid spaces. No gross or microscopic changes were observed and the specimens were indistinguishable from non-perfused animals.

PAR In view of the above, those of ordinary skill in the art will recognize that various modifications can be made to the methods and apparatus described above without departing from the scope of the present invention. For example, it should be understood that, the injection and withdrawal catheters used to perform the herein described method should be sealed with respect to the skull so that a water and bacteria tight seal is created between these catheter and skull. Although conventional bone wax has been used for creating this seal in the feline experiments described above, fitting 22(a) preferably comprises a double threaded sleeve which is threaded into a bone aperture, and in turn receives complimental threads formed on injection catheter 20a. Such attachment means, particularly when used with a ventricular injection catheter, should eliminate any need for total head immobilization during human treatment.

PAR It should also be understood that the oxygenated nutrient emulsions of the present invention may contain various therapeutic agents including free fatty acids, prostaglandins, prostacyclins, cyclic nucleotides and hormones.

PAR As seen from the above, it is desired to maintain the the p0.sub.2 level in the withdrawn fluid at levels which are substantially above the minimum level of efficient oxygen exchange of the subject fluorocarbon. For the fluorocarbon nutrient emulsion described above, that minimum (unsaturated condition) occurs at a p0.sub.2 equal to about 190, which is about 30% of the readily achieved maximum p0.sub.2 level. (p0.sub.2 =645) As described above, it is preferred to perform the treatment method of this invention so as to maintain the p0.sub.2 of the withdrawn oxygenated nutrient emulsion at a p0.sub.2 above 400, that is, at a p0.sub.2 level which is about twice the minimum level of efficient oxygen exchange for the subject fluorocarbon. It is presently anticipated that a similar differential should be maintained in practicing the present invention utilizing oxygenated nutrient emulsions having other oxygenatable components exhibiting different ranges of efficient oxygen exchange.

PAR The methodology described requires the formulation of a physiochemical fluid which must be adequately oxygenated, temperature controlled and delivered under well controlled conditions. The perfusion system of the present invention may be routinely placed by trained animal surgeons. Neurosurgeons commonly possess skills necessary to implant treatment ports in accordance with the present invention in humans. The procedure is relatively simple and can be quickly accomplished with available instruments. The oxygenated nutrient emulsion treatment delivery system of the present invention has certain similarities to the arterial heart-lung machine. Major differences, however, include the use of a complex synthetic fluid for cerebral spinal perfusion, the route performed by cerebral spinal perfusion is an extravascular one, and there is no known limitation on perfusion time in accordance with the herein disclosed method. Oxygenated fluorocarbon nutrient emulsion tolerates pumping mechanics well and the exit fluid can either be discarded or recirculated. Formed blood elements, on the other hand, are fragile and lyse under prolonged recirculation conditions. It is presently contemplated that cerebral-spinal fluid perfusion support will need to be carried out until the vascular system can once again take over. Surgical revascularization or bypass procedures will in some cases be necessary to accomplish this end. The return of cerebral vascular compentency can be assessed by measurements of regional blood flow, electro cerebral activity, and the metabolic configuration of the exit perfusion fluid. One foreseeable complication of this technique is bacterial infection, and rigorous attention to ambient sterility, millipore filtering, and antibiotics should reduce this hazard to acceptable levels. Safeguards have been built into the pumping system to immediately stop delivery if either the inlet or outlet become obstructed.

PAC Conclusion

PAR As seen from the above examples, and the foregoing description, circulation of the preferred embodiment nutrient liquid is capable of sustaining cellular integrity, aerobic metabolism and ongoing neuronal function. Even for neurons deep within the spinal cord (grey matter) the process has been successful in nurturing the ischemic neurons. The ability to sustain the central nervous system in a lethally ischemic field which persists for longer than a few minutes has never been accomplished before. The extravascular pathway has not been employed as a global nutrient route prior to the present invention, nor has the combined use of oxygen rich emulsion which also contains the other disclosed novel components been know to the art.

PAR As seen from the above experiments, the methods, compositions and system of the present invention are capable of providing substantial amounts of oxygen to neurologic tissues to be treated, while at the same time, removing the by-products of aerobic metabolism, including carbon dioxide, which have been found to exist in substantially higher concentrations in the exit, diagnostic fluid. Similarly, as discussed above, rapid, normally lethal, lyses of anterior horn cells is readily preventable through the treatment of the present invention, protecting at least 60% of the cells through this modality. Similarly, high energy phosphate metabolism utilizing both oxygen and glucose is maintained at substantial levels. Accordingly, the methodology of the present invention represents a substantial advance in the treatment of central nervous system tissue. Prior to this invention there was not a method available to sustain central nervous tissues after a few minutes of profound ischemic insult. This invention should revolutionize the therapeutic capabilities by providing therapeutic approaches for stroke, aneurysm, brain injury, vasospasm, senility, tumors, coma, spinal cord injury, ischemia, post shock, post cardiac arrest and central nervous system poisoning.

PAR It is further anticipated that the treatment method of the present invention should make it possible to interrupt the cerebral blood supply with some impunity for surgical maneuvers not heratofore possible without skill in the art will recognize that future development may result in perfection of the oxygenated nutrient emulsion composition, delivery rates, treatment times, the width of the therapeutic window in which treatment may be instituted and the correlation of behavioral functions in surviving animals with normalization of cerebral chemistry and electrographic activity. Nonetheless, by any standard, the present invention provides a dramatic, yet clinically acceptable, therapeutic method for treating ischemic neurologic tissue.

CLMS
STM What is claimed is:
NUM 1.
PAR 1. A method of treating hypoxic-ischemic central nervous system tissue comprising:
PA1 (a) providing a physiologically acceptable oxygenated fluorocarbon emulsion as treatment fluid;
PA1 (b) establishing a circulation of said fluid through an oxygenator at a first preselected flow rate to oxygenate said fluid;
PA1 (c) injecting said oxygenated fluid into the cerebrospinal pathway at a first injecting point and at a second preselected rate;
PA1 (d) substantially continuously withdrawing fluid from said cerebrospinal fluid pathway at a second point which is selected to create a circulation of said oxygented fluid in the vicinity of said hypoxic-ischemic tissue sufficient to support significant aerobic respiration of a portion of said tissue,
PAL whereby said portion of said tissue will be metabolically sustained during said treatment.
NUM 2.
PAR 2. The method of claim 1 wherein step (b) further comprises establishing a circulation of said fluid through a heat exchanger to adjust the temperature of said fluid prior to injection.
NUM 3.
PAR 3. The invention of claim 2 wherein step (a) further comprises providing a reservoir means for containing said fluid and step (b) further comprises establishing a separate circulation through said heat exchanger to said reservoir.
NUM 4.
PAR 4. The method of claim 3 wherein said separate circulation is established at a third preselected flow rate.
NUM 5.
PAR 5. The method of claim 1 wherein step (c) further comprises first forcing said fluid through a filter.
NUM 6.
PAR 6. The method of claim 5 wherein said filter is a bacterial filter.

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PATN
WKU  044459700
SRC  6
APN  2679418
APT  1
ART  173
APD  19810601
TTL  High mineral composite fine paper
ISD  19840501
NCL  28
ECL  1,2,3
EXP  Chin; Peter
NDR  1
NFG  1
INVT
NAM  Post; Richard L.
CTY  Ridgway
STA  PA
INVT
NAM  Fort; Robert G.
CTY  St. Marys
STA  PA
ASSG
NAM  Penntech Papers, Inc.
CTY  White Plains
STA  NY
COD  02
RLAP
COD  72
APN  199165
APD  19801022
PSC  03
CLAS
OCL  162135
XCL  162136
XCL  1621646
XCL  1621682
XCL  1621683
XCL  1621811
XCL  1621812
XCL  1621814
XCL  1621816
XCL  1621818
EDF  3
ICL  D21F 1100
FSC  162
FSS  169;183;181.1;168.1;181.2;175;181.4;135;181.8;136;158;164.1;164.6;168.2
     ;168.3;181.6
UREF
PNO  2657991
ISD  19531100
NAM  Walsh et al.
OCL  162169
UREF
PNO  3119731
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NAM  Strole et al.
OCL  162183
UREF
PNO  3844880
ISD  19741000
NAM  Meisel et al.
OCL  162169
UREF
PNO  4225383
ISD  19800900
NAM  McReynolds
OCL  162169
FREF
PNO  619559
ISD  19610500
CNT  CAX
OCL  162169
FREF
PNO  627550
ISD  19610900
CNT  CAX
OCL  162169
FREF
PNO  0006390
ISD  19800100
CNT  EPX
LREP
FR2  Flocks; Karl W.
FR2  Neimark; Sheridan
ABST
PAL  Composite fine paper suitable for offset and gravure printing at high
      speeds and containing over 30% filler up to 70% filler for basis weights
      of 30-150 lbs/3300 ft.sup.2, is produced on a high speed paper-making
      machine from a furnish containing large quantities of filler, preferably a
      mixture of clay and talc, and including 3-7% of an ionic latex which is
      selected to provide good retention and good strength without leaving a
      residue on the screen.
PARN
PAC  DESCRIPTION
PAC  FIELD OF INVENTION
PAR  This application is a continuation-in-part of patent application Ser. No.
      193,165, filed Oct. 22, 1980 by Richard L. Post and Robert G. Fort,
      entitled "HIGH MINERAL COMPOSITE FINE PAPER" and now abandoned.
BSUM
PAR  The present invention relates to offset or gravure printable fine paper
      and, more particularly, to highly mineral filled fine paper weighing from
      30 to 150 lbs/3300 ft.sup.2 and having sufficient strength to be usable
      for offset or gravure printing.
PAC  BACKGROUND OF THE INVENTION
PAR  Normal fine paper contains internally some filler up to a maximum of about
      30% mineral filler. As fine paper suitable for offset and gravure printing
      must have sufficient strength to resist the printing operation which is
      carried out under high speed, and this includes both tensile and
      Z-direction strength, it has been found that the use of high quantities of
      mineral filler are not suitable. Indeed, the normal offset printable fine
      paper has a very low mineral filler content, and this paper is normally
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surface sized after the paper web has been dried. The term "fine" paper is used in the conventional industry sense and includes tablet, bond, offset, coated printing papers, text and cover stock, coated publication paper, book paper and cotton paper; it does not include so-called "high-strength" paper products.

PAR The use of filler internally in the manufacture of paper in general and fine paper in particular has been practiced for many years using common fillers such as kaolin clay, talc, titanium dioxide, calcium carbonate, hydrated aluminum silicate, diatomaceous earth and other insoluble inorganic compounds. The use of filler accomplishes two objectives: one is the extension of the paper-making fibers to reduce cost and the other is to obtain certain optical and physical properties such as brightness and opacity. In fine paper manufacture, fillers are normally added at a level of 4-20% by weight of the finished paper, although rarely as much as 30% filler has been used in Europe and 25% in the United States. Fine paper manufacture in part depends on hydrogen bonding and one problem which occurs in the use of more than 20% filler in fine paper manufacture is that too much filler reduces hydrogen bonding and causes the web to lose its strength. Using external methods of application, such as coating with pigment/adhesive mixture on the size press or coater, the total filler content can easily be increased.

PAR Fine paper containing up to a maximum of 30% filler is normally made by adding 15-20 pounds of cationic starch or 1-5 pounds of guar gum per ton of dry furnish, as normal internal strength agents. Latices are sometimes used in paper manufacture as noted below, but not in fine paper manufacture because such latices are normally sticky and difficult to use on a Fourdrinier machine for making fine paper at high speed.

PAR The U.S. Pat. No. 3,184,373 to Arledter discloses the production of paper having greater than normal quantities of mineral fiber, but no mention is made of the properties of the resultant paper. The Arledter process depends on what is referred to as a synergistic mixture of filler retention aids, including a water soluble mucilaginous material, such as guar gum, and a water-soluble polyethylene imine resin. An earlier patent in the name of the same patentee, U.S. Pat. No. 2,943,013, contains similar subject matter, but the resultant paper is specified to be for use in the manufacture of decorative laminates, i.e. there is no requirement for the high strength necessary for fine papers which are to be printed by the offset method.

PAR It has been common knowledge in the paper industry that the addition of an anionic latex to the wet end of a paper machine combined with a cationically charged chemical, such as alum, causes the latex to precipitate in the presence of the paper-making fibers and fillers and thereby gives the paper increased strength. This procedure is normally used in the manufacture of certain so-called "high-strength" products such as gasket material, saturated paperboard, roofing felt, flooring felt, etc. No similar technique has heretofore been suggested for the manufacture of fine paper having greater than normal quantities of mineral filler.

PAR A number of prior patents disclose the general idea that a charged latex can be added to the paper-making furnish. Because of the basic electro-chemical reaction of an anionic paper-making system, a cationic latex precipitates easily and provides additional fiber bonding and, accordingly, strength to the resultant paper. These patents relate primarily to so-called "high-strength" papers which are largely devoid of fillers, or at best contain only very small quantities of fillers or the use of a cationic latex, but pigment is not essential. Also the U.S. Pat. No. 4,187,142 to Pickleman et al discloses the use of an anionic polymer co-additive with a cationic latex, with the use of a sufficient amount of latex to make the entire paper-making system cationic; the use of fillers in any example is not mentioned. Foster et al U.S. Pat. No. 4,189,345 discusses extremely high levels of cationic latex.

PAR It has been proposed noting the McReynolds U.S. Pat. No. 4,225,383, in the manufacture of relatively thick paper product, similarly to the manufacture of roofing and flooring felt papers, to use the combination of a cationic polymer with an anionic latex, and substantial quantities of mineral filler. Once again, however, the product is not designed for printing using the offset method, and its strength requirements are accordingly relatively low. Moreover, because of the substantial thickness of the products produced by such a technique, the product is given some additional strength merely by means of its mass.

PAR The Riddell et al U.S. Pat. No. 4,181,567 is directed to the manufacture of paper using an agglomerate of ionic polymer and relatively large quantities of filler. The patentees indicate that either anionic or cationic polymers may be used, and fillers mentioned are calcium carbonate, clay, talc, titanium dioxide and mixtures. In example 1, an 80 basis weight paper having 29% ash is produced using calcium carbonate as the filler. This patent in essence discusses precipitation of the pigment with a retention aid system prior to its addition to the paper-making system.

PAR Such Riddell et al patent mentions German Offenlegunschrift No. 25 16 097 near the bottom of column 1 thereof, the latter of which corresponds to U.K. Pat. No. 1,505,641 which discloses the pre-treatment of calcium carbonate with a styrene-butadiene latex to produce a protected pigment which can then be used in paper making preferably at the 20% by weight level, although the patent does state that there is little or no reduction in strength up to the 50% by weight level. In more detail, the U.K. patent discloses mixing an anionic latex with an aqueous suspension of the special filler having a cationic charge, e.g. made by mixing with positively charged starch. One to twenty parts of latex are used per 100 parts of filler, and the filler composition is added to the beater, pulper or elsewhere before the breast box. Example III shows the use of 400 parts of filler to 700 parts of wood fiber. A point to be emphasized, however, is that the technique of the U.K. patent requires extra equipment and extra processing, as the filler is first encapsulated and then only later added to the paper-making system; in other words, the technique of the U.K. patent is unduly complex. Moreover, the encapsulation provides inadequate protection to enable the calcium carbonate to be used in acidic medium without undesirable foaming.

PAC SUMMARY OF THE INVENTION

PAR It is, accordingly, an object of the instant invention to overcome deficiencies in the prior art, such as indicated above.

PAR It is another object to provide fine paper suitable for use in offset printing, which paper contains more than normal quantities of mineral filler.

PAR It is a further object to provide good quality, fine paper of thickness 1.5-15 mils, preferably 2-8 mils, and a weight of 0.009-0.945 lbs/ft.sup.2, having adequate strength for offset printing and having a high mineral filler content ranging from about 30% filler for 30 pound paper (based on 3300 ft.sup.2) to 70% filler for 70-150 pound paper.

PAR It is yet another object of the invention to provide a process for making good quality, fine printing paper containing large amounts of mineral filler, in an economical manner, at less cost, and at a higher production rate.

PAR It is yet a further object to provide high mineral content paper of good quality containing a synergistic mixture of mineral fillers.

PAR These and other objects and the nature and advantages of the instant invention will be more apparent from the following detailed description of various embodiments of the instant invention, taken in conjunction with the following drawing of an exemplary embodiment.

DRWD

PAC BRIEF DESCRIPTION OF THE DRAWING

PAR The sole FIGURE is a schematic flow sheet showing a system, upstream of the paper-making machine, for preparing a paper-making furnish in accordance with the invention.

DETD

PAC DETAILED DESCRIPTION OF EMBODIMENTS

PAR Generally in accordance with the invention, fine paper of thickness 1.5-15 mils, preferably 2-8 mils, and weight 9-45.times.10.sup.-3 lbs/ft.sup.2, preferably 9-24.times.10.sup.-3 lbs/ft.sup.2, is produced containing from 30% mineral filler to 70% mineral filler, although it will be understood that the invention can be used in making other types of paper and that the filler range will depend on the ultimate use for which the paper is intended. However, for fine paper suitable for use in offset printing, 30% mineral filler will normally be used for 30 pound paper, 40% for 40 lbs, 50% for 50 lbs, 60% for 60 lbs and 70% mineral filler for 70-150, preferably 70-80, pound paper, all based on 3300 ft.sup.2.

PAR The fine paper is suitably produced on a conventional Fourdrinier paper machine at increased speeds with a major energy saving which permits production increases, although it will be understood that other types of paper-making equipment can also be used, e.g. cylinder machines, twin wires, etc. Because of the exceptional strength of the present paper-making system in relation to other high filler content fine paper systems, the paper machine runs better and the resultant fine paper can be used in general printing processes and functions as a bond paper.

PAR The use of large quantities of mineral filler drastically reduces the cost of the fine paper manufacture. In the first place, there is provided a savings of $30-70 per ton in the materials from which the fine paper is made. This number will increase as fiber is much more costly than filler material and tends to increase in cost more rapidly. Moreover, the high mineral filled paper is much easier to dry than normal paper and therefore the machinery can be run more rapidly, e.g. 10-25% more rapidly, which reduces production costs. Furthermore, the amount of steam necessary to dry the paper is reduced, conservatively, at least 15% and, more realistically, as much as 30%.

PAR In addition to the mineral filler, the fine paper is normally made from hardwood and softwood pulps prepared by various conventional pulping processes, as well as the conventional paper-making chemicals such as rosin size, alum and polymeric retention aids. It will be understood, however, that the invention can also be used in the manufacture of synthetic paper. With regard to the wood fibers used, any conventional stock may be used. Desirably, however, the wood fibers in the furnish will be from 50-100% hardwood kraft, with 0-50% softwood kraft, most desirably 25% softwood kraft and 75% hardwood kraft. Calculated on the basis of total solids in the furnish, it is preferred to have 15-30% by weight softwood kraft and 15-50% hardwood kraft.

PAR The paper-making slurry in accordance with the invention is preferably at and rosin size are preferably but not essentially present, and by term "rosin size" it is intended to encompass dispersed rosin size, synthetic rosin size and rosin derivatives. Other methods of internal sizing can also be used. Polymeric polyacrylamide (such as Accostrength) dry strength additives can also be used in this system to promote additional dry strength and some wet web strength on the paper-making machine.

PAR The preferred furnishes all contain alum and rosin size, preferably in the ratio of approximately 3 parts of alum to one part of rosin size, although it will be understood that these ratios may be varied. Suitable quantities are 5-10 pounds of rosin size per ton of dry furnish, and an amount sufficient of alum, usually about 10-20 and preferably 15 pounds of alum per ton of dry furnish to provide a pH of 4.0-5.0.

PAR An important aspect of the present invention is the use of a suitable latex. The latex can be a styrene-butadiene latex, an acrylic latex, a polyvinyl acetate latex, or another type of latex, but most latices which have been used for wet-end saturation are not necessarily suitable because they will not exhaust onto the fibers and fillers when precipitated. It has been found that the most satisfactory latex is an amphoteric latex which is cationic under the preferred conditions of use, e.g. cationic under acid conditions. Cationic latices may also be used. Even an anionic latex can be used, although it has been found that the anionic latex is less satisfactory. Cationic latex, compared to anionic latex, is easier to use, provides good strength and better retention.

PAR The latex, preferably cationic (positive) under the preferred conditions of use, is of a charge opposite to and less than that of the anionic (negative) paper-making system, and thereby precipitates easily on the negatively charged paper fibers and filler (clay) particles thereby forming a paper floc nucleus which, however, remains anionic because the net charge of the fibers and clay filler is greater than that of the cationic latex. As is known, the normal paper-making slurry has an anionic charge because this is the normal charge of the cellulose fibers. In addition, most mineral fillers, i.e. clays, are also strongly anionic, and this adds to the negative charge of the system. Where the filler used is non-ionic or slightly cationic, precipitation of the latex occurs mostly on the cellulose fibers, but floc formation still occurs with the filler becoming entrained in the floc and thereby attaching to the fiber.

PAR It will be understood that in order to reduce the anionic charge it is desirable to add to the system a cationic polymer. Indeed, in accordance with the preferred embodiment, two cationic polymers, alum (which is also cationic), rosin and latex, are added to the system. It will be understood that when an anionic latex is used, the quantity of cationic polymer used should be sufficient to precipitate the anionic latex.

PAR The floc formed by the precipitated latex can either be anionic or cationic and is dependent upon the amount and charge density of the latex used, the pH of the paper-making system and the materials other than the latex used, e.g. type of fiber, type of filler, the charge density of the anionic materials used, etc. This is so because the quantity of latex used is small compared with amounts used to make paperboard or saturated felt, generally running between only 3 and 7% based on the dry furnish. Nevertheless, in spite of the small amount of latex used, which itself is an economic advantage, the characteristics of the floc formed provide excellent retention on the wire of the paper-making machine. Use of this system, as opposed to a standard wet-end saturation approach, gives better filler retention; and, of course, when filler retention is poor, filler is lost which is difficult to recover. In addition, lost filler tends to build up in the wet-end system which can cause runnability problems. At the 5% by weight latex addition levels and with the addition of cationic polymer, the systems allows approximately 87% total retention in the first pass.

PAR As mineral filler, there can be used almost any material that is not water soluble. Most common paper-making filler materials may be used, e.g. kaolin clay, talc, titanium dioxide, aluminum hydrate, hydrated silica, calcium carbonate, etc., and these fillers are accordingly referred to as being "system compatible". Certain fillers have, however, been found to be undesirable when used by themselves; these include diatomaceous earth. Another filler found less satisfactory than others is porous calcined clay, such as high opaque clay and Ansilex. On the other hand, fillers which have been found particularly desirable are various forms of talc, including Mistron vapor talc which is a high brightness talc, and Yellowstone talc. Calcium carbonate is system compatible only in neutral or basic media, and not in paper-making slurrys below the pH of 7.0, as calcium carbonate reacts at acidic pH to generate carbon dioxide which causes foam problems, and therefore calcium carbonate cannot be used in the standard acidic paper-making system where the pH is between 4 and 5.

PAR A particular blend of fillers has been shown to provide superior results, i.e. the two components of the blend act synergistically to provide improved results, primarily increased strength at given filler contents. Thus a mixture of talc, which is neutral in charge, and kaolin clay, which is strongly anionic, act together synergistically to give a stronger product, it being theorized that the talc particles have a physical affinity for the latex and therefore sequester and absorb the latex and act as nuclei for the flocculation. The talc does not disrupt the fiber bonding as much as the kaolin clay. The blend of kaolin clay and talc may range from 95:5 to 5:95 parts by weight, although the preferred range is 5-75% talc for 95-25% kaolin clay. Calculated on the basis of total solids in the furnish, the preferred filler content is 10-30% talc and 10-30% kaolin clay.

PAR The clay, preferably kaolin clay, ranges in particle size from very fine, e.g. about 0.5 microns, to relatively coarse, e.g. maximum size about 15 microns. A highly suitable clay is Astraplate (Georgia kaolin) which is a kaolin clay composed of thin hexagonal plates, 80-82% of which are finer than 2 microns and only 0.005% of which are retained on a 325 mesh screen. Suitable special kaolin clays are disclosed in U.S. Pat. Nos. 2,904,267; 3,477,809; and 4,030,941. The talc is desirably ground to 325 mesh, although its size also is subject to considerable variation.

PAR The synergistic filler system of talc and kaolin clay can be used in high filler content fine papers containing up to 70% by weight filler. When used with the preferred amphoteric latex system, as described above, or even with the next-preferred cationic latex system, the resultant sheet has excellent strength. Even if anionic latex is used instead of the cationic latex, the system will still have good strength because of the filler synergism, although there are operating problems using the anionic latex because it is more difficult to control the precipitation and insure adequate paper floc strength in an acid furnish with the anionic latex due to its charge compatibility with the other components of the furnish. Another problem with the anionic latex system is that the fillers are normally dispersed in water and the dispersion agents normally used are anionic; as the filler must be flocculated with the cationic polymer, excessive polymer usage is required which creates problems in standard paper-making systems and in the handling of the filler.

PAR With reference to the attached drawing, it is seen that hardwood pulp, plural fillers are used they may be pre-blended together) and the slurry then fed to a funnel where latex and rosin are then added, with the mixture flowing into the machine chest; or the latex and rosin may be added directly to the machine chest. From the machine chest the slurry is pumped to a stuff box and on the way alum and a first cationic polymer, e.g. Dow XD-30440.01, are added. From the stuff box the slurry is diluted with water from the white water system, then pumped to the conventional cleaners and screens. Finally the furnish is pumped to a paper machine head box, and on the way a second cationic polymer, e.g. Betz 1260, which also serves as a retention aid, is added.

PAR With reference to the FIGURE, it will be seen that cationic polymer is added at two different points. These polymers are each added to the furnish in an amount of about 0.25 to 3 pounds per ton of dry furnish, preferably about 0.5 pounds per ton. As the stock leaves the machine chest, e.g. at a solid consistency of about 3%, a first cationic polymer is added to the system, preferably Dow XD-30440.01. This cationic polymer is a high M. W. polyacrylamide polymer of pH 4.6, density of 1.1, solids content of 8% and a bulk viscosity of 15,000-20,000 cps.

PAR After the furnish has left the screens and cleaners and before it reaches the paper machine head box, e.g. head box approach piping, a second cationic polymer, preferably Betz 1260, is added to the furnish normally in an amount of 0.25 to 1 pound per ton based on the dry furnish. The second cationic polymer acts in concert with the other components as indicated above to insure maximum flocculation, and also serves as a conventional retention aid. The Betz 1260 cationic polymer is an extremely high M. W. acrylamide copolymer and is sold as a white, free-flowing, water-soluble powder of density approximately 28 lbs/ft.sup.3. It will be understood that the first cationic polymer addition may be at any location upstream of the second cationic polymer addition, the latter of which should be at any location downstream of the first addition, the precise addition points depending on the paper machine system.

PAR As indicated above, selection of a proper latex is an important consideration in the successful operation of the present process in order to achieve maximum strength for a given high load of mineral filler. As indicated above and shown in the FIGURE, the latex is preferably added at the machine chest, most desirably in an amount between 3 and 7% based on the dry furnish. It is presently unknown why some latices work well and others do not, but it is believed that possibly important characteristics include particle size, charge, charge density and glass transition temperature. Successful operation has been carried out with the following three latices, listed in the order of their desirability.

PAR (1) Rhoplex P-57 Amphoteric Acrylic Latex (Rohm and Haas). This acrylic latex is characterized by being non-ionic under neutral conditions, but becoming cationic under acid conditions. It is sold in the form of milky-white liquid of 50% solid content having a density of 8.8 lbs per gallon and a specific gravity of 1.06 and a Brookfield LVF Viscosity at 25.degree. C. (No. 2 Spindle 60 rpm) of 200 CPS.

PAR (2) Dow XD-30288.00 Cationic Latex (Dow Chemical Co.). This is a carboxylated styrene-butadiene latex.

PAR (3) Dow XD-30374.01 Anionic Latex (Dow Chemical Co.). This is a carboxylated styrene-butadiene latex of pH 8.0, solids content of 45-47%, particle size of approximately 1600 .ANG. and a specific gravity of 1.01. It is disclosed in the McReynolds U.S. Pat. No. 4,225,383.

PAR Also satisfactory are a cross-linkable styrene-butadiene latex of 60% styrene and 40% butadiene; and a styrene-butadiene latex of 90% styrene and 10% butadiene.

PAR Other successful latices can, in view of the present disclosure, be determined by routine testing, key requirements of the latex being that it must precipitate on the fibers and filler to exhaustion or near exhaustion, that it provide good retention, and that it give adequate strength at high filler contents to enable offset or gravure printing when used at levels not substantially exceeding 7%. Such routine testing may be carried out using a furnish of 3-7% of the test latex and a 50:50 mixture of clay filler and wood pulp on a Noble and Wood hand-sheet machine or equivalent laboratory paper-former with white water recirculation using a standard screen of 100 mesh, the paper sheet being pressed once through a felted Noble and Wood or equivalent presser, and then contact dried. A suitable ionic latex is capable of exhaustion or near exhaustion if, in the test, the paper sheet leaves the wire without a latex residue being left behind; provides good retention if in such test about 75% or more, preferably at least 88%, of the filler and fiber is retained; and provides good strength if in such test the resultant paper sheet has at least 10%, preferably at least 16%, mullen.

PAR With all the furnish combinations discussed above, treatment on the paper machine at the size press position or later for external treatment, e.g. coating or sizing, is desirable to produce the best results, as is also true in the production of normal paper. The material used at e.g. the size press may be selected from those normally used including starch size or polyvinyl alcohol, polyvinyl acetate, styrene-butadiene latex, acrylic latices, clay, titanium dioxide, calcium carbonate, talc, and other commonly used material in the coating of paper and any combination thereof which provides the proper functional surface for printing or other functional end use. By "starch size" it is intended to encompass unmodified potato starch, tapioca starch, corn starch, anionic starch and derivatives of such starches. A particularly suitable material is ethylated corn starch having a solids content of 8-12%, and one example of such a material is Penford Gum 280 (Penick and Ford) which is an 80 fluidity, 2% substituted hydroxyethyl corn starch. It may be applied at the rate of between 30-200 pounds, preferably 60 to 150 pounds per ton.

PAR The following examples are offered illustratively. As adequate strength is a most important function of the resultant paper, strength is set forth in percent mullen, defined as mullen in pounds per square inch (psi) divided by the weight of the paper at 3300 square feet.

PAC EXAMPLE 1

PAR Two series of runs of hand sheets were prepared in a Noble and Wood sheet machine. The filler system was 50% kaolin clay and 50% talc. Both furnishes contained 5% latex and 0.39 lbs/ton of cationic polymer. The latex in the first furnish was Dow anionic XD-30374.01, and in the second furnish was Rohm & Haas P-57 amphoteric latex, the pH of the furnish being adjusted to 4.5 making the latex cationic.

PAR Retention was good, strength was adequate, and no residue was left on the screen for both series of trials. However, the filler in the resultant paper was more concentrated in the paper made with the cationic latex, thereby indicating a larger and more stable floc.

PAC EXAMPLE 2

PAR Using a Noble and Wood laboratory sheet machine, samples were prepared with a furnish of 55% kaolin clay, 45% wood pulp comprising a mixture of 75% hardwood and 25% softwood, 5% Dow XD-30374.01 anionic latex, 0.3 lbs/ton of Dow cationic polymer XD-30440.01, 2.5 lbs/ton of dispersed rosin size (Neuphor 100), and 10 lbs/ton of alum.

PAR The quantity of filler retained was 88%, and the quantity of clay in the

XD-30374.01 anionic carboxylated styrene-butadiene latex, 5 lbs/ton of Neuphor 100 and 12 lbs/ton of alum. The ash efficiency was 74.9% and the first pass retention was 74.5%. The paper was not sized externally. The resultant paper contained 42.8% filler and had a strength of 15.3% mullen.

PAC EXAMPLE 9

PAR Example 8 was repeated except that the quantity of paper pulp in the furnish was reduced to 46% and the quantity of coating grade kaolin clay was increased to 54%, and also the latex used was Rhoplex P-57 amphoteric acrylic latex, cationic under the conditions of use. The ash efficiency was 73.19% and the first pass retention was 76.7%. The resultant product contained 46.6% filler and had a strength of 13.5% mullen.

PAC EXAMPLE 10

PAR Example 8 was repeated except that the relative quantities of kaolin clay and wood pulp were adjusted to provide 55% clay and 45% wood pulp. The ash efficiency was 66% and the first pass retention was 66.1%. The resultant product contained 44.7% filler and had a strength of only 9.8% mullen.

PAR Examples 8-10 demonstrate that while the anionic latex approaches the cationic latex in efficiency when the furnish contains no more than about 50% filler, its efficiency drops off considerably, particularly relative to the strength of the product, when the quantity of filler in the slurry reaches 55%.

PAC EXAMPLE 11

PAR Using the pilot paper machine, paper was made from a furnish comprising 46% wood pulp and 54% filler, of which 50% was talc and 50% clay. Also present in the furnish was 5% Dow XD-30374.01 anionic carboxylated styrene-butadiene latex, 5 lbs/ton of Neuphor 100 rosin, 12 lbs/ton of alum and 0.5 lbs/ton of Dow XD-30440.01 cationic polyacrylamide. The ash efficiency was 73.9% and the first pass retention was 79.5%.

PAR The resultant paper was size press treated with starch. It had a filler content of 50.9% and a strength of 20.9% mullen.

PAC EXAMPLE 12

PAR Example 11 was repeated except that the filler comprised 46% talc and 54% clay. The basis weight of the paper produced was 48.8 lbs/3300 ft.sup.2. The ash efficiency was 67.8% and the first pass retention 83.6%. The resultant paper contained 46.9% filler and had a strength of 20% mullen.

PAC EXAMPLE 13

PAR Example 12 was repeated except that the 5% anionic styrene-butadiene latex was replaced with 5% Rhoplex P-57 amphoteric acrylic latex. The ash efficiency was 78.2% and the first pass retention was 87.9%. The product contained 49.3% filler and had a strength of 22.1% mullen.

PAR A comparison between Examples 13 and 12 again shows the superiority of the amphoteric acrylic latex, cationic in use, compared with the anionic latex, other variables remaining constant.

PAC EXAMPLE 14

PAR Example 13 was repeated except that the quantity of filler was increased to 54%, and the relative quantities of talc and clay were changed to provide 21.5% talc and 78.5% clay. The ash efficiency was 72.6% and the first pass retention 87.8%. The resultant paper contained 50.9% filler and had a strength of 17.1% mullen.

PAR Comparing Example 14 to Example 13, it is seen that the strength is reduced, although the retention remains very high.

PAC EXAMPLE 15

PAR Example 12 was repeated except that the basis weight of the paper produced was 96.8 lbs/3300 ft.sup.2, approximately double the weight of the paper of Example 12. The ash efficiency was 83.4% and the first pass retention of 26.5% mullen.

PAR A comparison of Examples 15 and 12 shows that an increase in basis weight, all other factors remaining constant, provides a significant increase in strength for high filler content, fine paper containing a mixture of talc and clay as the filler. Examples 11-15 demonstrate the synergism of the combination of clay and talc, these examples showing that talc at the 50% level is synergistic using all satisfactory latex systems, but is particularly effective with the amphoteric latex where it produces a stronger composite paper.

PAC EXAMPLE 16

PAR Paper sheets of Examples 4, 7 and 14 were printed on a full size Mhiele 1000, four-color offset press, with no problems, with inks designed for coated paper. All of these papers had sufficient strength to withstand the printing process, the press running at 600 ft/min.

PAC EXAMPLE 17

PAR A comparative test was conducted to determine the economics of producing fine paper according to the present invention. Four paper furnishes were prepared from which paper was formed.

PAR The first furnish, the blank or comparative test, comprised 90% wood fiber (75% hardwood, 25% softwood), 12 lbs/ton alum, 5 lbs/ton of rosin and 10% kaolin clay.

PAR Samples 1, 2 and 3 in accordance with the invention comprised similar furnishes except that each of these samples contained 5% of Rhoplex P-57 amphoteric acrylic latex, as well as increased amounts of kaolin clay, Sample 1 comprising 40% clay, Sample 2 comprising 50% clay, and Sample 3 comprising 60% clay.

PAR The four samples were dried to a 5% moisture level at the reel. The results are shown in Table I below:

TBL

TABLE I

Laboratory Dryness Evaluation - Based on 5% Moisture at the Real

Sample	Filler in Furnish	% Filler in Paper	% Dryness	Lbs. Steam to Dry to 5% Moisture	Lbs. Steam Saved Compared to Blank	Cost Saving	% Production Increase
Blank	10%	6.70%	29.34%	5370 lbs.			
1	40%	41.24%	37.39%	3698 lbs.	1672 lbs.	$4.18	31.1%
2	50%	48.46%	38.45%	3530 lbs.	1840 lbs.	$4.60	

```
                                          34.3%
  3   60%  59.16%
               40.36%
                    3249 lbs. 2121 lbs. $5.30
                                          39.5%
```

PAR As shown in the table above, the comparative paper containing 10% clay and no latex after pressing had a dryness of 29.34% while an identically formed and pressed 60% clay and 5% latex paper had a 40.36% dryness after pressing. Consequently, the high filler paper required far less steam heat to dry to a 5% moisture level, and consequently there resulted an important energy savings as indicated in the table. Also, because less drying is required, the production speed is increased as shown.

PAC EXAMPLE 18

PAR A series of hand sheet comparisons were made using different latices and different filler contents. All furnishes were the same except for the differences shown in Tables II and III, which tables also give the comparative results.

TBL TABLE II

```
Clay/Talc Series
          Target
               Basis Wt.                gms    Scott  Actual
          %    lbs/3300 ft.sup.2
                     Caliper
                          Caliper/
                               Mullen
                                    %   Elmendorf
                                               Bond
                                                 %   %   % Filler
Latex     Filler
               Product
                     Mils wt.  psi  Mullen
                                    Tear   Units
                                              Ash Filler
                                                     Retention

BLANK (no latex)
          20   60.2  7.4  1.23 14.0 23.26
                                    64     84 16.5
                                                18.3
                                                     .92

Cross-linkable
60% styrene-
          20   57.7  6.9  1.20 18.0 31.2
                                    74  .  134
                                              17.6
                                                 19.5
                                                     .98

40% butadiene+
90% styrene-
          20   59.1  7.1  1.20 18.2 30.8
                                    76     108
                                              15.3
                                                 17.0
```

```
40% butadiene**
P-57       20   55.0  6.5   1.18 21.3 38.7
                                          60      162
                                                     16.0
                                                         17.8
                                                             .89
BLANK (no latex)
           30   60.4  7.3   1.21 7.7  12.75
                                          48      50 24.5
                                                         27.2
                                                             .91
Cross-linkable
60% styrene-
           30   57.3  6.8   1.19 14.3 25.0
                                          62      141
                                                     25.5
                                                         28.3
                                                             .94
40% butadiene
90% styrene-
           30   55.6  6.7   1.21 12.7 22.8
                                          58      87 21.4
                                                         23.8
                                                             .79
40% butadiene
P-57       30   50.1  6.3   1.26 15.4 30.7
                                          48      136
                                                     21.9
                                                         24.3
                                                             .81
BLANK (no latex)
           40   57.5  7.2   1.25 4.2  7.3 30      40 32.4
                                                         36.0
                                                             .90
latex (i) 40    56.8  6.6   1.16 10.2 18.0
                                          44      85 31.7
                                                         35.2
                                                             .88
latex (ii)
           40   50.6  6.3   1.25 8.0  15.8
                                          44      80 28.5
                                                         31.6
                                                             .79
P-57       40   48.5  6.1   1.26 10.7 22.1
                                          42      114
                                                     27.9
                                                         31.0
                                                             .78
BLANK (no latex)
           50   52.6  6.7   1.27 2.3  4.37
                                          24      32 35.9
                                                         39.9
                                                             .80
latex (i) 50    55.9  6.9   1.23 8.0  14.3
                                          42      101
                                                     39.7
```

```
                                                                 44.1
                                                                     .88
latex (ii)
            50    46.7  6.0  1.29 4.7   10.1
                                             34       63 34.9
                                                                 38.7
                                                                     .77
P-57        50    44.8  5.8  1.30 7.1   15.9
                                             28       91 35.4
                                                                 39.3
                                                                     .79
-------------------------------------------------------------------------------------------
*latex (i)
**latex (ii)
TBL                                         TABLE III
-------------------------------------------------------------------------------------------
Clay Series
            Target
                  Basis Wt,                  gms      Scott  Actual
            %     lbs/3300 ft.sup.2
                         Caliper
                               Caliper/
                                     Mullen
                                           %  Elmendorf
                                                      Bond
                                                         %    %   % Filler
Latex       Filler
                  Product
                         Mils wt.  psi  Mullen
                                             Tear     Units
                                                         Ash Filler
                                                              Retention
-------------------------------------------------------------------------------------------
BLANK (no latex)
            20    60.2  7.7  1.28 10.6 17.61
                                             72       62 15.5
                                                                 17.5
                                                                     .88
latex (i)   20    62.6  7.2  1.15 20.1 32.1
                                             84       126
                                                         15.4
                                                                 17.4
                                                                     .87
latex (ii)
            20    61.7  7.4  1.20 16.0 25.9
                                             78       81 13.9
                                                                 15.7
                                                                     .79
P-57        20    59.1  6.9  1.17 18.7 31.6
                                             50       140
                                                         15.7
                                                                 17.7
                                                                     .89
BLANK (no latex)
            30    58.7  7.3  1.24 6.1   10.39
```

```
                                                          24.8
                                                              .83
latex (i) 30   61.2  7.0  1.14 17.0 27.8
                                         74     113
                                                   21.9
                                                       24.8
                                                           .83
latex (ii)
          30   58.5  7.0  1.20 12.4 21.2
                                         64     70 20.2
                                                       22.8
                                                           .76
P-57      30   55.4  6.5  1.17 12.3 22.2
                                         62     85 22.4
                                                       25.3
                                                           .84
BLANK (no latex)
          40   56.5  6.9  1.22 2.95 5.22
                                         32     35 29.9
                                                       33.8
                                                           .85
latex (i) 40   57.2  6.6  1.15 13.1 22.9
                                         58     108
                                                   29.3
                                                       33.1
                                                           .83
latex (ii)
          40   56.1  6.9  1.23 8.2  14.6
                                         50     58 25.0
                                                       28.8
                                                           .72
P-57      40   50.3  6.3  1.25 9.5  18.9
                                         46     93 26.1
                                                       29.5
                                                           .74
BLANK (no latex)
          50   48.4  6.3  1.30 1.1  2.27
                                         18     29 32.3
                                                       36.5
                                                           .73
latex (i) 50   56.9  6.3  1.11 8.0  14.1
                                         44     101
                                                   36.9
                                                       41.7
                                                           .83
latex (ii)
          50   50.7  6.2  1.22 5.2  10.3
                                         42     54 30.7
                                                       34.7
                                                           .69
P-57      50   44.7  5.7  1.28 6.1  13.7
                                         34     80 30.3
                                                       34.2
                                                           .68
```

PAR To compare the process U.K. Pat. No. 1,505,641 with the present invention, a series of comparative tests were carried out. Consistent with Example 1 of the U.K. patent, the furnish comprised 50 parts of cellulose fibers, 48 parts of filler and 5% latex, based on the total quantity of cellulose fibers and filler. In the trials according to the U.K. patent, the filler was calcium carbonate and such calcium carbonate was pretreated with the latex. In the trials according to the invention, the filler was clay or an equal mixture of clay and talc. Where an anionic latex was used it was Dow XD-30374.01 carboxylated styrene-butadiene anionic latex. Where the latex was cationic, it was Rhoplex P-57. The paper was formed on a laboratory hand-former. The results are given below in Table IV.

TBL TABLE IV

Filler	Latex	pH	Basis Wt. lbs/3300 ft.sup.2	Actual % Filler	% Mullen	% Filler Retention
U.K. Patent 1505641	Anionic	7.5	42.8	39.1	8.2	81.5
U.K. Patent 1505641	Anionic	5.5	43.8	31.1	10.2	64.8
Clay	Anionic	4.6	53.2	41.5	12.5	86.5
Clay Talc 1:1	Anionic	4.7	53.1	39.9	8.5	83.1
Clay	Cationic	4.8	52.5	41.0	13.3	85.4
Clay Talc 1:1	Cationic	4.6	51.6	40.9	14.0	85.2

PAR From the second trial given in Table IV above, it is clear that the system of the U.K. patent is not suitable for use at an acid pH, as the latex did not adequately protect the calcium carbonate which, to some extent, reacted with the acid and caused foaming; 8% of the filler was lost due to reaction with the alum and it can be seen that the calcium carbonate buffered the system to a pH of 5.5. In the trials carried out in an acid pH the target pH was 4.5, achieved by the addition of alum.

PAR The strength of the hand sheets made using the cationic amphoteric latex exceeded the strength obtained by the U.K. patent system at the selected filler level. The U.K. patent system at alkaline pH 7.5 retained 39.1% filler with an 8.2% mullen. The cationic amphoteric latex system with clay and talc retained 40.9% filler with a 14% mullen, and thus was superior to the U.K. system.

PAC EXAMPLE 20

PAR A series of runs were made on a full-size Fourdrinier paper-making machine. The furnish to the machine consisted of 50% wood fiber, 25% kaolin clay (Kaopaque 10) and 25% Yellowstone talc, the fiber constituting 35-40% hardwood kraft and 10-15% softwood kraft based on the total solid content of the furnish. Amphoteric latex P-57 was added at the machine chest in an amount of 4.4% based on the total solids in the furnish. Rosin size was also added in the machine chest at the rate of 7.6 lbs/ton. Alum at the rate of 20 lbs/ton and Dow XD-30440.01 at the rate of 3.2 lbs/ton were added at the suction side of the machine chest pump. Betz 1260 cationic polymer was added prior to the machine head box at the rate of about 0.4 lbs/ton. After paper formation, a size of 10% solids Penford Gum 280 was applied at the size press at a pickup rate of 111-117 lbs/ton. The machine speed was 600 ft/min with a production rate of 4.5-5.0 tons/hr.

PAR Table V shows the average results on the eight runs conducted. Table VI shows the average results on the eight runs conducted after sizing. Table VI shows the average base sheet results.

PAR Results were generally excellent, with very high strength at 40% filler levels. First pass retention levels ranged from 60-80%. The sheets were easily dried, allowing an increase in the production rate. Several rolls were printed successfully with no noticeable buildup on the printing presses.

PAR The tensile properties of the papers so produced are shown in Table VII.

TBL TABLE V

AVERAGE RESULTS AFTER SIZING

	Sets 201-205	Sets 206-208
Basis Weight in lbs/3300 ft.sup.2	75.9	76.7
Moisture %	3.6	3.1
Caliper in mils	6.0	5.3
Smoothness (Sheffield units)		
FS (felt side)	239	136
WS (wire side)	207	156
Gurley Density (seconds/100 ml. air passage)	8.8	15.0
Mullen (psi)	24.2	22.7
GE Brightness	82.9	82.9
% Opacity	95.9	96.1
% Ash	34.7	36.7
Scott Bond (10.sup.-3 ft-lbs)	128	126
Taber Stiffness	3.36	3.40
Bulk/Weight Ratio	0.79	0.69
% Mullen	31.9	29.6
% Filler	38.5	40.5

TBL TABLE VI

AVERAGE BASE SHEET RESULTS

Basis Weight in lbs/3300 ft.sup.2	75.2
Caliper in mils	7.5
B/W Ratio	1.00
Smoothness (Sheffield units)	
FS	340
WS	357
Gurley Density	9

```
     (seconds/100.ml. air passage)
     Mullen (psi)        12.9
     % Mullen            17.2
     GE Brightness       83.4
     % Opacity           97.1
     % Ash               39.6
     % Filler            43.9
     Scott Bond (10.sup.-3 ft-lbs)
                         63
     Taber Stiffness     3.16
      NOTE:
      Sample taken before size press at the end of the trial.
TBL                                    TABLE VII
                         TENSILE PROPERTIES
                         Peak
                            Peak      Breaking
                                           Tensile
                                                 Tensile
                                                     TEA
          Basis Weight
                 %   Caliper
                         Load
                            Elongation
                                  %   Length
                                           Strength
                                                 Energy
                                                     (ft-lb)
     Set  (lb/3300 ft.sup.2
                 Filler
                     (in)
                         (lb)
                            (in)  Strain
                                      (km) (lb/in.sup.2)
                                                 (ft-lb)
                                                     ft.sup.2
     201  59.6   19.8
                     .00511
                         31.97
                            .0621 2.24
                                      1.270
                                           6.26 .times. 10.sup.3
                                                 0.1080
                                                     5.65
     202  74.4   34.0
                     .00578
                         29.75
                            .0523 1.89
                                      0.835
                                           5.15 .times. 10.sup.3
                                                 0.0873
                                                     4.56
     203  77.2   38.2
```

```
           27.31
             .0479 1.73
                   0.730
                      4.67 .times. 10.sup.3
                         0.0743
                           3.83
204  79.1   44.7
         .00603
           23.63
             .0496 1.79
                   0.598
                      3.92 .times. 10.sup.3
                         0.0682
                           3.56
205  81.1   45.8
         .00563
           25.15
             .0440 1.59
                   0.665
                      4.47 .times. 10.sup.3
                         0.0630
                           3.29
206  62.9   38.4
         .00444
           20.51
             .0465 1.64
                   0.887
                      4.62 .times. 10.sup.3
                         0.0549
                           2.87
207  78.6   44.8
         .00491
           25.17
             .0502 1.81
                   0.787
                      5.13 .times. 10.sup.3
                         0.0716
                           3.74
208  75.3   41.6
         .00491
           27.85
             .0517 1.86
                   0.909
                      5.67 .times. 10.sup.3
                         0.0817
                           4.27
PenWeb
   66.9   16.0
         .00539
           34.00
             .0423 1.52
                   1.138
                      6.31 .times. 10.sup.3
                         0.0800
                           4.18
Offset
```

PAC EXAMPLE 21

PAR Using the same machine as used in Example 20, a series of runs were conducted to make 60 lb, 50 lb, and 45 lb paper containing 32-42% filler. Essentially the same procedure was followed as in Example 20, although relatively larger quantities of softwood in relation to hardwood were used in the production of the 50 lb and 60 lb paper. Once again, results were excellent, with the paper drying rapidly and having excellent printability. Results are shown in Tables VIII through XI.

TBL TABLE VIII -

AVERAGE TEST RESULTS

	Set # 534-544	Set # 545-547	Set # 548-551	Set # 552
Basis Weight	58.6	56.4	50.6	45.7
Moisture %	3.7	4.2	3.0	--
Caliper	4.2	3.7	3.4	3.9
Smoothness FS	130	125	115	105
WS	145	140	135	125
Gurley Density	11	13	12	9
Mullen (psi)	23.2	17.5	16.2	18.0
% Mullen	39.6	31.0	32.1	39.4
Brightness	82.6	83.2	83.3	82.3
% Opacity	93.0	93.6	91.5	89.5
% Ash	28.6	35.7	36.0	33.6
% Filler	31.7	39.6	40.0	37.3
Scott Bond (10.sup.-3 ft-lbs)	110	98	107	150
Taber Stiffness	1.82	1.50	1.09	0.75
Bulk/Weight Ratio	0.72	0.66	0.66	0.68

TBL TABLE IX

DRY END CONDITIONS

	Set 543	Set 544	Set 545	Set 546	Set 547	Set 548	Set 549	Set 550	Set 551	Set 552	Common Offset Paper
Basis Weight	58.0	59.3	57.6	56.4	55.3	50.8	50.7	50.5	50.5	45.7	60 50 40
Speed (fpm)											

```
         800 825 825 900 900 900 900 900 900 900 725 775 --
Production
         4.92
              5.19
                   5.04
                        5.38
                             5.28
                                  4.85
                                       4.85
                                            4.85
                                                 4.85
                                                      4.36
                                                           3.83
                                                                3.83
                                                                     3.75
(tons/hr)
Dryer Steam
Pressure:
Main Section
         13.5
              16.0
                   16.0
                        14.5
                             13.5
                                  10.5
                                       10.5
                                            10.5
                                                 10.5
                                                      9.0 20   20   20
(psi)
After Section
         21.0
              24.0
                   18.0
                        20.5
                             19.0
                                  15.0
                                       15.0
                                            16.0
                                                 17.0
                                                      17.0
                                                           30   30   30
(psi)
TBL
                  TABLE X

I.G.T. PRINTING TEST RESULTS
Westvaco Rod Applicator; #7 Ink;
A-spring tension; 50 kg pressure
Set #         Felt Side (fpm)
                             Wire side (fpm)

543            190           400
544            190           420
545            110           290
546             90           260
```

547	100	290
548	110	340
549	130	330
550	130	310
551	90	310
552	190	420

NOTE: 420 denotes no picking

TBL TABLE XI

MATERIAL ANALYSIS

Set #	% Hardwood	% Softwood	% Latex	% Starch	% Moisture	% Filler
543	38.1	15.5	3.9	7.7	3.7	31.1
544	39.6	13.2	3.9	7.3	3.7	32.3
545	28.6	12.8	4.1	7.6	4.2	42.7
546	29.0	18.5	4.1	7.0	4.2	37.2
547	22.9	22.8	4.1	7.2	4.2	38.8
548	26.8	17.8	4.6	7.8	3.0	40.0
549	27.5	17.6	4.6	7.8	3.0	39.5
550	27.0	18.7	3.0	7.8	3.0	40.5
551	24.0	22.2	3.0	7.8	3.0	40.0
552	32.7	15.4	3.3	8.3	3.0	37.3

PAR It will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is shown in the drawings and described in the specification.

CLMS

STM What is claimed is:

NUM 1.

PAR 1. A method of manufacturing fine paper containing mineral filler at a high speed comprising:

PA1 preparing an acidic paper furnish including paper-making fibers; an amount sufficient of mineral filler to retain internally in the fine paper web formed of 30-70% mineral filler, and wherein said mineral filler is system compatible; at least one retention aid agent which comprises a water soluble cationic polymer; and 3-7%, based on the dry furnish, of a cationic latex or amphoteric latex which is cationic at acid pH, said cationic or amphoteric latex being selected from latices which provide good mineral filler retention without substantial reduction in strength, which have a charge opposite to and less than the sum of the charges of the other ingredients of said furnish, and which precipitate on the fibers and fillers to exhaustion or near exhaustion;

PA1 forming a wet paper web from said furnish such as to produce fine paper of thickness 1.5-15 mils and weight 30-150 lbs/3300 ft.sup.2 containing internally greater than 30% mineral filler up to 70% mineral filler, and having tensile and Z-directional strength sufficient to withstand high-speed offset or gravure printing;

PA1 drying said web; and surface treating the dried web to improve the printability thereof.

NUM 2.

PAR 2. A method according to claim 1 wherein

Fourdrinier paper machine.

NUM 3.

PAR 3. A method according to claim 1 wherein said furnish also comprises alum.

NUM 4.

PAR 4. A method according to claim 3 wherein said furnish comprises approximately 5-10 lbs of rosin size per ton of dry furnish and sufficient of said alum to provide a pH of 4.0-5.0.

NUM 5.

PAR 5. A method according to claim 1 wherein said paper-making fibers are cellulose fibers and comprise 50-100% hardwood kraft and 0-50% softwood kraft.

NUM 6.

PAR 6. A method according to claim 5 wherein said cellulose fibers comprise approximately 25% softwood kraft and 75% hardwood kraft.

NUM 7.

PAR 7. A method according to claim 1 wherein said latex is selected from styrene-butadiene latex, acrylic latex, and polyvinyl acetate latex.

NUM 8.

PAR 8. A method according to claim 1 wherein said latex is amphoteric at a pH of 7.0, and is cationic under acidic conditions.

NUM 9.

PAR 9. A method according to claim 1 wherein said retention aid agent comprises two said cationic polymers, each of which is added to the furnish at a different stage during the preparation of said furnish.

NUM 10.

PAR 10. A method according to claim 1 wherein said mineral filler is selected from the group consisting of kaolin clay, talc, titanium dioxide, aluminum hydrate, hydrated silica and mixtures thereof.

NUM 11.

PAR 11. A method according to claim 1 wherein said filler comprises a mixture of talc and kaolin clay.

NUM 12.

PAR 12. A method according to claim 11 wherein said mixture of kaolin clay and talc is in the ratio of 95:5 to 5:95 parts by weight.

NUM 13.

PAR 13. A method according to claim 11 wherein said mixture comprises 5-75% talc and 95-25% kaolin clay.

NUM 14.

PAR 14. A method according to claim 10 or 11 or 12 or 13 wherein the particle size of said filler ranges from 0.5 to 15 microns.

NUM 15.

PAR 15. A method according to claim 1 wherein said preparation of the paper furnish comprises mixing hardwood pulp, broke, softwood pulp and filler, feeding the resultant slurry to a funnel where latex and rosin are added, passing the resultant mixture into a machine chest, adding alum and a first cationic polymer, adding dilution water, and adding a second cationic polymer.

NUM 16.

PAR 16. A method according to claim 15 wherein each of said cationic polymers is added in an amount of about 0.25 to 3 lbs per ton of dry furnish.

NUM 17.

PAR 17. A method according to claim 1 wherein said surface treating of the dried web comprises surface sizing of the dried web comprising coating the dried web with starch size at the rate of 30-200 lbs of said starch size per ton of paper.

NUM 18.

PAR 18. Method according to claim 1 wherein said surface treating of the dried web comprises coating the dried web with starch, polyvinyl alcohol, styrene-butadiene latex, polyvinyl acetate latex, clay, titanium, calcium carbonate, talc, or any combination thereof to improve the surface of printing or other functional end use.

NUM 19.

PAR 19. Method according to claim 1 wherein the thickness of the said paper ranges from 2.0-8.0 mils.

NUM 20.

PAR 20. Method according to claim 1 wherein said paper-making fibers are cellulose fibers comprised of bleached and unbleached hardwood and softwood fibers pulped by various pulping methods, i.e. groundwood, sulfite and kraft pulping including thermomechanical, semichemical and soda pulping process.

NUM 21.

PAR 21. Method according to claim 1 wherein said paper-making fibers contain 1-100% synthetic fibers.

NUM 22.

PAR 22. A method according to claim 1 wherein said fine paper produced has a filler content no greater than 50% by weight.

NUM 23.

PAR 23. Fine paper of 2-13 mils thickness produced according to the method of claim 1 and containing about 40% mineral filler for a basis weight of about 40 lbs/3300 ft.sup.2, about 50% mineral filler for a basis weight of about 50 lbs/3300 ft.sup.2, about 60% mineral filler for a basis weight of about 60 lbs/3300 ft.sup.2, or about 70% mineral filler for a basis weight of about 70-150 lbs/3300 ft.sup.2.

NUM 24.

PAR 24. Fine paper of 3-10 mils thickness having sufficient tensile and Z-directional strength to withstand high-speed offset or gravure printing, of weight 30-150 lbs/3300 ft.sup.2, containing 30-70% mineral filler, produced according to the method of claim 1.

NUM 25.

PAR 25. Fine paper of 3-10 mils thickness having sufficient tensile and Z-directional strength to withstand high-speed offset or gravure printing, of weight 30-150 lbs/3300 ft.sup.2, containing 30-70% mineral filler, produced according to the method of claim 14.

NUM 26.

PAR 26. Fine paper according to claim 23 having a filler content no greater than 50% by weight.

NUM 27.

PAR 27. Fine paper according to claim 25 or 26 wherein said filler has a particle size no greater than about 325 mesh.

NUM 28.

PAR 28. Fine paper of 2-13 mils thickness produced according to the method of claim 3 and containing about 40% mineral filler for a basis weight of about 40 lbs/3300 ft.sup.2, about 50% mineral filler for a basis weight of about 50 lbs/3300 ft.sup.2, about 60% mineral filler for a basis weight of about 60 lbs/3300 ft.sup.2, or about 70% mineral filler for a basis weight of about 70-150 lbs/3300 ft.sup.2, said fine paper having sufficient tensile and Z-directional strength to withstand high-speed offset or gravure printing.

```
PATN
WKU  044460600
SRC  6
APN  4783530
APT  1
ART  124
APD  19830324
TTL  Mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives,
      organoleptic uses thereof and processes for preparing same
ISD  19840501
NCL  12
ECL  1
EXP  Sneed; Helen M. S.
NDR  25
NFG  29
INVT
NAM  Sprecker; Mark A.
CTY  Sea Bright
STA  NJ
INVT
NAM  Hanna; Marie R.
CTY  Hazlet
STA  NJ
INVT
NAM  Tokarzewski; Richard J.
CTY  Keyport
STA  NJ
INVT
NAM  Belko; Robert P.
CTY  Woodbridge
STA  NJ
INVT
NAM  Watkins; Hugh
CTY  Lincroft
STA  NJ
INVT
NAM  Vock; Manfred H.
CTY  Locust
STA  NJ
ASSG
NAM  International Flavors & Fragrances Inc.
CTY  New York
STA  NY
COD  02
RLAP
COD  74
APN  354387
APD  19820302
PSC  01
PNO  4391284
CLAS
OCL  252522R
EDF  3
ICL  A61K  746
ICL  C11B  900
FSC  252
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FSS  522 R
UREF
PNO  3786075
ISD  19740100
NAM  Teisseire et al.
OCL  252522R
UREF
PNO  4293453
ISD  19811000
NAM  Sprecker et al.
OCL  252522R
OREF
PAL  Chemical Abstracts 87:22563j, (1977).
PAL  Chemical Abstracts 64:15763f, (1966).
LREP
FR2  Liberman; Arthur L.
ABST
PAL  Described are mono-oxomethyl substituted polyhydrodimethanonaphthalene
      derivatives having the generic structure:
      ##STR1##
      wherein the dashed line represents a carbon-carbon single bond or a
      carbon-carbon double bond; wherein R.sub.1, R.sub.1 ', R.sub.1 ", R.sub.1
      '", R.sub.1 "", R.sub.3, R.sub.5, R.sub.5 ', R.sub.5 ", R.sub.5 '",
      R.sub.5 "" and R.sub.6 represent hydrogen or methyl with the provisos:
PA1  (i) at least four of R.sub.1, R.sub.1 ', R.sub.1 ", R.sub.1 '" and R.sub.1
      "" are hydrogen; and (ii) at least four of R.sub.5, R.sub.5 ', R.sub.5 ",
      R.sub.5 '" and R.sub.5 "" represent hydrogen;
PAL  and wherein Z represents one of the moieties:
PA1  (i) carboxaldehyde having the structure:
      ##STR2##
      (ii) alkylene dioxy or dialkoxy methyl having the structure:
      ##STR3##
      (iii) hydroxy methyl having the structure:
      ##STR4##
      (iv) acetoxymethyl having the structure:
      ##STR5##
      and wherein R.sub.7 and R.sub.8 take separately represent C.sub.1 -C.sub.4
      lower alkyl or R.sub.7 and R.sub.8 taken together represent C.sub.2
      -C.sub.4 alkylene; wherein the line represented by:
EQU  [++++]
PAL  is either (i) a carbon-carbon single bond when R.sub.7 and R.sub.8 taken
      together are C.sub.2 -C.sub.4 alkylene or (ii) no bond at all when R.sub.7
      and R.sub.8 taken separately represent C.sub.1 -C.sub.4 lower alkyl. Also
      described are processes for preparing such mono-oxomethyl substituted
      polyhydrodimethanonaphthalene derivatives, and processes for using the
      above defined mono-oxomethyl substituted polyhydrodimethanonaphthalene
      derivatives for their organoleptic properties and compositions containing
      said mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives
      including perfumes, perfumed articles (such as solid or liquid anionic,
      cationic, nonionic or zwitterionic detergents, perfumed polymers, fabric
      softeners and cosmetic powders), foodstuffs, chewing gums, toothpastes,
      medicinal products, chewing tobaccos, smoking tobaccos and smoking tobacco
      articles.
PARN
PAR  This is a divisional of application Ser. No. 354,387, filed Mar. 2, 1982
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BSUM

PAC BACKGROUND OF THE INVENTION

PAR Materials including mixtures of natural products which can provide, augment or enhance melony, cucumber, violet-like, green, leafy green, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic and spicy fragrance notes are known in the art of perfumery. Many of the natural materials which provide such fragrances and contribute desired nuances to perfumery compositions are high in cost, vary in quality from one batch to another and/or are generally subject to the usual variations in the natural products.

PAR There is, accordingly, a continuing effort to find synthetic materials which will replace the essential fragrance notes provided by such natural essential oils or compositions thereof. Unfortunately, many of these synthetic materials either have the desired nuances only to a relatively small degree or else contribute undesirable or unwanted odor to the perfume compositions, perfumed articles or colognes using the same. The search for materials which can provide a more refined patchouli-like fragrance, for example, or a more refined floral fragrance, for example, or combination thereof ("floral/patchouli") has been difficult and relatively costly in the areas of both natural products and synthetic products.

PAR In addition, artificial flavoring agents for foodstuffs have received increasing attention in recent years. For many years, such food flavoring agents have been preferred over natural flavoring agents at least in part due to their diminished costs and their reproducible flavor qualities. For example, natural food flavoring agents such as extracts, concentrates and the like are often subject to wide variations due to changes in quality, and type and treatment of the raw materials. Such variations can be reflected in the end product and result in unfavorable flavor characteristics in said end product. Additionally, the presence of the natural product in the ultimate food may be undesirable because of increased tendency to spoil. This is particularly troublesome in food and food uses where such products as dips, soups, chips, saugages, gravies and the like are apt to be stored prior to use.

PAR The fundamental problem in creating artificial flavor agents is that the artificial flavor to be achieved be as natural as possible. This generally proves to be a difficult task since the mechanism for flavor development in many foods is not completely known. This is noticeable in products which have orange flavors, mint flavors, peppermint flavors, and even artichoke-like flavors and corresponding aroma characteristics.

PAR Thus, reproduction of sweet, aldehydic, floral, melony, herbaceous, green, and artichoke-like aroma and taste characteristics has been the subject of long and continuing searches by those engaged in the production of foodstuffs and beverages. The severe shortage of food in many parts of the world has given rise to the development of previously unused sources of protein which have heretofore been unpalatable. Accordingly, the need has arisen for the use of flavoring materials which will make such sources of protein palatable to human sensory organs.

PAR The use of tricyclohydrocarbyl oxomethyl derivatives is known in the art of perfumery. Thus, U.S. Pat. No. 4,123,394 issued on Oct. 31, 1978 discloses specifically the compound having the structure:

##STR6##

and generically the compound having the structure:

##STR7##

wherein R.sub.8 ' is hydrogen, acyl, alkyl or alkenyl.

PAR French Pat. No. 2,424,244 (corresponding to British patent application No.

2,019,841) discloses 8-exo-hydroxymethyl-endo-tricyclcdecanes useful as perfumery agents in soaps, shampoos, cosmetics and waxes wherein the fragrances range from green, green grass-like, fruit-like to wood-like. The generic structure of the compounds disclosed in French Pat. No. 2,424,244 (assigned to the Kao Soap Company of Japan) is:

##STR8##

wherein R is unsaturated C.sub.1 -C.sub.5 alkyl, C.sub.1 -C.sub.5 acyl or glycidyl and the esters are prepared from the compound wherein R is hydrogen by means of esterification with a carboxylic acid and a mineral acid catalyst and ethers are prepared from the compound wherein R equals H using a sodium hydride/alkyl iodide compound and the glycidyl ethers are prepared from allyl ethers by treatment with peracids.

PAR A number of the aldehydes found to be useful in our invention are known in the prior art.

PAR Thus, Japanese Pat. No. J76-011625 of April 1976 (assigned to Nado Research Institute Company) discloses a genus of compounds defined according to the structure:

##STR9##

wherein R.sub.1 ""' represents hydrogen, alkyl, or one of the moieties:

##STR10##

and R.sub.21 is hydrogen or alkyl; and wherein Y represents hydrogen, alkyl or one of the moieties:

##STR11##

wherein R.sub.31 represents hydrogen or alkyl.

PAR In addition, Japanese Pat. No. J75-135071 abstracted at Vol. 84, Chem. Abstracts 43466h discloses the compound having the structure:

##STR12##

and Chem. Abstract Vol. 60, 4026g (1964) Abstract of Compt. Rend. 257 (20) 2995-8 (1963) discloses the compound having the structure:

##STR13##

PAR None of the references disclosing the foregoing tetracyclic carboxaldehydes discloses their utilization for augmenting or enhancing the aroma or taste of consumable materials.

PAR In addition, nothing in the prior art discloses the other compounds of our invention or organoleptic utilities of any mono-oxomethyl substituted polyhydrodimethanonapnthalene derivatives.

DRWD

PAC BRIEF DESCRIPTION OF THE DRAWINGS

PAR FIG. 1 is the GLC profile for the reaction product of Example I containing the compound having the structure:

##STR14##

PAR FIG. 2 is the NMR spectrum for the reaction product of Example I containing the compound having the structure:

##STR15##

PAR FIG. 3 is the infra-red spectrum for the reaction product of Example I containing the compound having the structure:

##STR16##

PAR FIG. 4 is the GLC profile for the reaction product of Example II containing the compound having the structure:

##STR17##

PAR FIG. 5 is the NMR spectrum for fraction 11 of the distillation product of the reaction product of Example II containing the compound having the structure:

##STR18##

PAR FIG. 6 is the infra-red spectrum for fraction 11 of the distillation

```
      having the structure:
      ##STR19##
PAR  FIG. 7 is the GLC profile for the reaction product of Example III
      containing the compound having the structure:
      ##STR20##
PAR  FIG. 8 is the NMR spectrum for Peak 13 of the GLC profile of FIG. 7 for the
      reaction product of Example III containing the compound having the
      structure:
      ##STR21##
PAR  FIG. 9 is the GLC profile for bulked fractions 3-11 of the distillation
      product of the reaction product of Example IV containing the compound
      having the structure:
      ##STR22##
PAR  FIG. 10 is the NMR spectrum for bulked fractions 3-11 of the distillation
      product of the reaction product of Example IV containing the compound
      having the structure:
      ##STR23##
PAR  FIG. 11 is the infra-red spectrum for bulked fractions 3-11 of the
      distillation product of the reaction product of Example IV containing the
      compound having the structure:
      ##STR24##
PAR  FIG. 12 is the GLC profile for the reaction product of Example V containing
      the compound having the structure:
      ##STR25##
PAR  FIG. 13 is the NMR spectrum for fraction 8 of the distillation product of
      the reaction product of Example V containing the compound having the
      structure:
      ##STR26##
PAR  FIG. 14 is the infra-red spectrum for fraction 8 of the distillation
      product of the reaction product of Example V containing the compound
      having the structure:
      ##STR27##
PAR  FIG. 15 is the GLC profile for the reaction product of Example VI
      containing the compound having the structure:
      ##STR28##
PAR  FIG. 16 is the NMR spectrum for fraction 6 of the distillation product of
      the reaction product of Example VI containing the compound having the
      structure:
      ##STR29##
PAR  FIG. 17 is the infra-red spectrum for fraction 6 of the distillation
      product of the reaction product of Example VI containing the compound
      having the structure:
      ##STR30##
PAR  FIG. 18 is the GLC profile for the reaction product of Example VII
      containing the compound having the structure:
      ##STR31##
PAR  FIG. 19 is the NMR spectrum for fraction 9 of the distillation product of
      the reaction product of Example VII containing the compound having the
      structure:
      ##STR32##
PAR  FIG. 20 is the infra-red spectrum for fraction 9 of the distillation
      product of the reaction product of Example VII containing the compound
      having the structure:
      ##STR33##
PAR  FIG. 21 is the GLC profile for the reaction product of Example VIII
      containing a mixture of compounds defined according to the structures:
```

```
      ##STR34##
PAR  FIG. 22 is the NMR spectrum for Peak 51 of the GLC profile of FIG. 21 for
      the mixture of compounds defined according to the structures:
      ##STR35##
PAR  FIG. 23 is the infra-red spectrum for Peak 51 of the GLC profile of FIG. 21
      for the reaction product of Example VIII containing a mixture of compounds
      defined according to the structures:
      ##STR36##
PAR  FIG. 24 is the GLC profile for the reaction product of Example IX
      containing the compound defined according to the structure:
      ##STR37##
PAR  FIG. 25 is the NMR spectrum for the distillation product of the reaction
      product of Example IX containing the compound having the structure:
      ##STR38##
PAR  FIG. 26 is the infra-red spectrum for the distillation product of the
      reaction product of Example IX containing tha compound having the
      structure:
      ##STR39##
PAR  FIG. 27 is the GLC profile for the reaction product of Example X containing
      the compound having the structure:
      ##STR40##
PAR  FIG. 28 is the NMR spectrum for the distillation product of the reaction
      product of Example X containing the compound having the structure:
      ##STR41##
PAR  FIG. 29 is the infra-rad spectrum for the distillation product of the
      reaction product of Example X containing the compound having the
      structure:
      ##STR42##
DETD
PAC  DETAILED DESCRIPTION OF THE DRAWINGS
PAR  FIG. 1 is the GLC profile for the reaction product of Example I containing
      the compound having the structure:
      ##STR43##
      The peak indicated by the reference numeral 1 is the peak for the compound
      having the structure:
      ##STR44##
PAR  FIG. 7 is the GLC profile for reaction product of Example III. The peak
      indicated by the reference numeral 11 is for the compound defined
      according to the structure:
      ##STR45##
      The peak indicated by the reference numeral 12 is for the compound defined
      according to the structure:
      ##STR46##
      The peak indicated by the reference numeral 13 is for the reaction product
      defined according to the structure:
      ##STR47##
PAR  FIG. 9 is the GLC profile for the reaction product of Example IV, bulked
      distillation fractions 3-11. The peak indicated by the reference numeral
      21 is for the reaction product having the structure:
      ##STR48##
PAR  FIG. 12 is the GLC profile for the reaction product of Example V. The peak
      indicated by the reference numeral 31 is for the reaction product having
      the structure:
      ##STR49##
PAR  FIG. 15 is the GLC profile for the reaction product of Example VI. The peak
```

the structure:
##STR50##

PAR FIG. 21 is the GLC profile for the reaction product of Example VIII. The peak indicated by the reference numeral 51 is for the reaction product which is a mixture of compounds defined according to the structures:
##STR51##

PAC THE INVENTION

PAR It has now been determined that certain mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives are capable of imparting a variety of flavors and fragrances to various consumable materials.

PAR Briefly, our invention contemplates augmenting or enhancing the flavors and/or fragrances of such consumable materials by adding thereto a small but effective amount of at least one such mono-oxomethyl substituted polyhydrodimethanonaphthalene derivative defined according to the generic structure:
##STR52##
wherein the dashed line represents a carbon-carbon single bond or a carbon-carbon double bond; wherein R.sub.1, R.sub.1 ', R.sub.1 ", R.sub.1 "', R.sub.1 "", R.sub.3, R.sub.5, R.sub.5 ', R.sub.5 ", R.sub.5 "', R.sub.5 "" and R.sub.6 represent hydrogen or methyl with the provisos:

PA1 (i) at least four of R.sub.1, R.sub.1 ', R.sub.1 ", R.sub.1 "' and R.sub.1 "" are hydrogen and (ii) at least four of R.sub.5, R.sub.5 ', R.sub.5 ", R.sub.5 "' and R.sub.5 "" represent hydrogen;

PAL and wherein Z represents one of the moieties:

PA1 (i) carboxaldehyde having the structure:
##STR53##
(ii) alkylene dioxy or dialkoxy methyl having the structure:
##STR54##
(iii) hydroxymethyl having the structure:
##STR55##
(iv) acetoxymethyl having the structure:
##STR56##
and wherein R.sub.7 and R.sub.8 taken separately represent C.sub.1 -C.sub.4 lower alkyl or R.sub.7 and R.sub.8 taken together represent C.sub.2 -C.sub.4 aklylene; wherein the line represented by:

EQU [++++]

PAL is either a carbon-carbon single body when R.sub.7 and R.sub.8 taken together are C.sub.2 -C.sub.4 alkylene or no bond at all when R.sub.7 and R.sub.8 taken separately represent C.sub.1 -C.sub.4 lower alkyl.

PAR Also described are processes for preparing such monooxomethyl substituted polyhydrodimethanonaphthalene derivatives, and processes for using the above defined mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives for their organoleptic properties and compositions containing said mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives including perfumes, perfumed articles such as solid or liquid anionic, cationic, nonionic or zwitterionic detergents, perfumed polymers, fabric softeners and cosmetic powders; and foodstuffs, chewing gums, toothpastes, medicinal products, chewing tobaccos, smoking tobaccos and smoking tobacco articles; and flavoring compositions (e.g., for foodstuffs, chewing gums, chewing tobaccos, medicinal products, toothpastes and smoking tobaccos) and fragrance compositions (e.g., for perfume compositions and compositions for augmenting or enhancing the aroma of perfumed articles such as solid or liquid anionic, cationic, nonionic or zwitterionic detergents or fabric softeners or fabric softener articles or cosmetic powders or perfumed polymers) containing such mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives:

PAR The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives produced according to the processes of our invention which are used in practicing that part of our invention concerning flavoring and fragrance compositions are actually racemic mixtures rather than individual optical isomers such as is the case concerning isomers of patchouli alcohol which are obtained from patchouli oil.

PAR The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention insofar as their fragrance profiles are concerned have intense and long lasting melony, cucumber, violet-like, green, leafy, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic and spicy aromas. Insofar as their flavor uses are concerned (e.g., foodstuffs, chewing gums, medicinal products, chewing tobaccos and toothpastes) the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention have sweet, aldehydic, floral, melony, herbaceous, green and artichoke-like aroma and taste profiles.

PAR Insofar as smoking tobacco flavors are concerned the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention have sweet, floral and green aroma profiles prior to smoking and sweet, floral and aramatic aroma and taste nuances on smoking both in the main stream and in the side stream.

PAR The following table sets forth the structure and organoleptic property profiles for specific compounds according to the examples listed herein and located infra:

TBL TABLE I

Structure of Compound	Fragrance Profile	Food Flavor Profile	Tobacco Flavor Profile
##STR57## Produced according to Example I.	A melony, cucumber- like, violet-like, green, herbaceous, wormwood-like, and floral aroma.	Sweet, aldehydic, floral, melony and herbaceous aroma at 0.0001 ppm.	A sweet, floral, herbaceous aroma prior to smoking and a sweet, floral and aramatic flavor and taste on smoking in both the main stream and the side stream.
##STR58## Produced according to Example II.	A floral, fruity (melony) cinnamic aroma.	A sweet, melony, cinnamon-like aroma and taste profile.	A cinnamon/floral aroma prior to smoking and intense cinnamon-like nuances and aramatic tobacco notes on smoking in both the main stream and the side stream.
##STR59##	A sandalwood-like- patchouli-like and vetiver-like aroma profile.	A walnut-like aroma and taste profile.	A nutty/tobacco nuances prior to smoking and woody aroma and taste nuances on smoking in the main stream and the side stream

Produced according to Example IV. ##STR60##	A floral, fruit (pineapple) aroma profile.	An intense pineapple aroma and taste	A sweet, floral, fruity aroma and taste prior to smoking and fruity virginia-like tobacco notes on smoking in both the main stream and the side stream.
Produced according to Example VI. ##STR61##	A sweaty, musk-like aroma profile.	A green, artichoke- like aroma and taste profile.	
Produced according to Example VII. ##STR62##	An animalic, leafy, green, herbaceous, floral and violet-like aroma profile with cinnamic and cucumber-like undertones.	A green, melony, minty, herbaceous and floral aroma and taste profile at 2 ppm.	A minty tobacco nuance prior to smoking and minty cooling-like notes on smoking in both the main stream and the side stream.
Produced according to Example VIII, infra. ##STR63##	A spicy cinnamic-like aroma.	A spicy, cinnamon-like aroma and	A spicy, cinnamon-like aroma and taste profile prior to smoking and spicy turkish oriental- like tobacco nuances n smoking in the main stream and the side stream.
Produced according to Example X.			

PAR The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives produced according to the process of our invention which are used in practicing that part of our invention concerning flavor and fragrance compositions may be mixtures of isomers or they may be substantially pure forms of exo or endo isomers or specific stereoisomers such as in the case concerning isomers of patchouli alcohol which are obtained from patchouli oil.

PAR The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives prepared according to our invention can be obtained by reacting bicyclopentadiene or dimethyl bicyclopentadiene having the structures:
##STR64##
with an acrolein derivative according to the reaction:
##STR65##
wherein R.sub.1, R.sub.1 ', R.sub.1 ", R.sub.1 "', R.sub.1 "", R.sub.3, R.sub.5, R.sub.5 ', R.sub.5 ", R.sub.5 "', and R.sub.5 "" are defined, supra. The reaction is carried out at pressures in the range of from about 150 psig up to about 500 psig and at temperatures in the range of from about 150.degree. C. up to about 250.degree. C. in the presence of or in the absence of an inert solvent. When the solvent is used it is preferred to use a solvent such as toluene or xylene which can easily be separated

from the reaction mass after the completion of the reaction. The ratio of bicyclopentadiene derivative-acrolein derivative may vary from about 0.5:1 up to about 1:0.5 with the preferred mole ratio being about 1:1. The concentration of reactant in the reaction mass may vary from about 100 grams per liter up to about 500 grams per liter. At the end of the reaction the pressure vessel is opened and the contents are distilled preferably by means of fractional distillation. The reaction product can be used "as is" for its organoleptic properties or it may be further reacted as set forth, infra.

PAR The mechanism for this reaction is as follows:

##STR66##

wherein R.sub.1, R.sub.1 ', R.sub.1 ", R.sub.1 "', and R.sub.1 "" and R.sub.3, R.sub.5, R.sub.5 ', R.sub.5 " R.sub.5 '", R.sub.5 "" and R.sub.6 are defined, supra.

PAR The resulting aldehyde defined according to the structure:

##STR67##

may then be reduced to form the corresponding saturated polycyclic carboxaldehydes or unsaturated polycyclic carboxaldehydes or saturated polycyclic carbinols or unsaturated polycyclic carbinols or the resulting aldehyde may be then reacted with an alkanol or alkanediol to form polycyclic carbinyl acetals, or cyclic acetals. In turn, the resulting carbinols may be acylated as with acetic anhydride or acetyl chloride or acetyl bromide to form the corresponding saturated polycyclic carbinol acetates or unsaturated polycyclic carbinol acetates.

PAR Thus, when reacting the aldehyde derivative defined according to the genus having the structure:

##STR68##

with one mole of hydrogen per mole of aldehyde at a pressure in the range of from about 50 psig up to about 200 psig and in the presence of a catalyst such as palladium supported on carbon, palladium supported on barium sulfate, palladium supported on calcium sulfate or palladium supported on calcium carbonate (for example: 5% palladium supported on calcium sulfate, 5% palladium supported on calcium carbonate or 10% palladium on carbon) at a temperature in the range of from about 10.degree. C. up to 140.degree. C., the aldehyde will be reduced to the saturated polycyclic carboxaldehyde according to the reaction:

##STR69##

PAR On the other hand when two moles of hydrogen are used per mole of aldehyde, the reduction is such that a saturated polycyclic carbinol is formed according to the reaction:

##STR70##

PAR The aldehyde genus defined according to the structure:

##STR71##

may be reduced with an alkali metal borohydride or lithium aluminum hydride in the presence of an inert solvent to form the unsaturated polycyclic carbinol according to the reaction:

##STR72##

wherein M represents alkali metal such as lithium, sodium or potassium.

PAR The reaction is carried out in the presence of an inert solvent such as isopropyl alcohol, n-propyl alcohol, ethyl alcohol or methyl alcohol or diethyl ether or tetrahydrofuran. The reaction is carried out at a temperature in the range of from about 20.degree. C. up to reflux conditions (depending upon the solvent used) and is most conveniently and preferably carried out at atmospheric pressures since higher pressures do not give rise to higher yields or higher conversions. The mole ratio of hydride:aldehyde reactant may vary from about 0.2:1 up to about 1:1 with a preferred mole ratio of 0.25:1 up to 0.5:1.

PAR Both the saturated and unsaturated polycyclic carbinols defined according to the structures:

##STR73##

may be further reacted as by acetylation using acetic anhydride or acetyl chloride. The reaction with acetic anhydride is preferably carried out in the presence of an inert solvent at reflux conditions at atmospheric pressure. Such an inert solvent is toluene or xylene, the solvents being inert and having boiling points such that the reaction may proceed efficiently and in a minimum amount of time. Preferably the mole ratio of acetic anhydride:carbinol reactant is from about 0.5:1.5 up to about 1.5:0.5 with a most preferred ratio of acetic anhydride:carbinol reactant being 1-1.5:1. Each of these reactions is set forth as follows:

PAR In addition, the aldehyde derivatives defined according to the structure:

##STR74##

may be converted into cyclic or acyclic acetals by means of reaction of the aldehyde with a C.sub.1 -C.sub.4 alkanol or a C.sub.2 -C.sub.4 alkanediol according to the reaction:

##STR75##

wherein R.sub.1, R.sub.1 ', R.sub.1 ", R.sub.1 "', R.sub.1 "", R.sub.3, R.sub.5, R.sub.5 ', R.sub.5 ", R.sub.5 "', R.sub.5 "", R.sub.6, R.sub.7, R.sub.8 and the line [++++] are defined, supra.

PAL The reaction is carried out in the presence of a protonic acid catalyst or a Lewis acid catalyst at a temperature in the range of from about 30.degree. C. up to about 90.degree. C. Preferred catalysts are boron trifluoride etherate, 20% sulfuric acid, saturated aqueous, ammonium chloride and stannic chloride.

PAR The preferred mole ratio of alkane diol:aldehyde reactant may vary from about 1:1 up to aboue 2:1 and the preferred mole ratio of alkylenediol:aldehyde reactant may vary from about 2:1 up to about 4:1.

PAR At the end of each of the foregoing reactions the reaction product may, if desired, be separated from the resultant reaction mass by fractional distillation or preparative GLC (vapor phase, chromotography). However, if the desired reaction product is to be utilized as a reaction intermediate, the necessity of careful rectification of the reaction product in order to achieve odor acceptable substances or flavor acceptable substances is not usually necessary since the resultant reaction product will be further reacted.

PAR Thus, the individual mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be obtained in pure form or in substantially pure form by conventional purification techniques. The products can be purified and/or isolated not only by distillation (as mentioned, supra), but also using extraction, crystallization, preparative chromatographic techniques and the like. It has been found desirable to purify the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention by fractional distillation in vacuo.

PAR When the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention are used as food flavor adjuvants, the nature of the co-ingredients included with said mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives in formulating the product composition will also serve to alter, modify, augment or enhance the organoleptic characteristics of the ultimate foodstuff treated therewith.

PAR As used herein in regard to flavors, the terms "alter", "modify" and "augment" in their various forms mean "supplying or imparting flavor character or note to otherwise bland, relatively tasteless substances or augmenting the existing flavor characteristic where a natural flavor is deficient in some regard or supplementing the existing flavor impression to modify its quality, character or taste."

PAR The term "enhance" is used herein to mean the intensification of a flavor or aroma characteristic or note without the modification of the quality thereof. Thus, "enhancement" of a flavor or aroma means that the enhancement agents does not add any additional flavor note.

PAR As used herein, the term "foodstuff" includes both solid and liquid ingestible materials which usually do, but need not, have nutritional value. Thus, foodstuffs include soups, convenience foods, beverages, dairy products, candies, vegetables, cereals, soft drinks, snacks and the like.

PAR As used herein, the term "medicinal product" includes both solids and liquids which are ingestible, non-toxic materials which have medicinal value such as cough syrups, cough drops, aspirin and chewable medicinal tablets.

PAR The term "chewing gum" is intended to mean a composition which comprises a substantially water insoluble, chewable, plastic gum base such as chicle, or substitutes therefor, including guttakay rubber or certain comestible natural or synthetic resins or waxes. Incorporated with the gum base in admixture therewith may be plasticizers or softening agents, e.g., glycerine, and a flavoring composition which incorporates one or more of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention, and in addition, sweetening agents which may be sugars, including sucrose or dextrose and/or artificial sweeteners such as cyclamates or saccharin. Other optional ingredients may also be present.

PAR Substances suitable for use herein as co-ingredients or flavoring adjuvants are well known in the art for such use, being extensively described in the relevant literature. It is a requirement that any such material be "ingestibly" acceptable and thus non-toxic and otherwise non-deleterious particularly from an organoleptic standpoint whereby the ultimate flavor and/or aroma of the consumable material used is not caused to have unacceptable aroma and taste nuances. Such materials may in general be characterized as flavoring adjuvants or vehicles comprising, broadly, stablizers, thickeners, surface active agents, conditioners, other flavorants and flavor intensifiers.

PAR Stabilizer compounds include preservatives, e.g., sodium chloride; antioxidants, e.g., calcium and sodium ascorbate, ascorbic acid, butylated hydroxyanisole (mixture of 2- and 3-tertiary-butyl-4-hydroxy-anisole), butylated hydroxytoluene (2,6-di-tertiary-butyl-4-methyl phenol), propyl gallate and the like, and sequestrants, e.g., citric acid.

PAR Thickener compounds include carriers, binders, protective colloids, suspending agents, emulsifiers and the like, e.g., agar agar, carrageenan; cellulose and cellulose derivatives such as carboxymethyl cellulose and methyl cellulose; natural and synthetic gums such as gum arabic, gum tragacanth, gelatin, proteinaceous materials; lipids, carbohydrates; starches, pectins, and emulsifiers, e.g., mono- and diglycerides of fatty acids, skim milk powder, hexoses, pentoses, disaccharides, e.g., sucrose corn syrup and the like.

PAR Surface active agents include emulsifying agents, e.g., fatty acids such as capric acid, caprylic acid, palmitic acid, myristic acid and the like, mono- and diglycerides of fatty acids, lecithin, defoaming and flavor-dispersing agents such as sorbitan monostearate, potassium stearate, hydrogenated tallow alcohol and the like.

PAR Conditioners include compounds such as bleaching and maturing agents, e.g., modifiers such as peracetic acid, sodium chlorite, sodium hypochlorite, propylene oxide, succinic anhydride and the like, buffers and neutralizing agents, e.g., sodium acetate, ammonium bicarbonate, ammonium phosphate, citric acid, lactic acid, vinegar and the like; colorants, e.g., carminic acid, cochineal, tumeric and curcuma and the like; firming agents such as aluminum sodium sulfate, calcium chloride and calcium gluconate; texturizers, anti-caking agents, e.g., aluminum calcium sulfate and tribasic calcium phosphate; enzymes; yeast foods, e.g., calcium lactate and calcium sulfate; nitrient supplements, e.g., iron salts such as ferric phosphate, ferrous gluconate and the like, riboflavin, vitamins, zinc sources such as zinc chloride, zinc sulfate and the like.

PAR Other flavorants and flavor intensifiers include organic acids, e.g., acetic acid, formic acid, 2-hexenoic acid, benzoic acid, n-butyric acid, caproic acid, caprylic acid, cinnamic acid, isobutyric acid, isovaleric acid, alpha-methylbutyric acid, propionic acid, valeric acid, 2-methyl-2-pentenoic acid, and 2-methyl-3-pentenoic acid; ketones and aldehydes, e.g., acetaldehyde, acetophenone, acetone, acetyl methyl carbinol, acrolein, n-butanal, crotonal, diacetyl, 2-methylbutanal, beta-dimethylacrolein, methyl n-amyl ketone, n-hexanal, 2-hexenal, isopentanal, hydrocinnamic aldehyde, cis-3-hexenal, 2-heptenal, nonyl aldehyde, 4-(p-hydroxyphenyl)-2-butanone, alpha-ionone, beta-ionone, 2-methyl-3-butanone, benzaldehyde, .beta.-damascone, .alpha.-damascone, .beta.-damascenone, acetophenone, 2-heptanone, o-hydroxyacetophenone, 2-methyl-2-hepten-6-one, 2-octanone, 2-undecanone, 3-phenyl-4-pentenal, 2-phenyl-2-hexenal, 2-phenyl-2-pentenal, furfural, 5-methyl-furfural, cinnamaldehyde, beta-cyclohomocitral, 2-pentanone, 2-pentenal and propanal; alcohols such as 1-butanol, benzyl alcohol, 1-borneol, trans-2-buten-1-ol, ethanol, geraniol, 1-hexanol, 2-heptanol, trans-2-hexenol-1, cis-3-hexen-1-ol, 3-methyl-3-buten-1-ol, 1-pentanol, 1-penten- 3-ol, p-hydroxyphenyl-2-ethanol, isoamyl alcohol, isofenchyl alcohol, phenyl-2-ethanol, alpha-terpineol, cis-terpin hydrate, eugenol, linalool, 2-heptanol, acetoin; esters, such as butyl acetate, ethyl acetate, ethyl acetoacetate, ethyl benzoate, ethyl butyrate, ethyl caprate, ethyl caproate, ethyl carpylate, ethyl cinnamate, ethyl crotonate, ethyl formate, ethyl isobutyrate, ethyl isovalerate, ethyl laurate, ethyl myristate, ethyl .alpha.-methyl-butyrate, ethyl propionate, ethyl salicylate, trans-2-hexenyl acetate, hexyl acetate, 2-hexenyl butyrate, hexyl butyrate, isoamyl acetate, isopropyl butyrate, methyl acetate, methyl butyrate, methyl caproate, methyl isobutyrate, alpha-methyl-phenylglycidate, ethyl succinate, isobutyl cinnamate, cinnamyl formate, methyl cinnamate and terpenyl acetate; hydrocarbons such as dimethyl naphthalene, dodecane, methyldiphenyl, methyl naphthalene, myrcene, naphthalene, octadecane, tetradecane, tetramethylnaphthalene, tridecane, trimethylnaphthalene, undecane, caryophyllene, .alpha.-phellandrene, .beta.-phellandrene, p-cymene 1-.alpha.-pinene, beta-pinene, dihydrocarveol; pyrazines such as 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 2-ethyl-3,5,6-trimethylpyrazine, 3-isoamyl-2,5-dimethylpyrazine, 5-isoamyl-2,3-dimethylpyrazine, 2-isoamyl-3,5,6-trimethylpyrazine, isopropyl dimethylpyrazine, methyl ethylpyrazine, tetramethylpyrazine, trimethylpyrazine; essential oils such as jasmine absolute, cassia oil, cinnamon bark oil, black pepper oleoresin, oil of black pepper, rose absolute, orris absolute, oil of cubeb, oil of coriander, oil of pimento leaf, oil of patchouli, oil of nutmeg, lemon essential oil, safran oil, Bulgarian rose, capsicum, yara yara and vanilla; lactones such as .gamma.-nonalactone; .DELTA.-decalactone; .gamma.&.DELTA.-undecalactone;

.gamma.&.DELTA.-dodecalactone; sulfides, e.g., methyl sulfide and other materials such as maltol, and acetals (e.g., 1,1-diethoxyethane, 1-1-dimethoxyethane and dimethoxymethane), piperine, chavicine, and piperidine.

PAR The specific flavoring adjuvant selected for use may be either solid or liquid depending upon the desired physical form of the ultimate product, i.e., foodstuff, whether simulated or natural, and should, in any event, (i) be organoleptically compatible with the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention by not covering or spoiling the organoleptic properties (aroma and/or taste thereof); (ii) be non-reactive with the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention; and (iii) be capable of providing an environment in which the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be dispersed or admixed to provide a homogeneous medium. In addition, selection of one or more flavoring adjuvants, as well as the quantities thereof will depend upon the precise organoleptic character desired in the finished product. Thus, in the case of flavoring compositions, ingredient selection will vary in accordance with the foodstuff, chewing gum, medicinal product or toothpaste to which the flavor and/or aroma are to be imparted, modified, altered or enhanced. In contradistinction, in the preparation of solid products, e.g., simulated foodstuffs, ingredients capable of providing normally solid compositions should be selected such as various cellulose derivatives.

PAR As will be appreciated by those skilled in the art, the amount of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivative(s) of our invention employed in a particular instance can vary over a relatively wide range, depending upon the desired organoleptic effects to be achieved. Thus, correspondingly greater amounts would be necessary in those instances wherein the ultimate food composition to be flavored (e.g., with a peppermint flavor, or a specific vegetable flavor such as an artichoke flavor) is relatively bland to the taste, whereas relatively minor quantities may suffice for purposes of enhancing a composition merely deficient in natural flavor or aroma. The primary requirement is that the amount selected be effective, i.e., sufficient to alter, modify or enhance the organoleptic characteristics of the parent composition, whether foodstuff per se, chewing gum per se, medicinal product per se, toothpaste per se, of flavoring composition.

PAR The use of insufficient quantities of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention will, of course, substantially vitiate any possibility of obtaining the desired results while excess quantities prove needlessly costly and in extreme cases may disrupt the flavoraroma balance, thus proving self-defeating. Accordingly, the terminology "effective amount" and "sufficient amount" is to be accorded a significance in the context of the present invention consistent with the obtention of desired flavoring effects.

PAR Thus, and with respect to ultimate food compositions, chewing gum compositions, medicinal product compositions and toothpaste compositions, it is found that quantities of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention ranging from a small but effective amount, e.g., 0.00001 parts per million up to about 100 parts per million based on total composition, are suitable. Concentrations in excess of the maximum quantity stated are not normally recommended since they fail to provide commensurate enhancement of organoleptic properties. In those instances wherein the mono-oxomethyl added to the foodstuff as an integral component of a flavoring composition, it is of course essential that the total quantity of flavoring composition employed be sufficient to yield an effective mono-oxomethyl substituted polyhydrodimethanonaphthalene derivative concentration in the foodstuff product.

PAR Food flavoring compositions prepared in accordance with the present invention preferably contain the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention in concentrations ranging from about 0.01% up to about 15% by weight based on the total weight of the said flavoring composition.

PAR The composition described herein can be prepared according to conventional techniques well known as typified by cake batters and fruit drinks and can be formulated by merely admixing the involved ingredients within the proportions stated in a suitable blender to obtain the desired consistency, homogeneity of dispersion, etc. Alternatively, flavoring compositions in the form of particulate solids can be conveniently prepared by mixing the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention with, for example, gum arabic, gum tragacanth, carrageenan, xanthangum, guargum, mixtures of same and the like, and thereafter spray-drying the resultant mixture whereby to obtain the particular solid product. Prepared flavor mixes in powder form, e.g., a fruit flavored powder mix, are obtained by mixing the dried solid components; e.g., starch, sugar and the like, and one or more mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention in a dry blender until the requisite degree of uniformity is achieved.

PAR It is presently preferred to combine with the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention, the following adjuvants:

PA1 Oil of Cubeb;
PA1 .alpha.-phellandrene;
PA1 .beta.-phellandrene;
PA1 Oil of Coriander;
PA1 Oil of Pimento Leaf;
PA1 Oil of Patchouli;
PA1 Alpha Pinene;
PA1 Beta Pinene;
PA1 Beta-caryophyllene;
PA1 Dihydrocarveol;
PA1 Piperonal;
PA1 Piperine;
PA1 Chavicine;
PA1 Piperidine;
PA1 Oil of Black Pepper;
PA1 Black Pepper Oleoresin;
PA1 Capsicum;
PA1 Oil of Nutmeg.
PA1 Cardamom Oil;
PA1 Clove Oil;
PA1 Spearmint Oil;
PA1 Oil of Peppermint;
PA1 Ethyl-2-methyl butyrate;
PA1 Vanillin;
PA1 Butyl valerate;
PA1 2,3-Diethyl pyrazine;
PA1 Methyl cyclopentenolone;

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PA1  Benzaldehyde;
PA1  Valerian Oil Indian;
PA1  Propylene glycol;
PA1  Acetaldehyde;
PA1  Isobutyraldehyde;
PA1  Isovaleraldehyde;
PA1  Dimethyl sulfide;
PA1  Isobutyl acetate;
PA1  Isoamyl acetate;
PA1  Phenylethyl acetate;
PA1  Diacetyl;
PA1  Acetophenone;
PA1  Furfural
PA1  Phenylacetaldehyde
PA1  Isoamyl alcohol;
PA1  .beta.-Phenylethyl alcohol;
PA1  .alpha.-Phenyl ethyl alcohol
PA1  .gamma.-Butyrolactone;
PA1  y-Butyrolactone;
PA1  3-Phenyl-4-pentenal;
PA1  3-Phenyl-3-pentenal;
PA1  3-Phenyl-2-pentenal;
PA1  2-Methyl pyrazine;
PA1  2,6-Dimethyl pyrazine;
PA1  2,3,5,6-Tetramethyl pyrazine;
PA1  2,3,5-Trimethylpyrazine;
PA1  2-Ethyl-3-methylpyrazine;
PA1  2-Ethyl-3,5-dimethylpyrazine;
PA1  2-Ethyl-3,6-dimethylpyrazine;
PA1  2-Ethyl-5-methylpyrazine;
PA1  2(n-pentyl) thiazole;
PA1  2(i-butyl) thiazole;
PA1  2(i-propyl) thiazole;
PA1  2(n-propyl) thriazole;
PA1  2-phenyl-4-pentenal;
PA1  2-phenyl-4-pentenaldimethylacetal;
PA1  Methional;
PA1  4-methylthiobutanal;
PA1  2-ethyl-3-acetylpyrazine
PA1  trans-2-hexenal;
PA1  Hydrolyzed vegetable protein;
PA1  Monosodium glutamate;
PA1  Celery Oil;
PA1  Lemon Oil;
PA1  Mustard Oil;
PA1  2,4-dimethyl-.DELTA..sup.3 -thiazoline;
PA1  4,5-dimethyl-.DELTA..sup.3 -thiazoline;
PA1  2,4,5-trimethyl-.DELTA..sup.3 -thiazoline;
PA1  2-propyl-2,4,5-trimethyl-.DELTA..sup.3 -thiazoline;
PA1  2-ethyl-2,4,5-trimethyl-.DELTA..sup.3 -thiazoline;
PA1  2-(2'butyl)-4-methyl-.DELTA..sup.3 -thiazoline;
PA1  2-n-butyl-4,5-dimethyl-.DELTA..sup.3 thiazoline;
PA1  2-benzeyl-4-methyl-.DELTA..sup.3 -thiazoline;
PA1  2,5-dimethyl-2-benzyl-.DELTA..sup.3 -thiazoline;
PA1  2-(2'-methyl-n-propyl)-4.5-dimethyl-.DELTA..sup.3 thiazoline;
PA1  .beta.-Damascone ;
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PA1 .beta.-Damascenone; and

PA1 trans,trans.DELTA..sup.3 -Damascone

PAR The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be used to contribute melony, cucumber, violet-like, green, leafy, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic and spicy aroma nuances to perfume compositions, perfumed articles (such as solid or liquid anionic, cationic, nonionic or zwitterionic detergents, fabric softeners, fabric softener articles and perfumed polymers) and colognes. As olfactory agents the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be formulated into or used as components of a "perfume composition".

PAR The term "perfume composition" is used herein to mean a mixture of organic compounds including, for example, alcohols (other than the alcohols of our invention), aldehydes (other than the aldehydes of our invention), ketones, nitriles, ethers, lactones, acetals (other than the acetals of our invention), esters (other than the esters of our invention), and frequently hydrocarbons which are admixed so that the combined odors of the individual components produce a pleasant or desired fragrance. Such perfume compositions usually contain: (a) the main note or the "bouquet" or foundation-stone of the composition; (b) modifiers which round-off and accompany the main note; (c) fixatives which include odorous substances which lend a particular note to the perfume throughout all stages of evaporation, and substances which retard evaporation; and (d) top-notes which are usually low-boiling, fresh-smelling materials.

PAR In perfume compositions the individual component will contribute its particular olfactory characteristics, but the overall effect of the perfume composition will be the sum of the effects of each ingredient. Thus, the individual compounds of this invention, or mixtures thereof, can be used to alter the aroma characteristics of a perfume composition, for example, by highlighting or moderating the olfactory reaction contributed by another ingredient in the composition.

PAR The amount of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention which will be effective in perfume compositions depends on many factors, including the other ingredients, their amounts and the effects which are desired. It has been found that perfume compositions containing as little as 0.2% of one or more of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention, or even less, can be used to impart melony, cucumber-like, violet-like, green, leafy, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic, and spicy aroma nuances to soaps, cosmetics, solid or liquid anionic, cationic, nonionic, or zwitterionic detergents, fabric softeners, fabric softener articles, perfumed polymers, cosmetic powders, hair preparations and other products. The amount employed can range up to 50% or higher and will depend on considerations of cost, nature of the end product, the effect desired on the finished product and a particular fragrance sought.

PAR The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be used alone or in a perfume composition as an olfactory component in solid or liquid anionic, cationic, nonionic or zwitterionic detergents, fabric softeners, and soaps; space odorants and deodorants; perfumes; colognes, toilet waters; bath salts; hair preparations such as lacquers, brilliantines, pomades, and shampoos; cosmetic preparations such as creams, deodorants, hand lotions, and sun screens; powders such as talcs, dusting powders, face powder and the like. When used as an olfactory component of a perfumed article, as little as

0.005% of one or more of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention will suffice to impart an interesting melony, cucumber, violet-like, green, leafy, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic and spicy aromas. Generally, no more than 0.8% is required in the perfumed article. Thus, to be specific, the range of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention useful in perfumed articles varies from about 0.005% up to about 0.8%.

PAR In addition, the perfume composition of our invention can contain a vehicle or carrier for the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention. The vehicle can be a liquid such as an alcohol such as ethanol, a glycol such as propylene glycol, or the like. The carrier can be an absorbent solid such as a gum or components for encapsulating the composition by coacervation such as gelatin or for encapsulating the composition by forming polymers around a central liquid core such as a urea formaldehyde capsule.

PAR It is the further object of our invention to provide a smoking tobacco product treated with an additive which will enhance the tobacco aroma, as well as the flavor characteristics of the tobacco product made therefrom. Also, it is an object of the present invention to provide a smoking tobacco product having a material added to the tobacco which will readily transfer to the tobacco smoke and pass through a filter element (even of a high filtration type) so that the natural flavor qualities of the tobacco smoke are enhanced.

PAR Another object of our invention is the provision of smoking tobacco products, such as cigarettes, cigars, pipe tobacco, or tobacco smoke filters, having added thereto a releasable flavor additive which will impart a desirable fresh natural taste to the smoking product when smoked.

PAR Thus, in general, our invention further contemplates providing an organoleptically improved tobacco product having added thereto one or more mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention which imparts to the product the enhanced and desirable fresh flavor and aroma of natural tobacco. The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention are individually and in combination readily transferred either from the filter section or the tobacco section into the smoke stream when the tobacco product is smoked. The organoleptic qualities of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention particularly when transferred to the tobacco smoke, impart desirable fresh, oriental, spicy, floral, citrusy flavor and aroma nuances to tobacco causing the tobacco to be more desirable and causing a change from the "Virginia" and "Burley" types to the "Imported", "Turkish" types.

PAR The mono-oxomethyl substituted polyhydrodimethanonaphthalene of our invention employed to improve the organoleptic qualities of a tobacco product have odor characteristics which can be described as floral, spicy, woody, and cinnamon-like as well as citrusy. The amount of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention taken alone or in combination added to a tobacco product may vary greatly; however a sufficient amount should be used to achieve the desired organoleptic properties for the smoking tobacco product when smoked. We have found that the levels of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention (taken alone or in combination) added to a tobacco product, either to the filter or to the tobacco section, may be as low as 0.001% based on the weight of the polyhydrodimethanonaphthalene derivatives added to the tobacco product may be from about 0.001% up to about 0.1% based on the weight of the tobacco, preferably from about 0.005% up to about 0.05%, and more preferably from about 0.01% up to about 0.015%.

PAR The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention may be incorporated at any step into the treatment of the tobacco but it is preferred that they be added either separately or in admixture after the tobacco has been cured, aged and shredded and just prior to the manufacture of the desired tobacco product, for example, cigarettes, cigars, pipe tobacco, or other smoking products. Also, it may be added to tobacco smoke filter material prior to forming the filter rod. The additive is conveniently dissolved in a solvent, such as ethyl alcohol, and applied to the tobacco by spraying, dipping or other methods of application generally employed for treating tobacco. Also, it may be sprayed onto the filter material. Although solutions of this compound are preferred, suspensions thereof may be utilized. Other suitable solvents are, for example, acetone, diethyl ether, n-hexane, or the like. After treatment of the tobacco or the filter with at least one of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention, substantially all of the solvent is evaporated therefrom prior to its manufacture into tobacco products.

PAR The term "tobacco" will be understood herein to mean the natural products such as, for example, Burley, Turkish tobacco, Maryland tobacco, flue-cured tobacco and the like including tobacco-like or tobacco-based products such as reconstituted or homogenized leaf and the like, as well as tobacco substitutes intended to replace natural tobacco, such as lettuce and cabbage leaves and the like. The tobaccos and tobacco products in which the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention are useful include those designed or used for smoking such as in cigarette, cigar and pipe tobacco, as well as products such as snuff, chewing tobacco, and the like.

PAR The following examples I-X are given to illustrate methods for producing the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention. The examples following Example X are given to illustrate embodiments of the utilization of the mono-oxymethyl substituted polyhydrodimethanonphthalene derivatives of our invention. It will be understood that these examples are illustrative and that the invention is not to be considered as restrictive to these examples except as indicated in the appended claims.

PAC EXAMPLE I

PAC Preparation of 1,2,3,4,4A,5,5A,8 Octahydro-1,4:5,8 Dimethanonaphthalene-2-Carboxaloehyde

PAL Reaction
##STR76##

PAR Into a high pressure autoclave are placed the following ingredients:

PA1 396 dicyclopentadiene;

PA1 252 grams acrolein; and

PA1 500 ml toluene

PAL The autoclave is sealed, and with stirring, heated at 225.degree. C. at 200 psig for a period of three hours. At the end of the reaction, the autoclave is opened and a portion of the product is distilled in a "Rushover" apparatus yielding the following fractions:

TBL

Fraction	Vapor Temp.	Liquid Temp.	Vacuum mm.Hg.	Weight of Fractions

No.	(.degree.C.)	(.degree.C.)	Pressure	(mg)	
1	23/50	23/70	50/52	911.0	
2	56	77	50	802.0	
3	68	100	40	1031.0	
4	75	100	30	902.0	
5	83	115	15	200.0	
6	86	128	15	125.1	
7	100	133	10	91.6	
8	108	137	10	105.5	
9	120	143	8	96.0	
10	125	147	8	96.5	
11	135	168	2		1588.0
12	139	186	2		
13	156	220	2	339.0	

PAR Fractions 11 and 12 of this distillation are bulked and the resulting bulked fractions are distilled on a fractionation column yielding the following fractions:

TBL

Fraction No.	Vapor Temp. (.degree.C.)	Liquid Temp. (.degree.C.)	Vacuum mm.Hg. Pressure	Reflux Ratio	Weight of Fractions (mg)
1	23/77	23/122	2/2	9:1	20.8
2	78	125	2	9:1	17.3
3	78	126	2	9:1	18.9
4	78	125	2	9:1	21.3
5	79	126	2	9:1	27.8
6	80	127	2	9:1	23.5
7	80	128	2	9:1	106.5
8	80	127	2	9:1	122.4
9	80	129	2	9:1	44.0
10	80	129	2	9:1	31.1
11	83	130	2	9:1	39.0
12	83	130	2	9:1	42.4
13	83	130	2	1:1	106.4
14	83	130	2	1:1	102.3
15	83	130	2	1:1	106.9
16	83	133	2	1:1	128.1
17	83	134	2	1:1	130.1
18	84	136	2	1:1	128.7
19	86	170	2	1:1	132.0
20	78	187	2	1:1	64.2
21	50	220	2	1:1	44.1

PAR Fractions 14-19 are bulked and have an herbal, strong, green, aldehydic, wormwood-like, floral aroma profile. Bulked fractions 4-14 has a melony, PAR From a flavor standpoint fraction 14 has a sweet, aldehydic, floral, melony, herbaceous aroma and taste profile at 0.0001 ppm. In addition, it is an excellent vanilla flavor enhancer and orange oil flavor enhancer.

PAR FIG. 1 is the GLC profile of the reaction production prior to distillation (conditions: SE-30 packed column, programmed at 220.degree. C. isothermal (1/4".times.10 feet). The peak indicated on FIG. 1 by the reference "1" is for the reaction product having the structure:
##STR77##

PAR FIG. 2 is the NMR spectrum for the bulked fractions 4-20 of the foregoing distillation product containing the compound having the structure:
##STR78##

PAR FIG. 3 is the infra-red spectrum for bulked fractions 4-20 of the foregoing distillation product containing the compound having the structure:
##STR79##

PAC EXAMPLE II

PAC Preparation of Decahydro-1,4:5,8 Dimethanonaphthalene-2-Carboxaldehyde

PAL Reaction:
##STR80##

PAR Into a Parr shaker apparatus is placed the following ingredients;

TBL

Ingredients	Parts by Weight
Bulked fractions 22-26 of the distillation product of the reaction product of Example I containing the compound having the structure. ##STR81##	260 grams (1.3 moles)
1% Palladium on carbon	3 grams
Anhydrous isopropyl alcohol	80 ml

PAR The Parr shaker is pressurized with hydrogen to a pressure of between 87 and 109 psig while maintaining the reaction temperature at 48.degree.-54.degree. C. for a period of 14 hours. At the end of this period, the Parr shaker is depressurized, opened and the contents are filtered. The resulting product is then distilled on a fractionation column yielding the following fractions:

TBL

Fraction No.	Vapor Temp. (.degree. C.)	Liquid Temp. (.degree. C.)	Vacuum mm.Hg. Pressure	Weight of Fraction (gm)
1	35	37	20/20	13.6
2	119	120	1	10.6
3	122	122	1	15.6
4	127	127	1	15.1
5	127	140	1	16.7
6	127	140	1	16.7
7	127	140	1	18.1
8	127	140	1	19.5
9	127	140	1	16.0

10	127	140	1	15.6
11	127	147	1	17.3
12	127	147	1	21.2
13	127	147	1	22.5
14	130	200	1	22.7

PAR Fraction 7-13 of the foregoing distillation are bulked for subsequent evaluation and for subsequent reaction. Fractions 7-13, bulked, from a fragrance $tandpoint, have a floral, cinnamon-like and melony aroma profile.

PAR FIG. 4 is the GLC profile for the reaction product prior to distillation. (Conditions: SE-30 column programmed at 130.degree.-220.degree. C. at 8.degree. C. per minute).

PAR FIG. 5 is the NMR spectrum for fraction 11 of the foregoing distillation containing the compound having the structure:
##STR82##

PAR FIG. 6 is the infra-red spectrum for fraction 11 of the foregoing distillation containing the compound having the structure:
##STR83##

PAC EXAMPLE III

PAC Preparation of Dimethyl Acetal of 1,2,3,4,4A,5,5A,8 Octahydro-1,4:5,8 Dimethanonaphthalene-2-Carboxaldehyde

PAL Reaction:
##STR84##

PAR Into a 100 ml reaction flask equipped with stirrer, thermometer, reflux condenser and heating mantle is placed the following:

PA1 10.0 grams of the reaction product of Example I, bulked fractions 22-26, containing the compound having the structure:
##STR85##
4.0 grams borontrifluoride etherate 25.0 grams anhydrous methyl alcohol

PAR The reaction mass is heated to 60.degree. C. and maintained at 60.degree. C. for a period of three hours.

PAR The reaction product having the structure:
##STR86##
(as confirmed by NMR, IR mass spectral analyses) is trapped via preparative GLC. (Conditions: SE-30 column programmed at 220.degree. C., isothermal)

PAR FIG. 7 is the GLC profile for the reaction product of this example. The peak indicated by the reference "11" is the peak for the staring material, the aldehyde having the structure:
##STR87##
The peak indicated by the reference numeral "12" is for a side-product having the structure:
##STR88##
The peak indicated by the reference numeral "13" is the peak for the reaction product having the structure:
##STR89##

PAR FIG. 8 is the NMR spectrum for the peak "13" of the GLC profile of FIG. 7.

PAC EXAMPLE IV

PAC Preparation of 1,2,3,4,4A,5,8,8A-Octahydro 1,4:5,8-Dimethanonaphthalene-2-Methanol

PAL Reaction:
##STR90##

PAR Into a 1 liter reaction flask equipped with stirrer, thermometer, reflux condenser and heating mantle is placed 500 grams of isopropyl alcohol and

50.degree. C. While maintaining this mixture at 50.degree. C., over a period of one hour 300 grams of the aldehyde produced according to Example I, bulked fractions 22-26 having the structure:
##STR91##
is added to the reaction mass. The reaction mass is then maintained at 60.degree. C. for a period of 0.5 hours.

PAR The reaction mass is then cooled and washed with 2 liters of water. An aqueous 10% solution of hydrochloric acid is then added until the solution is clear. The reaction mass is then washed and neutralized with sodium carbonate.

PAR The reaction mass is then distilled on a 1".times.12" Goodloe column yielding the following fractions:

TBL

Fraction No.	Vapor Temp. (.degree. C.)	Liquid Temp. (.degree. C.)	Vacuum mm.Hg. Pressure	Reflux Ratio	Weight of Fraction (gm)
1	23/110	27/147	1/1	9:1	14.0
2	111	147	0.8	9:1	15.3
3	111	147	0.65	9:1	20.1
4	111	147	0.65	9:1	24.3
5	116	153	0.65	1:1	26.1
6	122	157	0.65	1:1	27.1
7	122	158	0.65	1:1	25.0
8	122	161	0 65	1:1	27.4
9	121	168	0.65	1:1	26.3
10	119	196	0.65	1:1	25.8
11	115	230	0.65	1:1	17.6
12	100	235	--	--	--

PAR Bulked fraction 6-10 of the foregoing distillation have a sandalwood-like, patchouli-like and vetiver-like aroma profile.

PAR FIG. 9 is the GLC profile for bulked fractions 3-11 of of the distillation product of the foregoing reaction product. The peak indicated by the reference numeral "21" is the peak indicating the product having the structure:
##STR92##
The conditions for the GLC operation are: SE-30 column operated at 220.degree. C. isothermal.

PAR FIG. 10 is the NMR spectrum for bulked fractions 3-11 of foregoing distillation containing the compound having the structure:
##STR93##

PAR FIG. 11 is the infra-red spectrum for bulked fractions 3-11 of the foregoing distillation containing the compound having the structure:
##STR94##

PAC EXAMPLE V

PAC Preparation of 1,4:5,8-Dimethanonaphthalene-2-Methanol Decahydro

PAL Reaction:
##STR95##

PAR Into a 1 liter reaction vessel equipped with reflux condenser, thermometer, addition funnel, heating mantle and stirrer is placed 500 grams of

isopropyl alcohol and 40 grams of sodium borohydride. Over a period of 20 minutes, 280 grams (1.3 moles) of bulked fractions 4-11 of the distillation product of Example II containing the compound having the structure:
##STR96##
is added to the reaction mass, with refluxing. The reaction mass is maintained at a temperature of 70.degree.-80.degree. C. for a period of 20 hours.

PAR At the end of the 20 hour period 200 ml acetone is added to the reaction mass. Then, 1.5 liters of water is added to the reaction mass and the aqueous phase is separated from the organic phase. The organic phase crystallizes, at room temperature. The organic phase is distilled on a fractionation column yielding the following fractions:

TBL

Fraction No.	Vapor Temp. (.degree. C.)	Liquid Temp. (.degree. C.)	Weight of Fraction (gm)
1	130	140	16.1
2	130	140	21.5
3	130	140	17.3
4	130	140	22.7
5	130	140	20.0
6	130	140	29.9
7	130	147	28.4
8	130	220	23.0

PAR FIG. 12 is the GLC profile for the reaction product prior to distillation. The peak indicated by the reference numeral "31" is for the reaction product, the compound having the structure:
##STR97##
(Conditions: SE-30 column operated at 220.degree. C. isothermal).

PAR FIG. 13 is the NMR spectrum for fraction 8 of the foregoing distillation containing the compound having the structure:
##STR98##

PAR FIG. 14 is the infra-red spectrum for fraction 8 of the foregoing distillation containing the compound having the structure:
##STR99##

PAC EXAMPLE VI

PAC Preparation of 1,4:5,8-Dimethanonaphthalene-2-Methanol-Decahydro Acetate

PAL Reaction:
##STR100##

PAR Into a 1 liter reaction flask equipped with stirrer, thermometer, and reflux condenser is placed 160.0 grams of acetic anhydride, 200.0 ml toluene and 178.9 grams of the alcohol reaction product produced according to Example V, bulked fractions 3-8 having the structure:
##STR101##
The reaction mass is heated to 116.degree. C. and maintained at 116.degree. C. for a period of 2 hours. At the end of the reaction, 1 liter of water is added to the reaction mass and the organic phase is separated from the aqueous phase. The organic phase is washed with saturated sodium carbonate and the resulting product is fractionally distilled yielding the following fractions:

Fraction No.	Vapor Temp. (.degree. C.)	Liquid Temp. (.degree. C.)	Vacuum mm.Hg. Pressure	Weight of Fraction (gm)
2	147	152	2	19.4
3	137	150$	1	14.1
4	135	140	1	14.1
5	120	130	1	17.2
6	117	135	1	21.0
7	117	140	1	24.3
8	120	140	1	18.5
9	127	148	1	15.8
10	128	152	1	23.0
11	131	163	1	10.9
12	134	270	1	11.9

PAR Fraction 8-10 are bulked for subsequent evaluation. Fractions 8-10 have a floral, pineapple-like aroma from a perfumery standpoint and a pineapple taste.

PAR FIG. 15 is the GLC profile for the reaction product prior to distillation (Conditions: SE-30 column, programmed at 220.degree. C. isothermal). The peak indicated by the reference numeral "41" is the peak for the reaction product having the structure:
##STR102##

PAR FIG. 16 is the NMR spectrum for fraction 6 of the foregoing distillation containing the compound having the structure:
##STR103##

PAR FIG. 17 is the infra-red spectrum for fraction 6 of the foregoing distillation containing the compound having the structure:
##STR104##

PAC EXAMPLE VII

PAC Preparation of 1,2,3,4,4A,5,8,8A-Octahydro-1,4:5,8-Dimethanonaphthalene-2-Methanol Acetate

FAL Reaction:
##STR105##

PAR Into a 1 liter reaction flask equipped with stirrer, thermometer and reflux condenser are placed 102 grams of acetic anhydride, 500.0 ml toluene and 72.0 grams of the alcohol reaction product produced according to Example IV, bulked fractions 6-10 having the structure:
##STR106##
The reaction mass is heated to 117.degree. C. and maintained at 117.degree. C. for a period of 1.5 hours. At the end of the reaction, the toluene solvent is stripped and the reaction mass is washed with concentrated aqueous sodium carbonate. The reaction mass is then distilled on a fractionation column yielding the following fractions:

TBL

Fraction No.	Vapor Temp. (.degree. C.)	Liquid Temp. (.degree. C.)	Weight of Fraction (gm)

1	126	180	1.9
2	128	190	6.2
3	130	195	4.7
4	130	200	9.2
5	130	205	3.5

PAR Fractions 2-4 are bulked. The bulked fractions from a perfumery standpoint have a sweaty aroma nuance. From a flavor standpoint, bulked fractions 2-4 at a concentration of 1 ppm have a green, artichoke-like aroma and taste profile making it useful for augmenting or enhancing the aroma and taste of salad dressings.

PAR FIG. 18 is the GLC profile of the reaction product of this example containing the compound having the structure:
##STR107##

PAR FIG. 19 is the NMR spectrum for fraction 4 of the foregoing distillation containing the compound having the structure:
##STR108##

PAR FIG. 20 is the infra-red spectrum for fraction 4 of the foregoing distillation product containing the compound having the structure:
##STR109##

PAC EXAMPLE VIII

PAC Preparation of Dimethyl 1,2,3,4,4A,5,8,8A-Octahydro-1,4:5,8-Dimethanonaphthalene-2-Carboxaldehyde

PAL Reaction:
##STR110##

PAR Into a 2 liter autoclave is placed the following materials;

PA1 (a) 400 grams of methyl cyclopentadiene dimer, a mixture of compounds defined according to the structures:
##STR111##
(b) 200 grams acrolein; and (c) 300 ml toluene.

FAR The autoclave is sealed and heated to 225.degree. C. (180 psig) and maintained at that temperature and pressure for a period of two hours. At the end of the two hour period, the autoclave is depressurized and opened. The reaction product is analyzed via GLC, NMR, IR and mass spectral analyses. The resulting product has an animalic, leafy, green, herbaceous, floral (violet-like) aroma with cinnamon-like and cucumber undertones from a fragrance standpoint. The resulting substance has a green, melony, minty, herbaceous and floral aroma and taste profile at 2 ppm making it useful for mint and peppermint flavors.

PAR FIG. 21 is the GLC profile for the reaction product. The peak indicated by the reference numeral "51" is the peak for the reaction product defined according to the structures:
##STR112##
(mixtures of compounds).

PAR FIG. 22 is the NMR spectrum for peak "51" of the GLC profile of FIG. 21 for the mixture of compounds defined according to the structures:
##STR113##

PAR FIG. 23 is the infra-red spectrum for peak "51" of the GLC profile of FIG. 21 for the mixture of compounds defined according to the structures:
##STR114##

PAC EXAMPLE IX

PAC Preparation of 1,2,3,4,4A,5,8,8A-Octahydro-3-Methyl-1,4:5,8 Dimethanonaphthalene-2-Carboxaldehyde

PAL Reaction:
##STR115##

TBL

(a) Dicyclopentadiene	400 grams
(b) Crotonaldehyde	255 grams
(c) Toluene	500 ml

PAR The autoclave is sealed and heated to 225.degree. C. at a pressure of 200-320 psig and maintained at a temperature of 25.degree. C. at a pressure in the range of 200-320 psig for a period of three hours. At the end of the three hour period, the autoclave is depressurized and opened. The reaction mass is then distilled on a fractionation column yielding a product boiling at a temperature in the range of 92.degree.-96.degree. C. (vapor temperature) and a liquid temperature in the range of 126.degree.-140.degree. C. at 1.0 mm/Hg pressure.

PAR The reaction product at that boiling point has a spicy, cinnamon-like aroma.

PAR FIG. 24 is the GLC profile for the reaction product (conditions: SE-30 column programmed at 220.degree. C. isothermal).

PAR FIG. 25 is the NMR spectrum for the resulting reaction product at the foregoing boiling range.

PAR FIG. 26 is the infra-red spectrum for the resulting reaction product at the above boiling range.

PAC EXAMPLE X

PAC Preparation of 1,2,3,4,4A,5,8,8A-Octahydro-2-Methyl-1,4:5,8-Dimethanonaphthalene-2-Carboxaldehyde

PAL Reaction:

##STR116##

PAR Into a 200 ml autoclave is placed the following ingredients:

PA1 (i) 400 grams Dicyclopentadiene;

PA1 (ii) 255 grams of methacrolein; and

PA1 (iii) 500 ml toluene

PAR The autoclave is sealed and heated to 225.degree. C. and maintained at 225.degree. C. and at a pressure of 200 psig for a period of three hours. At the end of the three hour period the autoclave is opened and the resulting product is fractionally distilled yielding the following fractions:

TBL

Fraction No.	Vapor Temp. (.degree.C.)	Liquid Temp. (.degree.C.)	Vacuum mm.Hg. Pressure	Reflux Ratio	Weight of Fraction (gm)
1	27/57	23/90	2/2	9:1	21.1
2	70	126	2	9:1	11.5
3	75	132	2	9:1	13.7
4	83	135	2	9:1	17.2
5	83	135	2	9:1	13.5
6	85	136	2	9:1	23.5
7	85	136	2	9:1	24.8
8	85	136	2	9:1	26.1
9	85	176	2	9:1	18.7
10	86	136	2	9:1	17.8

11	86	136	2	1:1	33.1
12	86	137	2	1:1	30.6
13	86	137	2	1:1	29.8
14	86	137	2	1:1	31.3
15	86	137	2	1:1	32.0
16	86	140	2	1:1	33.1
17	86	140	2	1:1	29.6
18	86	140	2	1:1	29.0
19	87	140	2	--	32.1
20	85	143	2	--	33.3
21	80	186	2	--	30.1

PAR Fractions 4-15 are bulked for subsequent evaluation for tobacco, food flavoring and fragrance properties.

PAC EXAMPLE XI

PAC Chypre Perfume Formulations

PAR The following formulation is prepared:

TBL

Ingredients	Parts by Weight
Texas Cedarwood Oil	200
Patchouli Oil	50
Vetiver Oil	30
Bergamot Oil	150
African Geranium Oil	50
Coumarin	60
Natural Oak Moss	80
Tolu Balsam Peru	200
Labdanum	150
Musk Xylene	10
##STR117##	135

PAL The addition of the compound having the structure:
##STR118##
to this Chypre essence causes said Chypre to have an interesting sandalwood-like, patchouli-like and vetiver-like series of topnotes.

PAR Accordingly, this formulation can be described as having a Chypre essence with patchouli-like, sandalwood-like and vetiver-like topnotes.

PAC EXAMPLE XII

PAC Preparation of Herbal Fragrances

PAR The following mixtures are prepared:

TBL TABLE I

	Parts by Weight			
Ingredients	XIIA	XIIB	XIIC	XIID
Amyl Cinnamic Aldehyde	20%	20%	20%	20%
Phenyl Acetaldehyde	4%	4%	4%	4%
Dimethyl Acetal				
Thyme Oil, White	8%	8%	8%	8%
Sauge Sclaree French	8%	8%	8%	8%
Galbanum Oil	4%	4%	4%	4%

Juniper Berry Oil	4%	4%	4%	4%
Methyl Octin Carbonate	2%	2%	2%	2%
Linalyl Acetate	10%	10%	10%	10%
Dihydro Methyl Jasmonate	20%	20%	20%	20%
Fenchyl Ethyl Ether	10%	10%	10%	10%
##STR119##	3%	0%	0%	0%
##STR120##	0%	6%	0%	0%
##STR121##	0%	0%	6%	0%
##STR122##	0%	0%	0%	5%

PAR When added to this herbal formulation the product of Example I imparts to the herbal formulation a melony, cucumber, violet-like, wormwood-like and generally pleasant floral undertone.

PAR The product of Example II when added to this herbal formulation imparts to it, a floral, melony and cinnamon-like undertones..

PAR When the product of Example VI is added to this herbal formulation a pineapple-like, pleasant floral undertone is added to the herbal essence profile.

PAR When the reaction product of Example VIII is added to this herbal formulation, animalic, leafy, floral, violet-like, cinnamon-like and cucumber-like undertones are imparted to this formulation.

PAC EXAMPLE XIII

PAC Patchouli/Spicy Perfume Formulation

PAR The following mixture is prepared:

TBL

Ingredients	Parts by Weight
Orange Oil	50
Beramot Oil	20
Lime Oil	100
1-Hydroxy-methyl-2,4,6 Trimethyl cyclohexane	45
Neroli Oil	5
4-(4-Methyl-4-Hydroxyamyl) .DELTA..sup.3 -cyclohexene carboxaldehyde	10
2,3,3A,4,5,7A-Hexahydro-6,7A,8,8-Tetramethyl-1,5-methano-[1H]-inden-1-ol	100
1',2',3',4',5',6',7',8'-octahydro 2',3',8',8'-tetramethyl-2'-aceto-naphthone isomer mixture produced according to the process of Example VII of the U.S. Letters Pat. No. 3,911,018 issued on October 7, 1975	20
Gamma Methyl Ionone	20
1-acetyl-2,5,5-trimethylcycloheptane	100
Substituted tricyclodecane derivatives prepared according	

```
     to Example XII of U.S. Pat.
                                  100
     No. 4,275,251 issued on
     June 23, 1981
      ##STR123##                  85
     ______________________________________
PAR  The compound produced according to Example IX having the structure:
      ##STR124##
      imparts to this patchouli/spicy formulation an intense, cinnamon-like,
      long lasting, oriental, spicy characteristic.
PAC  EXAMPLE XIV
PAC  Preparation of Soap Composition
PAR  A total of 100 grams of soap chips produced from unperfumed sodium base
      toilet soap made from talo and coconut oil is admixed with 1 gram of each
      of the perfume compositions set forth in Table II, below until a
      substantially homogeneous composition is obtained. The mixture is melted
      under 8 atmospheres pressure at 190.degree. C. and maintained at
      190.degree. C. with mixing for a period of five hours at 8 atmospheres
      pressure. At the end of the five hour period, the resulting mixture is
      cooled and cut into soap bars. Each of the soap bars manifest an excellent
      aroma as set forth in Table II, supra:
TBL                TABLE II
     ______________________________________
     Structure of Compound
     and example by which
     produced          Perfumery Profile
     ______________________________________
     Aldehyde produced An herbal, strong, green,
     according to Example I,
                       aldehydic, wormwood-like
     bulked fractions 14-19,
                       and floral aroma profile.
     having the structure:
      ##STR125##
       Compound produced according
                       A melony, cucumber-like,
     to Example I, having the
                       violet-like, green,
     structure:        aldehydic aroma profile.
      ##STR126##
     bulked fractions 8-12.
       Compound produced according
                       A floral, melony, cinnamon-
     to Example II, having the
                       like aroma.
     structure:
      ##STR127##
     bulked fractions 7-13.
       Compound produced according
                       A sandalwood, patchouli,
     to Example IV, having the
                       vetiver aroma profile.
     structure:
      ##STR128##
     bulked fractions 6-10
```

```
                     A floral, pineapple-like
to Example VI, having the
                     aroma profile.
structure:
 ##STR129##
bulked fractions 8-10.
  Compound produced according
                     A sweaty, animal-like, musk-
to Example VII, having the
                     like aroma profile.
structure:
 ##STR130##
bulked fractions 1-5.
  A mixture of compounds
                     An animalic, leafy, green,
produced according to
                     herbaceous, floral, violet-
Example VIII, containing
                     like aroma with cinnamon-
the compounds having
                     like and cucumber-like
structures:          undertones.
 ##STR131##
and
 ##STR132##
  Compound produced according
                     A spicy, cinnamon-like
to Example IX having the
                     aroma profile.
structure:
 ##STR133##
  Perfume composition of
                     A chypre aroma with
Example XI.          patchouli-like, vetiver-
                     like and sandalwood-like
                     topnotes.
Perfume composition of
                     A herbal aroma with melony,
Example XIIA.        cucumber, violet-like,
                     wormwood-like and pleasant
                     floral undertones.
Perfume composition of
                     A herbal aroma with floral,
Example XIIB.        melony and cinnamon-like
                     undertones.
Perfume composition of
                     A herbal aroma with floral
Example XIIC.        and pineapple-like
                     undertones.
Perfume composition of
                     A herbal essence with
Example XIID.        animal-like, leafy, floral,
                     violet-like, cinnamon-like
                     and cucumber undertones.
Perfume composition of
                     A patchouli/spicy
```

Example XIII.	formulation an intense, cinnamon-like, long lasting, oriental, spicy characteristic.

PAC EXAMPLE XV

PAC Preparation of a Detergent Composition

PAR A total of 100 grams of a detergent powder sold under the trademark "RINSO.RTM." are mixed with 0.15 grams of each of the perfumery substances as set forth in Table II of Example XIV, supra, until a substantially homogeneous composition is obtained. Each of the detergent powders manifest an excellent aroma as set forth in Table II of Example XIV.

PAC EXAMPLE XVI

PAC Preparation of Cosmetic Bases

PAR A cosmetic powder is prepared by mixing in a ball mill 100 grams of talcum powder with 0.25 grams of one of the perfumery substances as set forth in Table II of Example XIV. The cosmetic powders produced using the materials of Table II of Example XIV have aroma characteristics as set forth in Table II of Example XIV.

PAC EXAMPLE XVII

PAC Liquid Detergent Composition

PAR Concentrated liquid detergents with aromas as set forth in Table II of Example XIV containing 0.2%, 0.5% and 1.2% of one of the substances set forth in Table II of Example XIV are prepared by adding appropriate quantities of perfumery substances as set forth in Table II of Example XIV to a liquid detergent known as P-87. The aroma intensity of each of the liquid detergents so prepared increases with increasing concentration of each of the substances as set forth in Table II of Example XIV, each of the detergents manifesting aromas as set forth in Table II of Example XIV.

PAC EXAMPLE XVIII

PAC Preparation of Colognes and Handkerchief Perfumes

PAR Each of the perfume substances of Table II of Example XIV are incorporated into 80%, 85%, 90% and 95% foodgrade ethanol solutions at the rates of 2.0%, 2.5%, 3.0%, 3.5% and 4.0%; and into handkerchief perfumes at concentrations of 15%, 20%, 25%, 30% and 40% (in 80%, 85%, 90% and 95% aqueous foodgrade ethanol). These of each of the substances of Table II of Example XIV are for distinct and definitive aroma nuances in each of the handkerchief perfumes and colognes as indicated in Table II of Example XIV.

PAC EXAMPLE XIX

PAC Preparation of Detergent Composition

PAR A total of 100 pounds of a detergent powder prepared according to U.S. Pat. No. 4,058,472 (the disclosure of which is incorporated by reference herein) and containing 5% by weight of the sodium salts of a mixture of sulfonated C.sub.14 -C.sub.18 alkyl catechol as a surface active component, the mixture being 60 parts by weight of mono-C.sub.14 -C.sub.18 alkyl catechol and 40 parts by weight of di-C.sub.14 -C.sub.18 alkyl catechol, 35% of sodium tetrapyrophosphate, 30% of sodium silicate, 20% of sodium carbonate, 3% of sodium carboxymethyl cellulose and 7% of starch is mixed with 0.15 grams of one of the perfumery substances set forth in Table II of Example XIV, supra, until substantially homogeneous compositions are obtained. Each of the compositions have excellent aromas as set forth in Table II of Example XIV.

PAC EXAMPLE XX

PAR Scented polyethylene pellets having pronounced aromas as set forth in Table II of Example XIV are prepared as follows:

heated to about 230.degree. C. under 5 atmospheres pressure in a pressure vessel. 25 Pounds of each of the substances set forth in Table II of Example XIV, separately, are then quickly added to the liquified polyethylene. The temperature is maintained at 230.degree. C. under high pressure and the mixing is continued for about 15 minutes in each case. The pressure vessel is then depressurized and the molten polyethylene enriched with each of the perfumery substances is permitted to exit from the vessel by gravity. The liquid falling through orifices (in the apparatus) in droplets solidifies almost instantaneously on impact with a moving cooled conveyor operating immediately below the pressure vessel. Solid polyethylene pellets having pronounced aromas as set forth in Table II of Example XIV are thus formed. In each case 50 pounds of thus-formed master pellets are then added to 1000 pounds of unscented polyethylene powder and the mass is heated to the liquid state. The liquid is molded into thin sheets, films and container shapes. The thin sheets, films and container shapes have pronounced aromas as set forth in Table II of Example XIV.

PAC EXAMPLE XXI

PAR Utilizing the procedure of Example I at column 15 of U.S. Pat. No. 3,632,396 (the specification for which is incorporated by reference herein), a non-woven cloth substrate useful as a drier-added fabric softening article of manufacture is prepared wherein the substrate, the substrate coating and the outer coating and the perfuming material are as follows:

PA1 1. a water dissolvable paper as the substrate ("Dissolvo Paper");
PA1 2. Adogen 448 (melting point 140.degree. F.) as the substrate coating; and
PA1 3. an outer coating having the following formulation (melting point about 150.degree. F.):
PA2 57% C.sub.20-22 HAPS
PA2 22% isopropyl alcohol
PA2 20% antistatic agent
PA2 1% of one of the perfumery substances as set forth in Table II of Example XIV.

PAR A fabric softening composition prepared as set forth above having aroma characteristics as set forth in Table II of Example XIV consists of a substrate having a weight of about 3 grams per 100 square inches, a substrate coating weighing about 1.85 grams per 100 square inches of substrate and an outer coating weighing about 1.4 grams per 100 square inches of substrate is created, thereby providing a total aromatized substrate and outer coating weight ratio of about 1:1 by weight of the substrate. The aromas as set forth in Table II of Example XIV is imparted in pleasant manners to head spaces in the dryers on operation thereof using the drier-added fabric softening non-woven fabric articles.

PAC EXAMPLE XXII

PAC Vanilla Flavor

PAR The following formulation is prepared:

TBL

Vanillin	10.0	grams
Ethyl Vanillin	3.0	grams
Benzodihydropyrone	3.0	grams
Heliotropin	1.0	gram
Propenyl Guiacol	0.5	grams
Gamma Nonyl Lactone	0.25	grams
Gamma Undecalactone	0.25	grams
Delta-Dodecalactone	0.25	grams
##STR134##	0.001	grams

PAR The compound having the structure:
##STR135##
enhances the foregoing vanillin formulation (a) making it more natural-like; and (b) making it three times (3.times.) as powerful as the formulation without this compound added thereto. In addition, the formulation is rendered much more outstanding in a standard creme-de-Kahlua formulation causing the creme-de-Kahlua formulation to be more natural-like and preferred by a bench panel of five members, unanimously. The resulting formulation containing the compound having the structure:
##STR136##
is added to the following liqueur formulation:

TBL

Ingredients	Parts by Weight
Clove essential oils	780
Lemon essential oils	400
Orange essential oils	300
Cinnamon essential oils	250
Mace essential oils	180
Vanillin formulation (as set forth above)	150
Neroli essential oil	10
Citronellol	2
Rose absolute	1
Food grade ethanol	927

PAR The resulting liqueur is added to the following mixture in order to produce a consumable material:

TBL

Ingredients	Parts by Weight	
96% Food grade ethanol	301	kg
Sugar	40	kg
Distilled water	46.8	liters
Flavor (as set forth above) (0.5% in food grade ethanol)	0.5	kg

PAL The resulting liquer has an interesting, bitter almond taste and aroma making it useful as such or as a "Bagne" for a sauce used for soaking pound cakes such as "Rum BaBa".

PAC EXAMPLE XXIII

PAR The vanilla flavor of Example XII is placed into an ice cream mix at the rate of 0.05%. The resulting previously-unflavored ice cream has an

PAC EXAMPLE XXIV

PAC Salad Dressing

PAR To a portion of essentially flavorless salad dressing, the compound of Example VII, having the structure:

##STR137##

(bulked fractions 1-5) is added at the rate of 1 ppm and also at the rate of 2 ppm. The resulting mixtures have characteristic artichoke notes. The salad dressing is a mixture of the following:

TBL

Ingredient	Parts by Weight
Black pepper oil	3
Nutmeg oil	3
Celery Oil	3
Lemon oil	3
Mustard oil	1
Vinegar-citric acid (50-50 mixture)	120
Starch paste prepared from tapioca flour-water (50-50 mixture)	300
Liquid egg yolks	210
Sodium chloride	7
Sucrose	10
Mustard	20
Locust Bean gum	6

PAC EXAMPLE XXV(A), (B)

PAC Lemon/Fruity Flavor Formulation

PAR The following lemony, fruity flavor formulations are prepared:

TBL

Ingredient	Parts by Weight	
	XXV(A)	XXV(B)
Natural Lemon Oil, Terpeneless	10.0	10.0
Acetaldehyde	0.6	0.6
Alpha-terpineol	2.1	2.1
Citral	1.8	1.8
Carvone	0.24	0.24
Terpinolene	1.2	1.2
Alpha-terpinene	0.25	0.25
Diphenyl	0.25	0.25
Alpha Fenchyl Alcohol	0.25	0.25
Limonene	0.35	0.35
Linalool	0.25	0.25
Geranyl Acetate	0.25	0.25
Ncotkatone	0.25	0.25
Neryl Acetate	0.25	0.25
Geranyl nitrile	0.55	0.55
Citronellol nitrile	0.60	0.60
Fenchyl ethyl ether	0.05	0.05
##STR138##	0.50	0.0
##STR139##	0.0	0.75

PAR The compound of Example II adds to this lemon flavor formulation an excellent melony flavor causing the overall formulation to have a "lemon/melon" aroma and taste causing it to be useful in enhancing the taste of fresh papaya fruit when three or four drops of this flavor diluted at the rate of 1% in 50% aqueous foodgrade ethanol is placed on the open papaya fruit.

PAR The compound of Example VI adds an excellent pineapple aroma and taste nuance to this lemon flavor. When the flavor (in 2% dilution and 50% foodgrade ethanol) is added to cooking chicken, the resultant cooked chicken has an excellent "lemony nuance" which is enhanced by use of the compound of Example VI.

PAC EXAMPLE XXVI

PAC Root Beer Beverage

PAR The compound having the structure:

##STR140##

produced according to Example IV, bulked fractions 6-10 is added to root beer (Barrelhead, produced by Canada Dry Corporation of Maspeth, N.Y., a division of the Norton Simon Corporation) at the rate of 1.5 ppm and submitted to a bench panel. The tetracyclic carbinol improves the woody rooty notes insofar as the aroma and taste of the rootbeer are concerned. Therefore, the beverage containing the compound defined according to the structure:

##STR141##

is preferred by a bench panel (of five members) unanimously over the beverage which does not contain the tetracyclic carbinol derivative produced according to Example IV.

PAC EXAMPLE XXVII

PAC Amaretto Flavor

PAR The following formulation is prepared:

TBL

Ingredients	Parts by Weight
Lavender essential oil	105.0
Clary sage essential oil	100.0
Rosemary essential oil	100.0
Thyme essential oil	90.0
Fennel essential oil	40.0
Mint essential oil	20.0
##STR142##	5.9
Angelica essential oil	5.0
Anise essential oil	5.0
Lemon essential oil	4.0
Wormwood essential oil	2.0
Cinnamon essential oil (10% in alcohol solution)	0.1
Aqueous 95%, foodgrade ethanol	523.0

PAR The mixture of compounds produced according to Example VIII enhances this amaretto flavor in view of the green, melony, minty, herbaceous and floral aroma and taste nuances which particularly enhance the mint oil aroma and taste portion of this formulation.

PAR A liqueur is produced by using the foregoing formulation as follows:

TBL

Ingredient	Parts by Weight	
96% alcohol	46.1	l
Sugar	1.0	kg
Distilled Water	55.1	l
Amaretto flavor produced, supra (diluted at the rate of 0.8% in 95% aqueous foodgrade ethanol)	0.5	kg

PAR In addition, the wormwood essential oil component of the foregoing amaretto flavor can be replaced totally by the use of the compound of Example I having the structure:
##STR143##
bulked fractions 8-19. Actually the aldehyde having the structure:
##STR144##
can replace the 2 parts by weight of wormwood essential oil by using only 0.02 parts by weight of the aldehyde having the structure:
##STR145##

PAC EXAMPLE XXVIII

PAC Toothpaste Flavor Formulation

PAR The following basic toothpaste flavor formulation is prepared:

TBL

Ingredients	Parts by Weight
Cardamon Oil	0.2
Clove Oil	1.0
Spearmint Oil	2.0
Peppermint Oil	96.8

PAR This flavor formulation is divided into three portions. To the first portion, nothing is added. To the second portion, 8 parts by weight of the first portion is combined with 2 parts by weight of anethole. Eight parts by weight of the third portion of this flavor is then combined with 2 parts by weight of the compound of Example IX having the structure:
##STR146##
prepared according to Example IX and 2 parts by weight of anethole.

PAR Each of the three flavors are compared in water at the rate of 10 ppm and evaluated by a bench panel. Each of the second and third flavors has sweet anise-like characteristics, but the flavor containing the compound defined according to the structure:
##STR147##
also has cinnamic and spicy aroma and taste nuances. Therefore, the flavor containing the aldehyde produced according to Example IX is preferred over flavors not containing the aldehyde of Example IX and, in addition, the aldehyde of Example IX having the structure:
##STR148##
augments and enhances the anise-like flavor.

PAC EXAMPLE XXIX

PAC Mint Flavor Formulation

PAR The following mint flavor formulation is prepared:

TBL

Ingredients	Parts by Weight
Peppermint Oil	60.0
Spearmint Oil	38.0
##STR149##	2.0

PAR The mixture of compounds produced according to Example VIII imparts a minty, herbaceous, floral, green and melony aroma and taste nuance of great intensity to this mint flavor formulation.

PAC EXAMPLE XXX

PAC A. Powder Flavor Formulation

PAR 20 Grams of the flavor composition of Example XXIX is emulsified in a solution containing 300 gm gum acacia and 700 gm water. The emulsion is spray-dried with a Bowen Lab Model Drier utilizing 260 c.f.m. of air with an inlet temperature of 500.degree. F., an outlet temperature of 200.degree. F. and a wheel speed of 50,000 rpm.

PAC B. Sustained Release Flavor

PAR The following mixture is prepared:

TBL

Ingredients	Parts by Weight
Liquid mint Flavor Composition of Example XXIX	20.0
Propylene glycol	9.0
Cab-O-Sil .RTM. M-5 (Brand of Silica produced by the Cabot Corporation of 125 High Street, Boston, Mass. 02110;	5.00
Physical Properties: Surface Area: 200 m.sup.2 gm Nominal particle size: 0.012 microns Density: 2.3 lbs/cu. ft.)	

PAR The Cab-O-Sil is dispersed in the liquid mint flavor composition of Example XXIX with vigorous stirring, thereby resulting in a viscous liquid. 71 Parts by weight of the powder flavor composition of Part A of this example, supra, is then blended into the said viscous liquid, with stirring, at 25.degree. C. for a period of 30 minutes resulting in a dry, free flowing sustained release flavor powder.

PAC EXAMPLE XXXI

PAR 10 Parts by weight of 50 Bloom pigskin gelatin is added to 90 parts by weight of water at a temperature of 150.degree. F. The mixture is agitated until the gelatin is completely dissolved and the solution is cooled to 120.degree. F. 20 Parts by weight of the liquid flavor composition of Example XXIX is added to the solution which is then homogenized to form an emulsion having particle size typically in the range of 5-40 microns. This material is kept at 120.degree. F. under which conditions the gelatin will not jell.

PAR Coacervation is induced by adding slowly and uniformly 40 parts by weight of a 20% aqueous solution of sodium sulphate. During coacervation the gelatin molecules are deposited uniformly about each oil droplet as a

PAR Gelation is effected by pouring the heated coacervate mixture into 1,000 parts by weight of 7% aqueous solution of sodium sulphate at 65.degree. F. The resulting jelled coacervate may be filtered and washed with water at temperatures below the melting point of gelatin, to remove the salt.

PAR Hardening of the filtered cake, in this example, is effected by washing with 200 parts by weight of 37% solution of formaldehyde in water. The cake is then washed to remove residual formaldehyde.

PAC EXAMPLE XXXII

PAC Chewing Gum

PAR 100 Parts by weight of chicle are mixed with 4 parts by weight of the flavor prepared in accordance with Example XXIX. 300 Parts of sucrose and 100 parts of corn syrup are added. Mixing is effected in a ribbon blender with jacketed side walls of the type manufactured by the Baker Perkins Co.

PAR The resultant chewing gum blend is then manufactured into strips 1 inch in width and 0.1 inches in thickness. The strips are cut into lengths of 3 inches each. On chewing, the chewing gum has a pleasant, long lasting mint flavors.

PAC EXAMPLE XXXIII

PAC Chewing Gum

PAR 100 Parts by weight of chicle are mixed with 18 parts by weight of the flavor prepared in accordance with Example XXX(B). 300 Parts of sucrose and 100 parts of corn syrup are then added. Mixing is effected in a ribbon blender with jacketed side walls of the type manufactured by the Baker Perkins Co.

PAR The resultant chewing gum blend is then manufactured into strips 1 inch in width and 0.1 inches in thickness. The strips are cut into lengths of 3 inches each. On chewing, the chewing gum has a pleasant, long lasting mint flavor.

PAC EXAMPLE XXXIV

PAC Toothpaste Formulation

PAR The following separate groups of ingredients are prepared:

TBL

Parts by Weight	Ingredients
Group "A"	
30.200	Glycerine
15.325	Distilled Water
.100	Sodium Benzoate
.125	Saccharin Sodium
.400	Stannous Fluoride
Group "B"	
12.500	Calcium Carbonate
37.200	Dicalsium Phosphate (Dihydrate)
Group "C"	
2.000	Sodium N--Lauroyl Sarcosinate (foaming agent)
Group "D"	
1.200	Flavor Material of Example XXX(B)
100.00 TOTAL	

PROCEDURE:

1. The ingredients in Group "A" are stirred and heated in a steam jackete kettle to 160.degree. F.;

2. Stirring is continued for an additional three to five minutes to form homogeneous gel;
3. The powders of Group "B" are added to the gel, while mixing, until a homogeneous paste is formed;
4. With stirring, the flavor of "D" is added and lastly the sodiumn-lauroyl sarcosinate; and
5. The resultant slurry is then blended for one hour. The completed paste is then transferred to a three roller mill and then homogenized, and finally tubed.

PAR The resulting toothpaste when used in a normal toothbrushing procedure yields a pleasant mint flavor, of constant strong intensity throughout said procedure (1-1.5 minutes).

PAC EXAMPLE XXXV

PAC Chewable Vitamin Tablets

PAR The flavor material produced according to the process of Example XXX(B) is added to a Chewable Vitamin Tablet. Formulation at a rate of 10 gm/Kg which Chewable Vitamin Tablet formulation is prepared as follows:

PAR In a Hobart mixer, the following materials are blended to homogeneity:

TBL

Gms/1000 Tablets

Vitamin C (ascorbic acid) as
70.11
Ascorbic acid-sodium ascorbate
4.0
mixture 1:1
Vitamin B.sub.1 (thiamine mononitrate) as
Rocoat .RTM. thiamine mononitrate
5.0
331/3% (Hoffman LaRoche)
Vitamin B.sub.2 (riboflavin) as
Rocoat .RTM. riboflavin 331/3%
4.0
Vitamin B.sub.6 (pyridoxine hydrochloride) as
Rocoat .RTM. pyridoxine hydrochloride
33.0
331/3%
Niacinamide as Rocoat .RTM. niacinamide
331/3%
Calcium pantothenate 11.5
Vitamin B.sub.12 (cyanocobalamin) as
3.5
Merck 0.1% in gelatin
Vitamin E (dl-alpha tocopheryl
6.6
acetate) as dry Vitamin E acetate 331/3%
d-Biotin 0.044
Flavor of Example XXX(B)
(as indicated above)
Certified lake color 5.0
Sweetener - sodium saccharin
1.0
Magnesium stearate lubricant
10.0
Mannitol q.s. to make 500.0

PAL Preliminary tablets are prepared by slugging with flatfaced punches and grinding the slugs to 14 mesh. 13.5 gm dry Vitamin A Acetate and 0.6 gm Vitamin D are then added as beadlets. The entire blend is then compressed using concave punches at 0.5 gm each.

PAR Chewing of the resultant tablets yields a pleasant, longlasting mint flavor for a period of 15 minutes.

PAC EXAMPLE XXVI

PAC Chewing Tobacco

PAR Onto 100 pounds of tobacco for chewing (85% Wisconsin leaf and 15% Pennsylvania leaf) the following casing is sprayed at a rate of 30%:

TBL

Ingredients	Parts by Weight
Corn Syrup	60.0
Licorice	10.0
Glycerine	20.0
Fig Juice	4.6
Prune Juice	5.0
Mint flavor of Example XXX(I)	0.08

PAR The resultant product is redried to a moisture content of 20%. On chewing, this tobacco has an excellent cooling mint flavor nuance in conjunction with the tobacco notes.

PAC EXAMPLE XXXVI

PAC Tobacco Formulation

PAR A tobacco blend is made up by mixing the following materials:

TBL

Ingredient	Parts by Weight
Bright	40.1
Burley	24.9
Maryland	1.1
Turkish	11.6
Stem (flue cured)	14.2
Glycerine	2.8
Water	5.3

PAR The above tobacco is used in producing cigarettes, and the following formulation is compounded and incorporated into each of these cigarettes:

TBL

Ingredient	Parts by Weight
Ethyl butyrate	0.05
Ethyl valerate	0.05
Maltol	2.00
Cocoa extract	26.00
Coffee extract	10.00
Ethyl alcohol	20.00
Water	41.90

PAR The above flavor is incorporated into model "filter" cigarettes at the rate of 0.1%.

PAR One-fourth of these model cigaretts are treated in the tobacco section with th ixture of aldehydes produced according to Example VIII ing the

```
      structures:
      ##STR150##
PAR  One-fourth of these model cigarettes are treated in the tobacco section
      with the compound defined according to the structure:
      ##STR151##
      produced according to Example IX.
PAR  Each of the foregoing aldehydes is added at rates of 100, 200 and 300 ppm
      per cigarette.
PAR  Another one-fourth of these model cigarettes are treated in the filter with
      either the mixture of aldehydes of Example VIII or the aldehyde of Example
      IX at the rate of 2.times.10.sup.-5 gm per gm of filter.
PAR  When evaluated by paired comparison, the cigarettes treated both in the
      tobacco and the filter with the mixture of compounds produced according to
      Example VIII are found, in smoke flavor, to have sweet, floral, green,
      herbaceous, minty and cooling aroma and taste nuances, and also cause the
      tobacco to be more natural-like. Also an excellent hay tobacco aroma and
      taste is imparted prior to and on smoking in both the main stream and the
      side stream by the product of Example VIII.
PAR  When evaluated by a paired comparison, these cigarettes are treated in both
      the tobacco and the filter with the compound of Example IX are found in
      smoked flavored to have oriental, spicy, cinnamon-like aroma and taste
      nuances causing the tobacco to be "oriental" and also natural in its
      "oriental" character. In general, an excellent "Turkish" tobacco aroma and
      taste is imparted prior to and on smoking in the main stream and in the
      side stream by the product produced according to Example IX, supra.
CLMS
STM  What is claimed is:
NUM  1.
PAR  1. A process for augmenting or enhancing the aroma or taste of a consumable
      material selected from the group consisting of perfume compositions and,
      colognes, comprising the step of adding to said consumable material an
      aroma augmenting or enhancing quantity of at least one compound defined
      according to the structure:
      ##STR152##
      wherein the dashed line represents a carbon-carbon double bond or a
      carbon-carbon single bond; wherein R.sub.1, R.sub.1 ', R.sub.1 ", R.sub.1
      '", R.sub.1 "", R.sub.3, R.sub.5, R.sub.5 ', R.sub.5 ", R.sub.5 '",
      R.sub.5 "" and R.sub.6 represent hydrogen or methyl; with the provisos:
PA1  (i) at least four of R.sub.1, R.sub.1 ', R.sub.1 ", R.sub.1 '" and R.sub.1
      "" represents hydrogen; and
PA1  (ii) at leat four of R.sub.5, R.sub.5 ', R.sub.5 ", R.sub.5 '", R.sub.5 ""
      represent hydrogen;
PAL  with Z being a moiety selected from the group consisting of:
      ##STR153##
      with the line:
EQU  [++++]
PAL  representing a carbon-carbon single bond or no bond at all; and R.sub.7 and
      R.sub.8 being separately C.sub.1 -C.sub.4 lower alkyl or, taken together,
      being C.sub.2 -C.sub.4 alkylene.
NUM  2.
PAR  2. The process of claim 1 wherein the consumable material is a perfume
      composition.
NUM  3.
PAR  3. The process of claim 1 wherein the consumable material is a cologne.
NUM  4.
```

```
     material has the structure:
     ##STR154##
NUM  5.
PAR  5. The process of claim 1 wherein the compound added to the consumable
     material has the structure:
     ##STR155##
NUM  6.
PAR  6. The process of claim 1 wherein the compound added to the consumable
     material has the structure:
     ##STR156##
NUM  7.
PAR  7. The process of claim 1 wherein the compound added to the consumable
     material has the structure:
     ##STR157##
NUM  8.
PAR  8. The process of claim 1 wherein the compound added to the consumable
     material has the structure:
     ##STR158##
NUM  9.
PAR  9. The process of claim 1 wherein the substance added to the consumable
     material which substance is defined according to the structure:
     ##STR159##
     is a mixture having the structures:
     ##STR160##
NUM  10.
PAR  10. The process of claim 1 wherein the compound added to the consumable
     material has the structure:
     ##STR161##
NUM  11.
PAR  11. The process of claim 1 wherein the compound added to the consumable
     material has the structure:
     ##STR162##
NUM  12.
PAR  12. The process of claim 1 wherein the compound added to the consumable
     material has the structure:
     ##STR163##
```

```
PATN
WKU  044462263
SRC  6
APN  3970833
APT  1
ART  166
APD  19820712
TTL  Light-sensitive color photographic material
ISD  19840501
NCL  9
ECL  1
EXP  Downey; Mary F.
INVT
NAM  Yamashita; Kiyoshi
CTY  Hino
CNT  JPX
INVT
NAM  Iijima; Toshifumi
CTY  Hino
CNT  JPX
ASSG
NAM  Konishiroku Photo Industry Co., Ltd.
CTY  Tokyo
CNT  JPX
COD  03
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CNT  JPX
APD  19810710
APN  56-106908
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APD  19811213
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CLAS
OCL  430506
XCL  430502
XCL  430503
XCL  430509
XCL  430567
EDF  3
ICL  G03C  146
ICL  G03C  726
FSC  430
FSS  502;503;505;506;509;567;569
UREF
PNO  4153460
ISD  19790500
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OCL  430505
UREF
PND  4187110
ISD  19800200
NAM  Yagihara et al.
OCL  430957
LREP
FRM  Frishauf, Holtz, Goodman & Woodward
ABST
PAL  A light-sensitive color photographic material having a support and, coated
      thereon, at least two light-sensitive silver halide emulsion layers
      respectively sensitive to lights of different spectral regions,
      characterized in that each of the light-sensitive emulsion layers
      comprises at least two emulsion layers having different
      light-sensitivities and containing negative type light-sensitive silver
      halide crystals essentially consisting of silver iodobromide containing
      silver iodide at a proportion not higher than 4 mole %.
PAL  This invention provides a silver halide color photographic material, in
      which the proportion of the silver halide utilized for the information of
      a color image to the total silver halide used is enhanced remarkably.
BSUM
PAR  This invention relates to a light-sensitive color photographic material,
      and particularly to a light-sensitive color photographic material for use
      of photographing an object in a camera. More particularly, this invention
      relates to a multi-layer silver halide light-sensitive color photographic
      material for high-sensitivity photographing, in which the efficiency of
      utilizing the silver halide in a negative type silver halide emulsion for
      the formation of a dye image is improved.
PAR  Generally, light-sensitive color photographic materials used for the
      photographing purposes are required to exhibit a high sensitivity and a
      high image quality. Sensitivity of a silver halide depends on the size of
      silver halide crystals, and it is necessary to use relatively coarse
      silver halide crystals in order to obtain a high sensitivity. However,
      graininess of a dye image is decisively affected by the size of silver
      halide crystals. Therefore, it has been proposed to use a multi-layer
      light-sensitive color photographic material comprising two or more layers
      exhibiting sensitivity of light in the same spectral region and forming a
      dye of the same hue. Light-sensitive color photographic materials of this
      type are described for example in West German Patent No. 1121470, British
      Pat. No. 923,045, Japanese Patent Publication No. 15495/1974, Japanese
      Provisional Patent Publication Nos. 49027/1976, 143016/1977, 97831/1978
      and 97424/1978. It is also known to form a light-sensitive photographic
      material comprising only one layer by using a mixture of a
      high-sensitivity emulsion containing relatively coarse crystals sensitive
      to light in a particular visible spectral region and a low-sensitivity
      emulsion containing relatively fine crystals. However, the material of
      this type is not popular because of its inferior graininess.
PAR  The present invention relates to a multi-layer light-sensitive color
      photographic material comprising at least two layers exhibiting different
      spectral sensitivities, and each layer exhibiting the same spectral
      sensitivity i.e., each layer exhibiting sensitivity to light in the same
      visible spectral region and forming a dye of the same hue is further
      constituted by two or more layers.
PAR  In silver halide light-sensitive color photographic materials, silver is
      used as the raw material for light-sensitive substance. In spite of small
      amo   of silver deposits, silver is widely used for industr   trinketry
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and medical purposes and the like. Thus, need exists for reduction in the amount of silver used in silver halide light-sensitive photographic materials for the purpose of preserving resources and also reducing the cost of silver halide light-sensitive photographic materials because of recent remarkable rise in the price of silver.

PAR Usually, in silver halide light-sensitive color photographic materials for high-sensitivity photographing, negative type silver iodobromide containing silver iodide at a high molar percentage is used as the light-sensitive silver halide. However, with a light-sensitive material in which negative silver iodobromide containing silver iodide at a high molar percentage is used as the light-sensitive silver halide, the number of silver halide crystals not utilized for the image formation (hereinafter referred to as the dead grains) increases at the portion of maximum density in an image obtained upon exposure through an optical wedge. Thus, only about 40% of the exposed silver iodobromide crystals is utilized for the image formation. Although the mechanism of this phenomenon has not been completely clarified, it is assumed attributable to the occurrence of latent image bleaching during the development processing. In the color development, the proportion of the developed silver utilized for the formation of a color image is at most about 60% at the portion of maximum density because an oxidized product of the color developing agent is subjected not only to the reaction with a coupler but also to various reactions as described for example by T. H. James in "The Theory of the Photographic Process", Chapter 12, Section II, Macmillan Co., 1977. Therefore, because of the above-mentioned two factors affecting the utilization efficiency, the proportion of the silver halide actually utilized for the formation of a color image is 25% or less of the silver amount used.

PAR On the other hand, in a multi-layer light-sensitive color photographic material comprising at least two layers exhibiting different spectral sensitivities, and each layer exhibiting the same spectral sensitivity is further constituted by two or more layers, it is known to adjust the maximum color density of the high sensitivity layer by lowering the concentration of a coupler in the high sensitivity emulsion layer so as to improve graininess of the high sensitivity layer using relatively coarse silver halide crystals. However, if the concentration of the coupler is lowered, there is a serious drawback in that, many dead grains occur, resulting in low efficiency of silver halide utilization and low apparent sensitivity of the silver halide crystals.

PAR Silver halide light-sensitive color photographic materials are generally subjected to color development after the imagewise exposure. Recently, the temperature of the color development is gradually raised for the purpose of meeting the need for quick processing. In many cases, the color development is conducted at a temperature between 35.degree. and 40.degree. C. for 3 to 3.5 minutes. However, to maintain such high processing temperatures, it is necessary to use much energy and to keep the concentration of the processing solution at a constant level as the solvent evaporates. Further, the processing solution deteriorates quickly as the processing temperature rises. Thus, need exists for a silver halide light-sensitive color photographic material capable of being developed at as low temperatures as possible.

PAR The primary object of the present invention is to provide a silver halide light-sensitive color photographic material for high-sensitivity photographing which eliminates the disadvantages of the conventional techniques described above, and particularly a silver halide photographing in which the proportion of the silver halide amount utilized for the formation of a color image to the amount of silver halide used is enhanced remarkably.

PAR Another object of the present invention is to provide a silver halide light-sensitive color photographic material for high-sensitivity photographing, in which a negative type silver iodobromide emulsion having few dead grains is used.

PAR A further object of the present invention is to provide a silver halide light-sensitive color photographic material for high-sensitivity photographing, in which the degree of color formation is increased with respect to the unit amount of developed silver.

PAR A still further object of the present invention is to provide a silver halide light-sensitive color photographic material for high-sensitivity photographing, which is suitable for a low-temperature quick color development system.

PAR The present invention provides a light-sensitive color photographic material having a support and, coated thereon, at least two light-sensitive silver halide emulsion layers respectively sensitive to lights of different spectral regions, each of which emulsion layers comprises at least two emulsion layers having different light-sensitivities and containing negative type light-sensitive silver halide crystals essentially consisting of silver iodobromide containing silver iodide at a proportion not higher than 4 mol %. The light-sensitive color photographic material characterized as described above is hereinafter referred to as the light-sensitive color photographic material in accordance with the present invention.

PAR The above objects can be accomplished by the light-sensitive color photographic material described below in detail.

PAR Namely, in the light-sensitive color photographic material in accordance with the present invention, a negative type silver halide emulsion having the sensitivity speck mainly at the surfaces of the silver halide crystals is used as the silver halide emulsion. The emulsion is of the surface latent image type, which means reversely from the so-called internal latent image type direct positive emulsion, namely means an emulsion which yields a blackened silver image in inverse proportion to the lightness of the object when developed with a surface developing solution after the exposure.

PAR In the silver iodobromide emulsion, it is well known that more rapid development characteristics can be obtained as the molar percentage of silver iodide decreases. The inventors further studied this phenomenon and found that, although dead grains decrease as the molar percentage of silver iodide decreases in the case of a single layer, this feature does not occur remarkably if such a layer is stacked on or sandwiched between silver iodobromide emulsion layers containing a large molar percentage of silver iodide. Further studies revealed that, even in stacked layers, dead grains can be reduced if all of the negative type silver halide light-sensitive emulsions in the multi-layer silver halide light-sensitive material comprise silver iodobromide of low molar percentage of silver iodide. It was also revealed that the amount of dye formed per unit amount of developed silver increases considerably. The inventors presumes that dead grains occur because a small size latent image is bleached by an oxidized product of the developing agent. It is assumed that dead grains decrease in the case of low-iodine silver iodobromide because, if the development speed is high, the latent image quickly grows to a stable development nucleus, and that a relatively large amount of iodine occurring in a layer containing a large molar percentage of silver iodide restricts the development when a layer containing a small molar percentage of silver iodide is stacked on a silver iodobromide layer containing a large molar percentage of silver iodide.

PAR It is not clear why the amount of a dye formed per unit amount of developed silver increases.

PAR The silver halide used in the light-sensitive color photographic material in accordance with the present invention substantially consists of a negative type silver iodobromide containing 4 mole % or less of silver iodide. This means that the average content of silver iodide in the silver iodobromide crystals should be 4 mole % or less, and there may partially exist silver iodobromide crystals which contain more than 4 mole % of silver iodide and which are generated during the production process of silver halide. In the present invention, silver iodobromide preferably means the silver iodobromide containing 0.1 mole % or more of silver iodide. The preferable molar percentage of silver iodide in the present invention is between 1 and 3 mole %. The silver iodobromide may contain silver chloride, silver bromide, silver chlorobromide and/or a mixture thereof insofar as the effect of the present invention is not adversely affected. The silver iodobromide emulsion may contain large or small crystals, and may be monodispersed or polydispersed. However, the effect of the present invention is particularly remarkable when the emulsion is monodisperse. It is particularly preferable that the coefficient of variation obtained by dividing the standard deviation S (defined below) by the average crystal size r is 0.15 or less.

##EQU1##

PAR The average crystal size as used herein means the average value of the diameters of silver halide crystals when they are spherical. When the crystals are cubic or not spherical, their projected images are converted to circular images of the same area, and the average of the diameters of the circular images is taken as the average crystal size. The average crystal size is defined by:

##EQU2##

where r.sub.i designates the crystal sizes of individual grains, and n.sub.i designates the number of the crystals.

PAR In the silver halide light-sensitive color photographic material according to the present invention, each emulsion layer containing negative type silver halide crystals having the same spectral sensitivity is constituted by at least two negative type silver halide emulsion layers having different light sensitivities.

PAR It is preferable that the upper layer, viewed from the support, has a light sensitivity higher than that of the lower layer. Further, in the present invention, it is preferable that the at least two layers each having the same spectral sensitivity have the average crystal sizes of the silver halide crystals different from each other. For example, it is preferable that the average grain size of the silver halide grains contained in the emulsion layer having a higher light sensitivity is in the range between 0.5.mu. and 1.5.mu., while that in the emulsion layer having a lower light sensitivity is in the range between 0.3.mu. and 0.8.mu..

PAR The light-sensitive color photographic material in accordance with the present invention comprises at least two kinds of emulsion layers which contain negative type silver halide crystals exhibiting different spectral sensitivities and which respectively consist of a plurality of layers. In the case of a light-sensitive natural color photographic material, three emulsion layers exhibiting different spectral sensitivities are generally used, and these layers are positioned in the order of for example the side of the support towards the outermost layer. In this case, the proportion of silver iodide to the silver iodobromide in each layer should be 4 mole % or less. It is more preferable that the difference between the contents of silver iodide in the silver iodobromide emulsion layer containing the maximum molar percentage of silver iodide and that containing the minimum molar percentage of silver iodide is 2 mole % or less whereby the occurrence of dead grains is reduced much more. The molar percentage of silver iodide in the silver iodobromide contained in each layer is not limited in sofar as the silver halide light-sensitive emulsion contained in each of the two or more layers each exhibiting the same spectral sensitivity substantially consists of silver iodobromide containing 8 mole % or less of silver iodide. However, because of little occurrence of dead grains, it is preferable that the difference between the molar percentage of silver iodide in the silver iodobromide in the respective layers is small. Further, it is preferable that the difference between the molar percentage of silver iodide in the layer containing the maximum molar percentage of silver iodide and the layer containing the minimum molar percentage of silver iodide is 2 mole % or less.

PAR The silver halide crystals used in the light-sensitive color photographic material in accordance with the present invention may be the so-called twinned crystals having irregular shapes such as sherical or plate-like shape, or may be of a regular shape such as cube, octahedron and tetradecahedron. Preferably, they are octahedral or tetradecahedral since lesser dead grains are generated. It is also possible to be a mixture of grains having a regular shape and an irregular shape.

PAR The silver halide crystals used in the light-sensitive color photographic material in accordance with the present invention may be prepared by the acid process, neutral process or ammonia process. It is also possible to prepare seed crystals by the acid process, and grow them up to the predetermined size by the ammonia process which gives a high growth rate. When growing the silver halide crystals, it is desirable that the pH, pAg or the like in the reactor are controlled, and silver ions and halide ions are both poured sequentially and simultaneously and mixed in quantities matching the growth rate of silver halide grains, that is so called double jet method as described for example in Japanese Provisional Patent Publication No. 48521/1979.

PAR The silver halides may be chemically sensitized with active gelatin; a sulfur sensitizer e.g. allylthiocarbamide, thiourea or cystine; a selenium sensitizer; a reduction sensitizer e.g. tin (II) salt, thiourea dioxide and polyamine; a noble metal sensitizer, e.g. gold sensitizer such as potassium aurithiocyanate, potassium chloroaurate, water-soluble gold salts or a water-soluble salt of ruthenium, platinum, rhodium or iridium, e.g. potassium chloroplatinate (some of these serve as sensitizers or fog restrainers depending on the amount used). These sensitizers may be used alone or in combination (e.g. a combination of the gold sensitizer with the sulfur sensitizer, or a combination of the gold sensitizer with selenium sensitizer).

PAR Further, the silver halides may be optically sensitized (in which so-called super-sensitization may be obtained) to a desired wavelength region for example by using an optical sensitizer e.g. a cyanine dye such as zeromethine dye, monomethine dye, dimethine dye or trimethine dye, or a merocyanine dye singly or in combination of two or more.

PAR As for the coupler used in the light-sensitive color photographic material in accordance with the present invention, i.e. the compound forming a dye by the reaction with an oxidized product of the color developing agent, it is sufficient only if it exists substantially at the time of lor development. The coupler may be contained in the color developing solution or in the light-sensitive color photographic material. When the coupler is non-diffusion type, it is preferably contained in the light-sensitive color photographic material.

PAR Generally, the coupler is contained in the light-sensitive layer of the light-sensitive color photographic material.

PAR The coupler can be incorporated in the light-sensitive color photographic material in various ways in accordance with the present invention. When the coupler is soluble in an alkali, it may be added in the form of an alkaline solution. When it is soluble in an oil, it is preferably dissolved in a high boiling solvent optionally in combination with a low boiling solvent and finely dispersed in the silver halide emulsion according to the procedures described in U.S. Pat. Nos. 2,322,027, 2,801,170, 2,801,171, 2,272,191 and 2,304,940. In this case, it is also possible to additionally add a hydroquinone derivative, an ultra violet ray absorber, a discoloration preventing agent or the like as required. It is also possible to use a mixture of two or more couplers. In the incorporation of the coupler into the light-sensitive material, one or more couplers may be dissolved optionally together with another coupler, a hydroquinone derivative, a discoloration preventing agent, an ultra violet ray absorber or the like as required in a high boiling solvent such as an organic acid amide, a carbamate, an ester, a ketone, a urea derivative or the like, particularly di-n-butyl phthalate, tri-cresyl phosphate, triphenyl phosphate, di-isooctyl azelate, di-n-butyl sebacate, tri-n-hexyl phosphate, N,N-diethyl-caprylamide butyl, N,N-diethyllaurylamide, n-pentadecyl phenyl ether, dioctyl phthalate, n-nonyl phenol, 3-pentadecylphenyl ethyl ether, 2,5-di-sec.-amylphenyl butyl ether, monophenyl-di-o-chlorophenyl phosphate, or a fluoroparaffin, or if necessary in a low boiling solvent such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, butyl propionate, cyclohexanol, diethylene glycol monoacetate, nitromethane, carbon tetrachloride, chloroform, cyclohexane, tetrahydrofuran, methyl alcohol, acetonitrile, dimethylformamide, dioxane or ethyl methyl ketone. The solution thus formed may be mixed with an aqueous solution containing a hydrophilic binder such as gelatin and an anionic surface active agent such as alkylbenzenesulfonate or alkylnaphthalenesulfonate and/or a nonionic surface active agent such as sorbitan sesquioleate or sorbitan monolaurate. The mixture thus obtained may then be emulsified and dispersed in a high-speed rotating mixer, colloid mill, supersonic dispersing unit or the like, and added to a constituent of the light-sensitive color photographic material in accordance with the present invention, preferably the silver halide emulsion.

PAR Further, the coupler may be dispersed in the photosensitive material by a latex dispersing method.

PAR The latex dispersing method and its effect are described for example in Japanese Provisional Patent Publication Nos. 74538/1974, 59943/1976 and 32552/1979, and "Research Disclosure", August 1976, No. 14850, pages 77-79.

PAR Examples of suitable lateces are homopolymers, copolymers and terpolymers of monomers such as styrene, ethyl acrylate, n-butyl acrylate, n-buty methacrylate, 2-acetoacetoxyethyl methacrylate, 2-(methacryloyloxy) ethyltrimethylammonium sulfate, sodium 3-(methacryloyloxy) propane-1-sulfonate, N-isopropylacrylamide, N-[2-(2-methyl-4-oxopentyl)]acrylamide, and 2-acrylamido-2-methylpropane sulfonate.

to the light-sensitive color photographic material, it is preferably used in an amount between 10 g and 100 g per one mole of silver halide. When it is added to the color developing solution, it is used preferably in an amount between about 0.1 g and 3 g per liter of the color developing solution.

PAR For the purpose of preventing the dye from discolorating due to active rays having a short wavelength, it is advantageous to use ultraviolet ray absorbers such as thiazolidone, benzotriazole, acrylonitrile and benzophenone compounds together with the coupler in the light-sensitive color photographic material in accordance with the present invention. It is particularly advantageous to use Tinuvin P's, 320, 326, 327 and 328 (available from Ciba-Geigy AG) alone or in combination.

PAR The hydroquinone derivatives used together with the coupler in the light-sensitive color photographic material in accordance with the present invention also include their precursors. The precursors as used herein mean the compounds releasing hydroquinone derivatives by hydrolysis.

PAR Examples of the discoloration preventing agents used together with the coupler in the present invention preferably include coumarone, coumaran and spirochroman compounds and the like.

PAR The coupler used in the light-sensitive color photographic material in accordance with the present invention may be of either two or four equivalent type of an optional combination thereof.

PAR Further, the coupler may be a low molecular coupler or the so-called polymeric coupler.

PAR The coupler used in the light-sensitive color photographic material in accordance with the present invention may be any of the known photographic couplers, preferably .alpha.-acylacetamide yellow coupler (.alpha.-benzoylacetanilide yellow coupler, .alpha.-pivaloylacetanilide yellow coupler or the like), 5-pyrazolone magneta coupler, pyrazolinobenzoimidazole magenta coupler, phenol cyan coupler or naphthol cyan coupler.

PAR Typical examples of the .alpha.-acylacetamide yellow couplers used in the present invention are:
##STR1##

PAR The above-described .alpha.-acylacetamide yellow couplers used in the present invention can be prepared by the methods described for example in West German Offenlegungsschrift Nos. 2,057,941 and 2,163,812, Japanese Provisional Patent Publication Nos. 26133/1972 and 29432/1973, U.S. Pat. Nos. 3,227,550, 2,875,057 and 3,265,506, Japanese Provisional Patent Publication Nos. 66834/1973, 66835/1973, 94432/1973, 1229/1973, 10736/1974, 34232/1975, 65231/1975, 117423/1975, 3631/1976 and 50734/1976.

PAR The .alpha.-acylacetamide yellow couplers may be contained in the silver halide emulsion layer individually or as a mixture of two or more couplers. They may be incorporated by the above-mentioned procedures in an amount 1-30 mole % of blue-sensitive silver halide.

PAR Typical examples of the cyan couplers used in the present invention are:
##STR2##

PAR The cyan couplers used in the present invention can be prepared by the methods described for example in British Pat. No. 1,084,480, Japanese Provisional Patent Publication Nos. 117422/1975, 10135/1975, 37647/1976, 25228/1975 and 130441/1975. They are contained alone or in combination in the silver halide emulsion layer or contained in admixture with a so-called active-point arylazo-substituted colored coupler as described in U.S. Pat. No. 3,034,892, etc. They are incorporated by conventional procedure in an amount between 1 and 30 mole % of silver halide.

PAR Examples of the preferable magenta couplers used in the present invention

are:
##STR3##

PAR The magenta couplers used in the present invention also includes those described for example in U.S. Pat. Nos. 3,311,476, 3,419,391, 3,888,680 and 2,618,641, West German Offenlegungsschrift Nos. 20 15 814, 23 57 105 and 23 57 122, Japanese Provisional Patent Publication Nos. 129538/1974, 105820/1976, 12555/1979, 48540/1979, 112342/1976, 112343/1976, 108842/1976 and 58533/1977. The methods of preparing them are also described in these litaratures.

PAR As for the coupler used in the present invention, it is preferable that the speed of the reaction between the coupler and the oxidized product of the developing agent is high because in this case the number of dye molecules formed per unit amount of developed silver increases. Particularly, couplers exhibiting a specific rate, as measured by the method described below, which is higher than that of the compound M-1 are preferable.

PAR (Measurement of specific rate)

PAR In 30 ml of ethyl acetate and 15 ml of dibutyl phthalate, 0.02 mole of a coupler is dissolved. The solution thus obtained is mixed with 20 ml of a 10% aqueous solution of Alkanol B (alkylnaphthalenesulfonate available from du Pont) and 200 ml of a 5% aqueous gelatin solution. The mixture is then emulsified and dispersed in a colloid mill. The dispersion thus obtained is then added to a silver iodobromide emulsion containing 3.5 mole % of silver iodide so that the mole percentage of the coupler with respect to silver in the emulsion is 10%. The composition thus obtained is then applied to a triacetate film so that the silver amount is 15 mg/dm.sup.2, and dried to yield a specimen. The obtained specimen is exposed through an optical wedge and processed according to the processes described below by using the processing solutions described below.

PAR The percentage of the maximum density obtained with a color developing solution containing citrazinic acid with respect to the maximum density obtained with a color developing solution containing no cirtazinic acid is taken as the specific rate.

TBL

Processing (processing temperature: 38.degree. C.)	Processing time
Color development	3 minutes 15 seconds
Bleaching	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Fixing	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Stabilization	1 minute 30 seconds
Drying	

PAR Compositions of the processing solutions were used in the processing steps:

TBL

(Developing solution containing no citrazinic acid)

4-Amino-3-methyl-N--ethyl-N--(.beta.-hydroxyethyl)-aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine half-sulfate	2.0 g
Anhydrous potassium carbonate	

Sodium bromide	1.3	g
Trisodium nitrilotriacetate (monohydrate)	2.5	g
Potassium hydroxide	1.0	g

PAL Made up to 1 liter with water, and adjusted to pH 10.3 with a 1N aqueous potassium hydroxide or acetic acid.

PAR (Developing solution containing citrazinic acid)

PAR Citrazinic acid is added to the developing solution containing no citrazinic acid in an amount of 5 g per liter, and the resulting solution is adjusted to pH 10.3.

TBL

(Bleaching solution)

Ferric ammonium salt of ethylenediaminetetraacetic acid	100.0	g
Diammonium salt of ethylenediaminetetraacetic acid	10.0	g
Ammonium bromide	150.0	g
Glacial acetic acid	10.0	ml

Made up to 1 liter with water and adjusted to pH 6.0 with aqueous ammonia.

(Fixing solution)

Ammonium thiosulfate	175.0	g
Anhydrous sodium sulfite	8.6	g
Sodium metasulfite	2.3	g

Made up to 1 liter with water and adjusted to pH 6.0 with acetic acid.

(Stabilizing solution)

Formalin (37% aqueous solution)	1.5	ml
Konidax (available from Konishiroku Photo Industry Co., Ltd.)	7.5	ml

Made up to 1 liter with water.

PAR In the light-sensitive color photographic material in accordance with the present invention, it is preferable that at least one of the light-sensitive layers contain a compound releasing a development inhibitor by the reaction with an oxidized product of the color developing agent. By using such a compound, the sharpness, graininess, color purity and wide latitude of exposure are remarkably improved over the conventional light-sensitive color photographic material.

PAR Examples of known compounds releasing a development inhibitor by the the reaction with an oxidized product of the developing agent are compounds which couple with an oxidized product of a color developing agent to form a dye and release a development inhibitor (hereinafter referred to as the DIR couplers) as disclosed in U.S. Pat. Nos. 3,148,062 and 3,227,554, and compounds which release a development inhibitor without forming a dye by the coupling with an oxidized product of a color developing agent (hereinafter referred to as the DIR substances) as disclosed in U.S. Pat. No. 3,632,345. (Both DIR couplers and DIR substances are referred to as the DIR compounds.)

PAR For example, when the present invention is applied to an ordinary mul layer light-sensitive color photographic material cont ing a blue-, green- and red-sensitive emulsion layers, the DIR compounds should be contained in one or more of these layers. Particularly, it is preferable that they are contained at least in the green-sensitive emulsion layer. Further, when an emulsion layer exhibiting a color sensitivity comprises a plurality of layers exhibiting different sensitivities as in the present invention, the DIR compounds should be contained in at least one of the layers, preferably in the emulsion having a lower sensitivity.

PAR The DIR compounds preferably used in the present invention are represented by the following general formula (I) or (II):

EQU A-TIME-Z (I)

PAR In the general formula (I), A designates a coupling component capable of reacting with an oxidized product of a color developing agent. The coupling component may be any component which can release the group TIME-Z by the reaction with an oxidized product of a color developing agent.

PAR In the general formula (I), TIME designates a timing group, and Z designates a development inhibitor. Examples of the timing groups includes those based on the intramolecular nucleophilic substitution as described in Japanese Provisional Patent Publication No. 145135/1979, and those based on the electron movement along the conjugated chain as described in Japanese Provisional Patent Publication No. 17644/1980. In short, any compound may be used if it first releases the group TIME-Z through the breakage of the A-TIME bond and then releases Z through the breakage of the TIME-Z bond. Z includes the development inhibitors as described in "Research Disclosure", Vol. 176, No. 17643, Dec. 1978 (hereinafter referred to as the literature 1). Preferably, it is mercaptotetrazole, selenotetrazole, mercaptobenzothiazole, selenobenzothiazole, mercaptobenzoxazole, selenobenzoxazole, mercaptobenzimidazole, selenobenzimidazole, benzotriazole, benzodiazole or a derivative thereof.

EQU A-Z (II)

PAR In the general formula (II), A and Z have the same meanings as described above with respect to the general formula (I).

PAR Syntheses of the compounds represented by the general formula (I) are described for example in Japanese Provisional Patent Publication Nos. 14513/1979 and 17644/1980.

PAR The DIR compounds represented by the general formula (II) involve the DIR couplers and the DIR substances. Examples of the DIR couplers represented by the general formula (II) are described e.g. in U.S. Pat. Nos. 3,227,554 and 3,773,201, and British Pat. No. 2,010,818. Syntheses thereof are also described in these patents.

PAR Examples of the DIR substances represented by the general formula (II) are described e.g. in U.S. Pat. Nos. 3,958,993, 3,961,959 and 3,938,996, Japanese Provisional Patent Publication Nos. 147716/1975, 152731/1975, 105819/1976, 6724/1976 and 123025/1975, U.S. Pat. Nos. 3,928,041 and 3,632,345, and Japanese Provisional Patent Publication No. 125202/1975. Syntheses thereof are also described in these specifications.

##STR4##

PAR In the formula for [D-24].about.[D-31], Y, W, m and R.sup.3 each represent the following:

TBL

Compound No.	Y	W	m	R.sub.3
[D-24]	O	NO.sub.2	0	

```
                                          ##STR6##
   [D-26]  0     NO.sub.2       1
                                          ##STR7##
   [D-27]  0     NO.sub.2       1
                                          ##STR8##
   [D-28]  0     NO.sub.2       1
                                          ##STR9##
   [D-29]  0     NHSO.sub.2 C.sub.4 H.sub.9
                                0
                                          ##STR10##
   [D-30]  0     NHSO.sub.2 C.sub.8 H.sub.17
                                1
                                          ##STR11##
   [D-31]  S     H              0
                                          ##STR12##
 [D-32] .about.[D-36]
           ##STR13##
PAR  In [D-32].about.[D-36], Z represents the following:
PAC  Compound No.
PAO  [D-32]ethylthiotetrazole
PAO  [D-33]n-butylthiotetrazole
PAO  [D-34]cyclohexylthiotetrazole
PAO  [D-35]N-butylthiotetrazole
PAO  [D-36]5,6-dichlorobenzotriazole
      ##STR14##
PAR  The other compositions of the silver halide light-sensitive color
      photographic material in accordance with the present invention may be
      determined as described in the above-mentioned literature 1 or "Research
      Disclosure" No. 18431.
PAR  The silver halide light-sensitive color photographic material in accordance
      with the present invention is highly sensitive and used for photographing
      purposes, for example, for color negative films, color reversal films, 8
      mm color films, motion picture films and the like.
PAR  The light-sensitive color photographic material in accordance with the
      present invention can yield a color image by ordinary color development
      process following exposure. The basic processes in the negative-positive
      method include the color development, bleaching, and fixing processes. The
      basic processes of the reversal method include development with a black
      and white negative developing solution, followed by exposure to white
      light or treatment with a processing solution containing fogging agent,
      color development, bleaching and fixing. These basic processes are
      conducted independently or, two or more basic processes are conducted in
      one step using a processing solution having the respective functions. For
      example, a combined color processing method is conduced by using a
      processing solution containing a color developing agent, a ferric salt
      bleaching constituent and a thiosulfate fixing constituent, and a combined
      bleaching and fixing method is conducted by using a processing solution
      containing iron (III) complex of ethylenediaminetetraacetic acid as the
      bleaching constituent and a thiosulfate fixing constituent.
PAR  The light-sensitive color photographic material in accordance with the
      present invention may be processed by any processing method consisting for
      example of color development, combined bleaching and fixing, if necessary
      followed by washing and stabilization; color development, bleaching,
      fixing, if necessary followed by washing and stabilization; pre-hardening,
      neu   lization, color development, combined stopping and fix   washing,
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bleaching, fixing, washing, post-hardening, and washing; color development, washing, subsidiary color development, stopping, bleaching, fixing, washing, and stabilization; pre-hardening, neutralization, washing, first development, stopping, washing, color development, stopping, washing, bleaching, fixing, and washing; pre-hardening, neutralization, first development, stopping, washing, color development, stopping, washing, bleaching, organic acid bath, fixing, and washing; first development, non-fixing silver dye bleaching and washing, color development, acid rinsing, washing, bleaching, washing, fixing, washing, stabilization, and washing; halogenation belaching of developed silver generated by color development, followed by color development to increase the amount of dye formed; or processing of a low-silver light-sensitive material with an amplifier such as peroxide or cobalt complex.

PAR Typical examples of the color developing agents used in the developing solution are aromatic primary amino compounds such as p-phenylenediamines and p-aminophenols. The typical examples of these compounds are:

PAR N,N-Dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine,
3-methyl-N,N-diethyl-p-phenylenediamine,
N-carbamidemethyl-N-methyl-p-phenylenediamine,
N-carbamidemethyl-N-tetrahydrofurfuryl-2-methyl-p-phenylenediamine,
N-ethyl-N-carboxymethyl-2-methyl-p-phenylenediamine,
N-carbamidemethyl-N-ethyl-2-methyl-p-phenylenediamine,
3-.beta.-methanesulfonamidoethyl-4-amino-N,N-diethylaniline,
N-ethyl-N-tetrahydrofurfuryl-2-methyl-p-aminophenol,
3-acetylamino-4-aminodimethylaniline,
3-methyl-4-amino-N-ethyl-N-.beta.-hydroxyethylaniline,
N-ethyl-N-.beta.-methanesulfonamidoethyl-4-aminoaniline,
3-methyl-4-amino-N-ethyl-N-.beta.-methanesulfonamidoethylaniline,
N-ethyl-N-.beta.-methanesulfonamidoethyl-3-methyl-4-aminoaniline,
3-methyl-4-amino-N-ethyl-N-.beta.-methoxyethylaniline,
N-methyl-N-.beta.-sulfoethyl-p-phenylenediamine,
N-ethyl-N-.beta.-(.beta.-methoxyethoxy)ethyl-3-methyl-4-aminoaniline,
N-ethyl-N-.beta.-[.beta.-(.beta.-methoxyethoxy)ethoxy]-ethyl-3-methyl-4-aminoaniline, o-aminophenol, p-aminophenol, 5-amino-2-oxy-toluene inorganic acid salt such as hydrochloric acid or sulfuric acid, or organic acid salt such as p-toluenesulfonate and the like.

PAR Typical examples thereof are also described in Japanese Provisional Patent Publication Nos. 64932/1973, 131526/1975 and 95849/1976, and by Bent et al. in "Journal of the American Chemical Society", Vol. 73, pages 3100-3125, 1951.

PAR The amount of the aromatic primary amino compound used is determined by the desired activity of the developing solution. To increase the activity, the amount used should be raised. It is generally used in an amount between 0.0002 mol/liter and 0.7 mol/liter. According to the purposes, it is possible to use a combination of two or more compounds, for example,
3-methyl-4-amino-N,N-diethylaniline and
3-methyl-4-amino-N-ethyl-N-.beta.-methanesulfonamidoethylaniline;
3-methyl-4-amino-N-ethyl-N-.beta.-methanesulfonamidoethylaniline and
3-methyl-4-amino-N-ethyl-N-.beta.-hydroxyethylaniline;
3-methyl-4-amino-N-ethyl-N-.beta.-methanesulfonamidoethylaniline and
N-ethyl-N-.beta.-[.beta.-(.beta.-methoxyethoxy)ethoxy]ethyl-3-methyl-4-aminoaniline; 3-methyl-4-amino-N,N-diethylaniline and
3-methyl-4-amino-N-ethyl-N-.beta.-methanesulfonamidoethyl- and
3-methyl-4-amino-N-ethyl-N-.beta.-hydroxyethylaniline and
N-ethyl-N-.beta.-[.beta.-(.beta.-methoxyethoxy)ethoxy]ethyl-3-methyl-4-ami

and 3-methyl-4-amino-N-.beta.-methoxyethylaniline.

PAR The color developing solution may further contain various constituents ordinarily used in such solutions, for example, alkali agents such as sodium hydroxide, sodium carbonate and potassium carbonate, alkali metal sulfite, alkali metal bisulfite, alkali metal thiocyanate, alkali metal halide, benzyl alcohol, water softening agent, thickening agent and development accelerator. The pH value of the color developing solution is normally 7 or more, most generally between about 9 and about 13.

PAR Additives used as required in the color developing solution include for example hydroxides, carbonates, and phosphates of alkali metals and ammonium for keeping the pH value constant; pH adjusting or buffering agents (e.g. weak acids such as acetic acid and boric acid, weak bases, and their salts); development accelerators such as pyridinium compounds, cationic compounds, potassium nitrate and sodium nitrate, polyethylene glycol condensates, phenyl cellosolve, phenylcarbitol, alkyl cellosolve, phenylcarbitol, dialkylformamide, alkyl phosphate and derivatives thereof, nonionic compounds such as polythioethers, polymers having sulfite esters, organic amines such as pyridine and ethanolamine, benzyl alcohol and hydrazine.

PAR Examples of fog restrainers include bromides such as potassium bromide, sodium bromide and ammonium bromide, compounds used for quick processing solutions such as alkali iodide, nitrobenzoimidazole, mercaptobenzoimidazole, 5-methylbenzotriazole, and 1-phenyl-5-mercaptotetrazole, nitro benzoate, benzothiazolium derivatives and phenazine N-oxide.

PAR It is also possible to use stain preventing agents, sludge preventing agents, interlayer effect accelerators, preservatives (e.g. sulfite, acid sulfite, hydroxylamine hydrochloride, formsulfite, alkanolamine sulfite adduct), and chelating agents.

PAR Examples of the chelating agents are phosphates such as polyphosphates, aminopolycarboxylic acids such as nitrilotriacetic acid and 1-3-diamino-2-propanoltetraacetic acid, oxycarboxylic acids such as citric acid and gluconic acid, and 1-hydroxy-1,1'-diphosphonic acid. These chelating agents may be used in combination with each other or with lithium sulfate.

PAR Metal complexes of organic acids used as the bleaching agent in the bleaching solution or in the combined bleaching and fixing solution oxidize the metallic silver formed by the development and convert it into silver halides, and at the same time cause the noncolor-forming portion of the color forming agent to develop color. The metal complexes of organic acids have a structure in which metal ions such as iron, cobalt and copper are coordinated with organic acids such as aminopolycarboxylic acid, oxalic acid or citric acid. The most preferable organic acids used for forming such metal complexes are aminopolycarboxylic acids represented by the general formulas (III) and (IV):

EQU HOCO-A.sub.1 -Z-A.sub.2 -COOH (III)
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in which A.sub.1, A.sub.2, A.sub.3, A.sub.4, A.sub.5 and A.sub.6 each designate a substituted or unsubstituted hydrocarbon group, and Z designates a hydrocarbon group, oxygen atom, sulfur atom or >N-A.sub.7 wherein A.sub.7 denotes a hydrocarbon group or a lower aliphatic carboxilic acid.

PAR These aminopolycarboxylic acids may be used in the form of an alkali metal salt, an ammonium salt or a water-soluble amine salt. The typical examples of the aminopolycarboxylic acids represented by the general formulas (III) and (IV) and the other aminopolycarboxylic acids are:

PAO Ethylenediaminetetraacetic acid,
PAO diethylenetriaminepentaacetic acid,
PAO ethylenediamine-N-(.beta.-oxyethyl)-N,N',N'-triacetic acid,
PAO propylenediaminetetraacetic acid,
PAO nitrilotriacetic acid,
PAO cyclohexanediaminetetraacetic acid,
PAO iminodiacetic acid,
PAO dihydroxyethylglycine,
PAO ethyletherdiaminetetraacetic acid,
PAO glycoletherdiaminetetraacetic acid,
PAO ethylenediaminetetrapropionic acid,
PAO phenylenediaminetetraacetic acid,
PAO disodium ethylenediaminetetraacetate,
PAO tetra(trimethylammonium)ethylenediaminetetraacetate,
PAO tetrasodium ethylenediaminetetraacetate,
PAO pentasodium diethylenetriaminepentaacetate,
PAO sodium ethylenediamine-N-(.beta.-oxyethyl)-N,N',N'-triacetate,
PAO sodium propylenediaminetetraacetate,
PAO sodium nitrilotriacetate, and
PAO sodium cyclohexanediaminetetraacetate.

PAR In addition to the above-mentioned metal complexes of organic acids as the bleaching agents, various additives may be contained in the bleaching solution. The additives may preferably be re-halogenating agents such as alkali halides and ammonium halides e.g. potassium bromide, sodium bromide, sodium chloride and ammonium bromide. It is also possible to add pH buffering agents such as borate, oxalate, acetate, carbonate and phosphate, and other additives which is usually used in bleaching solutions such as polyaminocarboxylic acids and their salts, alkylamines and polyethylene oxides.

PAR When a combined bleaching and fixing solution (bleach-fixing solution) is used in the bleaching process, a bleach-fixing solution containing the above-mentioned metal complexes of organic acids as the belaching agents and silver halide fixing agents such as thiosulfates, thiocyanates and thioureas is used. The solution may also contain a small or large amount of halogen compounds such as potassium bromide. It is also possible to use a special bleaching and fixing solution consisting of a combination of a bleaching agent and a large amount of halogen compounds such as potassium bromide. The above-mentioned halogen compounds may be potassium bromide, hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, ammonium bromide, potassium iodide and ammonium iodide.

PAR Typical examples of the silver halide fixing agents contained in the bleach-fixing solution are the compounds forming water-soluble complexes by the reaction with silver halides, which are used in usual fixing, e.g. thiosulfates such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate, thiocyanates such as potassium thiocyanate, sodium thiocyanate, and ammonium thiocyanates, or thioureas and thioethers.

PAR Like a bleaching solution, the bleach-fixing solution may further contain pH buffering agents such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide alone or in combination. The solution may also contain various brightening agents, anti-foaming agents and surface active agents. It is also possible to add preservatives such as bisulfite addition compounds of hydroxylamine, hydrazine, and aldehyde compounds, organic chelating agents such as aminopolycarboxylic acids, stabilizers such as nitroalcohol dimethylsulfoxide.

PAR The silver halide fixing agents are the compounds forming water-soluble complexes by the reaction with silver halides, which are used in usual fixing. The typical examples thereof are thiosulfates such as potassium thiosulfate, sodium thiosulfate, and ammonium thiosulfate, thiocyanates such as potassium thiocyanate, sodium thiocyanate, and ammonium thiocyanate, or thioureas and thioethers. These agents may be used alone or in combination. In the latter case, they may be combined in any proportion. The halides of alkali metals or ammonium sometimes exhibit the fixing action.

PAR The fixing solution may be incorporated with various additives as required, e.g. pH buffering agents such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide alone or in combination. The solution may also contain various brightening agents, anti-foaming agents and surface active agents. It is also possible to add preservatives such as sulfurous acid, bisulfite addition compounds of hydroxylamine, hydrazine, and aldehyde compounds, organic chelating agents such as aminopolycarboxylic acids, stabilizers such as nitroalcohol nitrate, organic solvents such as methanol, dimethylsulfoamide, and dimethylsulfoxide. Conventional fixing accelerators may be added optionally.

PAR The present invention is hereinafter illustrated by the following nonlimitative examples.

PAR First, the preparations of the emulsions used in the examples are described below.

PAR (Preparation of polydispersed emulsion)

PAR An ammoniacal silver nitrate solution and an aqueous alkali halide solution were naturally dropped into a reactor containing an aqueous gelatin solution and an excess of halide and maintained at 60.degree. C. Then after an aqueous Demool-N (made by KAO Atlas Co. Ltd.

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solution and aqueous magnesium sulfate solution were added to cause precipitation, desalting was done, and gelatin was added to obtain an emulsion having a pAg value of 7.8 and a pH value of 6.0. Further, sodium thiosulfate, chloroauric acid and ammonium thiocyanate were added, and the resulting mixture was subjected to chemical ripening at 52.degree. C. for 70 minutes. Thereafter, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 6-nitrobenzoimidazole were added, and gelatin was added to obtain a polydispersed silver iodobromide emulsion. The molar percentage of the silver iodide was changed by changing the composition of the alkali halide, and the average crystal size and crystal size distribution were changed by changing the time for adding the ammoniacal silver nitrate solution and the aqueous alkali halide solution.

PAR (Preparation of monodispersed emulsion)

PAR An aqueous ammoniacal silver nitrate solution and an aqueous potassium bromide solution were added to a reactor containing potassium iodide and an aqueous gelatin solution while the pAg value in the reactor was maintained constant. This addition was done in proportion to the increase in the surface area of crystals during the growth thereof. Then, after an aqueous Demool-N (made by KAO Atlas Co., Ltd.

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solution and aqueous magnesium sulfate solution were added to cause precipitation, desalting was done, and gelatin was added to obtain an emulsion having a pAg value of 7.8 and a pH value of 6.0. Further, sodium thi[illegible]fate, chloroauric acid and ammonium thiocyanate were a[illegible], and the resulting mixture was subjected to chemical ripening. Thereafter, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 6-nitrobenzoimidazole were added, and gelatin was further added to obtain a monodispersed silver iodobromide emulsion. The molar percentage of the silver iodide was changed by changing the ratio of potassium iodide to potassium bromide. The crystal size was changed by changing the amounts of the ammoniacal silver nitrate and the potassium halide added. Furthermore crystal shape was changed by varying the pAg value during a precipitation procedure, which however should be kept constant during the reaction.

DETD

PAC EXAMPLE 1

PAR Specimen No. 1 was prepared by sequentially applying the layers described below on a transparent support made of an under-coated cellulose triacetate film. (In all examples below, addition amount to the silver halide light-sensitive color photographic material is the amount per 1 m.sup.2, and the amounts of the silver halide emulsion and the colloidal silver are expressed in terms of silver.)

PAC (Specimen No. 1)

PA1 Layer 1: Antihalation layer containing 0.4 g of black colloidal silver and 3 g of gelatin.

PA1 Layer 2: Low-sensitivity red-sensitive emulsion layer containing 1.5 g of silver iodobromide low-sensitivity red-sensitive emulsion (obtained by red-sensitization of emulsion 2 in Table 2), 1.6 g of gelatin and 0.4 g of tricresyl phosphate (hereinafter referred to as TCP) in which 0.80 g of 1-hydroxy-4-[.beta.-methoxyethylaminocarbonylmethoxy)-N-[.delta.-(2,4-di-tert-amylphenoxy)butyl]-2-naphthoamide (hereinafter referred to as cyan coupler C-18), and 0.028 g of 1-hydroxy-4-[4-(1-hydroxy-8-acetamido-3,6-disulfo-2-naphthylazo)phenoxy]-N-[.delta.-(2,4-di-tert-amylphenoxy)butyl]-2-naphthoamide disodium salt (hereinafter referred to as colored cyan coupler CC-1) were dissolved.

PA1 Layer 3: High-sensitivity red-sensitive emulsion layer containing 1.1 g of a silver iodobromide high-sensitivity red-sensitive emulsion (obtained by red-sensitive of emulsion 1 in Table 2), 1.2 g of gelatin and 0.15 g of TCP in which 0.23 g of the cyan coupler C-18, and 0.020 g of the colored cyan coupler CC-1 were dissolved.

PA1 Layer 4: Intermediate layer containing 1.2 g of gelatin and 0.04 g of di-n-butyl phthalate (hereinafter referred to as DBP) in which 0.07 g of 2,5-di-tert-octylhydroquinone (hereinafter referred to as stain preventing agent HQ-1) was dissolved.

PA1 Layer 5: Low-sensitivity green-sensitive emulsion layer containing 1.6 g of a silver iodobromide low-sensitivity green-sensitive emulsion (obtained by green-sensitization of emulsion 2 in Table 2), 1.7 g of gelatin and 0.3 g of TCP in which 0.30 g of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido]-5-pyrazolone (hereinafter referred to as magenta coupler M-1), 0.20 g of 4,4-methylenebis-[1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido]benzeneamido]-5-pyrazolone (hereinafter referred to as magenta coupler M-19) and 0.066 g of 1-(2,4,6-trichlorophenyl)-4-(1-naphthylazo)-3-(2-chloro-5-octadecenylsuccinimidoanilino)-5-pyrazolone (hereinafter referred to as colored magenta coupler CM-1) were dissolved.

PA1 Layer 6: High-sensitivity green-sensitive emulsion layer containing 1.5 g of a silver iodobromide high-sensitivity green-sensitive emulsion (obtained by green-sensitization of emulsion 1 in Table 2), 1.9 g of gelatin and 0.12 g of TCP in which 0.093 g of the maganta coupler M-1, 0.094 g of the magenta coupler M-19, and 0.040 g of the colored coupler CM-1 were dissolved.

PA1 Layer 7: Yellow filter layer containing 0.2 g of yellow colloidal silver, 0.11 g of DBP in which 0.2 g of stain preventing agent HQ-1 was dissolved, and 2.1 g of gelatin.

PA1 Layer 8: Low-sensitivity blue-sensitive emulsion layer containing 0.95 g of a silver iodobromide low-sensitivity blue-sensitive emulsion (emulsion 2 in Table 2), 1.9 g of gelatin and 0.93 g of DBP in which 1.84 g of .alpha.-[4-(1-benzyl-2-phenyl-3,5-dioxo-1,2,4-triazolidinyl)]-.alpha.-pivaloyl-2-chloro-5-[.gamma.-(2,4-di-tert-amylphenoxy)butylamido]acetanilide (hereinafter referred to as yellow coupler Y-4) was dissolved.

PA1 Layer 9: High-sensitivity blue-sensitive emulsion layer containing 1.2 g of a silver iodobromide high-sensitivity blue-sensitive emulsion (emulsion 1 in Table 2), 2.0 g of gelatin and 0.23 g of DBP in which 0.46 g of the yellow coupler Y-4 was dissolved.

PA1 Layer 10: Protective layer containing 2.3 g of gelatin.

PAR Other specimens were prepared in the same way as specimen No. 1, except that emulsions obtained by the color-sensitization of the silver iodobromide emulsions listed in Table 1 were used in respective light-sensitive layers. The physical values of respective silver iodobromide emulsions were as shown in Table 2.

TBL TABLE 1

	Specimen No. 1 (Comparative)	Specimen No. 2 (Comparative)	Specimen No. 3 (Comparative)	Specimen No. 4 (Comparative)	Specimen No. 5 (According to the present invention)	Specimen No. 6 (According to the present invention)
Layer 2	EM - 2	EM - 4	EM - 6	EM - 8	EM - 6	EM - 8
Layer 3	EM - 1	EM - 3	EM - 1	EM - 3	EM - 5	EM - 7
Layer 5	EM - 2	EM - 4	EM - 2	EM - 4	EM - 6	EM - 8
Layer 6	EM - 1	EM - 3	EM - 5	EM - 7	EM - 5	EM - 7
Layer 8	EM - 2	EM - 4	EM - 2	EM - 4	EM - 6	EM - 8
Layer 9	EM - 1	EM - 3	EM - 1	EM - 3	EM - 5	EM - 7

TBL TABLE 2

EM - 1 EM - 2 EM - 3
EM - 4
EM - 5 EM - 6 EM - 7
EM -

```
                                                       8
Mole % of silver iodide
           7%    7%    7%  7%  2%    2%    2%  2%
Average crystal size (.sup.-r)
         1.05.mu.
               0.65.mu.
                     1.04.mu.
                        0.65.mu.
                           1.06.mu.
                                 0.66.mu.
                                       1.05.mu.
                                          0.64.mu.
Standard deviation (S)
          0.25.mu.
                0.16.mu.
                     0.093.mu.
                        0.08.mu.
                           0.27.mu.
                                 0.16.mu.
                                       0.084.mu.
                                          0.05.mu.
S/.sup.-r  0.24  0.25  0.09
                        0.08
                           0.25  0.24  0.08
                                          0.08
Form of grains
          Twinned and
                Twinned and
                      Cubic
                         Cubic
                           Twinned and
                                 Twinned and
                                       Cubic
                                          Cubic
          cubic  cubic        cubic  cubic
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PAR The obtained six specimens were respectively subjected to exposure giving the maximum density (exposure giving the maximum density after the exposure to white light through an optical wedge and processing by the processes described below). They were then respectively processed gy the processes described below to yield the specimens having dye images.

TBL

Processing (processing temperature: 38.degree. C.)	Processing time
Color development	3 minutes 15 seconds
Bleaching	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Fixing	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Stabilization	1 minute 30 seconds
Drying	

processing steps:

TBL

(Color developing solution)		
4-Amino-3-methyl-N--ethyl-N--(.beta.-hydroxyethyl)-aniline sulfate	4.75	g
Anhydrous sodium sulfite	4.25	g
Hydroxylamine half-sulfate	2.0	g
Anhydrous potassium carbonate	37.5	g
Sodium bromide	1.3	g
Trisodium nitrilotriacetate (monohydrate)	2.5	g
Potassium hydroxide	1.0	g
Made up to 1 liter with water		
(Bleaching solution)		
Ferric ammonium salt of ethylenediamine-tetraacetic acid	100.0	g
Diammonium salt of ethylenediamine-tetraacetic acid	10.0	g
Ammonium bromide	150.0	g
Glacial acetic acid	10.0	ml
Made up to 1 liter with water and adjusted to pH 6.0 with aqueous ammonia.		
(Fixing solution)		
Ammonium thiosulfate	175.0	g
Anhydrous sodium sulfite	8.6	g
Sodium metasulfite	2.3	g
Made up to 1 liter with water and adjusted to pH 6.0 with acetic acid.		
(Stabilizing solution)		
Formalin (37% aqueous solution)	1.5	ml
Konidax (available from Konishiroku Photo Industry Co., Ltd.)	7.5	ml
Made up to 1 liter with water.		

PAR Gelatin of the obtained image was decomposed with pronase for respective layers. Silver iodobromide crystals were separated by centrifuging, and observed by using a scanning type electronic microscope (JSM-T200 available from Nippon Denshi K.K.) to measure the percentage of the undeveloped grans with respect to the total crystals in each layer (dead grain percentage). The results were as shown in Table 3.

TBL

TABLE 3

Specimen No. 5

Specimen No. 6

Spcimen No. 1

Specimen No. 2

Specimen No. 3

Specimen No. 4

(According to the

(According to the
(Comparative)
(Comparative)
(Comparative)
(Comparative)
present invention)
present invention)

Layer 2					
47%	45%	45%	43%	27%	20%
Layer 3					
55%	52%	46%	44%	34%	27%
Layer 5					
53%	48%	44%	40%	29%	23%
Layer 6					
61%	57%	59%	55%	36%	30%
Layer 8					
50%	45%	48%	46%	29%	22%
Layer 9					
59%	55%	57%	52%	34%	28%

PAR As shown in Table 3, specimen Nos. 5 and 6 in accordance with the present invention exhibited reduced dead grains.

PAC EXAMPLE 2

PAR Specimen No. 1 used in Example 1 was exposed to blue, green and red light through an optical wedge, and developed in the same way as in Example 1. In this way, the minimum exposure log Eo in the exposure to blue, green, and red light, which gave the maximum density, was determined. On the other hand, specimen Nos. 1 to 6 used in Example 1 were respectively divided into two sections, and all of these specimens were subjected to the minimum exposure. One section of each specimen was developed in the same way as in Example 1 to obtain a dye image. The other section of each specimen was subjected to the color development conducted in Example 1, a stop processing with a 2% aqueous acetic acid solution, and the fixing and subsequent processes in Example 1 so as to obtain a dye image in which the silver image was not removed. As for the dye image in which the silver image was not removed, the amount of developed silver (Ag) per m.sup.2 of the specimen was determined by X-ray fluorimetry. The utilization efficiency of silver for the formation of dye image was determined as the quotient of the image density divided by the amount of developed silver (D/Ag). The results were as shown in Table 4. The amount of developed silver was the value compensated for the colloidal silver amount added during coating.

TBL TABLE 4

Specimen		Amount of developed silver (g/m.sup.2)	D/Ag
1	Exposure to blue light		
		0.82	0.96
	Exposure to green light		
		0.96	1.89
	Exposure to red light		

2	Exposure to blue light	0.90	0.98
	Exposure to green light	1.06	1.92
	Exposure to red light	0.52	1.57
3	Exposure to blue light	0.85	0.97
	Exposure to green light	0.99	1.90
	Exposure to red light	0.55	1.59
4	Exposure to blue light	0.92	0.99
	Exposure to green light	1.17	1.94
	Exposure to red light	0.57	1.60
5	Exposure to blue light	1.24	1.08
	Exposure to green light	1.51	2.03
	Exposure to red light	0.7	1.66
6	Exposure to blue light	1.35	1.10
	Exposure to green light	1.65	2.16
	Exposure to red light	0.75	1.69

PAR As shown in Table 4, specimen Nos. 5 and 6 according to the present invention in which a silver iodobromide emulsion containing a low molar percentage of iodine exhibited lesser dead grains and increased developed silver amount compared with specimen Nos. 1 and 2 in which a silver iodobromide emulsion containing a high molar percentage of silver iodide and specimen No. 3 partially containing a layer of a silver iodobromide emulsion containing a low molar percentage of silver iodide. Further, the specimens in accordance with the present invention exhibited remarkably increased density of dye image obtained from silver iodobromide per unit, and increased utilization efficiency of silver for the formation of dye image.

PAC EXAMPLE 3

PAR Specimen No. 7 was prepared by sequentially applying the layers described below on a transparent support made of an under-coated cellulose triacetate film.

PAC (Specimen No. 7)

PA1 Layer 1: Antihalation layer containing 0.4 g of black colloidal silver and 3 g of gelatin.

PA1 Layer 2: Low-sensitivity red-sensitive emulsion layer containing 1.5 g of silver iodobromide low-sensitivity red-sensitive emulsion (obtained by red-sensitization of emulsion 9 in Table 6), 1.6 g of gelatin and 0.4 g of TCP in which 0.80 g of the cyan coupler C-18 and 0.018 g of the DIR compound D-100 were dissolved.

PA1 Layer 3: High-sensitivity red-sensitive emulsion layer containing 1.1 g of a silver iodobromide high-sensitivity red-sensitive emulsion (obtained by red-sensitization of emulsion 1 in Table 2), 1.2 g of gelatin and 0.15 g of TCP in which 0.23 g of the cyan coupler C-18 and 0.013 g of the DIR compound D-100 were dissolved.

PA1 Layer 4: Intermediate layer containing 1.2 g of gelatin and 0.04 g of DBP in which 0.07 g of stain preventing agent HQ-1 was dissolved.

PA1 Layer 5: Low-sensitivity green-sensitive emulsion layer containing 1.6 g of a silver iodobromide low-sensitivity green-sensitive emulsion (obtained by green-sensitization of emulsion 9 in Table 6), 1.7 g of gelatin and 0.3 g of TCP in which 0.30 g of magenta coupler M-1, 0.20 g of magenta coupler M-19 and 0.025 g of the DIR compound D-100 were dissolved.

PA1 Layer 6: High-sensitivity green-sensitive emulsion layer containing 1.5 g of a silver iodobromide high-sensitivity green-sensitive emulsion (obtained by green-sensitization of emulsion 1 in Table 2), 1.9 g of gelatin and 0.12 g of TCP in which 0.093 g of the magenta coupler M-1, 0.094 g of the magenta coupler M-19 and 0.008 g of the DIR compound D-100 were dissolved.

PA1 Layer 7: Yellow filter layer containing 0.2 g of yellow colloidal silver, 0.11 g of DBP in which 0.2 g of stain preventing agent HQ-1 was dissolved, and 2.1 g of gelatin.

PA1 Layer 8: Low-sensitivity blue-sensitive emulsion layer containing 0.95 g of a silver iodobromide low-sensitivity blue-sensitive emulsion (emulsion 9 in Table 6), 1.9 g of gelatin and 0.93 g of DBP in which 1.84 g of yellow coupler Y-4 and 0.025 g of the DIR compound D-100 were dissolved.

PA1 Layer 9: High-sensitivity blue-sensitive emulsion layer containing 1.2 g of a silver iodobromide high-sensitivity blue-sensitive emulsion (emulsion 1 in Table 2), 2.0 g of gelatin and 0.23 g of DBP in which 0.46 g of the yellow coupler Y-4 and 0.008 g of the DIR compound D-100 were dissolved.

PA1 Layer 10: Protective layer containing 2.3 g of gelatin.

PAR Specimen Nos. 8 to 12 were prepared in the same way as specimen No. 7, except that emulsions obtained by the color-sensitization of the silver iodobromide emulsions listed in Table 5 were used in respective light-sensitive layers. The physical values of respective emulsions were as shown in Table 6. The amount of the DIR compound was altered to obtain the equal gamma value. The addition amount for respective specimens were as shown in Table 5.

TBL TABLE 5

	Layer 2	Layer 3	Layer 5	Layer 6	Layer 8	Layer 9
Specimen No. 7						
Emulsion used	EM-9	EM-1	EM-9	EM-1	EM-9	EM-1
(Comparative)						
Amount of D-100 used (g)						

0.013
0.025
0.008
0.025
0.008

Specimen No. 8
Emulsion used
EM-10
EM-3
EM-10
EM-3
EM-10
EM-3

(Comparative)
Amount of D-100 used (g)
0.027
0.019
0.036
0.012
0.035
0.012

Specimen No. 9
Emulsion used
EM-9
EM-1
EM-6
EM-11
EM-9
EM-1

(Comparative)
Amount of D-100 used (g)
0.018
0.013
0.032
0.010
0.025
0.008

Specimen No. 10
Emulsion used
EM-10
EM-3
EM-8
EM-12
EM-10
EM-3

(Comparative)
Amount of D-100 used (g)
0.027
0.019
0.038
0.014
0.035
0.012

Specimen No. 11
Emulsion used
EM-6

EM-11
EM-6
EM-11
EM-6
EM-11
(According to the
Amount of D-100 used (g)
0.026
0.018
0.032
0.010
0.031
0.011
present invention)
Specimen No. 12
Emulsion used
EM-8
EM-12
EM-8
EM-12
EM-8
EM-12
(According to the
Amount of D-100 used (g)
0.030
0.020
0.038
0.014
0.038
0.014
present invention)

PAR In Table 5, EM-1, EM-3, EM-6 and EM-8 were the emulsions listed in Table 2 and used in Example 1. EM-9, EM-10, EM-11 and EM-12 were the emulsions listed in Table 6.

TBL TABLE 6

	EM-9	EM-10	EM-11	EM-12
Mole % of silver iodide	6%	6%	3%	3%
Average crystal size (.sup.-r)	0.64.mu.	0.66.mu.	1.05.mu.	1.04.mu.
Standard deviation (S)	0.17.mu.	0.06.mu.	0.27.mu.	0.09.mu.
S/.sup.-r	0.27	0.09	0.26	0.09
Form of grains	Twinned and cubic	Cubic	Twinned and cubic	Cubic

transparent square wave chart or wedge, and exposed to blue, green and red monochromatic light, followed by the color development according to the procedure described in Example 1. The results of the photographic characteristics, sharpness and graininess were as shown in Table 7.

PAR The effect of improvement in the image sharpness was evaluated by determining the modulation transfer function (MTF) and comparing the MTF values at spatial frequencies of 10 lines/mm and 30 lines/mm.

PAR The graininess (RMS) was evaluated by obtaining the standard deviation of the fluctuation in the density values occurring when a color image having a color image density of 1.0 is scanned with a microdensitometer having a circular scanning aperture of diameter of 25.mu., and comparing the value obtained by magnifying the standard deviation by a factor of 1000.

PAR The gamma value is expressed by tan .alpha. in which .alpha. designates the angle between the extension of the straight section of the photographic characteristic curve and the horizontal axis. The sensitivity is expressed by the relative value of the logarithm of the reciprocal of the exposure that is able to give the density of fog density plus 0.1. The blue, green and red sensitivities of each specimen were expressed by the relative values, with those of specimen No. 7 taken as 100.

TBL TABLE 7

Specimen No.		Relative sensi- tivity	.gamma. (gamma)	MTF value (%) 10 lines/mm	MTF value (%) 30 lines/mm	RMS
7 (Comparative)	Exposure to blue light	100	0.87	89	57	55
	Exposure to green light	100	0.85	86	49	34
	Exposure to red light	100	0.88	78	33	39
8 (Comparative)	Exposure to blue light	105	0.86	111	82	47
	Exposure to green light	106	0.86	112	75	27
	Exposure to red light	104	0.88	98	53	32
9 (Comparative)	Exposure to blue light	99	0.87	90	56	54
	Exposure to green light	100	0.85	80	52	35
	Exposure to red light	98	0.88	77	35	40
10 (Comparative)	Exposure to blue light	107	0.87	110	79	46
	Exposure to green light					

		105	0.85	118	78	28
	Exposure to red light	105	0.85	103	59	31
11 (According to the present invention)	Exposure to blue light	103	0.86	128	85	53
	Exposure to green light	102	0.88	127	80	36
	Exposure to red light	103	0.85	109	65	39
12 (According to the present invention)	Exposure to blue light	106	0.88	132	101	45
	Exposure to green light	107	0.85	130	97	27
	Exposure to red light	105	0.86	119	78	30

PAR The above six specimens were respectively subjected to exposure giving the maximum density. They were then developed and subjected to the separation processing for respective layers in the same way as in Example 1. The dead grain percentage was measured to obtain the results shown in Table 8.

TBL TABLE 8

	Specimen No. 7 (Comparative)	Specimen No. 8 (Comparative)	Specimen No. 9 (Comparative)	Specimen No. 10 (Comparative)	Specimen No. 11 (According to the present invention)	Specimen No. 12 (According to the present invention)
Layer 2	45%	44%	45%	43%	27%	21%
Layer 3	54%	52%	52%	50%	36%	29%
Layer 5	82%	46%	42%	39%	30%	23%
Layer 6						

Layer 8	48%	43%	47%	43%	29%	24%
Layer 9	57%	53%	57%	52%	35%	29%

PAR As shown in Table 8, the present invention can reduce dead grains even when the gamma characteristics are controlled with the DIR compound. Table 8 also shows that the sharpness is greatly improved if the light-sensitive material in accordance with the present invention is combined with the DIR compound. Thus, the present invention is advantageous also for improving the image quality.

PAC EXAMPLE 4

PAR Specimen No. 13 was prepared by sequentially applying the layers described below on a transparent support made of an under-coated cellulose triacetate film.

PAC (Spcimen No. 13)

PA1 Layer 1: Antihalation layer containing 0.4 g of black colloidal silver and 3 g of gelatin.

PA1 Layer 2: Low-sensitivity red-sensitive emulsion layer containing 1.5 g of silver iodobromide low-sensitivity red-sensitive emulsion (obtained by red-sensitization of EM-8 used in Example 1), 1.6 g of gelatin and 0.80 g of the cyan coupler C-18.

PA1 Layer 3: High-sensitivity red-sensitive emulsion layer containing 1.1 g of a silver iodobromide high-sensitivity red-sensitive emulsion (emulsion obtained by red-sensitization of EM-7 used in Example 1), 1.2 g of gelatin and 0.15 g of TCP in which 0.23 g of the cyan coupler C-18 was dissolved.

PA1 Layer 4: Intermediate layer containing 1.2 g of gelatin and 0.04 g of DBP in which 0.07 g of the stain preventing agent HQ-1 was dissolved.

PA1 Layer 5: Low-sensitivity green-sensitive emulsion layer containing 1.6 g of a silver iodobromide low-sensitivity green-sensitive emulsion (emulsion obtained by green-sensitization of EM-8 used in Example 1), 1.7 g of gelatin and 0.3 g of TCP in which 0.40 g of 1-(2,4,6-trichlorophenyl)-3-[3-(octadecenylsuccinimide)-2-chloro]anilino-5-pyrazolone (magenta coupler M-6) was dissolved.

PA1 Layer 6: High-sensitivity green-sensitive emulsion layer containing 1.5 g of a silver iodobromide high-sensitivity green-sensitive emulsion (obtained by green-sensitization of EM-7 used in Example 1), 1.9 g of gelatin and 0.12 g of TCP in which 0.14 g of the magenta coupler M-6 was dissolved.

PA1 Layer 7: Yellow filter layer containing 0.2 g of yellow colloidal silver, 0.11 g of DBP in which 0.2 g of stain preventing agent HQ-1 was dissolved, and 2.1 g of gelatin.

PA1 Layer 8: Low-sensitivity blue-sensitive emulsion layer containing 0.95 g of a silver iodobromide low-sensitivity blue-sensitive emulsion (EM-8 used in Example 1), 1.9 g of gelatin and 0.93 g of DBP in which 1.84 g of .alpha.-[4-(1-benzyl-2-phenyl-3,5-dioxo-1,2,4-triazolidin-4-yl)]-.alpha.-pivaloyl-2-chloro-5-[.gamma.-(2,4-di-tert-amylphenoxyl)butaneamido]acetanilide (yellow coupler Y-5) was dissolved.

PA1 Layer 9: High-sensitivity blue-sensitive emulsion layer containing 1.2 g of a silver iodobromide high-sensitivity blue-sensitive emulsion (EM-7 in Example 1), 2.0 g of gelatin and 0.23 g of DBP in which 0.46 g of the yellow coupler Y-5 was dissolved.

PA1 Layer 10: Protective layer containing 2.3 g of gelatin.

PAR Specimen No. 14 was prepared in the same way as specimen No. 13 except that 1-hydroxy-2-[.delta,-(2,4-di-tertamylphenoxybutyl]naphthoamide (cyan coupler C-1) was used instead of C-18, the magenta coupler M-[illegible]as used instead of M-6, and .alpha.-(1-benzyl-2,4-dioxo-imidazolidin-3-yl)-.alpha.-pivaloyl-2-chloro-5-[.gamma.-(2,4-di-tertamylphenoxy)butaneamido]acetanilide (yellow coupler Y-2) was used instead of the yellow coupler Y-4.

PAR The obtained two specimens were respectively subjected to exposure giving the maximum density. They were then developed and subjected to the separation processing for respective layers in the same way as in Example 1. The dead grain percentage was measured to obtain the results shown in Table 9.

TBL TABLE 9

	Specimen No. 13	Specimen No. 14
Layer 2	20%	26%
Layer 3	28%	35%
Layer 5	19%	27%
Layer 6	27%	34%
Layer 8	17%	25%
Layer 9	23%	31%

PAR The couplers used in respective specimens and the specific rates with respect to M-1 were as shown in Table 10.

TBL TABLE 10

	Specimen No. 13		Specimen No. 14	
	Coupler	Specific rate	Coupler	Specific rate
Layer 2, 3	C - 18	1.22	C - 1	0.98
Layer 5, 6	M - 6	1.28	M - 1	1.00
Layer 8, 9	Y - 5	1.39	Y - 2	0.70

PAR Both specimen Nos. 13 and 14 fall within the scope of the present invention. Table 10 shows that dead grains reduce to a larger degree when a coupler exhibiting a specific rate larger than that of M-1 is used.

PAC EXAMPLE 5

PAR Specimen Nos. 15 to 17 were prepared by sequentially applying the layers described below on a transparent support made of an under-coated cellulose triacetate film.

PA1 Layer 1: Antihalation layer containing 0.4 g of black colloidal silver and 3 g of gelatin.

PA1 Layer 2: Low-sensitivity red-sensitive emulsion layer containing 1.5 g of silver iodobromide low-sensitivity red-sensitive emulsion (obtained by red-sensitization of an emulsion in Table 11), 1.6 g of gelatin and 0.4 g of TCP in which 0.80 g of the cyan coupler C-18 was dissolved.

PA1 Layer 3: High-sensitivity red-sensitive emulsion layer containing 1.1 g of a silver iodobromide high-sensitivity red-sensitive emulsion (obtained by red-sensitization of an emulsion in Table 11), 1.2 g of gelatin and 0.15 g of TCP in which 0.23 g of the cyan coupler C-18 was dissolved.

in which 0.07 g of the stain preventing agent HQ-1 was dissolved.

PA1 Layer 5: Low-sensitivity green-sensitive emulsion layer containing 1.6 g of a silver iodobromide low-sensitivity green-sensitive emulsion (obtained by green-sensitization of an emulsion in Table 11), 1.7 g of gelatin and 0.3 g of TCP in which 0.40 g of the magenta coupler M-1 was dissolved.

PA1 Layer 6: High-sensitivity green-sensitive emulsion layer containing 1.5 g of a silver iodobromide high-sensitivity green-sensitive emulsion (obtained by green-sensitization of an emulsion in Table 11), 1.9 g of gelatin and 0.12 g of TCP in which 0.14 g of the magenta coupler M-1 was dissolved.

PA1 Layer 7: Yellow filter layer containing 0.2 g of yellow colloidal silver, 0.11 g of DBP in which 0.2 g of stain preventing agent HQ-1 was dissolved, and 2.1 g of gelatin.

PA1 Layer 8: Low-sensitivity blue-sensitive emulsion layer containing 0.95 g of a silver iodobromide low-sensitivity blue-sensitive emulsion (an emulsion in Table 11), 1.9 g of gelatin and 0.93 g of DBP in which 1.84 g of the yellow coupler Y-1 was dissolved.

PA1 Layer 9: High-sensitivity blue-sensitive emulsion layer containing 1.2 g of a silver iodobromide high-sensitivity blue-sensitive emulsion (an emulsion Table 11), 2.0 g of gelatin and 0.23 g of DBP in which 0.46 g of the yellow coupler Y-1 was dissolved.

PA1 Layer 10: Protective layer containing 2.3 g of gelatin.

TBL TABLE 11

	Specimen No. 15	Specimen No. 16	Specimen No. 17
Layer 2	EM - 8	EM - 13	EM - 15
Layer 3	EM - 7	EM - 14	EM - 16
Layer 5	EM - 8	EM - 13	EM - 15
Layer 6	EM - 7	EM - 14	EM - 16
Layer 8	EM - 8	EM - 13	EM - 15
Layer 9	EM - 7	EM - 14	EM - 16

PA1 EM-7, EM-8: Emulsions listed in Table 2 and used in Example 1.

TBL TABLE 12

	EM-13	EM-14	EM-15	EM-16.
Mole % of silver iodide	2%	2%	2%	2%
Average crystal size (,sup.-r)	0.64.mu.	1.03.mu.	0.63.mu.	1.05.mu,
Standard deviation (S)	0.05.mu,	0.10.mu.	0.06.mu.	0.09.mu.
S/.sup.-r	0.08	0.10	0.10	0.9
Form of grains	octa- hedral	Octa- hedral	Tetra- deca-	Tetra- deca-

hedral
hedral

PAR The obtained three specimens were respectively subjected to exposure giving the maximum density. They were then developed and subjected to the separation processing for respective layers in the same way as in Example 1. The dead grain percentage was measured to obtain the results shown in Table 13.

TBL TABLE 13

	Specimen No. 15	Specimen No. 16	Specimen No. 17
Layer 2	20%	17%	18%
Layer 3	28%	24%	24%
Layer 5	23%	19%	19%
Layer 6	31%	28%	27%
Layer 8	23%	17%	18%
Layer 9	28%	23%	24%

PAR Specimen Nos. 15, 16 and 17 fall within the scope of the present invention. As shown in Table 11, the effect of the present invention is larger when octahedral or tetradecahedral silver iodobromide crystals are used than when cubic crystals are used.

PAC EXAMPLE 6

PAR The light-sensitive photographic materials in accordance with the present invention, which were used in Example 3 (specimen Nos. 7, 8, 11 and 12), were separation-exposed to blue, green and red light through a wedge, and processed by the processes described below to yield the specimens having the dye images.

TBL

Processes (processing temperature: 25.degree. C.)	Processing time
Color development	3 minutes 30 seconds
Bleaching	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Fixing	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Stabilization	1 minute 30 seconds
Drying	

PAR The compositions of the processing solutions used in the above-mentioned processes were the same as those in Example 1.

PAR The photographic characteristics of the obtained color images were compared with those obtained by processing the specimen Nos. 7, 8, 11 and 12 in Example 3 at a processing temperature of 38.degree. C. The results were as shown in Table 14.

TBL TABLE 14

Processing at 38.degree. C.
Processing at 25.degree. C.

Specimen No.		sensitivity	Gamma	sensitivity	Gamma
7	Exposure to blue light	100	0.87	65	0.57
	Exposure to green light	100	0.85	57	0.48
	Exposure to red light	100	0.88	51	0.45
8	Exposure to blue light	105	0.86	70	0.60
	Exposure to green light	106	0.86	63	0.50
	Exposure to red light	104	0.88	57	0.50
11	Exposure to blue light	103	0.86	98	0.84
	Exposure to green light	102	0.88	97	0.85
	Exposure to red light	103	0.85	96	0.81
12	Exposure to blue light	106	0.88	101	0.88
	Exposure to green light	107	0.85	99	0.84
	Exposure to red light	105	0.86	98	0.84

PAR As shown in Table 14, even when the specimens in accordance with the present invention are processed at a low temperature, they exhibit characteristics equivalent to those obtained with a high-temperature development conducted for the same development time. This indicates that the light-sensitive material in accordance with the present invention allows quick processing even at low temperatures.

CLMS

STM We claim:

NUM 1.

PAR 1. A light-sensitive color photographic material having a support and, coated thereon, at least two light-sensitive silver halide emulsion layers respectively sensitive to light of a different spectral region, each of said emulsion layers comprising at least two light-sensitive emulsion sublayers having different sensitivity to light and containing negative type light-sensitive silver halide crystals consisting essentially of silver iodobromide containing silver iodide in an amount of from 1 to 3 mole %.

NUM 2.

PAR 2. The light-sensitive color photographic material according to claim 1 wherein the negative type silver halide crystals contained in at least one of said at least two light-sensitive emulsion sublayers have a monodispersed size distribution satisfying the following relationship:

##EQU3##

in which $ designates the standard deviation, r designates the average crystal size, r.sub.i designates the crystal sizes of the individual crys[illegible]s, and n.sub.i designates the number of crystals.

NUM 3.

PAR 3. The light-sensitive color photographic material according to claim 2 wherein the negative type silver halide crystals contained in all of said light-sensitive emulsion sublayers have a monodispersed size distribution satisfying the following relationship:

##EQU4##

in which S designates the standard deviation, r designates the average crystal size, r.sub.i designates the crystal sizes of the individual crystals, and n.sub.i designates the number of crystals.

NUM 4.

PAR 4. The light-sensitive color photographic material according to claim 2 wherein the negative type silver halide crystals contained in at least one of said at least two light-sensitive emulsion sublayers consists essentially of octahedrons, tetradecahedrons, or a combination of octahedrons and tetradecahedrons.

NUM 5.

PAR 5. The light-sensitive color photographic material according to claim 4 wherein the negative type silver halide crystals contained in all of said light-sensitive emulsion sublayers consist essentially of octahedrons, tetradecahedrons or a combination of octahedrons and tetradecahedrons.

NUM 6.

PAR 6. The light-sensitive color photographic material according to claim 1 wherein at least one of said emulsion layers comprises at least two light-sensitive emulsion sublayers containing silver halide crystals having different average crystal sizes.

NUM 7.

PAR 7. The light-sensitive color photographic material according to claim 2, wherein at least one of said emulsion layers comprises at least two light-sensitive emulsion sublayers containing silver halide crystals having different average crystal sizes.

NUM 8.

PAR 8. The light-sensitive color photographic material according to claim 3 wherein at least one of said emulsion layers comprises at least two light-sensitive emulsion sublayers containing silver halide crystals having different average crystal sizes.

NUM 9.

PAR 9. The light-sensitive color photographic material according to claim 5 wherein at least one of said emulsion layers comprises at least two light-sensitive emulsion sublayers containing silver halide crystals having different average crystal sizes.

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PATN
WKU  044462905
SRC  6
APN  3617548
APT  1
ART  144
APD  19820325
TTL  Process for producing conjugated diene polymer
ISD  19840501
NCL  12
ECL  1
EXA  Kulkosky; Peter F.
EXP  Schofer; Joseph L.
INVT
NAM  Ikematu; Takeshi
CTY  Yokohama
CNT  JPX
INVT
NAM  Hattori; Yasuo
CTY  Yokohama
CNT  JPX
ASSG
NAM  Asahi Kasei Kogyo Kabushiki Kaisha
CTY  Osaka
CNT  JPX
COD  03
PRIR
CNT  JPX
APD  19810327
APN  56-43993
CLAS
OCL  526174
EDF  3
ICL  C08F13608
ICL  C08F23608
ICL  C08F  446
ICL  C08F  450
FSC  526
FSS  174
UREF
PNO  3629213
ISD  19711200
NAM  Onishi et al.
OCL  526181
UREF
PNO  3846385
ISD  19741100
NAM  Hargis et al.
OCL  526174
UREF
PNO  4080492
ISD  19780300
NAM  de Zarauz
OCL  526177
UREF
PNO  4129705
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ISD 19781200
NAM de Zarauz
OCL 526174
UREF
PNO 4136244
ISD 19790100
NAM Massoubre
OCL 526174
FREF
PNO 37616
ISD 19811000
CNT EPX
OCL 526174
LREP
FRM Birch, Stewart, Kolasch & Birch
ABST

PAL Conjugated diene polymers and copolymers having a high ratio of a trans-1,4 structure content to a cis-1,4 structure content in the diene moiety can be advantageously solution polymerized by using a novel catalyst complex consisting essentially of the following components (a) and (b) or (a), (b), and (c): (a) an organosodium compound, metallic sodium or a sodium amide compound, or a mixture of at least one thereof with an organic compound of sodium other than the sodium amide compound; (b) an organic or organometallic compound of barium, strontium, or calcium; (c) an organometallic compound of an electron deficient metal selected from lithium, beryllium, magnesium, zinc, cadmium, boron, aluminum, gallium, or indium.

BSUM

PAR The present invention relates to a process for producing conjugated diene polymers and copolymers having a high ratio of a trans-1,4 structure content to a cis-1,4 structure content in the diene moiety by means of a solution polymerization method by using a novel catalyst complex.

PAR Various processes for polymerizing conjugated dienes by using as a polymerization catalyst alkali metals or organometallic compounds of alkali metals have been proposed. On the other hand, only a few processes for polymerizing conjugated dienes by using as a polymerization catalyst alkaline earth metals (i.e. II A metals of the periodic table of elements) or organometallic compounds of alkaline earth metals have been proposed. Of the II A metals, the organometallic compounds of beryllium and magnesium can be relatively readily synthesized. However, the reactivity thereof is inferior to that of the organometallic compounds of alkali metals and, therefore, the polymerization activity thereof in the case of conjugated dienes can only be effective under limited conditions although the polymerization activity is remarkably low. For this reason, the organometallic compounds of beryllium and magnesium can not be practically used in the polymerization of conjugated dienes. Furthermore, the organometallic compounds of barium, strontium, and calcium are extremely difficult to synthesize. Polymerization processes of conjugated dienes in the presence of special organometallic compounds of alkaline earth metals have recently been proposed. However, the polymerization activity is extremely low and, therefore, these polymerization processes cannot now be utilized commercially.

PAR On the other hand, several polymerization processes of conjugated dienes using a combination catalyst of the organic compounds of alkaline earth metals such as barium, strontium, and calcium and other organometallic discloses a method for preparing butadiene polymers using a catalyst consisting of, for example, an organolithium compound and an organic compound of barium. U.S. Pat. No. 3,846,385 discloses a method for preparing butadiene polymers using a catalyst complex of barium di-tert-butoxide and dibutyl magnesium. Furthermore, U.S. Pat. No. 4,080,492 discloses a process for preparing conjugated diene polymers using a catalyst composition of an organo-lithium, -barium or -strontium compound and an organometallic compound of the II B or II A metals. These polymerization processes using catalyst complexes or compositions containing organometallic compounds of alkaline earth metals can provide rubberlike polymers having a high ratio of a trans-1,4 structure content to a cis-1,4 structure content in the diene moiety thereof and having a relatively high molecular weight. These polymers are believed to be useful in the manufacture of various rubber products including automotive tires since they have excellent characteristics including green strength, tensile strength, and abrasion resistance of the vulcanizates thereof.

PAR However, these polymerization processes using the above-mentioned catalyst complexes or compositions involve various disadvantages or problems. For example, in the case where polymers having a molecular weight sufficient to provide the desired properties are to be obtained, the amounts of the catalysts to be used should be decreased, which decrease would result in a remarkable decrease in the polymerization activity. In the case where the desired polymers are to be obtained at a high yield, the molecular weight distribution of the resultant polymers is remarkably broad, resulting in a remarkable decrease in the strength and abrasion resistance of the vulcanizates. In the case where copolymers of conjugated dienes and aromatic vinyl hydrocarbons are to be obtained, the copolymerization characteristics are not sufficient to produce the desired copolymers having the desired strength and heat buildup properties of the vulcanizates. Furthermore, although the polymers having a high trans-1,4 structure content and being obtained by the use of the above-mentioned catalyst complexes or compositions have the excellent physical properties mentioned above, these polymers have disadvantages such as poor processability and undesirable heat build-up of the vulcanizates, which disadvantages are due to the crystallization of the polymers at non-extension conditions, which crystallization is believed to be caused by the presence of long trans-1,4 structure chains.

PAR Accordingly, an object of the present invention is to eliminate the above-mentioned disadvantages or problems of the prior art and to provide a process for preparing conjugated diene polymers or copolymers having a high ratio of trans-1,4 structure content to a cis-1,4 structure content in the diene moiety, a relatively narrow molecular weight distribution, and no crystallization property as determined by a differential thermal analyzer.

PAR Another object of the present invention is to provide a catalyst complex suitable for use in the polymerization and copolymerization of conjugated dienes which has a remarkably excellent polymerization activity compared with that of conventional catalysts and can produce copolymers of conjugated dienes with aromatic vinyl hydrocarbons having an excellent random property.

PAR Other objects and advantages of the present invention will be apparent from the following description.

PAR In accordance with the present invention, there is provided a process for producing a conjugated diene polymer, a copolymer of a conjugated diene with at least one other conjugated diene, or a copolymer of a conjugated diene with an aromatic vinyl hydrocarbon comprising the step o polymerizing said monomer or monomers in the presence of a catalyst complex consisting essentially of the following components (a) and (b) or (a), (b), and (c):

PAR (a) an organosodium compound, metallic sodium or a sodium amide compound, or a mixture of at least one thereof with an organic compound of sodium other than the sodium amide compound;

PAR (b) an organic or organometallic compound of barium, strontium, or calcium;

PAR (c) an organometallic compound of an electron deficient metal selected from lithium, beryllium, magnesium, zinc, cadmium, boron, aluminum, gallium, or indium.

PAR The term "an organometallic compound (e.g. an organosodium compound)" used herein means an organic compound containing a metallic atom (e.g. sodium) directly bonded to a carbon atom, whereas the term "an organic compound of a metal (e.g. sodium)" used herein means an organic compound containing only a metallic atom (e.g. sodium) bonded to a carbon atom via an atom such as oxygen, sulfur, nitrogen, or the like.

PAR The catalyst complexes used in the present invention have a remarkably excellent polymerization activity as compared to that of conventional catalysts and can produce copolymers having an excellent random structure of conjugated dienes such as butadiene and isoprene and aromatic vinyl hydrocarbons such as styrene. Furthermore, the polymers or copolymers of conjugated dienes obtained by the use of the above-mentioned catalyst complexes have the following advantages:

PAR (i) The conjugated diene polymers or copolymers have a high trans/cis ratio in the micro-1,4-structure, for example, a trans/cis ratio of 2.0 or more in the case of butadiene.

PAR (ii) The conjugated diene polymers or copolymers have no crystallization property as determined by a differential thermal analyzer.

PAR (iii) The conjugated diene polymers or copolymers have a relatively narrow molecular weight distribution, for instance, a ratio of weight-average molecular weight/number-average molecular weight of 1.2 through 3.0.

PAR According to the present invention, the conjugated diene polymers or copolymers having excellent rubber characteristics and being suitable for use as raw materials in the manufacture of automotive tires can be produced in good yield in a relatively short period of time.

PAR The monomers usable in the process of the present invention are selected from the group of (1) conjugated dienes, (2) mixtures of a certain conjugated diene and one or more conjugated dienes, and (3) mixtures of conjugated diene(s) and aromatic vinyl hydrocarbon(s). The conjugated dienes desirably used in the present invention are those having 4 through 12 carbon atoms in a molecule thereof. Examples of such conjugated dienes are 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene, and 2-phenyl-1,3-butadiene. The aromatic vinyl hydrocarbons usable in the process of the present invention are those containing at least one vinyl group bonded to the carbon atom of the aromatic ring. The aromatic vinyl compounds desirably used in the present invention are those having 8 through 20 carbon atoms in a molecule thereof. Examples of such aromatic vinyl hydrocarbons are styrene, divinylbenzene, vinyltoluene, 1-vinylnaphthalene, .alpha.-methylstyrene, and methoxystyrene.

PAR The most desirable commercial polymerization processes of the present invention are butadiene homopolymerization, butadiene-isoprene copolymerization, and styrene-butadiene copolymerization.

PAR The sodium compounds usable as the first component (a) of the novel catalyst complexes of the present invention are selected from the group of organosodium compounds, metallic sodium or sodium amide compounds, or sodium) and organic compound(s) of sodium other than the sodium amide compounds.

PAR The organosodium compounds are represented by the following general formula:

EQU R'(Na).sub.m

PAL wherein R' is an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms or an unsaturated hydrocarbon group having at least one allyl hydrogen and desirably having 3 to 30 carbon atoms, and m is an integer of 1 through 4.

PAR Examples of the desirable R' group are the methyl, ethyl, iso-propyl, n-butyl, sec-butyl, n-amyl, tert-octyl, n-decyl, phenyl, naphthyl, 4-butylphenyl, cyclohexyl, 4-butylcyclohexyl, benzyl, allyl, triphenylmethyl, and fluorenyl groups.

PAR The metallic sodium can be desirably used in the form of a dispersion in, for example, mineral oil, paraffin or wax. However, the metallic sodium can also be used in the form of an alloy such as an amalgam.

PAR The sodium amide compounds are represented by the following general formula:

##STR1##

represents either a cyclized structure or a non-cyclized structure and R.sup.2 and R.sup.3 represent, in combination, a methylene chain having 2 to 10 carbon atoms in the case of a cyclized structure and R.sup.2 and R.sup.3 independently represent an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms in the case of a non-cyclized structure.

PAR Examples of the desirable amide groups are the dimethylamide, diethylamide, di-iso-propylamide, di-n-butylamide, di-iso-butylamide, dioctylamide, diallylamide, dicyclohexylamide, diphenylamide, dibenzylamide, and N-ethylanilide groups. Examples of cyclized structures are the ethyleneimide, trimethyleneimide, pyrrolidido, piperidido, and hexamethyleneimide groups.

PAR The organic compounds of sodium are selected from the group of compounds having the following general formulae:

##STR2##

wherein R.sup.4 is an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms, Y is an oxygen or sulfur atom, and n is an integer of 1 through 4.

PAR Examples of such desirable compounds are sodium salts of the following compounds: ethyl alcohol, n-propyl alcohol, iso-propyl alcohol, tert-butyl alcohol, n-hexyl alcohol, cyclohexyl alcohol, allyl alcohol, cyclopentenyl alcohol, benzyl alcohol, ethanethiol, n-butanethiol, phenol, catechol, 1-naphthol, 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, nonylphenol, 4-phenylphenol, thiophenol, 2-naphthalenethiol, capric acid, lauryl acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, naphthoic acid, benzoic acid, hexane thio acid, decane thio acid, tridecane thio acid, thiobenzoic acid, acid tert-butyl carbonate, acid hexyl carbonate, acid phenyl carbonate, thio acid tert-butyl carbonate butane sulfonic acid, hexane sulfonic acid, decane sulfonic acid, tridecane sulfonic acid, dodecylbenzene sulfonic acid, tetradecylbenzene sulfonic acid, octadecylbenzene sulfonic acid, dibutylnaphthalene sulfonic acid, di-iso-propylnaphthalene sulfonic acid, n-hexylnaphthalene sulfonic acid, dibutylphenyl sulfonic acid, sulfate ester of lauryl alcohol, sulfate ester of oleyl alcohol, and sulfate ester of stearyl alcohol.

PAR The organic compounds or organometallic compounds of barium, strontium, or calcium usable as the second component (b) of the novel catalyst complexes of the present invention are selected from the group of compounds having the following general formulae:

##STR3##

wherein R.sup.5 is an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms,

##STR4##

represents either a cyclized structure or a non-cyclized structure, and R.sup.6 and R.sup.7 represent, in combination, a methylene chain having 2 to 10 carbon atoms in the case of a cyclized structure and R.sup.6 and R.sup.7 independently represent an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms in the case of a non-cyclized structure provided that one of R.sup.6 and R.sup.7 can be hydrogen, Y is an oxygen or sulfur atom, Me' is a barium, strontium, or calcium atom, and X is a halogen atom such as fluorine, chlorine, bromine, or iodine.

PAR Examples of the desirable organic compounds of the II A metals are barium, strontium, or calcium salts of the following compounds: ethyl alcohol, n-propyl alcohol, iso-propyl alcohol, tert-butyl alcohol, n-hexyl alcohol, cyclohexyl alcohol, allyl alcohol, cyclopentenyl alcohol, benzyl alcohol, ethanethiol, n-butanethiol, phenol, catechol, 1-naphthol, 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, nonylphenol, 4-phenylphenol, thiophenol, 2-naphthalenethiol, capric acid, lauryl acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, naphthoic acid, benzoic acid, hexane thio acid, decane thio acid, tridecane thio acid, thiobenzoic acid, acid tert-butyl carbonate, acid hexyl carbonate, acid phenyl carbonate, thio acid tert-butyl carbonate butane sulfonic acid, hexane sulfonic acid, decane sulfonic acid, tridecane sulfonic acid, dodecylbenzene sulfonic acid, tetradecylbenzene sulfonic acid, octadecylbenzene sulfonic acid, dibutylnaphthalene sulfonic acid, di-iso-propylnaphthalene sulfonic acid, n-hexylnaphthalene sulfonic acid, dibutylphenyl sulfonic acid, sulfate ester of lauryl alcohol, sulfate ester of oleyl alcohol, sulfate ester of stearyl alcohol, dimethylamine, diethylamine, di-iso-propylamine, di-n-butylamine, mono-n-butylamine, di-iso-butylamine, mono-iso-butylamine, dioctylamine, diallylamine, dicyclohexylamine, phenylamine, diphenylamine, benzylamine, dibenzylamine, and N-ethylaniline.

PAR Examples of the desirable organometallic compounds of the II A metals are dimethyl calcium, n-butyl calcium iodide, ethyl strontium iodide, dimethyl strontium, ethyl barium iodide, dimethyl barium, phenyl barium iodide, dicyclopentadienyl barium, bistriphenylmethyl barium, dipropargyl barium, and barium di-2-ethylacetylide.

PAR The organometallic compounds of electron deficient metals usable as the third component (c) of the novel catalyst complexes of the present invention are lithium (Li) in the Group I A metals of the Mendeleev Periodic Table of Elements, beryllium (Be) and magnesium (Mg) in the Group II A metals, zinc (Zn) and cadmium (Cd) in the Group II B metals, and boron (B), aluminum (Al), gallium (Ga), and indium (In) in the Group III A metals and mixtures thereof.

PAR These compounds are represented by the following general formula:

EQU R.sup.9.sub.n-q Me.sup.2 X.sub.q

PAL wherein R.sup.9 is an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms, X is a halogen atom such as fluorine, chlorine, bromine, or iodine, a hydrogen atom, or an alkoxy group, Me.sup.2 is Li, Be, Mg, Zn, Cd, B, Al, Ga, or In, p is the valence of Me.sup.2, and q is 0.ltoreq.q.ltoreq.p-1.

PAR Examples of such desirable compounds are ethyl lithium, n-propyl lithium, iso-propyl lithium, n-butyl lithium, tert-butyl lithium, n-amyl lithium, n-hexyl lithium, allyl lithium, n-propenyl lithium, benzyl lithium, phenyl lithium, polybutadienyl lithium, polyisoprenyl lithium, polystyryl lithium, diethyl beryllium, di-n-propyl beryllium, di-n-butyl beryllium, ethyl beryllium chloride, diethyl magnesium, di-n-propyl magnesium, di-iso-propyl magnesium, di-tert-butyl magnesium, ethyl-n-butyl magnesium, di-n-hexyl magnesium, diphenyl magnesium, ethyl magnesium chloride, ethyl magnesium hydride, ethyl magnesium-iso-propoxide, iso-propyl magnesium chloride, n-butyl magnesium chloride, n-butyl magnesium bromide, phenyl magnesium chloride, diethyl zinc, ethyl zinc chloride, di-n-propyl zinc, di-iso-propyl zinc, diethyl cadmium, di-iso-propyl cadmium, ethyl cadmium chloride, trimethyl boron, triethyl boron, triethyl aluminum, tri-iso-butyl aluminum, diethyl aluminum chloride, diethyl aluminum hydride, diethyl aluminum propoxide, di-iso-butyl aluminum chloride, di-iso-butyl aluminum hydride, trihexyl aluminum, triphenyl aluminum, triethyl gallium, and triethyl indium.

PAR The amounts of the components (a) and (b) or the components (a), (b), and (c) can vary greatly depending upon, for example, the purposes of polymerization and upon the polymerization methods and conditions. However, generally speaking, the use of the components in the following range is recommended:

PA1 Component (a): 0.01 through 50 m mol per 100 g of the total monomer(s)

PA1 Component (b): 0.01 through 10 times based on the mol of the component (a)

PA1 Component (c): 0 through 5 times based on the mol of the component (a)

PAR In the case where the amount of the component (a) is too small, the polymerization activity tends to decrease. Contrary to this, in the case where the amount of the component (a) is too large, the molecular weight of the resultant polymer tends to decrease so that the resultant polymer is not suitable for use in general rubber industrial fields (e.g. the manufacture of automotive tires). In the case where the amount of the component (b) is too small, the molecular weight of the resultant polymer tends to decrease and the ratio of a trans-1,4/cis-1,4 structure content in the diene moiety also tends to decrease. Contrary to this, in the case where the amount of the component (b) is too large, the polymerization activity tends to decrease. Furthermore, in the case where the amount of the component (c) is too large, not only the polymerization activity tends to decrease but also the copolymerizability of conjugated dienes and aromatic vinyl hydrocarbons tends to decrease.

PAR Especially in the case of polymers (or copolymers) having a relatively high molecular weight and being suitable for use as a starting material in the manufacture of automotive tires, the components can be desirably used in the following range:

PA1 Component (a): 0.1 through 1 m mol per 100 g of the total monomer(s)

PA1 Component (b): 0.1 through 1 times based on the mol of the component (a)

PA1 Component (c): 0 through 2 times based on the mol of the component (a)

PAR The polymerization processes of the present invention can be desirably carried out in a solution polymerization manner using a hydrocarbon solvent, although a bulk polymerization method can be used. Examples of such hydrocarbon solvents are butane, pentane, hexane, heptane, octane, cyclohexane, cyclooctane, benzene, toluene, xylene, ethylbenzene, and mixtures thereof. Minor amounts of polar compounds can be added to the hydrocarbon solvent to improve the solubility and the catalytic activity of the catalyst complex. Examples of such polar compounds are ether compounds such as tetrahydrofuran, diethyl ether, and ethyleneglycol diethyl ether and amine compounds such as triethyl amine and tetramethyl ethylenediamine. The amount of hydrocarbon solvents used in the polymerization processes of the present invention can vary greatly depending upon the types and molecular weights of the polymers (or copolymers) to be produced. Generally speaking, the desirable amount of solvents to be used in 300 through 1000 parts by weight based on 100 parts by weight of the total monomer(s).

PAR The polymerization process of the present invention can be generally carried out at a temperature of -40.degree. C. through 160.degree. C. The desirable polymerization temperature is 30.degree. C. through 120.degree. C., especially when conjugated diene polymers or copolymers having a relatively high molecular weight and being suitable for use as starting materials in the manufacture of automotive tires are to be produced. The polymerization processes of the present invention should be carried out under an inert gas atmosphere such as nitrogen and argon. The contamination of the polymerization system with compounds capable of reacting with the organometallic compounds, such as water, carbon dioxide, oxygen, and halogen compounds, should be avoided. The pressure of the polymerization system may be sufficient to maintain the polymerization mixture in a liquid state. Usually, about 1 through 5 atmosphere are used.

PAR The conjugated diene polymers or copolymers obtained from the process of the present invention have extremely excellent characteristics, for example, processabilities such as green strength and tackiness and vulcanizate properties such as tensile strength, abrasion resistance and heat build-up. The conjugated diene polymers or copolymers can be compounded and vulcanized in any conventional manner. These conjugated diene polymers or copolymers can, therefore, be used alone or after blending with natural rubber or other synthetic rubbers in the application fields of automotive tires including tire treads, carcasses and side walls, as well as extruded articles, automotive window frames and various industrial articles. Furthermore, the conjugated diene polymers or copolymers can be grafted onto or blended with various plastics to improve the physical properties such as the impact strength.

DETD

PAR The present invention will now be further illustrated by, but is by no means limited to, the Examples set forth hereinbelow.

PAC EXAMPLE 1

PAR One hundred grams of 1,3-butadiene and 400 g of a cyclohexane solvent were charged into an approximately one liter pressure-resistant glass bottle filled with dry nitrogen. A catalyst complex of 0.5 m mol of n-amyl sodium and 0.25 m mol of barium di-t-butoxide was then added to the bottle and the mixture was polymerized at a temperature of 50.degree. C. for 7 hours.

PAR The yield, molecular weight, molecular weight distribution and micro structure of the resultant polymer are shown in Table 1 below.

TBL TABLE 1

Molecular
weight
determined
by Microstructure* sup 2

Yield (%)	--Mw (.times. 10.sup.4)	--Mw/ --Mn	structure (%)	cis-1,4 structure (%)	structure (%)	trans/ cis ratio
100	22.6	1.29	53	36	11	3.3

*.sup.1 GPC : Gel Permeation Chromatography
*.sup.2 Microstructure was determined according to a D. Morero method by using an infrared absorption spectrum.

PAR As is clear from the results shown in Table 1, the butadiene polymer having a high trans-1,4 structure content and a relatively narrow molecular weight distribution could be obtained by using a catalyst complex of the organosodium compound and the barium compound.

PAC EXAMPLE 2

PAR Example 1 was repeated, except that isoprene was used as a monomer in lieu of butadiene. The results are shown in Table 2 below.

TBL TABLE 2

Yield (%)	Molecular weight by GPC --Mw (.times. 10.sup.4)	--Mw/--Mn	Microstructure*.sup.1 3,4-structure (%)	1,4-structure (%)
100	22.5	1.32	48	52

*.sup.1 Microstructure was determined by using an infrared absorption spectrum.

PAC EXAMPLES 3 TO 7 AND COMPARATIVE EXAMPLES 1 TO 6

PAR Twenty five grams of styrene, 75 g of 1,3-butadiene and 400 g of a cyclohexane solvent were added to an approximately one liter pressure-resistant glass bottle filled with dry nitrogen. A catalyst complex each listed in Table 3 below was then added to the bottle and the mixture was polymerized at a temperature of 50.degree. C. for 7 hours. A portion of the polymer solution was withdrawn from the bottle at the conversion of less than 20% during the course of the polymerization and the bound styrene of the initial polymer was determined.

PAR As comparative examples, the above-mentioned polymerization experiments were repeated, except that conventional catalysts listed in Table 3 below were used in lieu of the catalyst complexes.

PAR As is clear from Table 3 below, the polymers of Examples 3 to 7 obtained by using the catalyst complexes consisting essentially of the organosodium compounds and the organic compounds of the II A metals have a high trans/cis ratio in the 1,4-structure of the butadiene moiety, as compared with those of Comparative Examples 1 to 4. The polymers having a high trans/cis ratio, for example, a trans/cis ratio of 1.8 or more can also be obtained by using conventional catalysts as shown in Comparative Examples 5 and 6. These catalysts, however, result in a low polymerization conversion and a poor styrene-butadiene copolymerization reactivity ratio as sh in the initial bound styrene contents in Table 3. Fur more, these polymers have a disadvantage in that the molecular weight distribution thereof is broad.

PAR As is clear from a comparison of the Examples with the Comparative Examples in Table 3 below, the polymerization processes of conjugated dienes using the novel catalyst complexes according to the present invention have the following advantages:

PAR (a) The polymerization activity of the catalysts is high;

PAR (b) Copolymers having an excellent random distribution of conjugated dienes (e.g. butadiene) and aromatic vinyl hydrocarbons (e.g. styrene) can be obtained;

PAR (c) Copolymers having a high trans/cis ratio in the 1,4-structure of the butadiene moiety can be obtained; and

PAR (d) Copolymers having a relatively narrow molecular weight distribution can be obtained.

PAR It is also clear from the results shown in Table 3 below that the 1,2-structure content and the ratio of the trans-1,4 structure/cis-1,4 structure of the copolymers can be controlled by changing the combination and composition of the catalyst complexes.

```
TBL                          TABLE 3
    ________________________________________________________________
                                       Microstructure in butadiene
                                       moiety
    Catalyst            Initial     Block
                                       Molecular 1,2-      Cis-1,4
    Catalyst  Catalyst bound     Bound
                                    sty-
                                       weight by GPC
                                       struc-
                                          Trans-1,4
                                                struc-
                                                   Trans/
    compo-    component*.sup.4
                        styrene*.sup.1
                            Yield
                               styrene
                                  rene*.sup.2
                                     --Mw      ture
                                          structure
                                                ture
                                                   cis
    nent*.sup.4 (1)
              (2)       (%)  (%) (%) (%) (.times. 10.sup.4)
                                         --Mw/--Mn
                                            (%) (%)  (%) ratio
    ________________________________________________________________
    Ex-
    ample
    3   nC.sub.5 H.sub.11 Na
              Ba[OC(CH.sub.3).sub.3 ].sub.2
                        26   96  25  0.  24.9 1.31 44  45   11  4.1
        0.5   0.5
    4   nC.sub.5 H.sub.11 Na
              Ba[OC(CH.sub.3).sub.3 ].sub.2
                        26   100 25  0   22.8 1.33 53  37   10  3.7
        0.5   0.25
```

```
          Ba[OC(CH.sub.3).sub.3 ].sub.2
                      27    100 25  0    19.6 1.34 58   33    9    3.7
    0.5    0.125
 6  nC.sub.5 H.sub.11 Na
          Sr[OC(CH.sub.3).sub.3 ].sub.2
                      29    100 25  0    18.2 1.40 59   30    11   2.7
    0.5    0.25
 7  nC.sub.5 H.sub.11 Na
          Ca[OCH(CH.sub.3).sub.2 ].sub.2
                      29    98  25  0    11.8 1.76 64   25    11   2.3
    0.5    0.25
Com-
para-
tive
Ex-
ample
 1  nC.sub.5 H.sub.11 Na
          None        32    41  30  0    3.2  1.94 68   20    12   1.7
    0.5
 2  nC.sub.5 H.sub.11 Na
          LiOC(CH.sub.3).sub.3
                      30    100 25  0    24.3 1.22 60   25    15   1.7
    0.5    0.5
 3  nC.sub.4 H.sub.9 Li
          None        3     84  8   17.0
                                         17.5 1.03 10   52    38   1.4
    0.5
 4  nC.sub.4 H.sub.9 Li
          Tetrahydrofuran
                      15    100 25  0    22.1 1.03 34   40    26   1.5
    0.5    5.0
 5  nC.sub.4 H.sub.9 Li
          Ba[OC(CH.sub.3).sub.3 ].sub.2
                      15    89  22  0    11.6 2.21 12   63    25   2.5
    0.5    0.25
 6  (C.sub.4 H.sub.9).sub.2 Mg
          Ba[OC(CH.sub.3).sub.3 ].sub.2
                      13    62  21  0    6.7  1.91 9    79    22   3.6
           0.25
```

---

*.sup.1 Determined by ultraviolet absorption spectrum

*.sup.2 Determined according to Kolthoff method (I. M. Kolthoff, J. Polymer Sci., 1,429-433 (1946))

*.sup.3 Determined by infrared absorption spectrum according to a Hampton method

*.sup.4 M mol per 100 g of the total monomers

PAC EXAMPLES 8 TO 22

PAR The copolymerization runs were repeated in the same manner as described in Examples 3 to 7, except that the components of the catalyst complexes of the present invention were changed. The amounts of the catalyst components used in these runs, based on 100 g of the total monomers, were as follows.

PA1 Component (a): 0.5 m mol

PA1 Component (b): 0.25 m mol

PA1 Component (c): 0.25 m mol

PAR The results are shown in Table 4 below.

PAR Examples 8 to 10 used sodium amide, metallic sodium and a mixture of the organosodium compound and the organic compound of sodium as the catalyst component (a). As is clear from the results shown in Table 4 below, these catalyst components (a) result in the advantages similar to those obtained by using the organosodium compounds.

PAR Examples 11 to 13 used the barium salts of various organic compounds as the catalyst component (b). As is clear from the results shown in Table 4, these various barium salts are effective as the catalyst component (b) of the catalyst complexes of the present invention.

PAR Examples 14 to 22 use the organometallic compounds of various electron deficient metals as the component (c). As is clear from the results in Table 4, the ratio of trans-1,4/cis-1,4 structures can be further increased.

TBL TABLE 4

```
                                                  Microstructure
                                                  in butadiene
                                                  moiety
Catalyst complex          Initial     Molecular
                                                  1,2-
Catalyst          Catalyst
                               bound   Bound
                                          Block
                                             weight by
                                                  struc-
                                                     Trans/
   component
         Catalyst component
                  component
                       styrene
                          Yield
                            styrene
                               styrene
                                  --Mw --Mw/
                                                  ture
                                                     cis
Example
   (a)      (b)        (c)     (%) (%) (%) (%) (.times. 10.sup.4)
                                                --Mn
                                                  (%) ratio
-----------------------------------------------------------------
    ##STR5##
         Ba[OC(OH.sub.3).sub.3 ].sub.2
                     None   26  80  26  0   16.3 1.46
                                                 54   4.1
  9  Sodium dispersion
         "           "      26  86  26  0   41.6 1.44
                                                 48   4.5
10   *1     "        "      26  99  25  0   35.7 1.32
                                                 51   3.9
 11 nC.sub.5 H.sub.11 Na
         ##STR6##    "      26  100 25  0   22.9 1.31
                                                 52   3.8
 12 "
         ##STR7##    "      26  98  25  0   25.3 1.40
```

		"		26	97	25	0	25.6	1.41	51	3.9
14	"	Ba[OC(CH.sub.3).sub.3].sub.2	LinO.sub.4 H.sub.9	26	100	25	0	12.7	1.29	32	4.3
15	"	"	Be(C.sub.2 H.sub.5).sub.2	24	99	25	0	23.1	1.35	25	4.8
16	"	"	Mg(nC.sub.4 H.sub.9).sub.2	25	100	25	0	11.9	1.31	26	4.7
17	"	"	Zn(C.sub.2 H.sub.5).sub.3	25	100	25	0	23.8	1.29	46	4.7
18	"	"	Cd(C.sub.2 H.sub.5).sub.3	26	100	25	0	22.4	1.30	47	4.6
19	"	"	B(C.sub.2 H.sub.5).sub.3	23	95	24	0	26.7	1.28	40	5.1
20	"	"	Al(C.sub.2 H.sub.5).sub.3	24	99	25	0	25.5	1.24	41	5.6
21	"	"	Ga(C.sub.2 H.sub.5).sub.3	25	100	25	0	22.3	1.30	45	4.6
22	"	"	In(C.sub.2 H.sub.5).sub.3	25	100	25	0	22.6	1.31	45	4.6

*1 A mixture of 0.25 m mol of nC.sub.5 H.sub.11 Na and 0.25 m mol of (CH.sub.3).sub.3 CONa

PAC EXAMPLE 23

PAR The copolymerization run of Example 1 was repeated, except that 25 g of styrene and 75 g of isoprene were used as monomers. The results are shown in Table 5 below.

TBL TABLE 5

	Styrene	Molecular weight		Microstructure	
Yield (%)	content (%)	--Mw (.times. 10.sup.4)	--Mw/--Mn	3,4-structure (%)	1,4-structure (%)
99	25	19.8	1.41	46	54

PAC EXAMPLE 24

PAR The copolymerization run of Example 1 was repeated, except that a mixed solvent of 400 g of cyclohexane and 1.0 m mol of tetramethyl ethylenediamine was used. The results are shown in Table 6 below.

TBL TABLE 6

Molecular Microstructure in butadiene moiety

```
weight by GPC 1,2      Trans-1,4
                                 Cis-1,4
                                          Trans
Yield --Mw      --Mw/  structure
                                structure
                                         structure
                                                  cis
(%)  (.times. 10.sup.4)
                 --Mn   (%)     (%)      (%)      ratio

100   21.1       1.21   80      15       5        3.0
```

PAC EXAMPLE 25 AND COMPARATIVE EXAMPLE 7

PAR The monomers and the catalyst complexes having the compositions listed in Table 7 below were charged, together with 4 kg of a cyclohexane solvent, into an approximately 10 liter autoclave filled with dry nitrogen and polymerized at a temperature of 65.degree. C. for 3 hours. After completing the polymerization, a small amount of methanol was added to the polymerization mixture to deactivate the living polymer. Thereafter, 0.3 parts by weight of BHT (i.e. 3,5-di-tert-butyl-3-hydroxytoluene) based on 100 parts by weight of the copolymer was added as a stabilizer and the cyclohexane was vaporized and removed from the polymer solution. Thus, polymers A to E of Example 25 and polymers F to K of Comparative Example 7 were obtained. The Mooney viscosity, molecular weight distribution, styrene content, microstructure in the butadiene moiety and melting point of the resultant polymers are also shown in Table 7 below. Polymers F and G of Comparative Example 7 had a high 1,2-structure content and a low trans/cis ratio in the 1,4-structure. Polymers H through K were those having a high trans/cis ratio in the 1,4-structure of the butadiene moiety, prepared from conventional processes.

TBL TABLE 7

```
                  Example 25         Comparative Example 7
                  A   B    C    D    E    F    G    H    I    J    K

Butadiene (kg) 1   0.82
                            0.75
                                 0.75
                                      0.75
                                           1    0.75
                                                     1    0.75 1    0.75
Styrene (kg)   0   0.18
                            0.25
                                 0.25
                                      0.25
                                           0    0.25
                                                     0    0.25 0    0.25
Catalyst and additive
                  nC.sub.5 H.sub.11 Na
                                      nC.sub.4 H.sub.9 Li
                                                nC.sub.4 H.sub.9 Li
                                                           (C.sub.4 H.sub.9).sub
                                                           .2 Mg
(m mol)           .rarw.4 m mol.fwdarw.
                             *.sup.1
                              *.sup.2
```

```
                                   4 m mol 3 m mol    3 m mol
              Ba--[OC(CH.sub.3)].sub.3
                                   E D M E Ba--[OC(CH.sub.3).sub.3
                                           ].sub.2   Ba--[OC(CH.sub.3).sub
                                                     .3 ].sub.2
              2 m mol                      1.5 m mol 1.5 m mol
Conversion (%) 100 99  98  96  92  100 100 92   77   79   59
Mooney viscosity (ML.sub.1+4
                 47 52  51  46  48  55  46  42   43   47   41
100.degree. C.)
Molecular weight distribution
              1.32
                 1.36
                    1.38
                       1.41
                          1.46
                             1.08
                                1.10
                                   2.36 2.41 1.88 1.97
(Mw/Mn)
Bound styrene (%)
              0  18  25  25  25  0  25  0   22   0   20
Block styrene (%)
              0  0   0   0   0   0   0  0   0    0   0
1,2-structure (%)
              39 41  42  35  29  38  40 12  13   9   9
Trans/cis ratio
              3.1 3.4 3.5 3.7 3.9 1.5 1.5 2.5 2.4 3.6 3.5
Melting point (.degree.C.)*.sup.3
              None
                 None
                    None
                       None
                          None
                             None
                                None
                                   None None 23   None
```

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*.sup.1 nC.sub.5 H.sub.11 Na 3 m mol + Ba--[OC(CH.sub.3).sub.3].sub.2 2 mol + Mg(nC.sub.4 H.sub.9).sub.2 0.5 m mol

*.sup.2 nC.sub.5 H.sub.11 Na 2 m mol + Ba--[OC(CH.sub.3).sub.3].sub.2 2 mol + Mg(nC.sub.4 H.sub.9).sub.2 1 m mol

*.sup.3 Determined by a differential thermal analyzer

PAR Polymers A to E of Example 25 and polymers F to K of comparative Example 7 as well as a commercially available solution polymerization type butadiene polymer (i.e. Diene NF 50R available from Asahi Kasei Kogyo Kabushiki Kaisha in Japan), a solution polymerization type styrene-butadiene copolymer (i.e. Tufdene 2000R available from Asahi Kasei Kogyo Kabushiki Kaisha in Japan) and an emulsion polymerization type styrene-butadiene copolymer (i.e. SBR-1502 available from Nihon Gosei Gomu Kabushiki Kaisha) were independently mixed in the compositions listed in Table 8 below by using a B-type Banbury mixer to produce compounds.

TBL TABLE 8

Compounding Formulation Component	Parts by Weight

Polymer	100
Aromatic process oil*.sup.1	20
HAF carbon	60
Zinc oxide	4
Stearic acid	3
Antioxidant 8*.sup.2	1.3
Sulfur	2
Vulcanizing accelerator CZ*.sup.3	1.5

*.sup.1 Specific density = 0.951, VGC = 0.961
*.sup.2 Reaction product of diphenylamine and acetone
*.sup.3 N--cyclohexyl benzothiazole sulfenamide

PAR The processability of the compounds thus obtained and the properties of the vulcanizates thereof were evaluated. Vulcanization was carried out by heating the compounds at a temperature of 141.degree. C. for 40 minutes. The results are shown in Table 9 below.

PAR The roll operation ability of the compounds of polymers A to E of Example 25 was clearly superior to that of the compounds of polymers F to K of Comparative Example 7, and was substantially comparable to that of the commercially available products.

PAR The compound of polymer J of Comparative Example 7 having a high trans/cis ratio in the 1,4-structure of the butadiene moiety exhibited an extremely high green strength. However, unvulcanized polymer J showed a crystallization property in the DSC analysis and the tackiness of the compound was extremely low due to the crystallization property of polymer J. Contrary to this, polymers A to E of Example 25 according to the present invention have no crystallization property in the DSC analysis, in spite of their high trans/cis ratios in the 1,4-structure of the butadiene moiety. Furthermore, the balance of the processability represented by the roll operation ability, green strength, elongation and tackiness of polymers A to E of Example 25 was superior to that of polymers F to K of Comparative Example 7 and was comparable to that of commercially available emulsion polymerization type SBR (i.e. SBR 1502).

PAR The physical properties of the vulcanizates of, for example, the styrene-butadiene copolymers of Example 25 according to the present invention (i.e. polymers B to E) are advantageous in respect to the following points, as compared with the styrene-butadiene copolymers of Comparative Example 7 (i.e. polymers G, I, K), the commercially available solution polymerization type styrene-butadiene rubber (i.e. Tufdene 2000R) and the commercially available emulsion polymerization type styrene-butadiene rubber (i.e. SBR-1502).

PAR (a) The tensile strengths of copolymers B to E according to the present invention are comparable to the commercially available emulsion type SBR and are superior to the commercially available solution type SBR and copolymers G, I and K of Comparative Example 7.

PAR (b) Generally speaking, an anti-wet skid property is contrary to an abrasion resistance property. That is, a polymer having a good anti-wet skid property generally has a poor abrasion resistance. However, copolymers B to E according to the present invention have an anti-wet skid property comparable to or greater than that of the commercially available emulsion polymerization type SBR (i.e. SBR 1502) and superior to that of

2000R). On the other hand, copolymers B to E according to the present invention have an abrasion resistance property superior to that of SBR 1502 and near that of Tufdene 2000R. Contrary to this, copolymers G, I and K do not have a good balance of both properties, although the copolymers having either a good abrasion resistance property or a good anti-wet skid property are present.

PAR (c) Copolymers B to E according to the present invention have a low heat build-up property superior to those of all the comparative copolymers, that is, comparative copolymers G, I and J, Tufdene 2000R and SBR 1502.

PAR Furthermore, as is clear from the comparison of butadiene polymers, the polymer according to the present invention (i.e. polymer A) also has the above-mentioned good properties as compared with the comparative butadiene polymers (i.e. polymers F, H and J and the commercially available Diene NF50R).

PAR As is clear from the above discussion, the polymers (or copolymers) obtained from the polymerization processes using the catalyst complexes have a good balance of properties with respect to the processability of the polymers and the strength, heat build-up property, anti-wet skid property and abrasion resistance property of the vulcanizates thereof.

TBL TABLE 9

	Example 25				
	A	B	C	D	E
Compound mooney viscosity*.sup.1 (ML.sub.1+4 100.degree. C.)	65	68	67	64	65
Rolling ability	Good	Good	Good	Good	Good
Green characteristics					
Green strength (kg/cm.sup.2)	2.7	2.5	2.5	2.8	3.1
Elongation*.sup.2 (%)	450	450	500	500	550
Tackiness*.sup.3 (kg/cm.sup.2)	0.33	0.36	0.45	0.41	0.41
Vulcanizate properties					
Hardness*.sup.4 (JIS)	63	63	64	63	63
300% modulus*.sup.4 (kg/cm.sup.2)	74	87	94	91	91
Tensile strength*.sup.4 (kg/cm.sup.2)	206	228	243	244	252
Elongation*.sup.4 (%)	660	670	690	660	680
Anti-wet skid*.sup.5 (index)	88	100	106	102	100
Impact resilience*.sup.4 (%)	54	45	39	41	43
Abrasion resistance*.sup.6 (index)	163	112	101	109	116
Heat build-up*.sup.7 .DELTA.T(.degree.C.)	32	32	33	31	31

Comparative Example 7 -	Diene	Tufdene SBR

	F	G	H	I	J	K	NF50R*.sup.8	2000R*.sup.8	1502
Compound mooney viscosity*.sup.1 (ML.sub.1+ 4 100.degree. C.)	71	65	56	56	60	55	64	61	64
Rolling ability	Poor	Poor	Fair	Fair	Poor	Fair	Good	Good	Good
Green characteristics									
Green strength (kg/cm.sup.2)	2.6	2.3	1.8	1.5	20.3	2.8	2.5	2.2	1.7
Elongation*.sup.2 (%)	150	170	400	500	250	550	250	320	450
Tackiness*.sup.3 (kg/cm.sup.2)	0.13	0.16	0.33	0.37	0.05	0.31	0.18	0.26	0.37
Vulcanizate properties									
Hardness*.sup.4 (JIS)	63	63	62	62	60	60	62	64	64
300% modulus*.sup.4 (kg/cm.sup.2)	78	94	71	84	60	65	74	82	95
Tensile strength*.sup.4 (kg/cm.sup.2)	170	190	174	193	162	184	165	226	239
Elongation*.sup.4 (%)	560	560	620	610	620	640	580	670	650
Anti-wet skid*.sup.5 (index)	87	103	75	91	74	88	76	94	100
Impact resilience*.sup.4 (%)	54	39	53	46	53	47	54	46	44
Abrasion resistance*.sup.6 (index)	132	74	165	117	166	117	185	120	100
Heat build-up*.sup.7 .DELTA.T(.degree.C.)	33	35	41	40	44	43	40	38	39

*.sup.1 JIS-K6300

*.sup.2 JIS #1 dumbbell, stress rate 500 nm/min

*.sup.3 Monsanto tuckmeter

*.sup.4 JISK6301

*.sup.5 Gravitational friction coefficient between the vulcanizate and wetted concrete road surface was determined using a slide rheostat developed by British Road Institute.

*.sup.6 Pico abrasion tester, ASTM D2228

*.sup.7 Goodrich flexometer, ASTM D623-58(A)

*.sup.8 Available from Asahi Kasei Kogyo Kabushiki Kaisha

PAC EXAMPLES 26 TO 57

PAR The copolymerization runs were repeated in the same manner as described in Examples 3 to 7, except that the components of the catalyst complexes were changed. The structures and amounts of the catalyst components used and the results are shown in Table 10 below.

sodium or a sodium amide compound and organic compounds of sodium as the component (a) of the present catalyst complex. As is clear from the results of Examples 26 to 36, various sodium salts of organic compounds are effective as the organic compound of sodium of the catalyst component (a).

PAR Examples 37 to 48 use the organic compounds or the organometallic compounds of barium as the catalyst component (b). Barium is selected as a typical example of the metals of the component (a) (i.e. barium, strontium and calcium). It is clear from the results of Examples 37 to 48 that these compounds are effective as the component (b) of the present catalyst complexes.

PAR Examples 49 to 57 use the organometallic compounds of magnesium or aluminum, which is selected as a typical example of the electron deficient metals of the component (a). It is also clear from the results of Examples 49 to 57 that various organometallic compounds having the general formula

EQU R.sup.9.sub.p-q Me.sup.2 X.sub.q

PAL wherein R.sup.9, Me.sup.2, p and q are the same as defined above are effective as the component (c) of the present catalyst complexes.

```
TBL3 TABLE 10 Initial Molecular Microstructure in butadiene moiety*.sup.3
 bound Bound Block weight by GPC 1,2- Trans-1,4 Cis-1.4 styrene*.sup.1
  Yield styrene styrene*.sup.2 --Mn structure structure structure
 Trans/cis Example Catalyst system (%) (%) (%) (%) (.times. 10.sup.4)
 --Mw/--Mn (%) (%) (%) ratio Component*.sup.4 Component*.sup.4 Component
 *.sup.4 (1) (1') (2) 26 nC.sub.5 H.sub.11 Na NaSn-C.sub.4
 H.sub.9 Ba[OC(CH.sub.3).sub.3 ].sub.2 27 100 25 0 19.3 1.41 54 37 9
 4.1 0.5 0.25 0.25 27 nC.sub.5 H.sub.11
  NaO.5
 ##STR8##
  Ba[OC(CH.sub. 3).sub.3 ].sub.20.25 27 100 25 0 18.7 1.33 49 40 11 3.6
  0.25 28 nC.sub.5 H.sub.11
  NaO.5
 ##STR9##
  Ba[(OC(CH.sub.3).sub.3 ].sub.20.25 27 99 25 0 18.8 1.36 53 37 10 3.7
 0.25 29 nC.sub.5 H.sub.11 Na NaOCOn-C.sub.17
  H.sub.35 Ba[OC(CH.sub.3).sub.3 ].sub.2 27 97 25 0 19.5 1.42 5337 10 3.7
  0.5 0.25 0.25 30 nC.sub.5 H.sub.11 Na NaSCSn-C.sub.12
  H.sub.25 Ba[OC(CH.sub.3).sub.3).sub.2 27 96 25 0 20.2 1.41 55 36 9 4.0
  0.5 0.25 0.25 31 nC.sub.5 H.sub.11 Na NaOCOCOOn-C.sub.6 H.sub.13
 Ba[OC(CH.sub.3).sub.3 ].sub.2 28 96 25 0 20.4 1.44 56 35 9 3.9 0.5
 0.25 0.25 32 nC.sub.5 H.sub.11 Na NaSCSCSSn-C.sub.4
  H.sub.9 Ba [OC(CH.sub.3).sub.3 ].sub.2 28 95 26 0 20.9 1.46 55 36 9
 4.0 0.5 0.25 0.25 33 nC.sub.5 H.sub.11 Na nC.sub.18 H.sub.37 OSO.sub.3
 Na Ba[OC(CH.sub.3).sub.3 ].sub.2 28 98 25 0 19.0 1.39 53 38 9 4.2 0.5
 0.25 0.25 34 nC.sub.5 H.sub.11
  NaO.5
 ##STR10##
  Ba[OC(CH.sub.3).sub.3 ].sub.20.25 27 98 25 0 19.3 1.37 53 38 9 4.2
 0.25 35 Sodium NaOC(CH.sub.3).sub.3 Ba[OC(CH.sub.3).sub.3 ].sub.2 27 89
 26 0 27.1 1.46 52 38 10 3.8 dispersion 0.25 0.25 0.5
   36
 ##STR11##
  NaOC(CH.sub.3).sub.30.25 Ba[OC(CH.sub.3).sub.3 ].sub.20.25 27 83 26 0
 18.6 1.48 54 37 9 4.1 0.5 Component*.sup.4 Component*.sup.4 (1)
 (2) 37 nC.sub.4 H.sub.9 Na Ba(On-C.sub.3 H.sub.7).sub.2 27 100 25 0
 22.2 1.32 53 37 10 3.7 0.5 0.25 38 nC.sub.4 H.sub.9 Na Ba(Sn-C.sub.4
 H.sub.9).sub.2 27 100 25 0 22.1 1.34 50 40 10 4.0 0.5 0.25 39
```

```
     nC.sub.4 H.sub.9
      NaO.5
      ##STR12##
      27 100  25 0 21.3 1.35 55 35 10 3.5    0.25  40 nC.sub.4 H.sub.9 Na      S
     Ba(CSn-C.sub.9 H.sub.19).sub.2 27 99 25 0 23.7 1.3452 38 10 3.8  0.5
     0.25 41 nC.sub.4 H.sub.9 Na  Ba(OCOCOOn-C.sub.6 H.sub.13).sub.2 26 97 25
     0 24.1 1.44 51 39 10 3.9  0.5  0.25 42 nC.sub.4 H.sub.9
      Na  Ba(SCSCSStert-C.sub.4 H.sub.9).sub.2 26 95 26 0 24.3 1.48 50 39 11
     3.5  0.5  0.25  43 nC.sub.4 H.sub.9
      NaO.5
      ##STR13##
      27 100  25 0 22.3 1.33 54 36 10 3.6    0.25  44 nC.sub.4 H.sub.9 Na
     (n-C.sub.19 H.sub.37 OSO.sub.3).sub.2 Ba 27 99 25 0 22.5 1.30 52 37 11
     3.4  0.5  0.25 45 nC.sub.4 H.sub.5 Na  Ba[N(C.sub.2 H.sub.5).sub.2
     ].sub.2 26 100  25 0 19.6 1.34 57 34  9 3.7  0.5  0.25 46 nC.sub.4
     H.sub.9 Na  Ba(CCC.sub.2 H.sub.5).sub.2 27 100  25 0 20.1 1.43 55 35 10
     3.5  0.5  0.25 47 nC.sub.4 H.sub.9 Na  Ba(CH.sub.3).sub.2 28 100  25 0
     21.8 1.49 56 35  9 3.9  0.5  0.25 48 nC.sub.4 H.sub.9 Na  C.sub.2
     H.sub.5 BaI 28 100
      25 0 19.9 1.41 50 39 113.5  0.5  0.25  Component*.sup.4 Component*.sup.
     4 Component*.sup.4  (1) (2) (3) 49 n-C.sub.5 H.sub.11
      Na Ba[OC(CH.sub.3).sub.3 ].sub.2 C.sub.2 H.sub.5 MgCl 24 95 25 0 22.2
     1.32 23 64 13 4.9  0.5 0.25 0.25 50 n-C.sub.5 H.sub.11
      Na Ba[OC(CH.sub.3).sub.3 ].sub.2 C.sub.2 H.sub.5 MgH 25 98 25 0 18.5
     1.38 25 62 13 4.8  0.5 0.25 0.25 51 n-C.sub.5 H.sub.11
      Na Ba[OC(CH.sub.3).sub.3 ].sub.2 C.sub.2 H.sub.5 MgOCH(CH.sub.3).sub.2
     25 99 25 0 19.9 1.33 26 61 13 4.7  0.5 0.25 0.25 52 n-C.sub.5 H.sub.11
     Na Ba[OC(CH.sub.3).sub.3 ].sub.2 (C.sub.2 H.sub.5).sub.2 AlCl 24 95 25 0
     28.6 1.23 39 51 10 5.1  0.5 0.25 0.25 53 n-C.sub.5 H.sub.11
      Na Ba[OC(CH.sub.3).sub.3 ].sub.2 (C.sub.2 H.sub.5).sub.2 AlH 25 99 25 0
     25.3 1.21 41 50  9 5.6  0.5 0.25 0.25 54 n-C.sub.5 H.sub.11
      Na Ba[OC(CH.sub.3).sub.3 ].sub.2 (C.sub.2 H.sub.5).sub.2
      AlOCH(CH.sub.3).sub.2 25 98 250 25.5 1.25 42 49  9 5.4  0.5 0.25 0.25
     55 n-C.sub.5 H.sub.11 Na Ba[OC(CH.sub.3).sub.3 ].sub.2 C.sub.2 H.sub.5
     Al[OCH(CH.sub.3).sub.2 ].sub.2 25 96 25 0 26.7 1.32 43 48  9 5.3  0.5
     0.25 0.25  56 n-C.sub.5 H.sub.11 NaO.5 Ba[OC(CH.sub.3).sub.3 ].sub.20.25
      ##STR14##
      25 100  25 0 25.3 1.27 40 51  9 5.7    0.25  57 n-C.sub.5 H.sub.11
     NaO.5 Ba[OC(CH.sub.3).sub.3
      ].sub.20.25
     ##STR15##-
     *.sup.1, *.sup.2, *.sup.3 and *.sup.4 : Please refer to Remarks of Table
     3.
CLMS
STM  We claim:
NUM  1.
PAR  1. A process for producing a conjugated diene polymer, a copolymer of a
     conjugated diene with at least one other conjugated diene, or a copolymer
     of a conjugated diene with an aromatic vinyl hydrocarbon comprising the
     step of polymerizing said monomer or monomers in the presence of an
     effective catalytic amount of a catalyst complex consisting essentially of
     the following components (a) and (b) or (a), (b) and (c):
PA1  (a)(1) an organosodium compound, having the general formula
EQU  R'(Na).sub.m
PA1  wherein R' is an aliphatic group, desirably having 1 to 30 carbon atoms, an
```

group, desirably having 6 to 30 carbon atoms or an unsaturated hydrocarbon group having at least one allyl hydrogen and desirably having 3 to 30 carbon atoms, and m is an integer of 1 through 4, (2) metallic sodium or (3) a sodium amide compound having the general formula

##STR16##

represents either a cyclized structure or a non-cyclized structure and R.sup.2 and R.sup.3 represent, in combination, a methylene chain having 2 to 10 carbon atoms in the case of a cyclized structure and R.sup.2 and R.sup.3 independently represent an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms in the case of a non-cyclized structure of (4) a mixture of at least one of the above components (1), (2), and (3) with an organic compound of sodium other than said sodium amide compound;

PA1 (b) an organic or organometallic compound of barium, strontium, or calcium; and

PA1 (c) an organometallic compound of an electron deficient metal selected from lithium, beryllium, magnesium, zinc, cadmium, boron, aluminum, gallium or indium, the amount of component (a) being 0.01 to 80 m mol per 100 g of the total monomers, the amount of component (b) being from 0.01 to 10 times the molar amount of component (a) and the amount of component (c) being from 0 to 5 times the molar amount of component (a).

NUM 2.

PAR 2. A process as claimed in claim 1, wherein said catalyst component (b) is an organic compound of barium.

NUM 3.

PAR 3. A process as claimed in claim 1, wherein said catalyst component (c) is an organolithium compound, an organomagnesium compound, or an organoaluminum compound.

NUM 4.

PAR 4. A process as claimed in claim 1, wherein said conjugated diene is butadiene or isoprene and said aromatic vinyl hydrocarbon is styrene.

NUM 5.

PAR 5. A process as claimed in claim 1, wherein polymerization is carried out in 300 to 1000 parts by weight per 100 parts by weight of the total monomer of a hydrocarbon solvent at a temperature of 30.degree. to 120.degree. C. in the presence of a catalyst complex comprising 0.1 to 1 m mol of the component (a) based on 100 g of the total monomers, an amount of component (b) of 0.1 to 1 times the molar amount of component (a) and an amount of component (c) of 0 to 2 times the molar amount of component (a).

NUM 6.

PAR 6. A catalyst complex suitable for use in the production of a conjugated diene polymer, a copolymer of a conjugated diene with at least one other conjugated diene, or a copolymer of a conjugated diene with an aromatic vinyl hydrocarbon consisting essentially of the following components (a) and (b) or (a), (b) and (c):

PA1 (a)(1) an organosodium compound, having the general formula

EQU R'(Na).sub.m

PA1 wherein R' is an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms or an unsaturated hydrocarbon group having at least one allyl hydrogen and desirably having 3 to 30 carbon atoms, and m is an integer of 1 through 4, (2) metallic sodium or (3) a sodium amide compound having the general formula

##STR17##

```
EQU  R'(Na).sub.m
PA1  wherein R' is an aliphatic group, desirably having 1 to 30 carbon atoms, an
      alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic
      group, desirably having 6 to 30 carbon atoms or an unsaturated hydrocarbon
      group having at least one allyl hydrogen and desirably having 3 to 30
      carbon atoms, and m is an integer of 1 through 4, (2) metallic sodium or
      (3) a sodium amide compound having the general formula
      ##STR16##
      represents either a cyclized structure or a non-cyclized structure and
      R.sup.2 and R.sup.3 represent, in combination, a methylene chain having 2
      to 10 carbon atoms in the case of a cyclized structure and R.sup.2 and
      R.sup.3 independently represent an aliphatic group, desirably having 1 to
      30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon
      atoms, or an aromatic group, desirably having 6 to 30 carbon atoms in the
      case of a non-cyclized structure of (4) a mixture of at least one of the
      above components (1), (2), and (3) with an organic compound of sodium
      other than said sodium amide compound;
PA1  (b) an organic or organometallic compound of barium, strontium, or calcium;
      and
PA1  (c) an organometallic compound of an electron deficient metal selected from
      lithium, beryllium, magnesium, zinc, cadmium, boron, aluminum, gallium or
      indium, the amount of component (a) being 0.01 to 50 m mol per 100 g of
      the total monomers, the amount of component (b) being from 0.01 to 10
      times the molar amount of component (a) and the amount of component (c)
      being from 0 to 5 times the molar amount of component (a).
NUM  2.
PAR  2. A process as claimed in claim 1, wherein said catalyst component (b) is
      an organic compound of barium.
NUM  3.
PAR  3. A process as claimed in claim 1, wherein said catalyst component (c) is
      an organolithium compound, an organomagnesium compound, or an
      organoaluminum compound.
NUM  4.
PAR  4. A process as claimed in claim 1, wherein said conjugated diene is
      butadiene or isoprene and said aromatic vinyl hydrocarbon is styrene.
NUM  5.
PAR  5. A process as claimed in claim 1, wherein polymerization is carried out
      in 300 to 1000 parts by weight per 100 parts by weight of the total
      monomer of a hydrocarbon solvent at a temperature of 30.degree. to
      120.degree. C. in the presence of a catalyst complex comprising 0.1 to 1 m
      mol of the component (a) based on 100 g of the total monomers, an amount
      of component (b) of 0.1 to 1 times the molar amount of component (a) and
      an amount of component (c) of 0 to 2 times the molar amount of component
      (a).
NUM  6.
PAR  6. A catalyst complex suitable for use in the production of a conjugated
      diene polymer, a copolymer of a conjugated diene with at least one other
      conjugated diene, or a copolymer of a conjugated diene with an aromatic
      vinyl hydrocarbon consisting essentially of the following components (a)
      and (b) or (a), (b) and (c):
PA1  (a)(1) an organosodium compound, having the general formula
EQU  R'(Na).sub.m
PA1  wherein R' is an aliphatic group, desirably having 1 to 30 carbon atoms, an
      alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic
      group, desirably having 6 to 30 carbon atoms or an unsaturated hydrocarbon
      group having at least one allyl hydrogen and desirably having 3 to 30
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carbon atoms, and m is an integer of 1 through 4, (2) metallic sodium or (3) a sodium amide compound having the general formula
##STR17##
represents either a cyclized structure or a non-cyclized structure and R.sup.2 and R.sup.3 represent, in combination, a methylene chain having 2 to 10 carbon atoms in the case of a cyclized structure and R.sup.2 and R.sup.3 independently represent an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms in the case of a non-cyclized structure or (4) a mixture of at least one of the above components (1), (2), and (3) with an organic compound of sodium other than said sodium amide compound;

PA1 (b) an organic or organometallic compound of barium, strontium, or calcium; and

PA1 (c) an organometallic compound of an electron deficient metal selected from lithium, beryllium, magnesium zinc, cadmium, boron, aluminum, gallium or indium, the amount of component (a) being 0.01 to 50 m mol per 100 g of the total monomers, the amount of component (b) being from 0.01 to 10 times the molar amount of component (a) and the amount of component (c) being from 0 to 5 times the molar amount of component (a).

NUM 7.

PAR 7. A catalyst complex as claimed in claim 6, wherein said catalyst component (b) is an organic compound of barium.

NUM 8.

PAR 8. A catalyst complex as claimed in claim 6, wherein said catalyst component (c) is an organolithium compound, an organomagesium compound, or an organoaluminum compound.

NUM 9.

PAR 9. A catalyst complex as claimed in claim 9, wherein said conjugated diene is butadiene or isoprene and said aromatic vinyl hydrocarbon is styrene.

NUM 10.

PAR 10. A catalyst complex as claimed in wherein the catalyst complex comprises 0.1 to 1 m mol of the component (a) based on 100 g of the total monomers, an amount of component (b) of 0.1 to 1 times the molar amount of component (a) and an amount of component (c) of 0 to 2 times the molar amount of component (a).

NUM 11.

PAR 11. A catalyst complex as claimed in claim 9, wherein the catalyst complex comprises 0.1 to 1 m mol of the component (a) based on 100 g of the total monomers, an amount of component (b) of 0.1 to 1 times the molar amount of component (a) and an amount of component (c) of 0 to 2 times the molar amount of component (a).

NUM 12.

PAR 12. The process of claim 4, wherein polymerization is carried out in 300 to 1000 parts by weight per 100 parts by weight of the total monomer of a hydrocarbon solvent at a temperature of 30.degree. to 120.degree. C. in the presence of a catalyst complex comprising 0.1 to 1 m mol of the component (a) based on 100 g of the total monomers, an amount of component (b) of 0.1 to 1 times the molar amount of component (a) and an amount of component (c) of 0 to 2 times the molar amount of component (a).

APPENDIX E

Patent Documents as they appear when issued and printed.

United States Patent [19]

Ocker

[11] **Des. 264,735**

[45] ** **Jun. 1, 1982**

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[54] NOVELTY BINOCULARS

[76] Inventor: Anna M. Ocker, 1857 Santa Gertrudis Dr., Bismarck, N. Dak. 58501

[**] Term: 14 Years

[21] Appl. No.: 140,230

[22] Filed: Apr. 14, 1980

[51] Int. Cl. .... D21—01

[52] U.S. Cl. D21/59; D21/109

[58] Field of Search .... D16/133; D21/59, 60, D21/240, 109, 241; D9/307; 272/1 R, 8 R, 8 N; 46/1 R

[56] References Cited

U.S. PATENT DOCUMENTS

D. 14,423	11/1883	Bradley	D9/307
D. 116,921	10/1939	Sierad	D9/307
D. 123,103	10/1940	Murray	D9/341
D. 238,304	12/1975	Hengst et al.	D16/133

Primary Examiner—Charles A. Rademaker

Attorney, Agent, or Firm—Kinney, Lange, Braddock, Westman and Fairbairn

[57] CLAIM

The ornamental design for novelty binoculars, as shown.

DESCRIPTION

FIG. 1 is a perspective view of novelty binoculars, showing my new design;

FIG. 2 is a right side elevational view thereof;

FIG. 3 is a top view thereof; and,

FIG. 4 is a bottom plan view thereof.

Fig. 1

Fig. 2

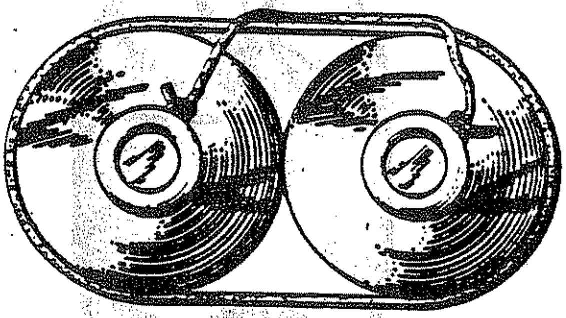
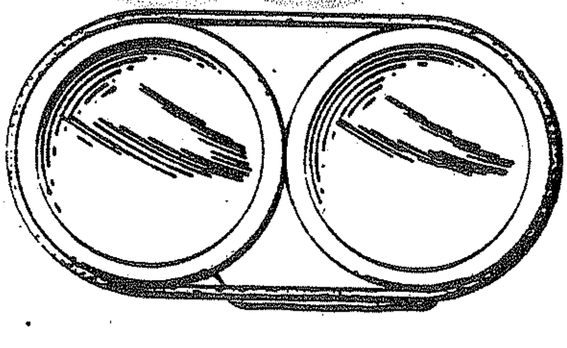


Fig. 3

Fig. 4



United States Statutory Invention Registration [19]

Buchanan, Jr. et al.

[11] **Reg. Number:** **H40**

[45] **Published:** **Apr. 1, 1986**

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[54] **FIELD SHIELDS FOR SCHOTTKY BARRIER DEVICES**

[75] Inventors: **William L. Buchanan, Jr.**, Reading; **James E. Kohl**, Wyomissing; **Robert S. Scott**, Spring Township, Berks County, all of Pa.; **Yiu-Huen Wong**, Berkeley Heights, N.J.

[73] Assignee: **AT&T Bell Laboratories**

[21] Appl. No.: **632,053**

[22] Filed: **Jul. 18, 1984**

[51] **Int. Cl.⁴** **H01L 29/48**; H01L 29/06

[52] **U.S. Cl.** **357/15**; 357/53; 357/20; 357/52

[58] **Field of Search** 357/15

[56] **References Cited**

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3,541,403	11/1970	Lepselter et al.	317/204
3,616,380	10/1971	Lepselter et al.	204/164
4,119,446	10/1978	Mastroianni	148/1.5
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FOREIGN PATENT DOCUMENTS

5224465	2/1977	Japan	357/15 M

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"Silicon Schottky Barrier Diode. . .", *Bell System Technical Journal*, vol. 47, No. 2, Feb. 1968 , pp. 195-208, Lepselter et al.

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"Optimum Doping Profile. . .", *IEEE Transactions on Electron Devices*, vol. Ed-26, No. 3, Mar. 1979, pp. 243-244, C. Hu.

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"High-Voltage Power Schottky. . .", *IBM Technical Disclosure Bulletin*, vol. 25, No. 5, Oct. 1982, pp. 2331-2333, Jambotkar.

"Electric-Field-Shielding Layers. . .", *Electronics Letters*, vol. 19, No. 15, Jul. 21, 1983, pp. 568-570, S. Nakashima et al.

Primary Examiner—S. C. Buczinski
Assistant Examiner—Linda J. Wallace
Attorney, Agent, or Firm—Wendy W. Koba

[57] **ABSTRACT**

The present invention relates to an improved Schottky barrier device wherein the leakage current present in the reverse bias mode attributed to the presence of an electric field at the Schottky barrier (**18**) is significantly reduced by the inclusion of one or more field shields (**22**), P+-type diffusions located under the metal anode (**16**) of the Schottky barrier device at the Schottky barrier (**18**). The P+-type field shields, which are disposed in a pattern on the surface of the Schottky barrier, reduce the surface electric field present, thereby significantly reducing the leakage current related thereto.

13 Claims, 8 Drawing Figures

A statutory invention registration is not a patent. It has the defensive attributes of a patent but does not have the enforceable attributes of a patent. No article or advertisement or the like may use the term patent, or any term suggestive of a patent, when referring to a statutory invention registration. For more specific information on the rights associated with a statutory invention registration see 35 U.S.C. 157.

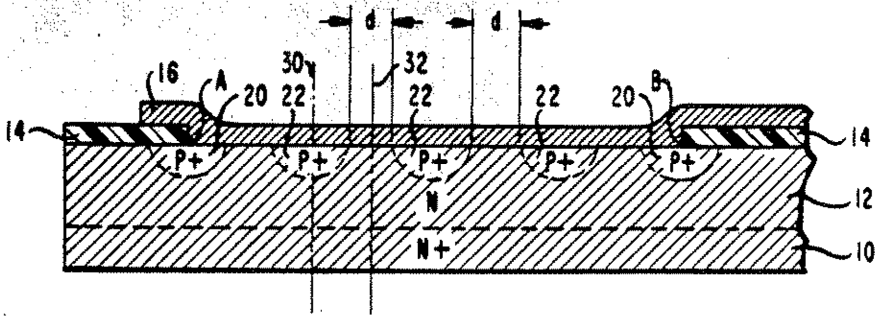


FIG. 1

(PRIOR ART)

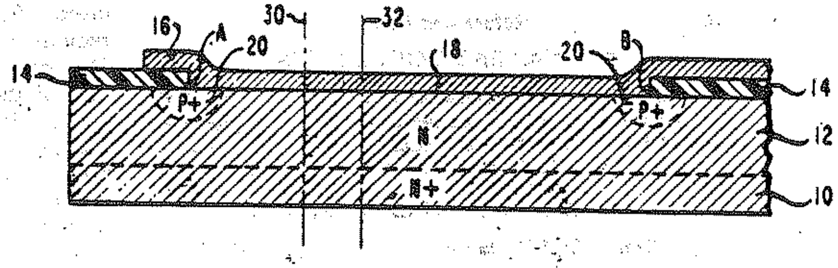


FIG. 2

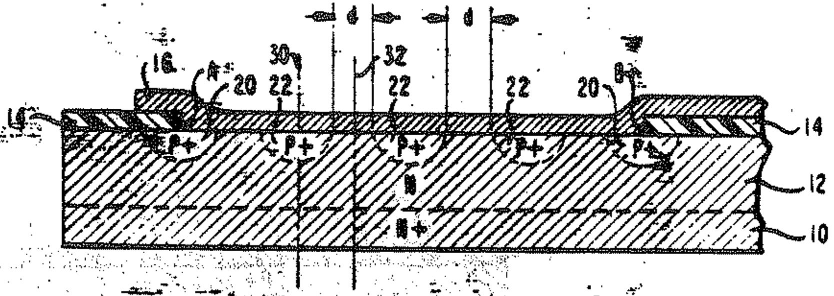


FIG. 3

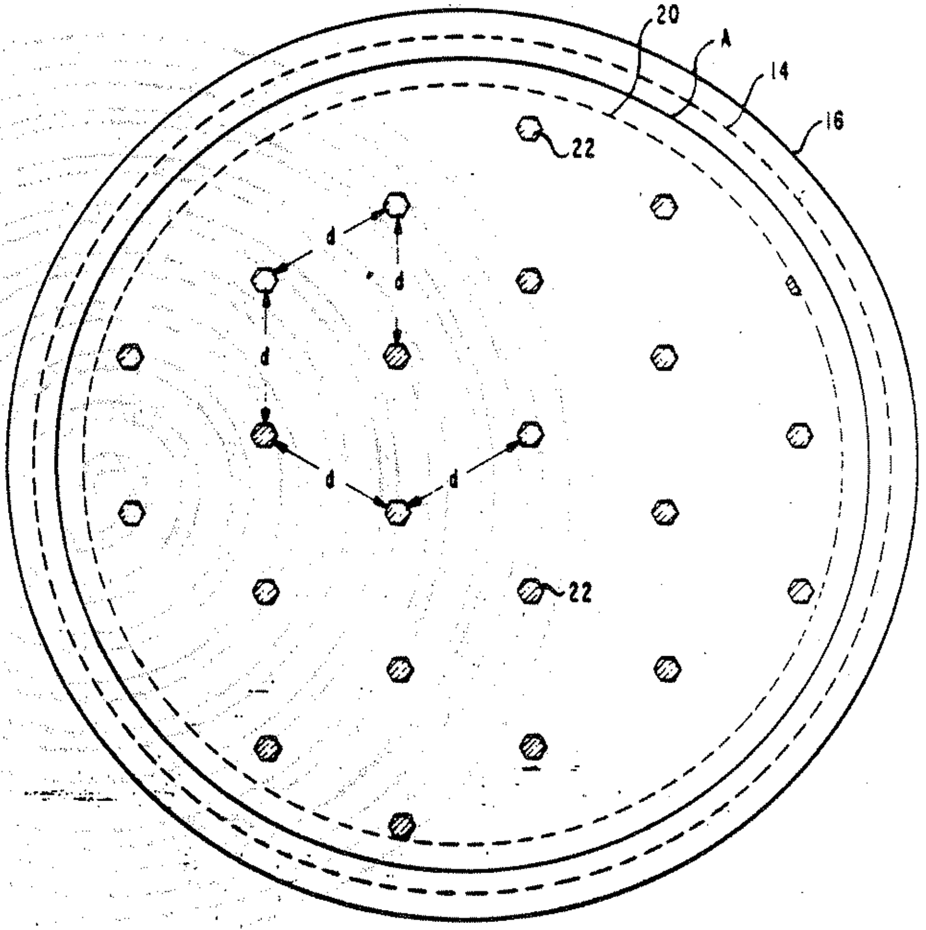


FIG. 4

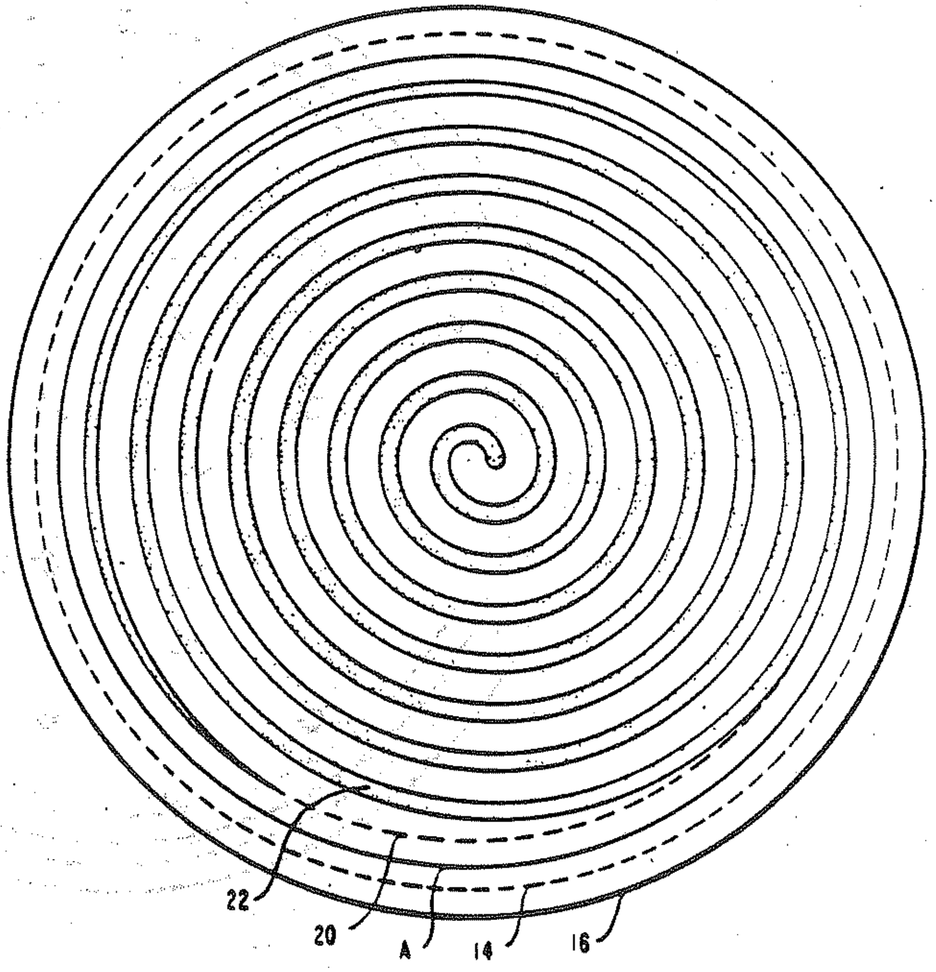


FIG. 6

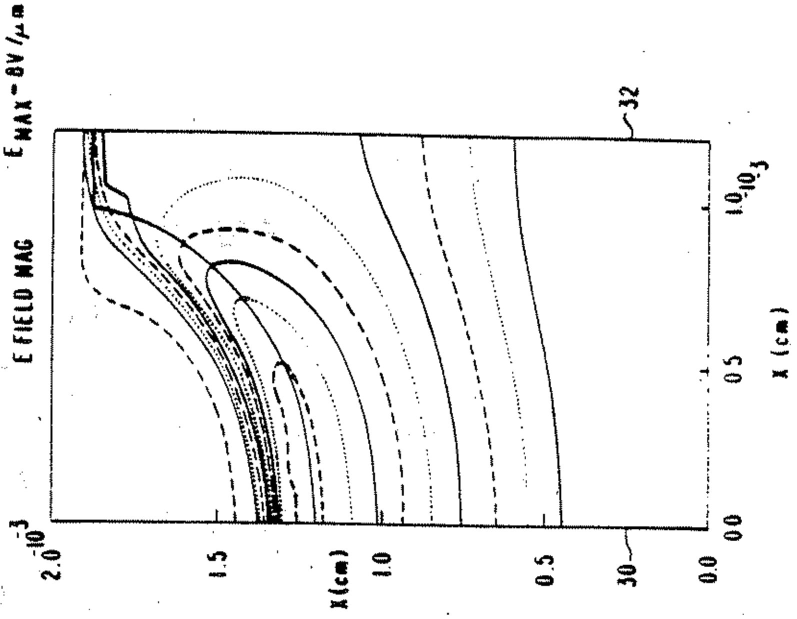


FIG. 5
(PRIOR ART)

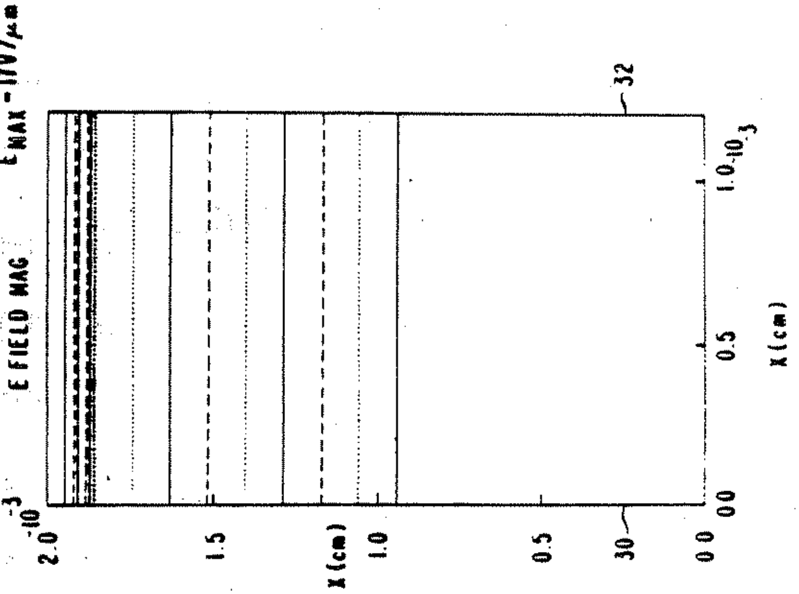


FIG. 7

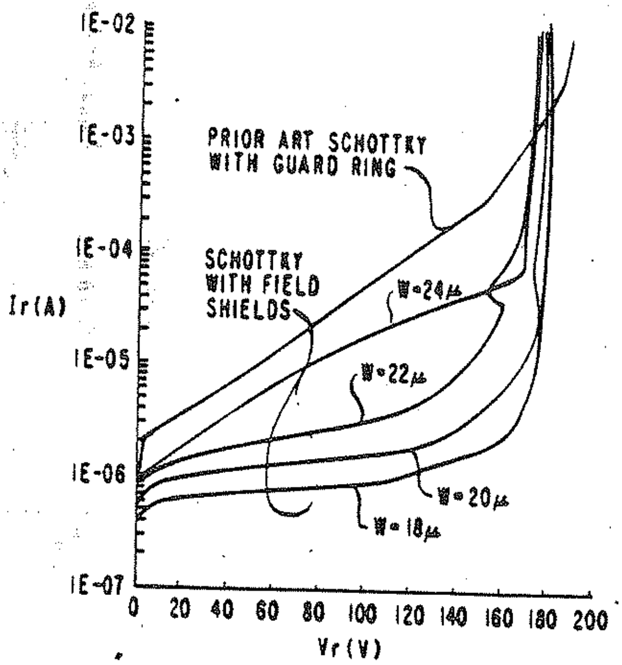
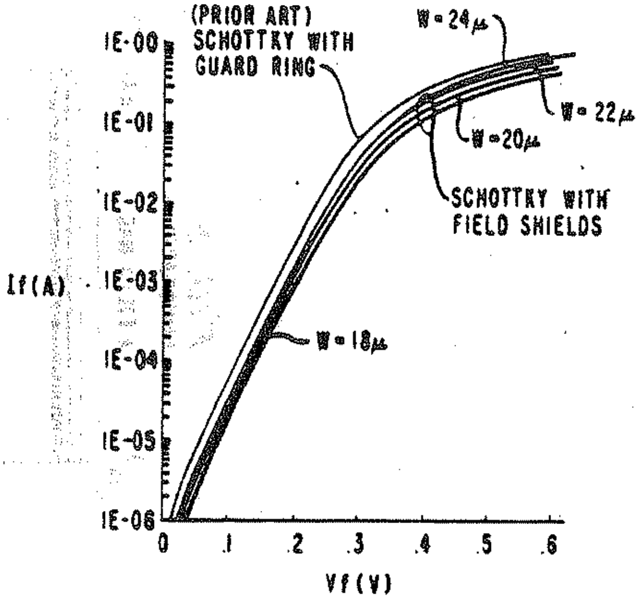

1E-02
1E-03
1E-04
1E-05
1E-06
1E-07
Ir(A)
PRIOR ART SCHOTTKY WITH GUARD RING
SCHOTTKY WITH FIELD SHIELDS
W=24μ
W=22μ
W=20μ
W=18μ
0
20
40
60
80
100
120
140
160
180
200
Vr(V)

FIG. 8


(PRIOR ART) SCHOTTKY WITH GUARD RING
W=24μ
W=22μ
W=20μ
SCHOTTKY WITH FIELD SHIELDS
W=18μ
1E-00
1E-01
1E-02
1E-03
1E-04
1E-05
1E-06
If(A)
0
.1
.2
.3
.4
.5
.6
Vf(V)

FIELD SHIELDS FOR SCHOTTKY BARRIER DEVICES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the inclusion of field shields in Schottky barrier devices, and more particularly, to the inclusion of one or more field shield diffusions at the metal-semiconductor interface to reduce the surface electric field along the interface, thereby decreasing the reverse bias leakage current of Schottky barrier devices.

2. Description of the Prior Art

Schottky barrier (metal-semiconductor) devices, in particular, diodes, are often used in circuits because they have a low forward voltage drop and a very fast reverse recovery time. These properties make Schottky diodes very useful in applications such as high-speed switching power supply rectifiers. However, compared with conventional p-n junction diodes, Schottky barrier diodes exhibit poor reverse bias characteristics manifested in an increased leakage, particularly at voltages approaching breakdown voltage.

In the past, the reverse characteristics of Schottky barrier diodes were improved by increasing the breakdown voltage of the device, utilizing p-type guard rings diffused into the n-type semiconductor material, as disclosed in U.S. Pat. No. 3,541,403 issued to M. P. Lepselter et al on Nov. 17, 1970. As disclosed, the guard ring is located in the substrate under the insulator-metal interface and functions to reduce the edge breakdown effects existing at the intersection of this interface and the semiconductor surface. The same guard ring structure is discussed in an article entitled "Silicon Schottky Barrier Diode with Near-Ideal I-V Characteristics" by M. P. Lepselter et al appearing in *Bell System Technical Journal*, Vol. 47, No. 2, pp. 195–208.

An improved method for forming guard rings in Schottky barrier diodes is disclosed in U.S. Pat. No. 4,119,446 issued to S. T. Mastroianni on Oct. 10, 1978. Here, the metal-semiconductor structure is formed first and the metal is then used in conjunction with another mask to form a guard ring self-aligned with the periphery of the metal.

Although the use of guard rings will improve the reverse characteristics of Schottky barrier diodes by reducing the edge breakdown effects, relatively large leakage current in the reverse blocking mode will still exist, due to the presence of a high surface electric field along the planar metal-semiconductor interface away from the edge of the interface. This leakage current generally increases very rapidly as the reverse potential is increased and may be several orders of magnitude larger than the leakage current of a diffused junction diode when the electric field approaches the silicon avalanche limit.

In order to reduce the Schottky barrier diode reverse leakage current, a Schottky metal (or metal silicide) which has a high barrier potential can be utilized. Although this will improve the reverse characteristics, the high barrier potential results in a higher forward voltage drop and, therefore, greater power dissipation than desired. In an alternative method, the electric field is reduced at the Schottky barrier when the device is under reverse bias, which results in reducing the leakage current. In particular, the electric field is reduced by increasing the resistivity and depth of the N-type silicon cathode (for the case of a metal-N silicon diode). However, this method of decreasing the leakage current will result in an increased series resistance between the anode and the cathode and thus will again result in an increased forward voltage drop. Further, this method is not very desirable in high-voltage integrated circuit technology since the N-type cathode material may also be used as collectors or drains of bipolar or MOS transistors, respectively, and the increased resistivity will adversely affect the characteristics of these devices.

There remains to be solved the problem of eliminating the leakage current present in Schottky barrier devices related to the presence of a surface electric field without unnecessarily increasing the forward voltage drop of the device.

SUMMARY OF THE INVENTION

The above-described problem is addressed by the present invention which relates to the inclusion of field shields in Schottky barrier devices and, more particularly, to the inclusion of one or more field shield diffusions at the metal-semiconductor interface to reduce the surface electric field along the interface, thereby decreasing the reverse bias leakage current of Schottky barrier devices without appreciably increasing the forward bias voltage drop.

It is an aspect of the present invention to diffuse a plurality of closely-spaced P-type regions, referred to as field shields, into an N-type semiconductor substrate (or to diffuse N-type regions into a P-type substrate). The field shields function to modify and thus reduce the surface electric field at the metal-semiconductor interface (Schottky barrier), thereby reducing the reverse leakage current and only moderately increasing the series resistance, without increasing the Schottky barrier height or the cathode material resistivity.

Another aspect of the present invention is to utilize a single P-type diffusion region to reduce the surface electric field, where the single diffusion forms a continuous pattern, for example, a spiral or snake pattern, on the Schottky barrier surface.

Yet another aspect of the present invention is the design of the spacing between the field shields as well as the overall pattern of the diffusions such that the reverse leakage current is reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the drawings,

FIG. 1 illustrates a cross-sectional view of a prior art Schottky barrier diode, including a guard ring structure which increases the breakdown voltage related to edge breakdown effects;

FIG. 2 illustrates a cross-sectional view of a Schottky barrier diode formed in accordance with the present invention which includes a plurality of field shields to reduce the leakage current associated with the surface electric field;

FIG. 3 illustrates a top view of an exemplary Schottky barrier diode formed in accordance with the present invention, where the field shields are distributed in a hexagonal array pattern;

FIG. 4 illustrates a top view of an alternative Schottky barrier diode formed in accordance with the present invention, where the field shield comprises a single diffusion disposed in a spiral pattern;

FIGS. 5 and 6 illustrate the calculated electric field contours associated with a prior art Schottky barrier diode (FIG. 5) and a Schottky barrier diode formed in accordance with the present invention (FIG. 6);

FIG. 7 illustrates the reverse bias current-voltage I-V characteristics for a prior art Schottky barrier diode and a plurality of Schottky barrier diodes formed in accordance with the present invention; and

FIG. 8 illustrates the forward I-V characteristics for a prior art Schottky barrier diode and a plurality of Schottky barrier diodes formed in accordance with the present invention.

DETAILED DESCRIPTION

In order to aid in the understanding of the present invention, the properties of a prior art Schottky barrier diode will be briefly explained with reference to FIG. 1. As shown, an exemplary prior art Schottky barrier diode comprises an N^+-type cathode layer 10 upon which is deposited an N^--type substrate region 12. An insulating layer 14 is subsequently deposited on N^- substrate region 12, where a central portion of insulating layer 14 is then etched away, exposing N^- substrate region 12. A metallic layer 16, which forms the anode of the prior art Schottky barrier device, is deposited into the opening created by the etchant and possibly overlaps a portion of insulating layer 14, as illustrated in FIG. 1. Many different metals and alloys may be used as layer 16, where nickel silicide is considered to be one alternative. It is to be understood that a Schottky barrier diode may also be formed with a P-type substrate region and the use of an N-type region throughout the present discussion is considered to be exemplary only.

As is well known, a Schottky barrier diode differs from a conventional diffused p-n junction diode in that Schottky barrier diodes are metal-semiconductor junction devices, where Schottky-barrier 18 is illustrated in FIG. 1. As previously discussed, prior art Schottky barrier diodes attempted to improve the reverse operating characteristics by increasing the reverse breakdown voltage which is related to edge breakdown effects. This was accomplished by the inclusion of an annular guard ring, illustrated in FIG. 1 (in a cross-sectional view) as P-type diffusion 20, where the edges which produce the breakdown effect are indicated at points A and B. As discussed in the above-cited prior art references, guard ring 20 forms a "protection" p-n diode in parallel with the Schottky barrier diode, thus increasing the reverse breakdown voltage of the device. The leakage current related to the electric field along the planar region of Schottky barrier 18 far from guard ring 20, however, is not reduced or eliminated by the inclusion of guard ring 20 in the Schottky barrier diode.

A Schottky barrier diode formed in accordance with the present invention, capable of significantly reducing the surface electric field, which in turn functions to reduce the reverse bias leakage current, is illustrated in FIG. 2. As can be seen, this device differs from the prior art arrangement of FIG. 1 by the addition of a plurality of field shields 22, P^+-type diffusions disposed in a predetermined geometric pattern inside guard ring 20, where the individual diffusions are separated from one another by predetermined distances. Although the cross-sectional view of FIG. 2 shows only three field shield diffusions, in the actual practice of the present invention, a large plurality of field shields, for example, hundreds or even thousands, may be diffused into substrate region 12 in the opening created by annular guard ring 20. Alternatively, field shield 22 could be formed using a single P^+-type diffusion in the form of a spiral, or any other type of continuous pattern, over the planar surface of Schottky barrier 18.

In accordance with the present invention, the illustrated distance d separating the plurality of field shields 22, for an embodiment utilizing a plurality of field shields, must be small enough such that their respective depletion regions merge together at reverse potentials well below the avalanche breakdown of the Schottky barrier diode in order to significantly reduce the surface electric field. In the case of a single field shield diffusion, the distance separating adjacent portions of the diffusion must also be small enough to allow the depletion region of the adjacent portions to merge in a similar fashion. Further, the deeper the plurality field shields 22 are diffused into N^--type substrate 12, and the closer they are spaced, the larger the two-dimensional field-lowering effect will be.

As stated before, the layout of field shields 22 may comprise one of many different geometrical patterns, where the chosen pattern affects the reduction of the surface electric field along the planar region of Schottky barrier 18 located between field shields 22, thus also affecting the resultant decrease in reverse bias leakage current. One exemplary pattern of field shields 22 is shown in FIG. 3, which illustrates a top view of an exemplary Schottky barrier diode with the plurality of field shields 22 disposed in a hexagonal array arrangement. In the hexagonal arrangement, the distance, d separating adjacent field shield diffusions will be constant. Alternatively, the layout pattern may be a set of concentric rings, where the separation between adjacent rings is designed to provide the desired reduction in reverse bias leakage while not greatly increasing the forward bias voltage drop. A single diffusion, as stated above, may also be utilized to reduce the surface electric field. For example, a continuous snake or spiral diffusion pattern over the surface of Schottky barrier 18 can be used to reduce this surface electric field. FIG. 4 illustrates one exemplary embodiment of the present invention where a spiral diffusion pattern is utilized. Other geometric patterns which may be utilized include a rectangular array, or a set of long, parallel stripes, where these patterns are illustrative only and many other patterns may be utilized in accordance with the present invention to provide sufficient improvement in reducing reverse bias leakage current without seriously degrading the forawrd bias voltage drop.

Referring now to FIGS. 5 and 6, the effect on the surface electric field related to the inclusion of the plurality of field shields 22 is demonstrated. FIG. 5 illustrates the calculated electric field contours associated with a prior art Schottky barrier diode, as discussed hereinabove in association with FIG. 1, and FIG. 6 illustrates the electric field contours associated with a Schottky barrier diode formed in accordance with the present invention at the same reverse bias potential as associated with FIG. 5. The illustrated electrical field contours correspond to the electric field present in N^- substrate region 12 as measured in the X (width) and Z (depth) directions, between vertical lines 30 and 32 shown in FIGS. 1 and 2. As can be seen, the inclusion of field shields 22 reduces the maximum magnitude of the electric field at Schottky barrier junction 18, thereby reducing the leakage current associated therewith.

FIG. 7 contains a semi-log graph illustrating the reverse I-V characteristics of both a prior art Schottky tially determine final bolt tension in production operations. Second, because of the selection of some parameter other than tension, there is introduced such widely variable factors as friction coefficients, speed related losses, and the like which grossly affect the relationship between the fixed tightening parameter or the fixed range thereof and the only important result in tightening, which is clamping load or bolt tension.

In one aspect, this invention contemplates the determination, during tightening, of the value of a tightening parameter which is sufficient to tighten each fastener pair to a final desired tension value, which parameter varies from one fastener pair to the next. Tightening of the fastener pair is then terminated in response to the variable value of the determined tightening parameter. By this approach, the variation in friction from one fastener pair to the next is largely eliminated. The technique of this invention produces typical tension scatters on the order of less than ±10% in production quantities whereas scatters with turn-of-the-nut techniques are at least 2–3 times higher and scatter with torque control techniques are at least 5–6 times higher. It is accordingly apparent that this invention produces substantially more consistent tightening results than do the significantly inaccurate techniques of the prior art.

In another aspect, an important part of this invention constitutes the quality control procedures that are conducted as a consequence of the acquisition of torque and angle data of each fastener tightened. Most of the quality control procedures are done well prior to the termination of tightening and include procedures for determining whether the prevailing torque of the fastener is too high, determining whether the torque rate of the fastener is linear or arcuate, determining whether the torque rate of the fastener is too low, determining whether the tool is performing normally and determining whether the fastener has exhibited significant nonlinear strain. Any of the fastener related quality control checks are used to prematurely terminate tightening in the event indications are that the fastener or its mating engagement with the clamped pieces is defective. The tool related quality control checks provide a warning so that maintenance attention can be given to the tool.

It is accordingly an object of this invention to provide a technique for tightening threaded fasteners which produces substantially more consistent results than the prior art.

Another object of the invention is to provide a tightening technique which provides sufficient data to conduct a number of quality control procedures during tightening.

Another object of this invention is to provide an improved technique for tightening threaded fasteners incorporating monitoring the torque-angle curve, calculating the tension in the fastener being tightened and instructing a tool to tighten the fasteners to a final desired tension value.

Another object of this invention is to provide an improved technique for tightening threaded fasteners incorporating the monitoring of the torque-angle relationship, calculating during tightening the tension appearing in the fastener being tightened and instructing the wrench to continue tightening until a predetermined value of torque or angle is obtained which corresponds to the final desired tension value.

Other aspects, objects and advantages of this invention will become apparent as the description proceeds.

IN THE DRAWINGS

FIG. 1 is an illustration of typical torque-angle and tension-angle curves generated during the continuous tightening of a fastener pair far beyond the elastic limit;

FIG. 2 is an enlarged illustration of the low end of a typical torque-angle curve illustrating very early torque-angle relationships;

FIG. 3 is an enlarged illustration of a typical torque-angle curve constituting a continuation of FIG. 2;

FIG. 4 is an illustration of a typical torque-speed relationship of an air powered tool;

FIG. 5 is a torque-angle diagram illustrating the determination of non-linear strain in the fastener at the mid-point stop;

FIG. 6 is an illustration of a typical tension-angle curve representing the relaxation of a joint at the termination of continuous tightening;

FIG. 7 is an illustration of a typical tension-angle curve representing the relaxation of the joint at the mid-point stop during tightening to a higher tension value;

FIG. 8 is a torque-angle diagram illustrating the determination of non-linear strain in the fastener during tightening toward a final tightening parameter;

FIG. 9 is an enlarged illustration of torque-angle and tension-angle curves graphically explaining another facet of the invention;

FIG. 10 is a schematic view of the mechanism of this invention;

FIG. 11 is a side view of a component of the mechanism of FIG. 10;

FIGS. 12A and 12B are circuit diagrams of another component of the device of FIG. 10;

FIG. 13 is a front view of a typical operator's console;

FIG. 14 is a graph illustrating the relative effectiveness of this invention compared to prior art techniques; and

FIG. 15 is a block diagram illustrating another mechanism of this invention.

Referring to FIG. 1, there is illustrated a typical torque-angle curve 10 and its corresponding tension-angle curve 12 which are developed during the continuous threading of a fastener pair to a point far beyond the elastic limit of the bolt, as may be measured in the laboratory by suitable equipment. In the torque curve 10, there is typically a free running region or period 14 where only a small torque is required to advance the nut and no appreciable bolt tension exists. This is followed by a region or period 16 of incipient clamp up where the joint parts are being brought toward engagement. This is followed by an engagement period or region 18 where the contact between the surfaces of the fastener and the clamped pieces are being established while the rate of angle advance is gradually being reduced in accordance with the torque-speed characteristics of the tool employed. The tension rate FR_1 in the region 18 is typically less than the ultimate tension rate FR_2 but is rather well defined. The engagement period 18 appears to cover an approximate tension range of about ten percent to about fifty percent of the elastic limit of the bolt. Above the engagement region 18 is a final tensioning region or period 20 which normally exhibits an increased tension rate FR_2. Fortunately, FR_1, FR_2 and the location of the bend therebetween are normally well defined and reproducible properties of the joint and are not related to friction or other variable factors which may develop in the course of tightening.

The torque rate is essentially zero in the free running region **14** and begins to rise substantially during the incipient clamp up period **16**. The torque rate TR in the engagement period **18** approaches linearity. Due to the existence of speed-dependent losses such as lubricant squeeze film and microplasticity of the surface irregularities between the fastener parts and clamped pieces, a linear approximation of the torque curve **10** in the region **18** does not intersect the angle axis at the point of origin of the tension curve **12**. An offset angle α_{os} exists which is proportional to such speed dependent losses. α_{os} describes the angular separation between the origin of the average torque slope TR and the origin of the average tension slope FR_1. Because of the torque-speed curve of the tool employed, it can be shown that α_{os} is torque rate dependent so that the offset torque T_{os} is the appropriate joint property and T_{os} is the product of the offset angle α_{os} and the torque rate TR.

The elastic limit **22** occurs at a point beyond which strain is not receivable upon unloading and appears toward the upper end of the final tightening region **20** as is well known in classical mechanics. Somewhere in the yield region **24**, the bolt commences to deform plastically rather than elastically. As alluded to previously, the normal definition of the yield point is in range of 0.1–0.2% strain which is somewhat arbitrary. The proportional limit occurs substantially below the yield point **22** and occurs where the stress/strain ratio is no longer constant.

In order to implement the hereinafter disclosed method of tension control, one needs to determine FR_1, FR_2, T_{os} and other parameters as discussed more fully hereinafter. This is conveniently accomplished by selecting a reasonably large sample of the fasteners that ultimately will be tightened by the technique of this invention and empirically determining the values in the laboratory. It will normally be experienced that scatters in FR_1 and either FR_2 or r, the ratio of FR_2/FR_1, will be quite small. In new bolts, FR_2 is normally 5–15% higher than FR_1. In fasteners that have previously been tightened, FR_2 is normally quite close to FR_1. The conclusion is that the difference between FR_1 and FR_2 is related to the microplasticity of surface irregularities between the mating faces of the joint. As is true in all torque measurements, T_{os} will have much larger scatters. Fortunately, the offset torque correction is normally quite small so that its lack of consistency has a quite minimal effect of the final tension values. One exception is in the use of so-called "prevailing torque" fasteners which usually comprise a bolt or nut having the threads intentionally deformed for various reasons. Another exception involves the use of a bolt or nut in which the threads are unintentionally deformed. In such situations, the normal value of T_{os} should be increased by the addition of the measured "free running" or prevailing torque or this effect compensated for as more fully explained hereinafter.

Broadly, the technique of this invention is to periodically or continuously sense the torque applied to the fastener pair and the angle of advance corresponding to the sensed torque, determine the tension appearing at least at one point **26**, calculate a value of a tightening parameter sufficient to achieve a final desired tension value F_D and instruct a tool to advance the fastener pair until the attainment of the tightening parameter.

During a study of torque-tension-angle relationships, it was discovered that the inverse of the rate with respect to angle of the logarithm of torque is theoretically a measure of bolt tension irrespective of joint friction. Defining,

$$P \equiv (d/d\alpha) \log T \tag{2}$$

$$F \propto (1/P),\ \alpha > \alpha_q \tag{3}$$

where α_q is the angle where P achieves a maximum value and conceivably could be used as the origin for the turn-of-the-nut method thereby totally eliminating the influence of joint friction. In practice, it is difficult to detect a single meaningful peak which can be labeled α_q because of the noise inherent in the actual torque-angle signal. Although the concept expressed in equation (2) is valid, it requires a different procedure for processing the torque-angle data to achieve a practical solution. As will be apparent to those skilled in the art, the solution may be analog or digital. The theoretical basis for equation (2) can be derived from equation (1). Differentiating equation (1) relative to angle,

$$\frac{dT}{d\alpha} = (f_h r_h + f_{th} r_{th}) \frac{dF}{d\alpha}. \tag{4}$$

Dividing equation (4) by equation (1),

$$(dT/d\alpha)/T = (dF/d\alpha)/F. \tag{5}$$

Since dT/T is the definition of d log T,

$$(dF/d\alpha)/F = (d/d\alpha) \log T. \tag{6}$$

If $dF/d\alpha$, the joint tension rate, is a constant, then:

$$F = \left(\frac{dF}{d\alpha}\right) \left(\frac{d}{d\alpha} \log T\right)^{-1} = FR/P. \tag{7}$$

Equation (7) shows that the constant of proportionality in equation (3) is the tension rate FR..

Several assumptions have been made in the above derivation:

(1) The tension rate is a constant. This is not precisely true throughout the tightening range. The more precise assumption would have been that tension at any angle of advance after the angle of origin, where the tension rate commences, is a unique function of the joint and therefore that the tension rate at any angle after the angle of origin is a unique function of the joint.

(2) Torque is not a function of the turning speed. This is not strictly true and for accurate application, it should be accounted for.

(3) Joint friction (f_h, f_{th}) is not load dependent for any one sample. This is a good assumption except when non-metallic (molybdenum disulfide, Teflon, etc.) coatings are utilized. Even in the case of non-metallic coatings, any changes in a finite tension range should be small.

For purposes of convenience, the tightening technique of this invention may be referred to as the logarithmic rate method.

The importance of equations (5) and (7) should now be appreciated. It has been demonstrated in the laboratory that the value of tension rate $dF/d\alpha$ is a function of the joint having small scatter and is independent of friction. The torque rate $dT/d\alpha$ can be determined from torque and angle measurements taken during the tightening of each fastener pair by suitable torque and angle sensors on the tightening tool. The torque value T is, of course, measured by same torque transducer. It will accordingly be apparent that the friction dependent parameters, i.e. torque rate and torque, are determined for each fastener during tightening, which is here defined as the time frame commencing with the onset of threading and stopping at the termination of tightening. Since tension rate $dF/d\alpha$ is a function of the joint which is determined empirically prior to the tightening of production fasteners, it is a simple matter to solve equation (5) for tension.

While theoretically correct, several adjustments should be made to equations (5) or (7) in order to enhance accuracy and reliability. First, the effect of prevailing torque T_{pv} should be taken into account. Prevailing torque is that torque necessary to overcome the thread-to-thread resistance to fastener advance which does not contribute to the inducement of bolt tension and which may be sensed during the threading advance of the fasteners in the region 14. Second, the effect of offset torque T_{os} should likewise be taken into account. Offset torque is that torque necessary, at zero prevailing torque, to advance the fastener to an angle location corresponding to the origin of tension. These accomodations may be expressed mathematically as:

$$F \propto \frac{d}{d\alpha_{\substack{smooth\\tense}}}[\log(T - T_{os} - T_{pv})]^{-1} \text{ or } \tag{8}$$

$$\frac{dT/d\alpha}{T - T_{os} - T_{pv}} = \frac{dF/d\alpha}{F}. \tag{9}$$

The importance of equations (8) and (9) should now be appreciated.

Referring to FIG. 1, it may be assumed that the fasteners are threaded together with measurements being taken of both torque and angle with tightening being advanced to the point 26. The average torque rate TR is calculated, as by the use of the least squares method. Since the tension rate FR_1 is known from empirical measurements of the joint in question, the tension in the joint can be calculated at the point 26 from equation (5) or (9). Graphically, the angle required to advance the fasteners from the tension value calculated at the point 26 to the final desired tension value F_D can be easily done since the tension rate FR_2 has likewise been determined empirically. After determining the additional angle α_{final}, the tool may be instructed to so advance the fasteners thereby attaining the desired final tension value F_D. In a similar fashion, the additional torque ΔT or the final desired torque T_D can be calculated.

There are substantial difficulties in applying these principles to production line operations. It will be apparent that the calculations being made are being done while tightening. It will be apparent that the duration of tightening should be minimized so far as practicable commensurate with the attainment of consistent results. In any event, it will be apparent that long tightening times, for example two minutes, would render the technique unsuitable for many production line operations although some suitability may remain for special purpose applications such as in the fabrication of reactor vessels, aircraft and the like where precision is paramount. It is accordingly evident that the use of electronic computation techniques is highly desirable for

processing the data obtained from measurements taken during tightening. Even with the use of electronic computation techniques, it is desirable to advance the fasteners for some initial distance, suspend tightening momentarily and then resume tightening to the final desired tension value. The momentary stop allows time to complete lengthly calculations and has the additional benefit of allowing the joint to relax at this point rather than at the final tension value attained. As will be more fully apparent hereinafter, many of the calculations are being done while the tool is running as well as when the tool is momentarily stopped. It will, however, be evident that simplified computations may be utilized thereby eliminating the necessity for a momentary pause in the tightening operation.

More specifically, the following steps may be taken to attain a consistent bolt tension utilizing an instructable tool equipped to measure torque and angle information only, after the acquisition of certain empirical information:

1. Engage the fasteners, start the tool and record torque at predetermined angle increments.

2. Shut the tool off in a tension range of 0.4–0.75 of elastic limit. Although a turn-of-the-nut approach or torque control strategy may be used to estimate the initial tool shut off, a simplified logarithmic rate method in accordance with this invention provides more consistent results.

3. Calculate the torque rate from the torque and angle measurements by a suitable smoothing technique, e.g. least squares. Calculate the torque at the mid-point of the range from which the torque rate was calculated, by averaging the torque value along this range. The intersection of the average torque rate with the axis represented by $(T_{pv}+T_{os})$ is accordingly established. Since the offset torque T_{os} is largely a function of the joint, the intersection of the tension curve with the angle axis is established.

4. The tension curve is then a straight line emerging from the origin or intersection determined in 3. above with the initial slope FR_1. This is typically valid up to about 0.5 elastic limit at which point the tension curve has a slope of FR_2. The location of the bend in the tension-angle curve is determined empirically when determining the values of FR_1, FR_2 and T_{os}.

5. Calculate the tension value appearing in the fasteners at some location, for example, point 26. Given the tension value at point 26, calculate the additional angle α_{final} or the additional torque ΔT necessary to tighten the fasteners to the final desired tension value F_D.

6. Instruct the tool to resume tightening and advance the fasteners through the angle α_{final} or for the increased torque ΔT.

As disclosed in applicant's copending application Ser. No. 766,429, the disclosure of which is incorporated herein by reference, the angle of advance measured by an angle encoder is not the true angle through which the fastener turns because of torsional twist in the tightening tool and because of torsional twist in the bolt. To achieve maximum accuracy, it is necessary to compensate the measured angle of advance for the torsional twist of the tool and bolt. In addition, it is necessary to take into account the torsional twist of the laboratory equipment utilized to acquire values for the tension rates FR_1 and FR_2.

For purposes of discussion, the implementation of the technique of this invention may be broken down into six generally chronological segments: (1) quality control procedures in the regions 14, 16; (2) reaching the midpoint stop and conducting torque rate determinations and quality control procedures; (3) procedures determining the final shut off parameters; (4) procedures involving restarting the tool; (5) procedures determining the occurrence of non-linear strain during tightening toward the final shut off point; and (6) quality control procedures conducted at the termination of tightening.

QUALITY CONTROL PROCEDURES IN THE REGIONS 14, 16

It has been learned that considerable information can be acquired about the quality of the fasteners during the free running region 14. Specifically, deductions can be made about cross threading, grossly imperfect threads, bolt bottoming, and whether the bolt is already tight. Because the joint has not clamped up, it is evident that the information so acquired concerns the fasteners only and is not affected by other joint properties. It has also been learned that deductions can be made during the incipient clamp up region 16 concerning the tool. Specifically, it can be determined whether the tool has engaged the fastener, whether a fastener is in place, the bolt is broken, one of the threaded members has no threads, or one of the threaded fasteners is the wrong size.

Prevailing Torque

Although the region 14 is referred to as the "free running" region, a small amount of torque is necessary to advance the fasteners because of friction between the mating threads. Some types of fasteners, known as prevailing torque fasteners, include intentionally imperfect threads which require more than a minimum amount of torque in order to threadably advance. Other fasteners which are unintentionally imperfect also require more than a minimum torque to effect threadable advance. For all practical purposes these types of fasteners may be treated identically with one caveat. Any batch of fasteners which are not intended to be prevailing torque fasteners will include some fasteners which have substantially perfect threads thereby requiring only a minimum torque and will also include some fasteners having imperfect threads which require more than a minimum torque for threadable advance. Thus, any technique which is intended to be universal or which is intended to be used with non-prevailing torque fasteners must have the capability of accomodating fasteners which vary from substantially perfect to grossly imperfect.

Broadly, one goal of this procedure is to detect, during tightening in the free running region 14, those fasteners which exhibit instantaneous prevailing torque values T_{pvi} which exceed a maximum expected prevailing torque $(T_{pv})_{max}$. The value of $(T_{pv})_{max}$ may be acquired in any suitable manner, as by relying on the published information of fastener manufacturers, by measuring the prevailing torque on a significant number of fasteners, or by adding an incremental percentage, for example 10–20%, to either published information or acquired values. Similarly, it may be desired to detect those fasteners which exhibit instantaneous prevailing torque values T_{pvi} which are less than a minimum prevailing torque $(T_{pv})_{min}$, as when using prevailing torque fasteners and assurance is required that the fasteners are up to specifications.

Another goal of this procedure is to acquire sufficient information to provide a reasonably accurate value for average prevailing torque T_{pv}. This may prove to be of value in correcting a final shut off parameter for the effect of prevailing torque.

Several precautions are desirably taken for the measuring of prevailing torque to assure that the data is reliable. First, it is essential that the acquisition of data occur before the commencement of clamp up of the joint parts. Otherwise, the normal torque required to begin tightening up the joint will be confused or erroneously deduced as abnormal prevailing torque. This error in data acquisition is fatal to proper results because applied torque rapidly increases during joint clamp up as is evident from the showing in region 16 is FIG. 1. Second, the acquisition of data should be delayed until the fastener parts are rotating or other steps should be taken to avoid spurious torque readings from the static friction exhibited between the fastener parts at rest or due to the transition from static to dynamic friction effects.

With the criteria outlined above, it is evident that there is considerable leeway in designing a system for acquiring prevailing torque data for a particular application. Because the need in a particular application may be to reject defective parts, to acquire values for average prevailing torque T_{pv}, or both, the design selections are subject to change.

In the system disclosed, utilizing the fasteners described immediately preceding Table II, it is desired to take prevailing torque data to reject fasteners at an early stage of tightening and to acquire an average prevailing torque value T_{pv} to compensate the final shut off parameter. Referring to FIG. 2, there is illustrated a typical torque-angle plot 28 of an acceptable fastener exhibiting an initial torque peak 30 caused by static friction between the fastener components and the change over from static to dynamic friction. After the initial torque peak 30, the curve 28 levels out to a reasonably constant value between a minimum expected prevailing torque $(T_{pv})_{min}$ and a maximum expected prevailing torque $(T_{pv})_{max}$. Although the curve 28 is illustrated as a continuously recorded value, in digital systems it is highly desirable to take torque sensings only at selected locations spaced apart by a predetermined angle increment $\Delta\theta$.

In operation, the tool is turned on to commence rotation of the fastener component and a delay of one $\Delta\theta$ angle increment is allowed before a first torque sensing 32 is taken. Thereafter, a torque sensing is taken at every angle increment $\Delta\theta$, indicated by the data points 34, until the expected rundown angle θ_{rd} is reached. During the expected rundown angle θ_{rd}, the instantaneous torque sensing T_{pvi} at each of the data points 32, 34 is compared with $(T_{pv})_{max}$. If the instantaneous prevailing torque T_{pvi} exceeds $(T_{pv})_{max}$ more than once, a shut off command to the tool is issued, an indication is made that the joint is unacceptable and the system is reset for the next tightening cycle. Although it is normally desirable to have the tool operator intervene following the rejection of a joint and although the typical air powered tools used to tighten fasteners are not reversible, it may be desired in some applications to automatically back off the nut by providing a reversible tool and instructing the tool to back the nut off prior to reset for the next tightening cycle. In connection with the fasteners exhibiting the curve 28, it is apparent that no shut off command is issued.

With the system designed in this manner, decisions need to be made about the size of the angle increments $\Delta\theta$, the size of the rundown angle θ_{rd}, and the size of a sampling region θ_s. The value of $\Delta\theta$ is selected so that the transient effect of the static-to-dynamic peak **30** and any other transient effect will be sensed only once if at all. It has been found that the transient torque effects in the free running region **14** are of quite short angular duration. Although the value of $\Delta\theta$ is susceptible to considerable compromise, a selection of 22° has proved satisfactory. The value of the rundown angle θ_{rd} is selected to assure that both the rundown angle θ_{rd} and the period of data acquisition θ_s immediately following θ_{rd} are completed substantially before the incipient clamp up region **16** commences. The value of θ_{rd} accordingly depends on the duration of the sampling period θ_s, the length of the threaded fastener compared to the size of the parts to be clamped up and the like. The selection of θ_{rd} and θ_s should be conservative to provide assurance that these angular periods are completed prior to the incipient clamp up region **16**. The value of θ_{rd} may thus vary widely and in one embodiment of the invention is five complete revolutions of the fastener or torque appling tool.

Similarly, the duration of the sampling region θ_s may also vary widely. It is not essential to take an enormous number of torque readings to establish a reasonably reliable value for average prevailing torque T_{pv} for the following reasons. It will be shortly apparent that the value of T_{pv} is relatively small when compared to the torque readings T from which T_{pv} will be subtracted. Accordingly, any difference between the true average prevailing torque and the calculated value will be smaller still. It is accordingly quite satisfactory to obtain an average value from a fairly modest number of data points, e.g. 5–30. Although the duration of the sampling period θ_s is susceptible to considerable compromise, a sampling duration on the order of one revolution has proved satisfactory. Since prevailing torque T_{pv} is created by circumferential asymmetry of the nut and bolt, a selection of one revolution for the sampling region θ_s is a natural one. The sampling interval between the data points **36** in the region θ_s may conveniently continue to be 22°. Accordingly, approximately sixteen data points **36** are used.

In calculating the average prevailing torque T_{pv} in the sampling region θ_s, there are a number of conceivable approaches. First, one may merely add the values of the torque sensings T_{pvi} and divide by the number of data points. In the alternative, one may elect to use a smoothing technique such as least squares. Furthermore, one could conceivably average the torque sensings after disregarding any value above $(T_{pv})_{max}$ and either arithematically averaging or smoothing the remaining data. For reasons mentioned previously, any reasonably accurate averaging technique will suffice because the difference between the calculated average and the true average will be a very small value.

It will be seen that by delaying the first data point **32** by the angle increment $\Delta\theta$ from the onset of rotation, the existence of the static-to-dynamic peak **30** will likely be masked. By separating the data points **32**, **34**, **36** by the angle increment $\Delta\theta$, any transient torque effect will be sensed only once if at all. By delaying the sampling period θ_s until after the rundown angle θ_{rd}, one is reasonably assured that sampling for averaging purposes avoids any spurious sensings related to the onset of tightening.

As will be more fully pointed out hereinafter, a reasonably reliable value for T_{pv} is desirable to compensate a final shut off parameter for the effect of prevailing torque. In this regard, it will be evident that the amount of torque applied to a fastener during the free running region **14** has nothing whatsoever to do with the attainment of tension in the bolt at the termination of tightening. The compensation made for the tightening strategy of this invention will be discussed more fully hereinafter. In a torque control strategy, however, the running torque sensed by the torque encoder in the final tightening region **18** should be adjusted by the amount of the noted prevailing torque to obtain a torque value which can be compared to the desired torque shut off parameter. For example, if empirical data suggests that the fastener needs to advance 30 ft-lbs above an average prevailing torque of 3 ft-lbs and the fastener being tightened exhibits a prevailing torque of 5 ft-lbs, the tool should be instructed either: (1) to advance the fastener to 35 ft-lbs, or (2) to advance the fastener 30 ft-lbs beyond the noted prevailing torque of 5 ft-lbs, or (3) to advance the fastener until the difference between the sensed torque and the noted prevailing torque equals 30 ft-lbs. In a turn-of-nut strategy, the torque sensings used in reaching the angle location known as snug torque should be similarly adjusted by the amount of the noted prevailing torque.

Also shown in FIG. 2 is a torque-angle curve **38** which clearly indicates an undesirable fastener pair. The curve **38** exhibits a torque peak **40** caused by the change over from static to dynamic friction and then levels out to a running value above $(T_{pv})_{max}$. A preferred technique for determining when a fastener pair is unacceptable is the occurrence of two torque sensings T_{pvi} above $(T_{pv})_{max}$. The torque sensing at the first data point **32** is above $(T_{pv})_{max}$ so that when the second data point **34** is likewise above this value, the tool shuts off, the joint is indicated as being unacceptable and the system is reset for the commencement of a new tightening cycle.

It is evident that any system which rejects fasteners having excessive prevailing torque sensings will reject the fastener pair exhibiting the curve **38** and will pass the fastener pair exhibiting the curve **28**. There are, however, a number of fasteners which exhibit a torque-angle curve **42** which is distinctly different than either of the curves **28**, **38**. The curve **42** includes a static-to-dynamic peak **44** and then levels out initially to a value below $(T_{pv})_{max}$. The curve **42** also exhibits a transient peak **46** which is above $(T_{pv})_{max}$ which is detected at the subsequent data point **34**. Thereafter, the curve **42** levels out below $(T_{pv})_{max}$. It is highly desirable not to reject the fasteners exhibiting the curve **42** because the transient torque peak **46** does not repeat or is not sensed more than once. Accordingly, the conclusion is that the transient peak **46** is not indicative of a serious thread imperfection.

A somewhat different situation is evidenced by a torque-angle curve **48** which exhibits a static-to-dynamic peak **50** and at least a pair of subsequent transient torque peaks **52**, **54**. In this situation, there are at least two instances where data taken at the points **34** indicate that the instantaneous prevailing torque T_{pvi} exceeds $(T_{pv})_{max}$. Although it is within the bounds of judgment to accept fasteners exhibiting several transient peaks, such as illustrated by the curve **48**, it is preferred to reject these fasteners.

It will accordingly be seen that there is provided a technique for rejecting threaded fasteners at an early stage of the tightening cycle in response to a torque sensing indicative of serious fastener imperfections.

If fasteners are often rejected because of high T_{pvi} sensings, it may be concluded that the batch of fasteners is suspect. Accordingly, a running average of rejections to fasteners run is conducted. If

$$R_{pv}/N \geqq E \qquad (10)$$

where R_{pv} is the number of fasteners rejected, N is the sample size and E is a fractional value acceptable to the user, such as 0.15, a signal is displayed at the operator's station to indicate a parts defect. The value of N is preferably not the cumulative number of joints tightened but is a running value, as by storing, on a first-in, first-out basis, a finite number of joints tightened, such as 30.

In the event that prevailing torque fasteners are being tightened and it is desired to determine that the fasteners do exhibit prevailing torque, it appears that the check to be made is to compare average prevailing torque T_{pv} with $(T_{pv})_{min}$. In the event that T_{pv} is less than $(T_{pv})_{min}$, the fasteners should be rejected.

Is Tool Advancing Fastener?

Another quality control procedure conducted early in the tightening cycle is to determine whether the fastener is threadably advancing. This is accomplished by measuring the time elapsed between the instant the tool is turned on until the torque encoder senses a predetermined minimum torque T_{sth} which is the threshold torque stored by the data processor after the preliminary data points 32, 34, 36. To establish T_{sth}, a torque value T_1 is empirically determined and is the first torque value utilized to calculate a preliminary torque rate as discussed hereinafter. T_1 is on the order of about 20–30% of the average final torque value obtained in running the same to empirically determine FR_1, FR_2 and T_{os}. When the storing threshold torque T_{sth} is sensed to be

$$T_{sth} = 0.25(T_1 + T_{pv}) \qquad (11)$$

the data processor begins to store torque values sensed by the torque encoder. If the data processor does not commence to store torque values within a very short period, on the order of 3–10 seconds, of the onset of tool turn-on, the conclusion is that no bolt is present, the tool socket has not engaged the bolt head, the bolt is broken, one of the threaded members has no threads, or one of the threaded members is the wrong size. In this event, a signal is generated by the data processor to turn off the tool, signal that one of these conditions exists and reset the tool for the next tightening cycle.

REACHING THE MID-POINT STOP, TORQUE RATE PROCEDURES, AND QUALITY CONTROL PROCEDURES

Reaching the Midpoint

The intent at the mid-point stop is for the joint to be tightened to an angular location corresponding to the break in the tension-angle curve for reasons more fully pointed out hereinafter. Although a torque control or turn-of-the-nut method can be used to determine the mid-point stop, it is preferred to use a simplified logarithmic rate method in accordance with this invention.

Referring to FIG. 3, which is a continuation of the normal torque-angle curve 28 of FIG. 2, the tool continues to turn the fasteners with torque values being recorded and stored at fairly small equal angle increments which may be, for example, in the range of 0.2°-3°.

The angle encoder may conveniently be of the digital type to deliver a pulse at small, equal angle increments. The unit of angle used for calculation purposes is $\Delta\alpha$ which is one or more multiples of the angle pulse. The value for $\Delta\alpha$ depends on the elastic properties of the joint and typically are in the range of 0.5°-6° although a wider range is acceptable in some circumstances. With fasteners of the type studied, a selection in the range of 2°-3° seems preferable. In getting to the mid-point, torque and angle measurements obtained in the region 16 are used.

Referring to FIG. 3, when running torque is first sensed to be equal to or greater than T_1, such as at the location 56, the angular position of the location 56 is noted and stored. When the tool passes the point 58 which is one α_k degrees beyond the location 56, the torque value T_2 is sensed and stored. The value of α_k is preferably large enough to give a rough approximation for a preliminary torque rate, which is calculated as $(T_2-T_1)/\alpha_k$. If α_k were very large, the tool would not be stopped until late, leaving little or no additional room to resume tightening. If α_k were very small, the value of torque rate calculated from $(T_2-T_1)/\alpha_k$ would be so influenced by noise in the torque sensings that it would be unreliable. The actual value of α_k depends on the elastic properties of the joint. A compromise of 9° for α_k has proved acceptable for the particular joint described preceeding Table II although other compromises are obviously acceptable.

The data processor then calculates α_1, in accordance with the following equations:

$$\alpha_1 = c + a(T_2 - T_{pv}) \qquad (12)$$

$$c = \alpha_d - \alpha_{or}\left(1 - \frac{T_{os}}{T_o}\right) - N_1\frac{T_1 - T_{os}}{K_o} - aT_1 \qquad (13)$$

$$a = \frac{1}{\alpha_k}\left[\frac{\alpha_{or}\alpha_d}{T_o} + N_2\frac{T_1 - T_{os}}{K_o^2} - \frac{\alpha_{or}^2}{T_o}\left(1 - \frac{T_{os}}{T_o}\right)\right] \qquad (14)$$

α_d is the desired angle from tension origin to mid-point and is F_M/FR_1 or slightly greater where F_M is the tension value at the junction of the two tension regions indicated by FR_1 and FR_2, α_{or} is the tool overrun at idle due to actuation delay, T_o is the stall torque of the tool, K_o is a typical torque rate for the particular fasteners involved and is determined empirically, and N_1 and N_2 are correction factors necessitated by the inaccurate algebraic expansion of more precise equations, which expansion substantially reduces calculation time compared to the exact equations. It will be apparent that, in a production line situation involving the same size bolts and the same size tools, every value in these equations, except T_2 and T_{pv} can be reduced to numbers before starting. Thus, the computations are actually easier and quicker than appears.

It might be questioned why the value of α_k is of any importance since neither equation (12), (13) or (14) appears to contain a value for preliminary torque rate.

Equations (12), (13) and (14) constitute one application of the logarithmic rate method to achieve a mid-point tension value of $FR_1\alpha_d$ with provisions made for tool overrun due solely to the time delay between the shut off command and exhaustion of air from the tool. The mathematical complexities have, by design, been transferred from equation (12) to equations (13) and (14) so that computation of equation (12) during tightening requires the least possible elapsed time. Equations (13) and (14) can be computed manually either prior to system installation or computed by the microprocessor when in a dormant portion of the tightening cycle, for example, prior to the initiation of tightening. Although the preliminary torque rate $(T_2-T_1)/\alpha k$ does not appear in equations (12), (13) or (14) as written, if one were to substitute the equations for a and c into equation (12), one would find that the preliminary torque rate appears. Accordingly, the reasons why α_k should not be too large or too small are as previously discussed.

As will be recognized by those skilled in the art, equations (13) and (14) do not include a tool overrun prediction due solely to the inertia of the rotating parts of the tool. For moderate and high torque rate bolts, the amount of angular overrun due solely to inertia is rather insignificant. The reason, of course, is that the tool is not rotating very fast. With low torque rate bolts, which the tool is able to turn faster, the amount of overrun due solely to inertia is still modest. For applications where maximum accuracy is desirable, equations (13) and/or (14) may be modified to incorporate a measure of overrun prediction based on inertia.

The determination of the mid-point stop is of some importance as may be visualized from an appreciation of FIG. 1. It will be recollected that it is desired to calculate the average torque rate TR. If the mid-point stop occurs, for example, in the lower part of the region **18**, the average torque rate will be substantially too low. If the mid-point stop is too late and well into the region **20**, two difficulties are presented: (1) the calculated torque rate TR may be substantially too high although some calculations can be done to disregard some of the later data in order to shift the range where torque rate calculations are actually being conducted, and (2) there may be little or no additional room available to resume tightening to the final desired tension value considering allowance for tool overrun.

Referring to FIG. 3, the tool is commanded to shut off at a point **60** which is α_1 degrees beyond point **56** which was where the torque value T_1 was first equalled or exceeded. Because of the time delay in the tool from the shut off command until the tool actually stops, which is represented by the point **62**, the tool has overrun by an angle $\delta\alpha$. The mid-point stop **62** typically falls in the range of about 0.4–0.75 of the elastic limit. For any given application, the empirically determined values act to establish the mid-point stop **62** at a given fraction of the elastic limit which is not changed until new empirical data is developed which, as for example, may occur when a different type fastener is selected.

Torque Rate Procedures

In order to calculate the average torque rate TR, a decision must be made of which torque and angle measurements are to be used. It has been learned that the torque sensings approaching the stopping point **62** are somewhat unreliable because of speed dependent variables. Accordingly, in the computations conducted to determine average torque rate TR, those sensings

which are affected by the act of stopping are disregarded. Although more than one torque sensing may be discarded in order to provide greater assurance, it is assumed for purposes of simplicity that only the last torque value is ignored. Accordingly, the highest torque value used in the torque rate calculations is at a location **64** which is one $\Delta\alpha$ backward from the point **62**. The torque value at the point **64** is T_3. The total number of values used in torque rate calculations, designated n for more general purposes, may vary widely and is subject to considerable compromise. A total of fourteen consecutive data points has proved quite acceptable. The mean torque T_m and the average torque rate TR are then calculated using the following summations where i is a designation for each point selected for the torque rate calculations and T_i is the torque value there sensed:

$$T_m = \frac{1}{n}\sum_{i=1}^{n} T_i \tag{15}$$

$$TR = -6\sum_{i=1}[(n+1-2i)T_i]/[n(n-1)(n+1)(\Delta\alpha)] \tag{16}$$

Equation (15) will be recognized as merely adding the torque values occuring at each of the points i and dividing this sum by the total number of data points n. Equation (16) will be recognized as a least squares fit for the data points i.

It is desirable to assure that the mean torque T_m and the average torque rate TR are taken over substantially the same tension range during the tightening of each fastener pair. This may be accomplished by checking to determine how close the angular position of the stopping point **62** is to the break in the tension-angle curve **12**. The angular position of the mean torque T_m along an abcissa $T_{os}+T_{pv}$ may be calculated from the equation:

$$\alpha_F=(T_m-T_{os}-T_{pv})/TR \text{ where } \alpha_F>0. \tag{17}$$

The angular distance from the point of origin of the tension curve **12** to the stopping point **62** may be calculated from actual data derived from the fastener being tightened from the equation:

$$\alpha_{origin}=-\tfrac{1}{2}(n+1)\Delta\alpha-\alpha_F \text{ where } \alpha_{origin}<0. \tag{18}$$

For calculation purposes, it is desirable that α_{origin} be a negative value. From empirically determined information done prior to the tightening of production fasteners, the start of the second tension region may be calculated from the equation:

$$\alpha_{FM}=(F_M/FR_1) \text{ where } \alpha_{FM}>0 \tag{19}$$

where F_M is the tension value at the break. The difference between α_{origin} and α_{FM} may be obtained from the equation:

$$X=-\alpha_{origin}-\alpha_{FM}. \tag{20}$$

It will be remembered that α_{origin} is a negative value.

If $X\geqq 0$, this means that the mid-point stop **62** is too late and consequently that the largest torque value T_3 in the torque rate calculations is too large. Without revising the value for TR, TR will tend to be too high as previously discussed. Accordingly, one needs to shift the range of torque rate calculations downwardly on the torque-angle curve illustrated in FIG. 3. Thus,

$$n_H = \downarrow (X/\Delta\alpha) + 1;\ \text{and} \tag{21}$$

$$n_1 = n. \tag{22}$$

From the stopping point 62, one moves downwardly along the torque-angle curve by n_H angle increments of $\Delta\alpha$ to define a new point 66 as the upper limit of the range through which torque rate will be calculated. The symbol $\downarrow$ means that any fractional value is dropped so that the number used is the next lowest integer from the calculated value. The total number of data points n remains the same.

If $X \leqq 0$, this means that the stopping point 62 occured too soon which would tend to give a value for torque rate that is too low. Since one cannot move upwardly on the torque-angle curve to obtain an additional area of measurement, the practical solution is to accept fewer data points for torque rate calculations thereby, in effect, lopping off the lower end of the range. Accordingly,

$$n_{H1} = 1;\ \text{and} \tag{23}$$

$$n_1 = \downarrow \left(\frac{F_o - F_L}{\Delta F} \right) + \downarrow \left(\frac{X}{\Delta\alpha} \right) \tag{24}$$

where n_{H1} indicates that the point or location where the largest torque value used in the torque rate calculations occurs. Since the largest torque value will remain the same, $n_{H1} = 1$ so that the torque T_3, being $\Delta\alpha$ removed from the stopping point 62, is the largest torque value used. The new value for n_1, which is the total number of data points used, is based on the assumption that the tension rate in the first region is substantially linear above a minimum tension value F_L, determined empirically, and that the tension F_o in the joint at the stopping point 62 lies in the first tension range. The symbol ΔF is the additional tension in the first range per angle increment $\Delta\alpha$ and may be expressed mathematically as:

$$\Delta F = FR_1 \Delta\alpha \tag{25}$$

The tension F_o in the joint at the stopping point 62 is

$$F_o = -FR_1 \alpha_{origin}\ \text{where}\ X \leqq 0,\ \text{or} \tag{26}$$

$$F_o = F_M + rFR_1 X\ \text{where}\ X > 0 \tag{27}$$

where F_M is the empirically determined tension value at the break in the tension curve 12 and r is the ratio of FR_2/FR_1.

It is conceivable that n_1 may be too small, e.g. two or three points, to give good results with the least squares equation (16). Accordingly, a check is made to determine if n_1 is less than one half of n. In this event,

$$n_2 = \downarrow \left(\frac{F_o - F_L}{\Delta F} \right) \tag{28}$$

and n_2 is used as the total number of data points.

Accordingly, a new summation is performed for mean torque T_m and torque rate TR in accordance with equations (15) and (16) utilizing the new starting place in the event that $X \geqq 0$ or starting with the same highest torque value but using fewer number of data points in the event that $X < 0$.

With revised values for mean torque T_m and torque rate TR, a revised value may be obtained for the angle of origin of the torque-angle curve using equation (17) and a revised value and for the origin of the tension-angle curve using equation (18). A calculation is again made to determine whether the tool has overshot or undershot the break in the tension curve in accordance with equations (19) and (20). Calculations are again made for the tension value F_o at the stopping point 62. It will be apparent that the values of mean torque T_m, torque rate TR, α_F, α_{origin}, F_o and the like may be revised as many times as desirable. It is also conceivable not to conduct the second pass under some circumstances.

Quality Control Procedures—Torque Rate Curvature

One of the defects in the technique heretofore described is the assumption that the empirically determined tension rate FR_1 correctly describes the elastic properties of the joint actually being tightened. For good quality joints, the tension rate FR_1 does not vary widely. There are, however, a number of relatively common situations, e.g. galled threads, misaligned fasteners, poor contact surfaces, dirt or other foreign particles between the contact surfaces, and the like, where the actual tension rate for the joint being tightened is significantly below the empirically determined tension rate FR_1. In such poor quality joints, the actual final tension value will be significantly below the desired tension value F_D and significantly below the final calculated tension value F_{final}. To determine the significance of such poor quality joints, two 5/16"-24, SAE grade 8 nuts and bolts were tightened with a shim, 0.015 inches in thickness, inserted from one end under the bolt in order to simulate poor contact due to misalignment. The final desired tension value F_D was 5500 pounds. The actual measured final tension value was 2400 pounds and 1700 pounds for the two fasteners, a percentage variation of −56% and −69% from desired. It will accordingly be apparent that the occurrence of such poor quality joints can have a major effect on the scatter seen in fasteners tightened by the technique of this invention. It will also be evident, upon reflection, that such poor quality joints will have a like effect on the scatter in fasteners tightened by a turn-of-the-nut method.

It has been learned that poor quality joints of the type exhibiting abnormally low tension rates can readily be detected by the data encoded and stored during the course of tightening a fastener pair with this invention. In such poor quality joints, the torque rate is not constant in the upper part of the region 18 where the average torque rate TR is calculated, as contrasted to the showing of FIG. 3. Instead, the torque-angle plot is arcuate and, if plotted, is upwardly concave. Thus, it is a relatively simple matter to measure or calculate and then directly compare the average torque rates in the upper and lower parts of the range where the torque rate TR is calculated. For example, in a situation where thirteen data points are being used to calculate TR, with the point 64 being the highest torque value used, the torque rate TR_a over an angle of six $\Delta\alpha$ increments backward from the point 64 would be calculated. The calculations may, of course, be a two point or a least squares technique. Next, the torque rate TR_b over an angle commencing with six $\Delta\alpha$ increments backward from the point **64** and ending twelve increments backward from the point **64** is calculated by a two point or least squares technique. Then, the ratio of TR_a/TR_b is computed. If the ratio of TR_a/TR_b is near unity, e.g. 1 ± 0.10, the conclusion is that the joint has an acceptable tension rate. If the ratio of TR_a/TR_b diverges significantly from unity, e.g. $TR_a/TR_b>1.10$, the conclusion is that the joint has an abnormally low tension rate FR_1 and, if tightened by the technique of this invention or by a turn-of-the-nut method, will result in a fastener stressed substantially below the desired tension value F_D. A suitable signal may be displayed at the operator's station, the joint rejected and the parts replaced.

Rather than directly checking the curvature of the torque-angle plot, indirect methods are available. One approach is to compare the values of the calculated mid-point tension F_o in the first pass with that in the second pass. This is, in effect, calculating a first tension value at a predetermined location using a torque rate in a first area, calculating a second tension value at the same location using a torque rate in a second area and then comparing the first and second tension values. If the two values deviate by more than about 13%, joint problems are highly likely. The figure 13% is, of course, somewhat arbitrary. It is based on the expectation of tension control of ±10% within three standard deviations, a mean shift of 2% plus 1% for other uncertainties. The selection of 13% rarely produces false signals when parts have reasonable quality. If a better number is available, it should be used.

Quality Control—Torque Rate Too Low

As will be appreciated, the torque rate calculations are conducted on each successive fastener in the same tension range, i.e. F_L-F_H, the values of which are determined empirically. If the torque rate TR is unusually high, the conclusion is that the fastener pair exhibits very high friction. In the practice of this invention, there is nothing wrong with high friction rates and consequently no upper limit on the torque rate TR is specified. Unusually low values of TR are, however, cause for concern. First, the theoretical minimum torque rate TR* is not zero because the tool does reversible work on the joint in the absence of friction by producing tensile stress in the bolt and compressive stress in the clamped pieces and nut. When friction is zero, it can be shown that

$$TR^*=(w/2\pi)FR>0 \tag{29}$$

where TR* is the theoretical minimum torque rate and w is the pitch of the threads. Accordingly, TR* is positive and its value depends on thread pitch and the joint tension rate. The observed torque rate TR is made up of TR* and TR_f which is the friction component. If it is assumed that friction can change at most ±60% from its expected value, represented by the typical torque rate TR_o, then the minimum expected torque rate TR_{min} under normal conditions can be expressed by:

$$TR_{min}=0.6TR^*+(1-0.6)TR_o \tag{30}$$

The factor 0.6, representing a 60% change in friction coefficient, is somewhat arbitrary. If a better estimate is available, it should be used. Whenever a torque rate less than TR_{min} is observed, it indicates a joint problem. This could mean wrong parts, poor contact between the parts, or poor data processing, e.g. if the mid-point tension F_o is far too low. In any event, when the calculated torque rate TR is less than TR_{min}, a signal is given to indicate that the joint is rejected. Because this calculation is conducted during the mid-point pause, the tool is already off. Accordingly, the tool is reset for a new tightening cycle. It will be appreciated that this approach is a direct technique for assuring that TR exceeds TR_{min} for acceptable joints.

There are, however, techniques for indirectly detecting very low torque rates. A first indirect technique involves the second pass or second calculations for TR. The second pass requires a value of n_H greater than one. When TR is abnormally low, the first estimate of F_o is very large leading to a value of n_H so great that the location of F_L lies outside the stored data, i.e. F_L appears to lie below the torque storing threshold T_{sth}. Another indirect approach is to compare the calculated tension F_o at the mid-point with the final desired tension F_D. If they are too close, the observed torque rate TR must be unusually low.

Quality Control—Tool Performance

One of the advantages of the mid-point stop is that one obtains a measurement of the actual amount of tool overrun $\delta\alpha$ occuring between the angular locations **60**, **62** corresponding to the torque values T_4 and T_d. This allows for a check of tool performance. Although the tool overrun at the termination of tightening may be used to determine tool malfunction, this operation is more conveniently and accurately monitored during overrun adjacent the mid-point stop **62**.

When the tool is instructed to stop, it takes some time for all motion to cease. For any given tool speed at the time of the shut off command, there exists a given angle of rotation that occurs before all motion ceases. There are two phenomena that affect tool overrun: (1) the time lapse between the issuance of the shut off commmand and the complete closing of the air control valve, and (2) the rotational inertia of the relevant parts. By selecting appropriately designed rotors, the overrun due to inertia is noticeable only when idling. For purposes of simplicity, tool overrun due to inertia may be neglected.

There are accordingly two assumptions in tool overrun calculations: (1) overrun is due solely to time delay and the motor stops immediately after the air supply valve is completely shut off; and (2) the tool has a linear torque-speed curve as shown in FIG. 4 which can be characterized by two parameters, the stall torque T_o and the idle angular speed ω_o such that:

$$(T/T_o)=1-(\omega/\omega_o) \tag{31}$$

where T is the sensed torque at any location and ω is the angular speed at that location. On this basis, it can be shown that:

$$\delta\alpha_a=\alpha_{or}\left(1-\frac{T_a}{T_o}\right)=\alpha_{or}\left(\frac{\omega_a}{\omega_o}\right) \tag{32}$$

with only a small error where $\delta\alpha_a$ is the anticipated angular overrun at the time applied torque is T_a, α_{or} is the angular overrun at idle and the tool speed is ω_a when the applied torque is T_a.

In an unregulated pneumatic vane motor, the stall torque T_o varies approximately with Δp which is the difference between the absolute air pressure upstream of the tool and atmospheric pressure which is, of course, the equivalent of the gauge pressure upstream of the tool. The speed of the tool varies with $\Delta p^{1/2}$. As shown in application Ser. No. 766,429, filed Feb. 7, 1977, a typical tightening tool used with this invention incorporates an air supply valve which is biased toward the closed position by inlet air pressure and moved toward the open position by a solenoid operator. In this situation, the time required to close the valve after energization of the solenoid decreases as gauge pressure increases. This relationship is approximately $\Delta p^{-1/2}$. If the line pressure changes, α_{or} remains substantially constant while the stall torque T_o varies linearly. On this basis, the actual tool overrun $\delta\alpha$ at the mid-point 62 is a measure of the actual stall torque. If:

$$T_s = T_o(1+\epsilon) \tag{33}$$

where T_s is the actual stall torque in any particular tightening cycle and ϵ is the relative change observed in stall torque. It can be shown that:

$$\epsilon = y/(1-z)-1 \tag{34}$$

where

$$y = T_a/T_o; \tag{35}$$

$$z = \delta\alpha/\alpha_{or} \tag{36}$$

T_a and $\delta\alpha$ are measured and are accordingly known at the mid-point 62. α_{or} and T_o are fixed input values. If ϵ is negative, the tool is underperforming and, if positive, the tool is overperforming.

Although equation (31) is set up on the basis of line pressure changes, it remains meaningful if changes in stall torque are related to lack of lubrication, blade abnormalities or impending bearing failure. The microprocessor will in each case calculate ϵ and, if it is less than a prescribed negative such as -0.25, then a signal is generated to indicate at the operator's station that the tool has underperformed. If tool underperformance occurs too frequently, as pointed out more fully hereinafter, this may also be displayed indicating the existance of a systematic problem requiring attention.

In the alternative, let

$$y_1 = (T_1 + \alpha_1 TR)/T_o; \tag{37}$$

$$z_1 = \delta\alpha/2\alpha_{or}; \text{ and} \tag{38}$$

$$\epsilon_1 = 100\,\frac{y_1 + 2z_1 - 1}{1 - z_1}\,\% \tag{39}$$

where α_1 is the angular distance (FIG. 3) from T_1 to the shut off point 60. It will be apparent that y_1 is a dimensionless number and basically is the ratio of T_4/T_o. As shown in FIG. 3, T_4 is the existing torque value at the mid-point shut off location 60 while T_o is the normal stall torque. It will be seen from FIG. 4 that Y_1 is an inverse function of tool speed. If the time delay between the giving of the shut off command and the closing of the valve remains constant, y_1 is a prediction of tool overrun. Since $\delta\alpha$ is the measured tool overrun, it will be seen that z_1 is a function of measured tool overrun while α_{or} is the normal angular overrun of the tool under no torque conditions. ϵ_1 will be recognized as a percentage change in tool and control performance.

If ϵ_1 is low, for example, $\leqq -10\%$, the deduction is that actual stall torque has decreased significantly, such as from a loss or decline in air pressure, lack of lubrication, worn or broken parts, or the like. In such an event, a signal may be displayed at the tool location to indicate that the tool requires inspection, maintenance, repair or replacement. It is conceivable, but quite unlikely, that a significant decrease in ϵ_1 could be caused by a decrease in time delay between the shut off command and the air valve closing.

If ϵ_1 is positive, i.e. greater than zero, complications arise. It appears that z_1 which is a simplification of a more complex equation, loses accuracy. The more complex equation indicates that if ϵ_1 is positive, z_1 should be reevaluated as:

$$z_2 = \delta\alpha/\alpha_{or} \tag{40}$$

Accordingly, ϵ should be reevaluated for greater accuracy, when positive, as:

$$\epsilon_2 = 100\,\frac{z_2 - 1}{1 - y_1} \tag{41}$$

If ϵ_2 is high, for example $\geqq +10\%$, the deduction is that the time delay between the shut off command and the air valve closing has decreased significantly or that air pressure supplied to the tool has increased. This normally indicates that the valve control solenoid is beginning to stick or that air pressure is too high. In such event, a signal may be displayed at the tool location to indicate that the air control system requires inspection, maintenance, repair or replacement. It is conceivable, but quite unlikely, that a significant increase in ϵ_2 could be caused by increased tool efficiency.

As will be apparent to those skilled in the art, the prediction of tool overrun embodied in equation (37) does not include a measure of overrun based on inertia, but instead based solely on time delay. As mentioned previously, inertial overrun is rather insignificant with moderate to high torque rate fasteners although accuracy can be improved somewhat for low torque rate fasteners by including an inertial overrun provision. In the event that it is desirable, a measure of inertial overrun can be incorporated into equation (39) through one or both of equations (37) or (38).

It is apparent that a single indication of tool malfunction is probably not significant but that an abnormal frequency of tool malfunction is significant. Thus, a running ratio of

$$C_{TL}/C_J \geqq C \tag{42}$$

is maintained where C_{TL} is the number of times that $\epsilon \leqq -10\%$, C_J is the number of joints tightened and C is a fraction acceptable to the user. The ratio C_{TL}/C_J is preferably a running ratio, as by storing on a first-in, first-out basis, rather than a cumulative ratio. From present information, it appears that C should be in the range of 0.1-0.2, for example 0.15.

Similarly, a running ratio of

$$C_{TC}/C_J \geqq D \tag{43}$$

is maintained where C_{TC} is the number of times that $\epsilon \geqq +10\%$ and D is a fraction acceptable to the user, for example, 0.15.

Another approach for predicting tool overrun and thereby detecting tool malfunction is pointed out by:

$$\alpha_p = \left(1 - \frac{T_4}{T_o}\right) \alpha_{or} \tag{44}$$

where α_p is the predicted tool overrun from the shut off command point **60** where the torque value T_4 appears. The measured value of overrun $\delta\alpha$ from the point **60** can be compared against α_p, as follows:

$$H \leqq \delta\alpha/\alpha_p \geqq G \tag{45}$$

where H and G are values acceptable to the user, such as 0.85 and 1.15 respectively. When measured overrun $\delta\alpha$ is too small, this indicates a motor malfunction while if $\delta\alpha$ is too large, it indicates a control system malfunction.

Quality Control—Non-Linear Strain

Another quality control procedure employed at the mid-point stop **62** is the detection of non-linear strain, whether elastic or plastic. If non-linear strain occurs before the mid-point stop, it could be detected by any of the following indirect techniques. First, if the joint is deeply within the plastic zone, the torque rate calculations will be askew so that an attempt will be made to search for torque data outside the memory. This indirect method is similar to indirectly determining whether the torque rate TR is abnormally low and will cause the joint to be rejected. Second, the joint might be rejected because the observed torque rate TR is less than the minimum expected torque rate TR_{min}. Third, it is possible that the joint will be rejected because the torque-angle plot is not linear but is instead demonstratably arcuate. In addition to or in lieu of relying on indirect techniques for detecting excessive non-linear strain, it is desirable to directly determine if it has been experienced by the fastener.

To this end, a classic yield point determination is made. Referring to FIG. **5**, there is illustrated a torque-angle curve **68** which is intended to represent a simplification of the showing of FIG. **3**. The curve **68** terminates at the mid-point stop **62** and describes, in the region **70**, a torque rate TR. Ideally, and in accordance with classic yield point determinations, an imaginary line **72** is spaced from the location of mean torque T_m and accordingly from the linear region **74** of the curve **68** by an offset angle or offset strain α_y. Although the value of α_y may vary as pointed out more fully hereinafter, a typical value to the particular fasteners disclosed immediately preceding Table II is 12°.

The angular location of T_m, which is α_F, is known as shown in FIG. **3** and as calculated from equation (17). The angular location of the mid-point stop **62** along an abcissa $T_{os}+T_{pv}$ is, of course, the absolute value of α_{origin}.

Thus, a torque value T_l on the imaginary line **72** which is used to compare with the torque reading at the mid-point stop **62** is:

$$T_l = T_m + (-\alpha_{origin} - \alpha_F - \alpha_y)TR \tag{46}$$

In the event that T_l is less than T_d, the conclusion is that the joint has not experienced significant non-linear strain. It will be apparent that the value of T_d is suppressed by the act of stopping rotation. Accordingly, if T_l is less than T_d, there is great assurance that the joint has experienced no significant non-linear strain. In the event that T_l is equal or greater than T_d, the conclusion is that the joint has experienced significant non-linear strain and the joint is rejected. A portion **76** of the torque-angle curve of an unacceptable joint is illustrated as crossing the imaginary line **72** at a torque value below T_l.

The actual digital logic for conducting a non-linear strain determination in the region surrounding the mid-point and a determination in the region adjacent the termination of tightening is somewhat complex. Accordingly, a more generalized version may be used which can accomodate both the mid-point and the final determinations.

FINAL SHUT OFF PARAMETER PROCEDURES

It will now be appreciated that the location **62** of calculated tension F_o appearing in the joint corresponds to the point **26** illustrated in the more general showing of FIG. **1**. The determination yet to be made is the additional angle α_{final} or the additional torque ΔT required to achieve the final desired tension value F_D. Compared to the manipulations used to assure consistently reliable values for torque rate TR and the angle of tension origin α_{origin}, these calculations are relatively straight forward.

Angle Option

One tightening parameter that may be selected to attain the final desired tension value F_D is the additional angle α_{final}.

$$\text{if } X \geqq 0,\ \alpha_{final} = \frac{F_D - F_o}{rFR_1}\text{; and} \tag{47}$$

$$\text{if } X < 0,\ \alpha_{final} = -X + \frac{F_D - F_M}{rFR_1} \tag{48}$$

F_o is, of course, obtained from equations (26) or (27) while F_M is the tension value at the break in the tension-angle curve and is determined empirically.

It will be appreciated that the tool overran an angle $\delta\alpha$ when stopping at the mid-point **62**. It is equally apparent that some amount of tool overrun will occur approaching the final desired tension value F_D. A typical torque-speed curve for an air powered tool is shown in FIG. **4**. Since the tool will be slowing down during tightening, it will be apparent that the tool overrun approaching the final desired tension value F_D will be less than the overrun approaching the point 62. Defining,

$$\alpha_a = (T_o - T_4)/TR - \delta\alpha \tag{49}$$

where T_4 is the torque value at the point **60** where the initial shut off command was given prior to reaching the stopping point **62**, T_o is the stall torque of the tool. TR is the calculated torque rate and $\delta\alpha$ is the measured angle overrun approaching the point **62**. The expected tool overrun $d\alpha$ approaching the final desired tension value F_D is:

$$d\alpha = \delta\alpha\left(1 - \frac{\alpha_{final}}{\alpha_a}\right) \tag{50}$$

In the alternative, it can be shown that:

$$d\alpha = \alpha_{or}\left(1 - \frac{T_4}{T_o}\right) \tag{51}$$

where T'_4 is the applied torque at the moment of final tool shut off. The overrun $\delta\alpha$ at the mid-point stop 62 is measured by the angle encoder while its theoretical value is:

$$\delta\alpha_1 = \alpha_{or}\left(1 - \frac{T_4}{T_o}\right) \tag{52}$$

where T_4 is the torque value at the shut off at the point 60 preceding the mid-point stop 62. Dividing equation (51) by equation (52), a relationship can be found between the two overruns which is independent of α_{or}. Accordingly, one can use a semiempirical approach to estimate $d\alpha$. In order to do so, an estimate of the final torque T_D must be provided.

$$\text{if } X \geqq 0,\ T_D = T_{sp} + u\alpha_{final} \tag{53}$$

$$\text{if } X > 0,\ T_D = T_{sp} + u\alpha_{final} + X(u - TR) \tag{54}$$

where

$$u = rRTR \tag{55}$$

and R is defined as TR_2/rTR. Consequently, equation (55) reduces to the proposition that $u = TR_2$.

It can be shown that the semiempirical relationship between final and mid-point overruns is:

$$d\alpha = \frac{T_o - T_D}{T_o - T_{sp} + (1 - rR)(T_{sp} - T_4)} \tag{56}$$

Regardless of how the amount of final overrun $d\alpha$ is determined, the shut off command to the tool is given at an angle location α_{final}—$d\alpha$. Overrun of the tool causes the fastener to move to the final angle location α_{final}. The next problem is where to commence the measurement of the angle increment α_{final}—$d\alpha$. The problem has two components: the effect of joint relaxation and the effect of a transient rise in torque during restarting.

It has become apparent that a typical joint will relax, i.e. lose tension without unthreading of the fasteners, at the mid-point stop 62 and/or at the termination of tightening. If the fasteners were continuously tightened, i.e. without a mid-point stop, the relaxation at termination of tightening can be rather significant while, with a mid-point stop, the relaxation at termination of tightening is quite modest. By stopping at the mid-point 62, the bulk of joint relaxation occurs prior to the resumption of tightening. Thus, the stopping at the mid-point 62 provides greater consistency in final joint tension although this phenomenon complicates the determination of the final shut off parameter, or more correctly, complicates the determination of where to commence measuring the final angle of advance.

If the joint did not relax at the mid-point stop 62, the tool would be instructed to go an additional angle α_{final}—$d\alpha$ beyond the mid-point stop 62 where the final shut off command would be given. As shown in FIG. 1, the final shut off command would occur at about the point 78 whereby the tool overruns to tighten the fastener pair through an angle $d\alpha$ until stopping at the final desired tension value F_D.

The phenomenon of joint relaxation is illustrated in FIG. 6 where the curve 80 represents the tension-angle relationship during continuous tightening to a location 82 below the elastic limit of the fastener. When tightening stops, the joint relaxes as suggested by the tailing off of tension along a constant angle line 84. The final tension appearing in the fastener is accordingly at the point 86. A typical value for joint relaxation along the line 84 is 7% of joint tension within twenty-one hours.

Referring to FIG. 7, the curve 88 represents the tension-angle relationship during tightening to the mid-point stop 62. Because the joint relaxes, tension in the fastener tails off along a constant angle line 90 to a tension value at the point 92.

One technique for accomodating joint relaxation is, instead of instructing the tool to go an additional angle α_{final}—$d\alpha$ from the mid-point stop 62, the instruction is to advance the fasteners an additional angle α_{final}—$d\alpha$ after the running torque equals or exceeds T_{sp} where

$$T_{sp} = T_3 + TR(\Delta\alpha) \text{ in the event that } X \leqq 0, \text{ or} \tag{57}$$

$$T_{sp} = T_3 + u(\Delta\alpha) \text{in the event that } X > 0. \tag{58}$$

T_{sp} will be recognized as the calculated torque value which would be expected at the mid-point 62 except for the effect of stopping. It will be recollected that the torque value T_3 is located at the point 64, which is one $\Delta\alpha$ backward from the mid-point stop 62. By advancing the tool until running torque equals or exceeds T_{sp}, the torque and tension values at the mid-point stop 62, before relaxation occurs, are essentially reproduced. This is indicated in FIG. 7 where the point 94 designates the location where running torque is equal to or greater than T_{sp}. Tightening will then be done correctly, regardless of prevailing tension in the bolt at the time the tool resumes tightening. As shown in FIG. 7, the final shut off command occurs at the point 96 whereby the tool overruns to tighten the fastener pair through an angle $d\alpha$ until stopping at the final desired tension value F_D. In order to shift the bulk of joint relaxation from the final stopping point to the mid-point stop 62, the mid-point stop is at least 0.4 of yield strength and conveniently is in the range of 0.4–0.75 yield strength. With the mid-point stop 62 so located, typical joint relaxation at the final stopping point is on the order of $\frac{1}{2}$-2% of final bolt tension within one hour. It should be clear that this amount of joint relaxation is the relaxation of a good quality joint rather than a joint suffering from misaligned parts, compressed gaskets and the like.

Although measuring the angle of advance from T_{sp} provides better results than merely measuring the advance from the mid-point stop 62, the results can be further improved upon. Accordingly, a preferred technique for accommodating joint relaxation, accommodating a transient torque rise immediately on restart and to take up any gear-socket backlash is to advance the fasteners the additional angle α_{final}—$d\alpha$ after the running torque equals or exceeds a value slightly greater than T_{sp}. This transient torque rise is caused by static friction and/or the change over from static to dynamic in much the same manner that the torque peak 30 is generated at the onset of tightening as shown in FIG. 2. The amount that T_{sp} should be increased is subject to compromise and is somewhat arbitrary. In the absence of joint relaxation, the transient torque rise has been observed to lie between 0–15% above the expected torque. Accordingly, a compromise adjustment of 8% is preferred so that the measurement of the angle α_{final}—$d\alpha$ is preferably measured from $1.08T_{sp}$. In the absence of joint relaxation, the transient torque rise is so fast that essentially only the backlash in the tightening tool is taken up, regardless of any compensating factor in the range of 0.9–1.1. In other words, in the absence of joint relaxation, essentially no angle error is created in restarting the tool and measuring the angle of advance from T_{sp}. When joint relaxation occurs, however, the compensating factor is material.

Torque Option

Another tightening parameter that may be selected to attain the final desired tension value F_D is the additional torque ΔT or the final torque T_D (FIG. 1). The final torque T_D is preferred since the joint may relax at the mid-point stop **62**. Because the tool instruction is to achieve an absolute torque value T_D, any relaxation in the joint is automatically accomodated. In using a torque governed shut off parameter, even a possible tightening of the joint at the mid-point stop will also be automatically compensated for.

In using a torque governed shut off, an interesting phenomenon has been noted for which no simple explanation appears. Referring to FIG. 1, it will be noted, as previously mentioned, that the tension rate FR_2 is greater than the tension rate FR_1, typically by 5–15% depending mainly on the value selected for F_M. This would lead one to believe that the torque rate in the region **20** would be greater by a similar amount than the torque rate in the region **18**. Laboratory investigations indicate that the torque rate in the region **20** typically exhibits a slightly smaller increase over the torque rate in the region **18**. Fortunately, the ratio of the torque rates in the regions **18, 20** to the ratio of the tension rates FR_1, FR_2 is more nearly constant for a single type fastener pair. In calculations for a final torque shut off command, this factor is taken into account, as follows:

$$T_{MC} = T_{os} + T_{pv} + \frac{TR}{FR_1}(F_M) \tag{59}$$

$$T_D = T_{MC} + \frac{R(TR)}{FR_1}(F_D - F_M) \tag{60}$$

where T_{MC} is a calculated value for the torque at the break in the tension curve, R is defined as TR_2/rTR, TR_2 is the torque rate in the region **20**, TR is the torque rate in the region **18**, and r is the ratio of FR_2/FR_1.

As is the case in the angle governed final shut off calculations, the tool will overrun after the final shut off command. Defining,

$$\delta T = TR_2(d\alpha) \tag{61}$$

$$T_a 32\ T_o - T_4 - \delta T \tag{62}$$

$$dT \doteq \delta T\left(\frac{T_o - T_D}{T_a}\right) \tag{63}$$

where $d\alpha$ is a calculated value for angle overrun from equation (50), (51) or (56). In the alternative,

$$T_b = T_D - TR_2 d\alpha \tag{64}$$

where T_b is the torque value at shut off.

After tightening is resumed, the final shut off command is given either when running torque $T \geqq T_b$ or T_D—dT. As shown in FIG. 1, the final shut off command will occur at about the point **78** whereby the tool overrun continues to tighten the fastener pair for an additional torque value dT until stopping at the final desired tension value F_D.

It is apparent that tightening of the fastener pair can be terminated in response to calculated tension which is derived by the techniques of this invention. Upon analysis, it will be evident that terminating tightening in response to calculated tension is in reality the same as terminating tightening in response to either angle or torque, depending on how the calculations of tension are conducted.

Torque—Angle Option

It will be apparent that tightening may be terminated in response to a combination of torque and angle, for example, a linear combination of torque and angle. Assuming that one wished to equally weigh the calculated advance derived from the torque and angle computations, the appropriate equation is generically:

$$F_D = F_o + \frac{rFR_1}{2}\left(\alpha_{final} + \frac{T_D - T_{sp}}{TR_2}\right] \tag{65}$$

where F_o is the calculated tension value at the mid-point stop **62** as may be calculated from equation (26) or (27) depending on whether $X \leqq 0$ or $X > 0$, and T_{sp} is the calculated torque value at the mid-point stop **62** as may be calculated from equation (57) or (58) depending on whether $X \leqq 0$ or $X > 0$. The calculations for α_{final} will depend on whether $X \geqq 0$ or $X > 0$ as pointed out in equations (47) and (48). Calculations for T_D are made using equations (53) and (54).

As with the use of other tightening parameters, it is desirable to provide an overrun correction. It is apparent that the angle overrun correction of equation (50) may be incorporated as an overrun prediction, as follows:

$$F_{or} = r(FR_1)d\alpha \tag{66}$$

where F_{or} is the increase in tension due to overrun. It may also be desirable to use an equally weighted linear combination of torque and angle in determining the predicted tool overrun. The tension produced in the bolt during overrun may be calculated as:

$$F_{or} = \frac{rFR_1}{2}\left(d\alpha + \frac{dT}{TR_2}\right) \tag{67}$$

It will be apparent that one cannot merely instruct the tool to proceed an additional angle or until a desired torque level is reached in order to stress the bolt to the desired tension value F_D when using a mixed parameter of torque and angle. Instead, one may calculate the tension appearing at any angular position α_3 beyond the point **62** as

$$\text{if } X \geqq 0,\ F_{\alpha 3} = F_o + \frac{rFR_1}{2}\left[\alpha_3 + \frac{T_{\alpha 3} - T_{sp}}{TR_2}\right] \tag{68}$$

-continued

$$\text{if } X < 0,\ F_{\alpha 3} = F_M + \frac{rFR_1}{2}\left[\alpha_3 - X + \frac{T_{\alpha 3} - T_{MC}}{TR_2}\right] \tag{69}$$

where $T_{\alpha 3}$ is the sensed torque value at the angular position α_3, T_{sp} is the calculated torque value at the mid-point stop 62, and T_{MC} is the calculated torque value at the location of F_M according to equation (59).

The calculated tension value at the point of shut off is:

$$F_{so} = F_D - F_{or} \tag{70}$$

where F_D is from equation (65) and F_{or} is from equation (67). By comparing the value of $F_{\alpha 3}$ at angle increments, such as $\Delta\alpha$, 1° or the like, with F_{so}, as soon as $F_{\alpha 3} \geqq F_{so}$, the shut off command is given. In this fashion, tightening may be terminated in response to a linear combination of torque and angle.

PROCEDURES INVOLVING RESTARTING OF THE TOOL

Decision to Advance

It is evident that the tension achieved in the fastener at the mid-point 62 may be substantially less than F_D, equal to or very close to F_D or greater than F_D. If the tension F_o achieved at the mid-point 62 is greater than or equal to F_D, the tool is not restarted but is instead reset to commence the tightening of the next fastener. In this circumstance, it may be desirable to provide an indication that the joint is satisfactorily tightened provided that the previously conducted quality control operations indicate that the joint is acceptable.

Accordingly, the question is whether to restart the tool when the mid-point tension F_o is less than F_D. Using, for purposes of illustration, the angle option technqiue for advancing the tool, if

$$\alpha_{final} - d\alpha > 0 \tag{71}$$

the tool is instructed to advance the angle increment $\alpha_{final} - d\alpha$ after either T_{sp} or $1.08T_{sp}$, depending on the election on how to handle joint relaxation. If $\alpha_{final} - d\alpha = 0$, the tool is instructed to commence turning and the shut off command is given immediately upon observing T_{sp} or $1.08T_{sp}$. If, however, $\alpha_{final} - d\alpha < 0$, two decisions are possible. The value of $d\alpha$ is normally greater than zero. Accordingly, if

$$d\alpha > 2\alpha_{final} \tag{72}$$

then the tool is instructed to open the air supply valve and issue a shut off command upon observing either T_{sp} or $1.08T_{sp}$. Otherwise, the best available final tension is the mid-point value F_o.

Torque Signal Filtering

There are many tools, for example the tool illustrated in copending application Ser. No. 766,429, that do not exhibit any substantial internal chattering which is reflected as noise in the torque signal. There are, however, a number of tools in which internal chattering produces undesirable noise in the torque signal. One such tool is of the type having the tool output angularly disposed relative to the motor shaft. In tools of this type, a set of meshing gear teeth effect the inclination of the output drive. In this situation, the meshing gear teeth apparently produce the noise that is reflected in the torque signal. It is desirable to filter the torque signal to reduce this noise. The difficulty is that a filter which will remove noise caused by internal chatter tends to slow the time response of the torque signal during startup for the final advance and causes response time problems near the termination of tightening.

To overcome these difficulties, there is preferably employed a pair of filters which are placed in circuit with the torque sensor by a switch controlled by the microprocessor. The first filter, which is conveniently of the resistance-capacitance type, has a substantial capacitance and accordingly acts to substantially filter the torque signal. The processor controls the switch to place the first filter in circuit with the torque sensor during the initial part of the tightening cycle, usually up to and including the mid-point stop 62. At the mid-point, the first filter is switched out of circuit with the torque sensor and a second filter is placed in circuit therewith. The second filter may also be of the resistance-capacitance type and has a much lower capacitance. The second stage filtering merely eliminates any very high frequency noise.

The difficulty with this approach is that the initial heavy filtering will cause a predictable torque-angle distortion that fortunately can be compensated for during the joint set up procedure. The other problem with filtering the torque signal is that deterioration or failure of the filter would cause tension errors.

NON-LINEAR STRAIN PROCEDURES DURING THE FINAL ADVANCE

Referring to FIG. 8, another feature of the invention is illustrated. When tightening to the final desired tension value, it is highly desirable to assure that the yield point is not reached or is at least not substantially exceeded. This may be done graphically as shown in FIG. 8 by drawing a line 98 parallel to the torque curve 10 in the region 20 or parallel to the tension curve 12 and spaced therefrom by an angle α_y in accordance with the classic offset strain technique. The value of α_y can be correlated with an acceptable amount of strain in the bolt since the amount of nut rotation in this region of the torque curve can be calculated into a percentage of bolt elongation because of the known pitch of the threads. When the running torque value T intersects the line 98 at the point 100, the tool is given a shut off command and ultimately comes to rest at a point 102 because of tool overrun.

In order to implement this technique, the torque value sensed by the tool is monitored after the tool is turned on again after the mid-point stop 62. One difficulty arises since the restarting torque applied to the fastener in order to resume tightening typically is relatively substantially larger than the running torque immediately prior to the mid-point stop 62 as is caused by the difference between the static and dynamic coefficients of friction and complicated dynamic factors. When the sensed value of running torque T first equals or exceeds the value of T_M where:

$$T_M = T_3 + TR(\Delta\alpha - X) \tag{73}$$

this location is marked and two $\Delta\alpha$ increments beyond this location, which is location 104, the running torque T is sensed and stored as T_5. T_M will be recognized as a calculated torque value which appears at the location on the torque-angle curve corresponding to the break in the tension curve.

As is apparent from FIG. 8, the calculations being done to detect the yield point or, in the alternative, an amount of non-linear strain below the yield point, occur in the region 20 where the torque rate is somewhat lower than the torque rate value calculated in the region 18. The torque rate in the region 20 can be expressed in accordance with equation (55).

Yield or non-linear strain calculations can be conducted periodically during tightening in the region 20 as often as is deemed desirable. Although the calculations can be done at every angle increment $\Delta\alpha$, results are quite satisfactory if done every other angle increment $\Delta\alpha$. Accordingly,

$$\Delta T_1 = 2u(\Delta\alpha) \quad (74)$$

$$\Delta T_y = u\alpha_y \quad (75)$$

where α_y is the angle corresponding to a desired strain level which can either be elastic but non-linear or plastic, ΔT_1 is the incremental torque over the incremental angle $2\Delta\alpha$ and ΔT_y is the incremental torque over the incremental angle α_y. By selecting small values for α_y, the shut off command will tend to be in the elastic but non-linear range below the yield point. If α_y is selected to be a large value, the shut off point will appear in the plastic range above the yield point. It is thus apparent that the detection of non-linear strain can encompass both elastic and plastic strain. The only difficulty is selecting very small values for α_y is that noise in the torque curve 10 in the range 20 might create a premature and false yield signal. At a point 106, which is two $\Delta\alpha$ degrees after the occurrence of T_5, the value of running torque T is compared with

$$T_{y1} = T_5 - \Delta T_y + \Delta T_1 \quad (76)$$

It is apparent that T_{y1} is a torque value on the line 98 at the point 108. If $T > T_{y1}$, tightening continues. At a point 110, which is two $\Delta\alpha$ degrees beyond the point 106, the value of running torque T is compared with

$$T_{y2} = T_{y1} + \Delta T_1 \quad (77)$$

$$= (T_5 - \Delta T_y + \Delta T_1) + \Delta T_1. \quad (78)$$

If $T > T_{y2}$, tightening continues. This procedure continues by adding an additional torque valve ΔT_1 to the preceding value of T_y at angle increments of two $\Delta\alpha$. In the event that $T \leqq T_y$ before the occurrence of the shut off command derived from the normal tightening parameter of torque or angle, a shut off command is given to the tool. It will be apparent that the actual shut off command from detection of non-linear strain or the actual detection of non-linear strain will not occur at exactly the point 100 since comparisons are being made every two $\Delta\alpha$. Thus, the actual yield detection will probably occur later, e.g. at the point 112 as shown in FIG. 8.

Thus, tightening is normally terminated in response to a torque governed, an angle governed or a mixed shut off command, but in the case of yield point detection or, in the alternative, detection of non-linear strain below the yield point, a premature shut off command is given. It will accordingly be apparent that the upper end of the scatter band is eliminated by a secondary yield point shut off. Thus, the total scatter will be reduced. It will also be apparent that the detection of non-linear strain may be conducted as disclosed in U.S. Pat. Nos. 3,643,501 or 3,693,726, although the technique herein disclosed in deemed preferable.

It will be appreciated that the non-linear strain detection conducted at the mid-point stop 62 is conceptually the same as the determination made during tightening toward the final desired tension value. The details of the determination as here disclosed are somewhat different. In order to simplify the program, it may be desirable to utilize a common approach.

It has been discovered that tightening can be consistently terminated in response to non-linear strain in the elastic region provided that certain precautions are taken. It is essential that a reliable value be obtained for the average torque rate of the fastener being tightened. Necessary to obtaining a reliable torque rate is conducting the calculations over an angle increment of significant size relative to the angular distance between the origin of stress and the proof load of the fastener. Typically, the minimum angle increment over which torque rate calculations are conducted should be in the range of 10–20% of this angular distance. Torque rate determinations made over smaller angle increments tend to be unduly influenced by noise in the torque signal. Another desirable feature is avoiding a two point torque rate calculation and instead using an averaging technique using at least 5 and preferably 10 different data points in order to minimize the effect of a single unusual torque sensing on the calculated torque rate. The approach of this invention is particularly suited to terminating tightening in response to non-linear strain in the elastic zone because of the pains taken to obtain a consistently reliable average torque rate. It will be appreciated that this feature is of considerable importance because of the desire of joint designers to achieve high tension stresses in the bolts without advancing threading into the zone of plastic deformation.

PROCEDURES AT TERMINATION

Frequency of Shut Off Due to Non-linear Strain

It is preferred that the selection of F_D will be low enough so that the cutoff due to detection of non-linear strain will be rare, e.g. 0.1%. In the event that the percentage of premature tightening termination due to non-linear strain detection rises substantially during a production run, this indicates that the fasteners, i.e. bolts and/or threaded parts, employed do not meet design specifications. Accordingly, a high percentage of non-linear strain detections is a signal that quality control investigations need to be conducted on the fasteners employed. For example, if the normal occurrence of non-linear strain is on the order of 0.1%, and a running average of non-linear strain detections is 10%, it is likely that the fasteners being run do not meet specifications.

To identify batches of fasteners which do not meet specifications, a running count of the number of joints tightened is maintained and a running count of the number of joints exhibiting non-linear strain is maintained. A frequency determination is accordingly made, as follows:

$$(C_Y/C_J) \geqq A \quad (79)$$

where C_J is the number of joints tightened, C_Y is the number of joints experiencing non-linear strain and A is some fraction acceptable to the user. From present information, it appears that the value of A should be in the range of 0.10–0.20, e.g. 0.15. The ratio of C_Y/C_J is preferably a running ratio, rather than a cumulative ratio, as by storing, on a first-in, first-out basis, a finite number of joints tightened C_J, e.g. 30, and any instances of non-linear strain detection C_Y. When the running ratio of C_Y/C_J equals or exceeds the selected value A, a suitable signal may be provided indicating that the frequency of non-linear strain is much too high. The investigations to be conducted normally include analysis of the strength and material composition of the fasteners, a technique well known in the art.

When to Conduct Extensive Quality Control Procedures

It will be appreciated that termination of tightening may occur normally, i.e. in response to the final shut off parameter, may occur in response to the detection of non-linear strain during tightening toward the final shut off parameter, may occur because the mid-point tension F_o is too close to the final desired tension value F_D or may occur in response to one of the quality control procedures done at the mid-point **62**. If tightening is terminated because the mid-point tension F_o is too close to F_D so that the tool cannot be restarted, one of two conclusions can be reached: (1) the joint has an unusually low value for torque rate TR and should be rejected or (2) the joint is acceptable provided that F_o passes the final tension check discussed hereinafter. The decision depends on the other quality control procedures conducted at the mid-point **62** and the decision of the system designer. In the circumstance where tightening is terminated because the joint is rejected by one of the quality control procedures, nothing further needs to be done. Accordingly, there are two situations where extensive quality control procedures are desirable, i.e. when tightening is terminated normally and when tightening is terminated in response to the detection of non-linear strain occurring after the mid-point stop **62**.

Final Tension Determination in the Elastic Zone

It is desirable to calculate and store the final tension appearing in a fastener, the tightening of which is terminated normally, i.e. in response to torque and/or angle rather than non-linear strain. When using a torque approach, equation (87) gives a value for F_{final} regardless of whether yield has occurred or not. When using an angle approach, the final achieved tension value may be calculated from:

$$F_{final}=F_D-rFR_1(\alpha_{final}-\alpha_{actual}) \tag{80}$$

where α_{actual} is the actual measured angle increment between the T_{sp} or $1.08T_{sp}$ and the final stopping point.

Final Tension at Tool Stall

It is also desirable to calculate and store final tension appearing in a fastener in other circumstances, such as when the tool stalls. Tool stall may occur before the mid-point stop **62** or after. Before the mid-point stop **62**,

$$F_{final}=F_o \tag{81}$$

After the mid-point stop **62**, the final desired tension value F_{final} may be calculated using a torque approach as:

$$F_{final}=F_o+\frac{FR_1}{R(TR)}(T_{final}-T_{sp}) \tag{82}$$

where T_{sp} is the calculated torque at the mid-point stop by equation (57) and T_{final} is the last highest torque sensing obtained within one or two $\Delta\alpha$ increments of the final stopping point.

After the mid-point stop **62**, the final desired tension value F_{final} may alternatively be calculated, using an angle approach, as:

$$F_{final}=F_o+rFR_1\alpha_{actual},\ \text{where } X>0 \tag{83}$$

where α_{actual} is the actual measured angle from T_{sp} or $1.08T_{sp}$ to the final stopping point.

Non-linear Strain Detection

This is a theoretically redundant check on the possible occurrence of excessive non-linear strain. The joint is rejected or indicated as having experienced excessive non-linear strain in the event that:

$$T_{final}\leqq T_m+TR(-\alpha_{origin}-\alpha_F)+u(\alpha_{actual}-\alpha_y) \tag{84}$$

where T_m is the mean torque value at the angle location α_F. It will be recollected that α_{origin} is a negative value thereby requiring the minus sign. The technique is basically to add a calculated torque value to the mean torque T_m to obtain a calculated torque value at the mid-point stop and then add another calculated torque value representing the additional increase in torque from the mid-point stop to the final stopping place which occurs at the angle sensing α_{actual}. If this calculated value is equal to or greater than the highest torque sensing T_{final} obtained within one or two $\Delta\alpha$ increments of the final stopping place, the joint is flagged.

Final Tension Determination in the Plastic Zone

It is highly desirable to calculate and store the final tension appearing in a fastener which has been stopped prematurely because of non-linear strain detection. It may be that the final tension value achieved is well within an acceptable range. In the event, it would be disadvantageous to require removal and replacement of the fastener pair if the problems associated with marginally yielded fasteners are not material if the fasteners are sufficiently stressed to assure acceptable joint conditions.

Accordingly, when using an angle approach, the value of final tension may be calculated as follows:

$$F_{final}=F_D-rFR_1(\alpha_{actual}+\alpha_y-\alpha_2) \tag{85}$$

where α_2 is the angle from the stopping point **102** to the location where yield detection is sensed. It will be appreciated that any calculated value of F_{final} is somewhat of an approximation since the tension rate well above the proportional limit is unknown and perhaps unknowable with any degree of accuracy. FIG. 9 graphically illustrates the difficulty. If the final tension value were calculated:

$$F_{final}=F_D-rFR_1(\alpha_{final}-\alpha_2) \tag{86}$$

the tension actually being calculated would be at the point **114** which is at the same angular position α_2 from the stopping point **102** as the yield detection point **112**.

It will be appreciated that the difference in tension values between the points **112**, **114** may be significant in some circumstances. Since it is known that the tension rate falls off substantially immediately prior to the point **100**, it is safe to calculate the tension value at the point **116** which is spaced downwardly along the slope FR_2 by an angular distance α_y. Thus, the rationale for the equation (86) is apparent. It will be appreciated that the actual final tension appearing in the joint is that at the point **112** which differs from the calculated tension value appearing at the point **116**. It will be seen, however, that the tension value at the point **116** is a substantially better estimation of actual final tension than is the tension that would be calculated at the point **114**. This is particularly true since the tension rate in the range **118** is known to be quite low. The final tension value F_{final} along with a notation that the bolt has yielded may be displayed at the tool location, printed or otherwise recorded for further use or analysis.

In the event the torque governed final shut off parameter is being used, when $T \geqq T_y$, non-linear strain is detected and a shut off command is given the tool. The final tension value may be calculated from a torque approach, as follows:

$$F_{final} = F_D - \frac{FR_1(T_D - T_{final})}{R(TR)} \tag{87}$$

where T_{final} is the highest value of torque sensed within one or two $\Delta\alpha$ increments before the final stopping place **102**. This is likewise illustrated in FIG. 9. The detection of yield occurs at point **112** on the torque curve **10** which the point **102** being the final stopping point. The torque at the point **102** is unreliable for the same reasons that the torque reading at the mid-point stop **62** is unreliable. Accordingly, the torque value T_{final} is taken as the peak within one or two $\Delta\alpha$ increments backward from the point **102**, such as at the point **120**. The effect of this, graphically, is shown by the horizontal line **122** terminating on the torque slope TR_2 at the point **124** and the vertical line **126** terminating at the point **128** on the tension slope FR_2. Thus, the final tension value F_{final} is the calculated tension at the point **128**.

In the alternative, the following estimate is fairly accurate:

$$F_{final} = F_D - \left(\frac{T_{mm} + u\alpha_{final} - T_{final}}{u} \right) rFR_1 \tag{88}$$

where T_{mm} is T_{sp} provided that $T_{sp} \geqq T_{mm}$, where T_{mm}, is $T_m + TR(-\alpha_{origin} - \alpha_F)$. If $T_{sp} < T_{mm}$, then $T_{mm} = TR(-\alpha_{origin} - \alpha_F)$.

In the event the tool continues to run far beyond any reasonable angle of advance, the conclusion is that the bolt has failed without yield detection, as may occur before the mid-point stop **62**. Thus, no appreciable tension appears in the bolt and

$$F_{final} = 0. \tag{89}$$

Final Tension Check

In any circumstance where F_{final} is calculated, it may be desirable to compare it with the final desired tension value F_D. In this event, if

$$\left| \frac{F_{final} - F_D}{F_D} \right| \leqq B \tag{90}$$

where B is a fraction deemed acceptable to the user, a suitable signal may be displayed to indicate that calculated tension is substantially below desired tension. From present information, it appears that the magnitude of B should be greater than the expected scatter from use of this invention and preferably should be 3–4 normal deviations. Thus, B should be in the range 0.10–0.17.

Final Tension Consistency Check

Another approach of this invention is to normally terminate tightening in response to one parameter, e.g. torque, and check this shut off parameter against another shut off parameter, e.g. angle. If the results compare closely, this is an indication that the assumptions made, the empirically determined joint parameters and the like are reasonably correct. If the comparisons are significantly different, this is an indication that something is amiss and that the operation should be stopped or investigations instituted to determine the cause. When using torque as the tightening parameter, F_D has been placed in the calculations for the final torque value T_D by equation (53) or (54) depending on whether $X \geqq 7$ 0 or $X < 0$. The calculated value of final tension F_{final} using an angle approach at a final angle of advance of α_{final} is:

$$F_{final} = F_D - rFR_1(\alpha_{final} - \alpha_{actuul}) \tag{91}$$

where α_{actual} is the angle of advance from T_{sp} or $1.08T_{sp}$ to the final stopping point. If the different between F_D and F_{final} is small, e.g. ±5–10%, it is apparent that substantial confidence may be placed in the technique. If the difference between F_D and F_{final} is larger, e.g. ±20%, it is apparent that something is amiss and that the tightening operation should be stopped or investigations instituted to determine the cause.

Final Torque Consistency Check

Assuming that the final advance of the fastener was determined in terms of angle and the joint has not experienced non-linear strain, a check of the value of the actual final peak torque T_{final} against a calculated value of the expected final torque T_D provides an independent evaluation of the procedures. In order to make this determination, preliminary calculations are made. First, the actual attained final tension value F_{final} differs from the expected tension value F_D only if the actual amount of tool overrun is different from the estimate $d\alpha$. The actual attained tension value is

$$F_{final} = F_D + (\alpha_{actual} - \alpha_{final}) rFR_1 \tag{92}$$

where α_{actual} is the actual observed angle from T_{sp} or $1.08T_{sp}$. This calculation will provide a value for actual attained tension for F_{final}. Realizing that the actual attained tension value F_{final} will differ from F_D, a correction is made in the expected value of final torque T_D, as follows:

$$T_D' = T_D(F_{final}/F_D) \tag{93}$$

where T_D' is the revised value of T_D. The value of T_D' must be comparable with T_{final}. A torque-angle consistency factor η_T is then defined as

$$\eta_T=(T_D'-T_{final})/T_D' \qquad (94)$$

Ideally, η_T should be zero. It will be appreciated, however, that minor deviations in η_T from zero are not indicative of any substantial problem. In good quality joints, it has been found that values of η_T on the order of about 0.13 rarely give false indications of defective joints. Accordingly, this value is used. If a better value is available, it should be used instead. Thus, a joint is judged defective in the event that

$$-0.13\leqq\eta_T\geqq0.13, \qquad (95)$$

the tool is reset for the next tightening cycle and a signal is given that the joint has failed. In the event that parts quality is known to be subnormal, the value of η_T should be increased somewhat.

This quality control procedure causes the rejections of joints experiencing thread galling, joint where the mid-point analysis, for some reason, is performed in a very low tension range, joints which yield and the non-linear strain procedures do not detect if, joints tightened with faulty torque or angle instrumentation, or joints tightened with incorrect input parameters fed to the microprocessor.

Final Torque Rate Consistency

This quality control procedure is intended to provide additional insurance against a fairly flat torque-angle curve near the termination of tightening which may possibly indicate significant penetration of the plastic zone somehow not detected by other routines. In this procedure, the final torque rate is checked against the empirically determined torque rate u or TR_2 within the angle interval of actual tool overrun. Defining,

$$FRC=(T_{final}-T_{marker})/u \qquad (96)$$

where T_{marker} is the torque sensing at the shut off command and T_{final} is the peak torque value sensed in the last few $\Delta\alpha$ increments prior to stopping. If FRC is less than some suitable value, e.g. 0.25, the joint is indicated as failing this procedure. This procedure has its difficulty because the value of T_{final}, which is the peak value of torque within one or two $\Delta\alpha$ increments from the final stopping point, is influenced by the act of stopping rotation for the same reason that the last torque readings prior to the mid-point stop 62 are suspect. Experience indicates that if joints are rejected when $FRC<0.25$, there is a false indication of joint inacceptability approximating a 1% frequency. This is believed to be caused in large part by the suspect value of T_{final}. The procedure does, however, have its value in providing considerable assurance against premature yielding if that is of paramount concern to the user.

Frequency of Joint Rejections

It is desirable to indicate a parts integrity problem when the number of joints that have failed at least one of the quality control procedures is too frequent. In other words, the joint failure frequency determinations are desirably merged into one single frequency determination. The difficulty to be avoided is, of course, counting twice a joint which fails two of the quality control procedures. Under normal circumstances, this is not a substantial problem because the quality control procedures are conducted sequentially and not simultaneously. Accordingly, any joint that fails a single test causes the cycle to terminate and the tool to be reset for the next succeeding tightening cycle. Accordingly, when

$$(C_{FTR}+C_{TRC}+C_{TRL}+C_{NM}+C_{NLS}+C_F+C_{NF}+C_{TC}+C_{FT})/C_J\geqq J \qquad (97)$$

a signal is generated to energize a parts integrity indicator, where C_{FTR} is the number of failures of the final torque rate check, C_{TRC} is the number of failures of the torque rate curvature check, C_{TRL} is the number of occurrences where the torque rate is too low, C_{NM} is the number of failures of the non-linear strain determination at the mid-point stop 62, C_{NLS} is the number of times that tightening is terminated in response to non-linear strain rather than in response to the normal tightening parameter, C_{NF} is the number of failures of the final non-linear strain determination, C_F is the number of failures of the tension check, C_{TC} is the number of failures of the tension consistency check, C_{FT} is the number of failures of the final torque consistency check, C_J is the number of joints tightened and J is a fraction acceptable to the user. It will be apparent, of course, that a number of these quality control procedures may be omitted from any particular application and consequently will have no bearing on this frequency check. It is preferred, as in other frequency checks, that C_J be a finite running number of joints stored on a first in, first out basis. The quantity selected for this finite number should be sufficiently large to avoid statistical aberrations and accordingly is preferably on the order of 50–500. The value of J is inversely related to the selected quantity of C_J in the sense that the higher the value for C_J, the lower may be the selected value of J. From present information, it appears that J should be on the order of about 0.05–0.20 and is preferably about 0.10 to avoid giving false indications of a systematic parts problem when none exists.

Repair of Failed Joints

When a joint is rejected by the tightening technique of this invention, it is highly likely that at least one part constituting the joint is not up to specifications. In such cases, it is highly desirable that defective parts be replaced and the tightening process repeated. However, if the user so wishes, rejected joints can be automatically tightened to a different parameter and the shut off command given. Because of the stored values of torque and angle, it is conceivable that the repair technique could comprise a turn-of-the-nut approach so that the tool could be instructed to advance a predetermined number of degrees beyond a particular torque location. It appears, however, that a turn-of-the-nut approach is not the most desirable for repairing failed joints. Instead, it is preferred that the rejected joints be tightened to a specified minimum torque and the shut off command given. Because of overrun, the final torque achieved would be somewhat greater than the minimum specified. This could, of course, be accomodated by making a simple overrun prediction along the lines of equation (64). It is apparent that this procedure is applicable to joints tightened in accordance with this invention using either the torque or angle option or tightened in accordance with a turn-of-the-nut strategy.

Shear Joint Routine

In joints which are subjected to significant axial loads, i.e. loads parallel to the bolt axis, the only object of tightening is to induce a desired tensile stress in the bolt. This is not precisely true in joints where all or a substantial fraction of the external load is transverse, i.e. in a plane perpendicular to the bolt axis. In shear joints of this type, it is desirable from the standpoint of joint mechanics to assure that a minimum torque value has been applied in addition to assuring that the bolt stress is above a predetermined value. Accordingly, a typical fastener in a shear joint might be tightened to 90% proof and 40 foot pounds. Calculations are conducted in accordance with the previous disclosure to terminate tightening at 90% proof. If the estimated or actual torque value at the termination of threading advance or one or two $\Delta\alpha$ increments prior thereto is less than the minimum predetermined torque, the tool is restarted until the minimum torque value is attained. Accordingly, if the final estimated torque T_D or the final peak torque T_{final} is equal to or greater than the minimum torque T_{min}, tightening is terminated normally. On the other hand, if the estimated final torque T_D or the peak torque T_{final} is less than T_{min}, a value of shut off torque T_{sh} is calculated as

$$T_{sh} = T_{min} - ud\alpha \tag{98}$$

The tool is accordingly restarted and the air supply valve is closed at a location where the running torque value is T_{sh}. The tool overruns for an angle increment $d\alpha$ so that the final attained torque value is T_{min}.

Joint With Multiple Fasteners

When tightening seriatim a multiplicity of fasteners comprising part of a single joint using a conventional technique, it is well known that the first tightened fasteners will lose at least some tension by the time the last fasteners are tightened. This is, of course, related to joint relaxation and alignment of the joint parts. In accordance with this invention, one powered instructable tool as disclosed more fully hereinafter may be used for each fastener and used in the following manner.

The tools are started simultaneously. When all of the tools have stopped at the mid-point 62, all the tools are restarted simultaneously to accomplish the final advance. In this manner, the alignment of all the fasteners and all joint relaxation occurs at the mid-point stop **62**. Each tool would then compensate for any relaxation that may have occurred adjacent the fastener coupled thereto. It will be apparent that the control mechanism for the tools would be interconnected electronically in a fashion that will be apparent to those skilled in the art following the more complete description of the tool hereinafter.

EQUIPMENT

Referring to FIG. 10, there is illustrated a schematic showing of a mechanism **126** for performing the previously described technique. The mechanism **126** includes an air tool **128** connected to the air supply **130** and comprising an air valve **132**, an air motor **134** having an output **136** coupled to the fastener pair comprising part of the joint **138**, a torque transducer **140** and an angle transducer **142**. The torque transducer **140** is connected to a signal conditioner **144** of a data processing unit **146** by a suitable electrical lead **148**.

The signal conditioner **144** is designed to receive electrical signals from the transducer **140** and modify the voltage and/or amperage thereof into a form acceptable by an analog-to-digital converter **150** through a suitable connecting circuit **152** described more fully hereinafter. The converter **150** changes the analog signal received from the conditioner **144** into digital form for delivery to an interface logic unit **154** through a suitable connection **156**. The angle transducer **142** is connected to the interface logic unit **154** by a lead **158**.

The connecting circuit **152** provides the torque signal filtering function discussed. To this end, the circuit **152** includes a pair of parallel leads **158**, **160** connecting the signal conditioner **144** to the analog to digital converter **150**. The lead **158** is connected to a ground **162** by a lead **164**. The lead **160** includes a resistor **166**. Extending between the leads **158**, **160** is a lead **168** having a first capacitor **170** therein. A second lead **172** also extends between the leads **158**, **160** and has therein a second capacitor **174** as well as a switch mechanism 176 of a relay **178**. The relay **178** may be of any suitable type and is designed, when energized, to close the switch mechanism **176** to place the second capacitor **174** in parallel with the first capacitor **170** in the connecting circuit **152**.

In operation with the relay **178** unenergized, the resistance **166** and the first capacitor **170** act as an R-C filter to remove very high frequency noise from the conditioned torque signal passing across the leads **158**, **160**. When the relay **178** is energized, the second capacitor **174** is placed in parallel with the first capacitor **170**. Together, the resistor **166** and the capacitors **170**, **174** act to filter the analog torque signal appearing in the leads **158**, **160**. As mentioned, the circuit **152** is employed with tightening tools which produce a substantial amount of internal chatter. In such tools, the relay **178** is energized during an initial portion of the tightening cycle, usually up to and including the mid-point stop **62**. Accordingly, the resistance-capacitance network provided by the resistor **166** and the capacitors **170**, **174** act to substantially filter the analog torque signal appearing on the leads **158**, **160**. At the mid-point stop 62, the energizing signal delivered to the relay **178** is terminated so that the switch mechanism 174 opens to remove the capacitor 176 from the connecting circuit 152.

It will be appreciated that the relative sizes of the resistor **166**, first capacitor **170** and second capacitor **174** control the degree of filtering actually accomplished. Although the design of the filtering network is subject to design selections, the following sizings have proved acceptable: the resistance of the resistor **166** is 2000 ohms, the capacitance of the first capacitor **170** is 0.5 microfarads, and the capacitance of the second capacitor **174** is 5 microfarads.

The interface logic unit **154** comprises an interface logic section **180** designed to handle information and is connected through suitable connections **182**, **184** to a microprocessor unit **186** which is in turn connected to a data memory unit **188** and an instruction memory and program unit **190** through suitable connections **192**, **194**, **196**, **198**. The interface logic section **180** is also designed to receive input parameters such as T_{os}, FR_1, r, F_D and the like.

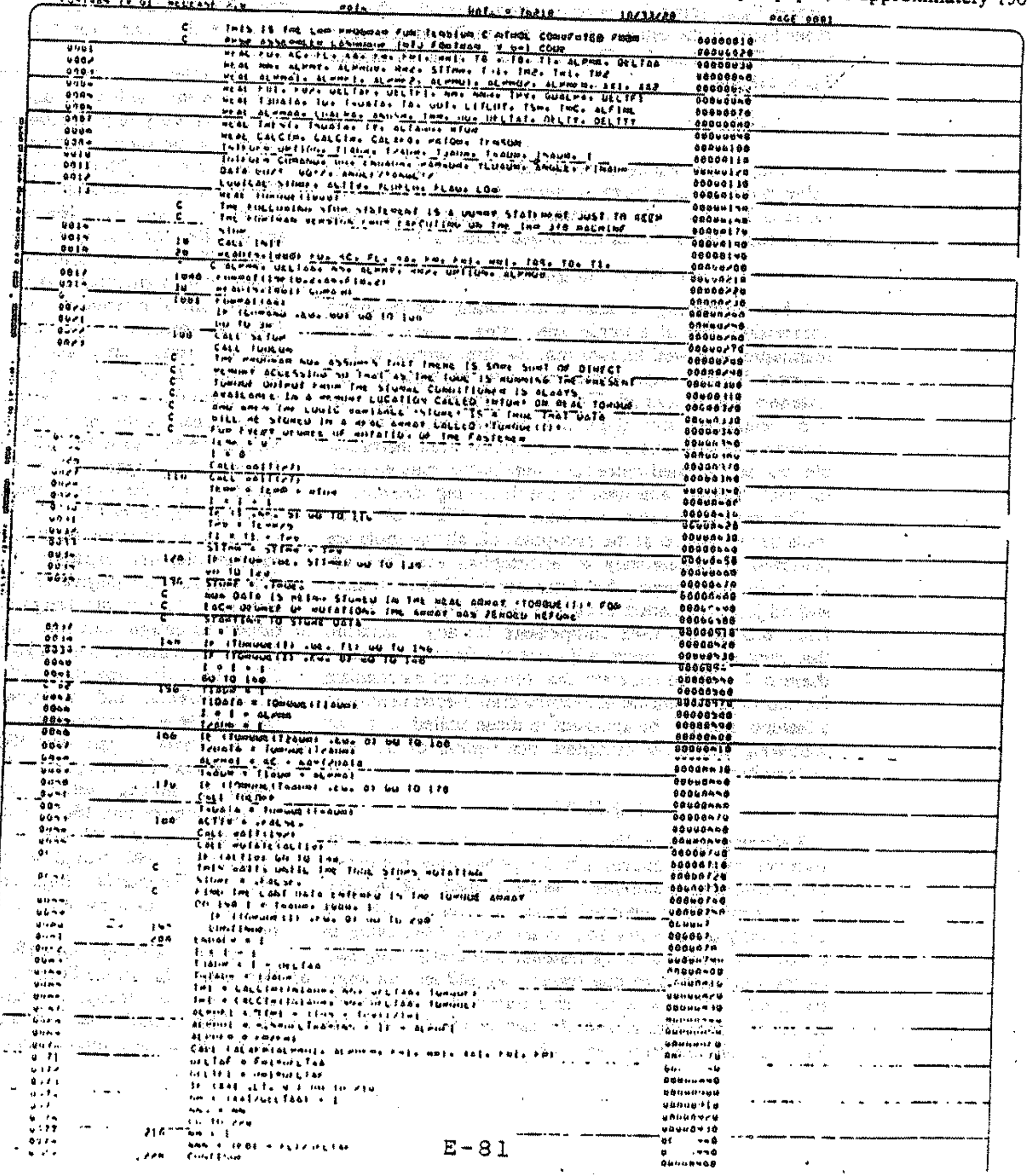
The interface logic unit **154** also comprises an amplifier section **200** controlling a solenoid (not shown) in the air valve **132** through a suitable electrical connection **202**. The amplifier section **200** also controls a display panel **204** having suitable signal lights through an electrical connection **206** as will be more fully explained hereinafter. The relay **178** is similar energized through a connection **208** from the amplifier section **200**.

The air tool **128** may be of any type desired such as a Rockwell model 63W which has been modified to reduce the amount of overrun or such as is shown in copending application Ser. No. 766,429. It has been surprising to learn that the bulk of the tool overrun occurs between the time the shut off command is given through the electrical connection **202** and the time that high pressure air downstream of the valve **132** is exhausted through the motor **134** while the amount of overrun attributable to inertia of the air tool **128** is rather insignificant at high running torque values because tool speed is rather slow.

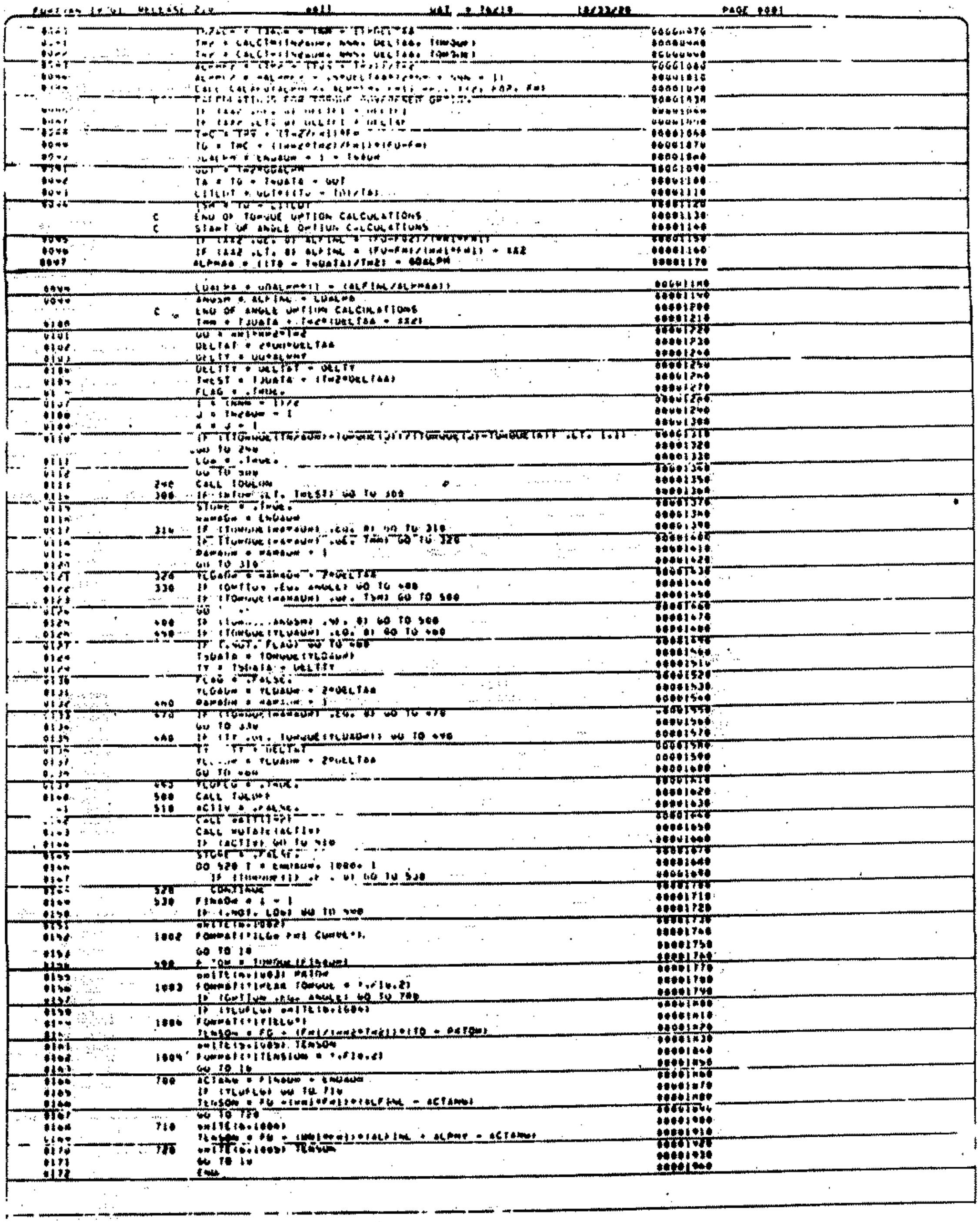
The data processor **146** is shown in greater detail in FIG. **11** and conveniently comprises a Rockwell microprocessor model PPS8. For a more complete description of the data processor **146**, attention is directed to publications of Rockwell International pertaining thereto.

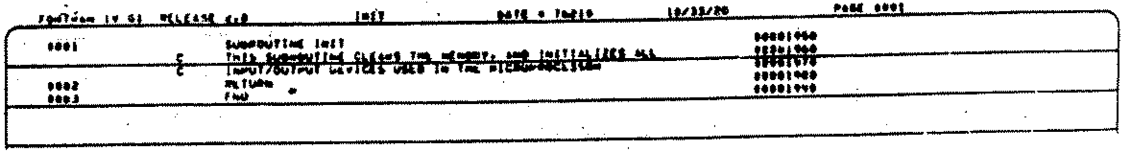
The data processor **146** comprises a chassis **210** having a power source **212** mounted thereon along with the signal conditioner **144**, the instruction memory and program unit **190**, the data memory unit **188**, the microprocessor unit **186**, the interface logic section **180**, the converter **150** and the logic interface amplifier section **200**. The signal conditioner **144**, the interface logic section **180**, the microprocessor unit **186**, and the data memory unit **188** are not modified in order to equip the data processor **146** to handle the calculations heretofore described.

The instruction memory and program unit **190** is physically a part of the data processor **146** and is physically modified to the extent that a suitable program has been placed therein. The initial machine language program developed during the investigation of this invention contains over 7,000 instructions and, on conventional computer output paper, is approximately 150



pages long. In the interests of brevity, economy and clarity, the following program is a FORTRAN version of the machine language program. This FORTRAN program will be understandable to any programmer skilled in the art and may be reconverted into a machine language program either manually or by the use of a standard language translation program. There are some input-output functions performed in the microprocessor 186 which cannot be converted into FORTRAN. These functions are pointed out in subroutines with comments describing what events should occur and be controlled by the subroutines. The FORTRAN program is as follows:





```
FORTRAN IV G1  RELEASE 2.0              INIT          DATE = 78210         10/23/80                 PAGE 0001

 0001                    SUBROUTINE INIT                                                   00001950
                   C     THIS SUBROUTINE CLEARS THE MEMORY, AND INITIALIZES ALL            00001960
                   C     INPUT/OUTPUT DEVICES USED IN THE MICROPROCESSOR                   00001970
 0002                    RETURN                                                            00001980
 0003                    END                                                               00001990
```

```
FORTRAN IV G1  RELEASE 2.0          SETUP            DATE = 78210        10/33/28            PAGE 0001
      0001                 SUBROUTINE SETUP
                  C        THIS SUBROUTINE CLEARS ALL THE WORK SPACE IN THE PROGRAM          00002000
                  C        AND PREPARES IT FOR A TIGHTENING OPERATION                        00002010
      0002                 RETURN                                                            00002020
      0003                 END                                                               00002030
                                                                                             00002040
```

```
FORTRAN IV G1  RELEASE 2.0          TOOLON           DATE = 78210        10/33/28            PAGE 0001
      0001                 SUBROUTINE TOOLON
                  C        THIS SUBROUTINE OUTPUTS A SIGNAL TO AN I/O DEVICE TO TURN         00002050
                  C        ON A POWER TRANSISTOR THAT TURNS ON THE AIR SOLENOID THAT         00002060
                  C        OPERATES THE AIR TOOL                                             00002070
      0002                 RETURN                                                            00002080
      0003                 END                                                               00002090
                                                                                             00002100
```

```
FORTRAN IV G1  RELEASE 2.0          TOLOFF           DATE = 78210        10/33/28            PAGE 0001
      0001                 SUBROUTINE TOLOFF
                  C        THIS SUBROUTINE OUTPUTS A SIGNAL TO AN OUTPUT DEVICE TO TURN      00002110
                  C        OFF THE AIR TOOL                                                  00002120
      0002                 RETURN                                                            00002130
      0003                 END                                                               00002140
                                                                                             00002150
```

```
FORTRAN IV G1  RELEASE 2.0          WAIT             DATE = 78210        10/33/28            PAGE 0001
      0001                 SUBROUTINE WAIT(TIME)
      0002                 REAL TIME                                                         00002160
                  C        THIS SUBROUTINE IS A WAIT LOOP THAT WAITS IN                      00002170
                  C        MILLISECONDS THE TIME SPECIFIED IN THE PARAMETER                  00002180
      0003                 RETURN                                                            00002190
      0004                 END                                                               00002200
                                                                                             00002210
```

```
FORTRAN IV G1  RELEASE 2.0          ROTATE           DATE = 78210        10/33/28            PAGE 0001
      0001                 SUBROUTINE ROTATE(RUN)
      0002                 LOGICAL RUN                                                       00002220
                  C        THIS SUBROUTINE CHECKS AN I/O DEVICE TO SEE IF THE AIR TOOL       00002230
                  C        IS RUNNING OR NOT AND SETS THE LOGIC VARIABLE RUN TRUE IF         00002240
                  C        THE TOOL IS STILL ROTATING                                        00002250
      0003                 RETURN                                                            00002260
      0004                 END                                                               00002270
                                                                                             00002280
```

```
FORTRAN IV G1  RELEASE 2.0          CALCTA           DATE = 78210        10/33/28            PAGE 0001
      0001                 REAL FUNCTION CALCTA(START,PTS,INCH,TORQUE)
      0002                 REAL START, PTS, INCH, TORQUE(1000), SUM                          00002290
      0003                 INTEGER I, COUNT                                                  00002300
      0004                 SUM = 0                                                           00002310
      0005                 COUNT = 0                                                         00002320
      0006                 I = START                                                         00002330
      0007           100   SUM = SUM + TORQUE(I)                                             00002340
      0008                 I = I + INCH                                                      00002350
      0009                 COUNT = COUNT + 1                                                 00002360
      0010                 IF (COUNT .NE. PTS) GO TO 100                                     00002370
      0011                 CALCTA = SUM/PTS                                                  00002380
      0012                 RETURN                                                            00002390
      0013                 END                                                               00002400
                                                                                             00002410
```

```
FORTRAN IV G1  RELEASE 2.0          CALCTR           DATE = 78210        10/33/28            PAGE 0001
      0001                 REAL FUNCTION CALCTR(START,PTS,INCH,TORQUE)
      0002                 REAL START, PTS, INCH, TORQUE(1000), SUM                          00002420
      0003                 INTEGER I, COUNT                                                  00002430
      0004                 COUNT = PTS                                                       00002440
      0005                 SUM = 0                                                           00002450
      0006                 I = START                                                         00002460
      0007           100   SUM = SUM + (PTS + 1 - 2*COUNT)*TORQUE(I)                         00002470
      0008                 I = I + INCH                                                      00002480
      0009                 COUNT = COUNT - 1                                                 00002490
      0010                 IF (COUNT .NE. 0) GO TO 100                                       00002500
      0011                 CALCTR = (-6/(INCH*(PTS*PTS*PTS - PTS)))*SUM                      00002510
      0012                 RETURN                                                            00002520
      0013                 END                                                               00002530
                                                                                             00002540
```

```
FORTRAN IV G1  RELEASE 2.0          CALAFO           DATE = 78210        10/33/28            PAGE 0001
      0001                 SUBROUTINE CALAFO(OMEGA,ALPHAO,FR1,RR1,A,FOA,FR)
      0002                 REAL OMEGA, ALPHAO, FR1, RR1, A, FOA, FR                          00002550
      0003                 A = -OMEGA - ALPHAO                                               00002560
      0004                 IF (A .GE. 0) FOA = FR + FR1*RR1**A                               00002570
      0005                 IF (A .LT. 0) FOA = -FR1*OMEGA                                    00002580
      0006                 RETURN                                                            00002590
      0007                 END                                                               00002600
                                                                                             00002610
```

Because of the limitations of the FORTRAN language, all of the abbreviations in lines 30–100 of the program may not be immediately recognizable. The abbreviations that may not be recognizable are:

KA is a in equation (8);

KC is c in equation (8);

RR_1 is r or FR_2/FR_1;

NN is n or the number of data points used in the first calculation of TR;

ALPHOV is the overrun angle under no torque conditions;

STTHR is T_{sth};

TM1 and TM2 are the mean torque values from equation (15) on the first and second calculations of the torque rate in the region **18**;

TR1 and TR2 are the average torque rates from equation (16) on the first and second calculations of the torque rate in the region **18**;

ALPHF1 and ALPHF2 are the results of equation (17) on the first and second torque rate calculations;

ALPHO1 and ALPHO2 are the results of equation (18) on the first and second torque rate calculations;

XX1 and XX2 are the values for X from equation (20) on the two torque rate calculations;

FO1 and FO2 are the calculated tension values at the mid-point stop **62** on the two torque rate calculations;

NNN is n_1 in equation (22);

TPV is the prevailing torque;

GDALPHA is actual measured overrun at the mid-point stop **62**;

GDT is the result of equation (61);

TSH is the torque value at the shut off command and is T_D—dT;

TMC is T_{MC} in equation (59);

ALPHAA is the result of equation (49);

LDALPHA is the result of equation (50) and is the calculated tool overrun;

ANGSH is the angle at the shut off command;

TMM is T_{sp} from equation (57) or (58);

UU is u from equation (55);

DELTAT is the result from equation (74);

DELTTY is the result from equation (75);

TREST is the torque value upon restarting from the mid-point stop **62**;

ACTANG is the actual angle from the mid-point stop **62** to the final stopping point;

PKTOR is the peak torque value sensed immediately prior to the final stopping point; and

TENSON is the final calculated tension value.

Since the filing of the parent application, a second generation program has been developed. Rather than unduly lengthen this specification, the following program instructions will enable anyone of ordinary programming skills to prepare a program in any suitable language for any suitable data processor.

Program Instructions

Fixed input: θ_{rd}, $(T_{pv})_{max}$, T_1 (time or loop number limit), α_k, a, c, S_T (number of counts from torque encoder per ft-lb), S_α (number of pulses from angle encoder per degree), α_{or}, T_o, Ω (correction for torsional flexibility of bolt and tool downstream of angle encoder), F_M, FR_1, r, R, T_{os}, $\Delta\alpha$, n, α_y, K_{min} (in these instructions, K=TR), (angle divisor), (special routine flags), and F_D.

1. Reset memory and registers.
2. $\Delta\theta = 22$ degrees.
3. Convert input values from engineering to internal units (degrees to pulses, ft-lb or N-m, etc to counts).
4. Let one (1) $\Delta\theta$ elapse, read torque there and every $\Delta\theta$ thereafter until:
   (i) $T \geqq (T_{pv})_{max}$ twice then call Subroutine (abnormal), or
   (ii) θ_{rd} is reached. Over the next revolution find the average T_{pv} and store. Continue to check for condition (i).
5. $T_1 = T_1 + T_{pv}$.
6. $T_{sth} = 0.25\ T_1$.
7. Search $T \geqq T_{sth}$, if time or loop number $\geqq$ (time or loop number limit), call Subroutine (abnormal); otherwise,
8. Search for $T \geqq T_1$, if time or loop number $\geqq$ limit, call Subroutine (abnormal), otherwise,
9. Pace ahead α_k pulses in torque memory and wait for appearance of data. If time or loop number $\geqq$ limit, call Subroutine (abnormal); otherwise, read and store T_2.
10. $\alpha_1 = c + a(T_2 = T_{pv})$.
11. Pace ahead α_1 pulses from T_1 address in torque memory and wait for appearance of data. If time or loop number $\geqq$ limit, call Subroutine (abnormal); otherwise,
12. Read and store T_4, turn tool off.
13. Verify tool has stopped.
14. $n_H = 3$. Values of 1 or 2 are acceptable as long as the product $n_H\Delta\alpha$ is approximately the same.
15. Call Subroutine (T_m, K).
16. Call Subroutine (α_{orig}, X).
17. If $X \geqq 0$, $n_H = \downarrow(X/\Delta\alpha) + 3$ and $n = n$;
    If $n_H + n > (T_{stop} - \text{address}) - (T_{sth} - \text{address})$, call Subroutine (abnormal);
    If $X < 0$, $n_H = 3$ and $n = n + \downarrow(X/\Delta\alpha)$.
18. Call Subroutine (T_m, K).
19. If $K \leqq K_{min}$, call Subroutine (abnormal).
20. Call Subroutine (α_{orig}, X).
21. If $X \geqq 0$, $F_o = F_M + rFR_{1c}X$; otherwise, $F_o = -\alpha_{orig}FR_{1c}$.
22. $n_H = n_H + \downarrow(n/2) + 1$.
23. $K_a = K$.
24. Call Subroutine (T_m, K).
25. $K_b = K$.
26. If $|(K_a/K_b) - 1| \geqq 0.13$, call Subroutine (abnormal).
27. Call Subroutine (peak torque, T_f).
28. $T_{fm} = T_f$.
29. $K = K_a$.
30. $T_{mm}' = T_m + K(-\alpha_{orig} - \alpha_F)$.
31. $u = rRK$.
32. If $T_{fm} \leqq T_{mm}' - u\alpha_y$, call Subroutine (abnormal).
33. $\delta\alpha = (T_{stop} - \text{address}) - (T_4 - \text{address})$.
34. $y = T_4/T_o$.
35. $z = \delta\alpha/\alpha_{or}$.
36. $\epsilon = Y/(1 - z) - 1$.
37. If $\epsilon \leqq -0.25$, give marginal tool signal, advance counter.
38. If $\epsilon > 0$ and

$$\delta\alpha > \alpha_{or}\left(1 - \frac{T_4}{T_o}\right) + 1 \text{ pulse, then}$$

$$\delta\alpha = \alpha_{or}\left(1 - \frac{T_4}{T_o}\right) + 1 \text{ pulse.}$$

39. Read torque one (1) $\Delta\alpha$ back from T_{stop}; store as T_3.
40. Call Subroutine (α_f, T_{rst}, T_D).

$$d\alpha = \frac{(T_o - T_D)\delta\alpha}{T_o - T_{rst} - (1 - rR)(T_{rst} - T_4)} \tag{41}$$

42. If $d\alpha > 2\alpha_f$, call Subroutine (end).
43. If $T_{rst} \geqq T_{mm}'$, $T_{mm} = T_{rst}$, otherwise, $T_{mm} = T_{mm}'$.
44. $T_6 = 1.08\ T_{rst}$.
45. $\alpha_{sh} = \alpha_f - d\alpha$.
46. $\Delta T = u\Delta\alpha$.
47. $T_y = T_{mm} + 3\Delta T - u(\alpha_y - 0.25\ d\alpha)$.
48. Turn tool on.
49. Search for $T \geqq T_6$ until:
    (i) Time or loop number $\geqq$ limit, then call Subroutine (stall).

(ii) Turn memory on and proceed.

50. Pace α_{sh} pulses adhead of T_6 address, wait until data appears. Turn tool off, call Subroutine (end).

51. Pace three (3) $\Delta\alpha$'s ahead of T_6 address and read torque T. If $T \leqq T_y$, turn tool off; call Subroutine (end).

52. $T_y = T_y + \Delta T$ pace ahead one (1) $\Delta\alpha$ and read T. If $T \leqq T_y$, turn tool off; call Subroutine (end). Otherwise, proceed repeating T_y and α_{sh} checks until one or the other is satisfied.

53. End.

SUBROUTINES

Subroutine (abnormal)

1. Turn tool off.
2. Verify tool has stopped. This is done by waiting for a short time or number of loops after the last data point appears.
3. Call Subroutine (peak torque, T_f).
4. If $T > T_1$, $T_1 = T_1 - T_{pv}$, read $\alpha_{T1} = (T_{stop}-\text{address}) - (T_1-\text{address})$.
5. Report Joint unacceptable (lights, error symbols, etc.)
6. Report T_f and α_{T1}.
7. Go to Start.
8. End.

Subroutine (T_m, K)

1. For torque array T_i at $\Delta\alpha$ angle intervals where $i=n$ is n_H spaces back from T_{stop} and $i=1$ is $(n-1)$ spaces beyond that.

$$T_m = \frac{1}{n}\sum_{i=1}^{n} T_i. \qquad 2.$$

$$K = -6\sum_{i=1}^{n} [(n+1-2i)T_i]/[n(n-1)(n+1)\Delta\alpha]. \qquad 3.$$

4. Return.

Subroutine (α_{orig}, X)

1. $\alpha_F = (T_m - T_{os} - T_{pv})/K$.
2. $FR_{1c} = FR_1(1 - \Omega K)$.
3. $\alpha_{orig} = -\alpha_F - 0.5(n - 1 + 2n_H)\Delta\alpha$.
4. $X = -\alpha_{orig} - (F_M/FR_{1c})$.
5. Return.

Subroutine (Peak Torque, T_f)

1. Inspect torque at each angle pulse within one (1) $\Delta\alpha$ from the stopping point. Find the highest and store under T_f. If $\Delta\alpha = 3$, for instance, four (4) locations are sampled, including the last data point.
2. Return.

Subroutine (α_f, T_{rst}, T_D)

1. If $X \geqq 0$, $\alpha_f = (F_D - F_o)/rFR_{1c}$ $T_{rst} = T_3 + u\Delta\alpha$, and $T_D = T_{rst} + u$ α_f. Otherwise, $\alpha_f = -X + (F_D - F_M)/rFR_{1c}$. $T_{rst} = T_3 + K\Delta\alpha$ and $T_D = T_{rst} + u\alpha_f + X(u - K)$.
2. Return.

Subroutine (end)

1. Verify tool has stopped.
2. $\alpha_{act} = (T_{stop}-\text{address}) - (T_6-\text{address})$.
3. Call Subroutine (peak torque, T_f).
4. $T_1 = T_1 - T_{pv}$.
5. $\alpha_{T1} = (T_{stop}-\text{address}) - (T_1-\text{address})$.
6. If NLS indicated, go to (A).
7. If $T_f \leqq T_{mm} + u(\alpha_{act} - \alpha_y)$, go to (A).
8. $F_f = F_D + (\alpha_{act} - \alpha_f)\, rFR_{1c}$. 9. $T_D' = T_D(F_f/F_D)$
10. $\eta_T = (T_D' - T_f)/T_D'$.
11. If $\eta_T \geqq 0.13$, go to (C).
12. If $(F_f - F_D)/F_D \geqq 0.13$, to go to (C).
13. Go to (B).

(A)

1. $F_f = F_D - (T_{mm} + u\alpha_f - T_f)\, rFR_{1c}/u$.

$$\text{If} \left| \frac{F_f - F_D}{F_D} \right| \geqq .13, \text{ to to (C).} \qquad 2.$$

(B)

1. If NLS indicated, give such output signal (NLS light, symbol, etc.).
2. Output "joint accepted" (light, symbol).
3. Output values of T_f, α_T and FF (display and/or print, etc.).
4. Return to Start.

(C)

1. Report "joint unacceptable" (lights, error symbols, etc.).
2. Report T_f and α_{T1}.
3. Go to Start
4. END

Subroutine (Stall)

1. Call Subroutine (peak torque, T_f). If $T_f/T_o \leqq 0.87$, give marginal tool signal, increment the counter.
2. Call Subroutine (end).
3. END

The interface logic and amplifier circuits 154, 200, illustrated schematically in FIGS. 12A and 12B, serve to provide interfacing of data and control signals between the microprocessor unit 186, a conventional teletype console (not shown), the torque and angle transducers, 140, 142, and the air valve 132 controlling tool operation.

Interfacing between the teletype console and the microprocessor 186 is necessitated by the fact that the console receives and transmits data in a serial format while the microprocessor 186 receives and transmits in a parallel format. The interface logic and amplifier circuits 154, 200 include a universal asynchronous receiver transmitter circuit 212 which receives input data, such as a desired tension value F_D, from the teletype console over the lines 214 in a serial or one bit at a time format, temporarily stores the data, and then transmits the data in parallel format over the lines 216 to the microprocessor 186. Thus a teletype console or other suitable means may provide an input 218 (FIG. 10) for variable empirical parameters, desired bolt tension and the like. Likewise, data from the microprocessor 186, which is to be printed out by the teletype console, is converted from the parallel format in which it is received from the microprocessor 186 over the lines 216 into the serial format for reception by the teletype console.

Timing pulses for the control of the universal asynchronous receiver transmitter 212 as well as other components of the interface logic and amplifier circuits are provided from the microprocessor 186 over line 220, the pulse train being supplied to a conventional divider circuit 222 to produce a timing signal on the line 224 which is a pulse train of lesser but proportional rate to that supplied by the processor 186. Timing pulses are also provided to other components of the interface logic and amplifier circuit over the line **226**. The microprocessor **186** also provides signals over the lines **228** which signals are generated in response to the program to control the transmission of data to and from the microprocessor **186**. Thus, for example, when the microprocessor **186** is in condition to input data, such as the final desired torque value T_D, a signal is transmitted from the microprocessor **186** over the lines **228** to a gating circuit **230** to furnish control inputs at **232**, **234** to the universal asynchronous receiver transmitter **212**. Control and status indication signals for the teletype console are also provided over the lines **236** and, via signal conditioner circuits **238**, over the lines **240**.

FIG. 12B schematically illustrates that portion of the circuit which provides interfacing between the microprocessor **186**, the torque and angle transducers **140**, **142** and the air valve **132**. Torque data from the torque transducer **140** (FIG. 10) is converted by the analog to digital converter **150** into twelve digit binary signals transmitted on the line **156**. The particular microprocessor employed is, however, only capable of receiving an eight digit input. In order to permit transmission of torque data to the processor, a multiplexing arrangement is provided. Thus, the twelve digit output of the analog to digital converter **150** is supplied, through logic level buffers **242**, **244** to a pair of steering gates **246**, **248**, the first four digits being supplied to the first inputs a of the gate **246** while the second four digits are supplied to the corresponding first inputs a of the gate **248**. The final four digits are supplied to the second inputs b of the gate **246**. The corresponding second inputs b of the gate **248** are connected to ground, supplying a constant zero input. The eight line output **250** of the steering gates **246**, **248** provides the torque data input to the microprocessor **186**. The gates **246**, **248** are controlled by signals on the lines **252**, **254** to first pass the a input signals, i.e.the first eight bits of the torque signal, to the output lines **250** followed by the b input signals, i.e. the final four bits and four zeros. In addition to being supplied to the steering gates **246**, **248**, the torque data transmitted on lines **156** is also temporarily stored in the registers **256**, **258**, **260**. These registers normally store the current torque value received from the analog to digital converter **150**. A hold signal furnished by the microprocessor **186** over the line **262** actuates a latching circuit **264** to temporarily freeze the registers **256**, **258**, **260** permitting the torque values stored therein to be read over the lines **266**. This arrangement permits reading of the torque data into the microprocessor **186** while updated torque data is being supplied from the analog to digital converter **150** without the danger of inadvertently reading into storage a data value which is a mixture of old and updated values.

The analog to digital converter **150** supplies an end of conversion signal over line **268** which signal is supplied to the latching circuit **264** over the line **270** to reset the circuit **264** when transmission of a torque value has ended permitting updating of the registers **256**, **258**, **260**. It should be noted that the analog to digital converter **150** is under the control of the microprocessor **186**. Thus the microprocessor **186** provides an enable signal over the line **272** and a convert signal over the line **274** to a gate **276** which also receives, over a line **278**, a tool rotation indicating signal, the origin of which will be described below. It will be understood that the enable and convert signals on lines **272**, **274** are generated in response to the program controlling the microprocessor **186**. The output of the gate **276** provides a start conversion signal to the analog to digital converter **150** over the line **280**.

As mentioned previously, the steering gates **246**, **248** receive control signals over the lines **252**, **254**. These control signals are generated by a pair of gating circuits **282**, **284**. The gating circuit **282** is responsive to the end of conversion signal from the analog to digital converter **150** on the line **268** and an enable signal on the line **286** which signal is derived from the enable signal supplied by the microprocessor **186** over the line **272**. The gating circuit **282** provides an input to the gating circuit **284** which also receives a signal over the line **288** from the microprocessor **186** in the form of a response back signal indicating that the previous data has been loaded into the microprocessor memory. In addition to controlling the steering gates **246**, **248**, the gating circuit **284** furnishes a data ready signal on the line **290** to the microprocessor **186**. A further input **292** is provided for the logic gating circuit **282**. The function of this input is to supply an event market to memory.

The circuitry of FIG. 12B also provides interfacing between the angle transducer **142** and the microprocessor **186**. The output signals of the angle transducer **142**, in the form of sine and cosine signals are supplied over the line **158** to a converting circuit **294** which, in response to the transducer signals, generates an output pulse for each degree of rotation of the tool. This pulse signal on the line **296** provides the tool rotation indicating signal on the line **278** and also provides an input to a gating circuit over a line **298**. The gating circuit **300** also receives an input signal from the microprocessor **186** over the line **302**. This latter signal is present during the tool on period and goes off simultaneously with the tool off signal. The output **304** of the gating circuit **300** provides an input to the microprocessor **186** in the form of a pulse train with one pulse for each degree of tool rotation. The portion of this signal occurring after the input signal on the line **302** has been removed is a measure of the degree of tool overrun.

Also included in the interface logic and amplifier circuits is a reset circuit **306** connected at **308** to a reset switch and providing output signals on lines **310**, **312** which serve to reset various of the circuit components when the system is turned on. Signal conditioner circuits are also provided, with the circuits **314** providing interfacing between the microprocessor **186** and external controls for reset, gain, internal calibration and external calibration while the circuit **316** serves to interface the tool on signal from the microprocessor **186** over the line **318** with a solid state relay controlling the air valve **132**, the output signal being provided over the line **320**. A further circuit **322** is connected to a single pole double throw external switch **324** serving as an emergency or panic switch. The output **326** of the circuit **322** supplies an interrupt signal to the microprocessor **186**.

The components illustrated in FIGS. 12A and 12B are more completely identified in Table I, below:

TABLE I

Identification or Standard Parts No.	Number
SN74LS04	1
SN7474L	3
SN7400L	5
SN741QL	7
SN7402L	9
Resistor Pack, 4.7K ohms	11

TABLE I-continued

Identification or Standard Parts No.	Number
Potentiometer, 1K ohms	13
72747, Texas Instruments	15
Diode, 1N914	unmarked
SN7404L, inverter	unmarked
SN7437L	17
Transistor	unmarked
SN74157L	246, 248
SN7496L	256, 258, 260
SN74161L	21
Resistor Pack, 15K ohm	23
SN7420L	25
SN7442L	27
TR1602	212
Transistor 2N2905	29
Resistors 33, 620 have ½ watt rating	unmarked

The number adjacent each resistor is the resistance in ohms. All resistors except 33, 620 have ¼ watt ratings. The number adjacent each capacitor is the capacitance in microfarads. The symbol "v" is used to designate that the particular lead is connected to a 5 volt buss through a resistor, e.g. of 1000 ohm capacity, to prevent damage to the component. The symbol "POR" is used to designate "power on reset" which means that power stays on about ½ second.

Although the computer program and the circuitry of the interface amplifier section **200**, previously described, are designed to activate a conventional teletype console in order to enter different values for the empirically determined parameters and to obtain a printed readout of certain calculated values such as the tension at the mid-point stop **62**, it is apparent that the details thereof can be adapted to manipulate a display panel **204** as shown in FIG. **13**. The display panel **204** is preferably located within view of the tool operator and comprises a base section **332** supported in any suitable fashion having a first group of signal lights **334**, **336**, **338**, **340** indicating features of the joint **138**. The signal light **334** indicates that the final desired tension value F_D has been reached or that the final calculated tension value F_{final} is within an acceptable range. The signal light **336** indicates that the joint has experienced non-linear strain. The signal light **338** indicates that the final calculated tension value F_{final} is in an unacceptable range. With the lights **334**, **336** lit, the deduction is that non-linear strain has occurred but that F_{final} is acceptable. With the lights **336**, **338** lit, the deduction is that non-linear strain has occurred but that F_{final} is not acceptable. The light **340** is energized when the fastener exhibits a low tension rate as pointed out by the ratio of TR_a/TR_b.

The display **204** also provides another group of lights **342**, **344**, **346** indicating quality control features. The light **342** is normally energized when the frequency of non-linear strain detection is minimal while the light **344** is energized when the frequency of non-linear strain detection is too high as pointed out in equation (79). The light **346** is energized when the final calculated tension F_{final} differs significantly from the final desired tension values F_D as pointed out by equation (90). It will be evident that additional lights may be provided to signal that other quality control procedures have indicated that the joint is subnormal. In the alternative, a single light may be used to signal joint abnormality and the microprocessor arranged to deliver a signal to another computer for record keeping purposes.

The display **204** also comprises a third group of lights **348**, **350**, **352** indicating tool operating features. The light **348** indicates that the tool is functioning normally. The light **350** is energized when the ratio $\delta\alpha/\delta\alpha_p$ is too small or when the frequency of low ratio values becomes significant. Similarly when the ratio of $\delta\alpha/\delta\alpha_p$ is too large, or when the frequency of high ratio values becomes significant, the light **352** is energized.

EXAMPLES

A typical fastener system for use with this invention may comprise 5/16", 24 threads/inch, SAE grade 8 nuts and bolts. With this fastener pair and the modified Rockwell 63W air tool, the following values were found for the empirically determined parameters:

FR_1 = 47 lb/degree	n = 14	r = 1.12
T_o = 54 ft-lb	F_M = 2900 lb	a = 11.6 degrees/ft-lb
F_L = 1000 lb	c = −52.3 degrees	T_1 = 5 ft-lb
α_d = 68 degrees	N_k = 0.80	R = 0.93
T_{os} = .4 ft-lb	α_y = 12 degrees	K_o = 21 ft-lb/degrees
α_{or} = 20 degrees	α_K = 9 degrees	$\Delta\alpha$ = 3 degrees

Using these parameters and the described fasteners, which have a grip length of 2.44", and having a cadmium dichromate coating, the following data was developed using part of the technique here disclosed. The stiffness of the load washer used to measure tension directly was a 5×10^6 lb/in and the clamped pieces were hardened steel. In running the tests reported in the following table, the angle option was used and execution was within +2 to −1 degrees, which corresponds to +104 to −52 pounds tension. The overall instrumentation repeatability and linearity, including the tension probe and the torque transducer, is estimated at 4%. The tension value reported in the second column was recorded approximately 15 seconds after the tool stopped. This is believed to involve a relaxation in the joint amounting to 1-2% of the recorded tension value.

A statistical analysis of the data gathered on the twenty fasteners reported in Table II shows that the partial technique of this invention acts to control tension to within ±11.1% of the desired value in 99 out of 100 cases, or within 2.58 standard deviations. It should be thoroughly understood that the above data was taken with a program which does not include a number of features disclosed herein, including (1) the use of a second calculation for TR and α_{origin}; (2) the provision of yield detection and shut off in response thereto; (3) the use of a curvature check of torque rate in the region where TR is calculated in order to identify and reject low tension rate fasteners; (4) the adjustment of the final tightening parameter for the effects of prevailing torque; and (5) the use of the quality control procedures disclosed herein which were not disclosed in copending application Ser. No. 712,554. The effect of these additions to the program is, of course, somewhat speculative. It is believed, however, that the inclusion thereof will reduce scatter still further.

With the same joint and tool, the use of a torque control method would have to produce an average final torque of 22.68 ft-lbs to achieve an average final tension value of 6267 pounds. The observed deviations from average is +43.0 to −45.5%. Thus the torque control method would have produced a tension scatter of ±82.3% of the desired value in 99 out of 100 cases, assuming that the bolts would have been capable of accepting any tension. In reality, 10.4% of the bolts

TABLE II

Run No.	LRM Set for 6,200 F_{final}, lb	T_{final}, ft-lb	Final Angle From 5 ft-lb α_{Tf}, deg	Exact α_{Tf} for 6,200 lb Tension	Exact Torque for 6,200 lb Tension	Condition
1	6355	28.91	108	105	28.22	As received
2	6179	32.33	109	109	32.44	As received
3	6517	34.00	107	101	32.18	As received
4	6356	27.61	107	104	26.93	As received
5	6274	28.23	105	104	27.90	As received
6	6147	30.65	108	109	30.91	As received
7	6221	28.91	106	106	28.81	As received
8	6205	30.77	108	108	30.75	As received
9	6151	28.85	102	103	29.08	As received
10	6742	31.02	109	99	28.37	As received
11	6377	16.38	90	87	15.93	Lubricated with SAE 10 oil
12	6706	18.05	96	87	17.18	Lubricated with SAE 10 oil
13	6407	16.81	100	96	16.27	Lubricated with SAE 10 oil
14	6103	12.16	70	72	12.35	Lubricated with SAE 10 oil
15	6045	15.14	88	91	15.53	Lubricated with SAE 10 oil
16	6030	16.00	87	90	16.45	Lubricated with SAE 10 oil
17	5634	14.64	84	95	15.59	Lubricated with SAE 10 oil
18	5891	15.20	83	89	15.73	Lubricated with SAE 10 oil
19	6618	17.68	91	83	16.88	Lubricated with SAE 10 oil
20	6381	16.56	91	88	16.09	Lubricated with SAE 10 oil
Average	6267	21.31	97.5	96.3	22.68	
Observed deviation from Avg. %	+7.8 −10.1	+59.5 −42.9	+11.9 −28.2	+13.2 −25.2	+43.0 −45.5	
One std. deviation, % of Avg.	4.3	—	—	10.6 8.4 on tension	31.9	

would have ruptured, producing no tension at the termination of tightening. Another 14.7% of the bolts would terminate in the plastic zone, i.e. past the yield point.

With the same joint and tool, the use of a turn-of-the-nut method would have to advance the nut 96.3° from a threshold torque of 5 ft-lbs to achieve a final tension value of 6267 pounds. The observed deviation is +13.2 to −25.2%. Thus, a turn-of-the-nut method would have produced a tension scatter of ±21.7% of the desired value in 99 out of 100 cases. It is interesting to note that the selection of 6200 pounds for a bolt having an elastic limit of 6950 pounds appears to be optimum because only about 0.6% of these bolts would end up in the plastic zone.

In another test on the same joint, the selected final tension F_D was 90% nominal proof or 6300 pounds. In this test, such refinements as a second pass for the determination of TR and α_{origin} was used, a non-linear strain procedure and the remaining quality control procedures were available. To obtain independent tension values, a load washer was incorporated into the joint. The load washer was carefully calibrated for mean setting and reading scatters were measured under the same load condition existing in the joint. Table III shows the experimental results. The data reported excludes any abnormal joints indicated as unacceptable by the system. Accordingly, any defective joint that would have passed a torque strategy or a turn-of-the-nut strategy is excluded even though conventional systems would not have rejected these fasteners. Thus, the reported data on torque control and turn-of-the-nut strategies are better than would be expected in practice. The reported results are corrected for load washer scatter of approximately 1.8%, one standard deviation.

TABLE III

	Tension and Torque Scatter One Standard Deviation		
	Tension Scatter, %		Torque Scatter
Lube Condition	LRM	T-O-T-N	at 6300 lbs, %
dry	2.2	6.4	18.5
oiled	2.4	5.0	13.8
mixed	2.6	8.2	29.9

Although the data of Table III appears to be substantially different than the data of Table II, the major difference lies in the adjustment in Table III of the load washer error of 1.8%, one standard deviation, whereas this adjustment has not been made in Table II.

It has been learned that torque scatter at constant tension is quite different from tension scatter at constant torque. Whereas torque scatter has a normal distribution, tension scatter at constant torque has a shifted or unsymmetrical distribution. The mixed lubrication condition, which involves the largest variation in friction, has been chosen to show the expectations in achieving tension control with various strategies. Referring to FIG. 14, the probability distributions in finite tension bands are illustrated. It will be apparent that the technique of this invention is substantially superior to the torque control and turn-of-the-nut strategies of the prior art.

ANALOG EMBODIMENT

Referring to FIG. 15, there is illustrated another device 354 for implementing the technique of this invention. The basis of this approach is equation (7) where the value of $dF/d\alpha$ indicates the tension rate. Rewriting equation (7),

$$\frac{d}{d\alpha}\log T = \frac{dF/d\alpha}{F}. \tag{99}$$

If $d/d\alpha \log T$ can in some fashion be determined, F in equation (99) can become the final desired tension value F_D or the tension value F_{so} at the point of shut off command while $dF/d\alpha$ is an empirically determined tension rate FR_3 which is an appropriate average of FR_1 and FR_2 over the angle interval in question. It will be apparent that

$$\frac{d}{d\alpha}\log T = \frac{\frac{d}{dt}\log T}{\frac{d\alpha}{dt}}. \tag{100}$$

As suggested in FIG. 15, the analog device 354 includes an angular speed pickup 356 of any suitable type, such as a tachometer, for continuously sensing a value for $d\alpha/dt$, which is the speed the fastener is being tightened.

A torque transducer 358 continuously senses the value of running torque T. The transducer 358 may be of the same type as the transducer 140. A logarithmic amplifier 360, such as is available from Analog Devices, Inc., Norwood, Mass., under the designation of Logarithmic Amplifier, Model 755, is connected to the torque transducer 358 by a suitable connection 362. The logarithmic amplifier 360 continuously converts the sensed value of running torque T into a continuous signal representative of log T.

A time differentiating device 364 is connected to the logarithmic amplifier 360 by a suitable lead 366 and continuously differentiates the signal from the logarithmic amplifier with respect to time in order to obtain the differential of the logarithm of running torque d/dt log T. The time differentiating device 364 may be of any suitable type, such as an operational amplifier 368 in parallel with a capacitor 370. A suitable operational amplifier is available from Analog Devices, Inc., Norwood, Mass., under the designation Operational Amplifier, Model 741.

The signal from the time differentiating device 364 is delivered through a lead 372 to a low pass filter 374 which acts to smooth out the signal from the time differentiating device 364 thereby removing some of the noise inherent in the torque signal from the transducer 358.

The angular speed pickup 356 and the low pass filter 374 are connected by suitable leads 376, 378 to an analog divide device 380 such as may be obtained from Analog Devices, Inc., Norwood, Mass. under the designation Divide Module 463B. The leads 376, 378 are connected to the divide device to produce an output signal along a lead 382 consisting of the ratio

$$\frac{\frac{d}{dt}\log T}{d\alpha/dt}$$

As indicated in equation (100), this signal is representative of d/dα log T. When the value of

$$d/d\alpha \log T \leqq FR_3/F_{so} \text{ when } T \geqq T_1 \qquad (101)$$

where F_{so} is the tension value in the bolt at the time of shut off, and T_1 is an early predetermined torque value, e.g. about 20–30% of the average final torque, the tool is commanded to shut off. It will be evident that the threshold may be measured in terms of angle, e.g. where $\alpha > \alpha_1$, rather than torque.

Because the tool will overrun after shut off, the value of F_{so} is selected so that average tool overrun advances the fasteners to the final desired tension value F_D. The average tool overrun may be determined empirically or from

$$\Delta F_{so} = (d\alpha/dt_{so})(\Delta t)FR_3 \qquad (102)$$

where $(d\alpha/dt_{so})$ is the average speed of the tool at shut off, ΔF_{so} is the average additional tension due to overrun, and Δt is the time delay between the giving of the shut off command and the closing of the air valve. Thus,

$$F_{so} = F_D - \Delta F_{so} \qquad (103)$$

Because F_{so} and FR_3 are assumed to be a constant, the ratio of FR_3/F_{so} is obviously constant. Thus, a constant signal representative of FR_3/F_{so} is placed on a lead 384. The leads 382, 384 are connected to another divide device 386. When the output signal from the divide device 386 on a lead 388 becomes unity, an amplifier 390 is triggered to energize a solenoid catch 392 to allow the solenoid spring (not shown) to close the air valve.

Although the analog device 354 of FIG. 15 is not believed to have the accuracy of the digital device 126, it is apparent that it has the advantage of simplicity, both physical and operational. The analog device 354 operates closer to the theoretical basis of the invention and contains fewer assumptions and simplifications. Some of the disadvantages of a simple analog device, such as the inability to vary the overrun prediction and the noise reduction in the filter 374, are capable of being surmounted by more sophisticated analog techniques as will be apparent to those skilled in the art.

As heretofore disclosed, the analog device 354 is designed to deliver a running torque signal T which is converted into a signal representative of log T which is then differentiated with respect to time to give d/dt log T. As explained previously, it is desirable to adjust the running torque value T by deducting the values of offset torque T_{os} and prevailing torque T_{pv}. It will be appreciated that this can be readily accomplished by suitable analog devices placed in the connection 362 between the torque transducer 358 and the log device 360.

As will be apparent to those skilled in the art, the technique of this invention can be used to monitor other tightening strategies thereby determining the accuracy thereof in tightening fasteners to a final desired stress value. This may readily be accomplished by modifying the amplifier section 200 in order not to manipulate the air valve solenoid in response to the tightening parameter.

Although the invention has been described in its preferred forms with a certain degree of particularity, it is understood that the disclosure of the preferred embodiments has been made only by way of example and numerous changes in the details of construction, combination and arrangement of parts, and mode of operation may be resorted to without departing from the spirit and scope of the invention as hereinafter claimed. It is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of patentable novelty exist in the invention disclosed.

I claim:

1. Apparatus for tightening seriatim a multiplicity of substantially identical joints having components including at least one threaded fastener to substantially the same final desired stress value, below the yield point of [any component] *all joint components* that can be correlated with stress, appearing in the fastener, comprising

a powered instructable tool, capable of terminating tightening in response to an instruction which varies from one fastener to the next, for applying torque to the fastener and tightening the same;

means for sensing the torque applied to the fastener at various angles of advance;

means responsive to the torque and angle sensings for determining, while tightening below the yield point of [any] *all* joint [component] *components* that can be correlated with stress, a tightening parameter value, variable from one fastener to the next, sufficient to tighten each fastener to the final desired stress value; and

means for instructing the tool to terminate tightening of each fastener in response to the determined tightening parameter value.

2. The apparatus of claim 1 wherein the determining means comprises means for determining the torque

values sufficient to tighten each fastener to the final desired stress value.

3. The apparatus of claim 2 wherein the determining means comprises means for calculating the sufficient torque value from the ultimate equation

$$F_D = \frac{(dF/d\alpha)(T_D - T_{os} - T_{pv})}{dT/d\alpha}$$

where F_D is the final desired stress value, $dF/d\alpha$ is the derivative of stress with respect to angle, T_D is the sufficient torque value, $dT/d\alpha$ is the derivative of torque with respect to angle, T_{os} is offset torque, and T_{pv} is prevailing torque.

4. The apparatus of claim 1 wherein the determining means comprises means for determining the angle of threading advance sufficient to tighten each fastener to the final desired stress value.

5. The apparatus of claim 4 wherein the determining means comprises means for calculating the angle of advance from the ultimate equation $F_D=\alpha FR$ where F_D is the final desired stress value, FR is the stress rate and α is the angular distance from the angle origin of stress to F_D.

[6. A method of tightening a multiplicity of substantially identical joints having components including at least one threaded fastener to a final desired stress value below the yield point of any joint component that can be correlated with stress, including
tightening the fastener with an instructable tool;
sensing torque at various angles of advance during tightening below the yield point of any joint component that can be correlated with stress;
calculating, while tightening below the yield point of any joint component that can be correlated with stress, the stress appearing in the fastener at least at one instant of tightening below the yield point of any joint component that can be correlated with stress from the sensed values of torque and angle;
determining the value of a tightening parameter sufficient to tighten the fastener to the final desired stress value below the yield point of any joint component that can be correlated with stress from the calculated stress;
instructing the tool to tighten the fastener to the determined parameter; and
terminating tightening in response to the attainment of the determined parameter.]

7. The method of claim [6] *51* wherein the tightening parameter is angle of advance.

8. The method of claim [6] *51* wherein the tightening parameter is torque.

9. The method of claim [6] *51* wherein the tightening parameter is a linear combination of torque and angle.

10. The method of claim [6] *51* wherein fastener is a bolt and the final desired stress value is final desired tension value in the bolt.

11. The method of claim [6] *51* wherein the tightening parameter includes a measure of tool overrun.

[12. Apparatus for tightening seriatim a multiplicity of substantially identical joints having components including at least one threaded fastener to substantially the same final desired stress value below the yield point, comprising
a powered instructable tool for tightening the fastener;
means for sensing torque at various angles of advance during tightening below the yield point of any joint component that can be correlated with stress;
means for calculating the stress appearing in the fastener at least at one instant of tightening below the yield point of any joint component that can be correlated with stress from the sensed values of torque and angle;
means for determining a tightening parameter value sufficient to tighten the fastener to the final desired stress value below the yield point of any joint component that can be correlated with stress from the calculated stress; and
means for instructing the tool to tighten the fastener to the determined parameter value.]

13. The apparatus of claim [12] *52* wherein the calculating means and the determining means respectively comprises means for calculating the stress and means for determining the tightening parameter value in a time period commencing with the onset of threading and stopping with the termination of tightening.

14. The apparatus of claim 13 wherein the time period is less than two minutes.

[15. A method of tightening a multiplicity of substantially identical joints having components including at least one threaded fastener to a final desired stress value below the yield point of any joint component that can be correlated with stress, comprising
tightening the fastener with an instructable powered tool;
sensing torque at various angles of advance during tightening;
determining the torque rate of the fastener from the sensed values of torque and angle;
calculating the stress appearing in the fastener at least at least at one instant of tightening below the yield point of any joint component that can be correlated with stress from the determined torque rate and from sensed torque;
determining the value of a tightening parameter sufficient to tighten the fastener to the final desired stress value below the yield point of any joint component that can be correlated with stress from the calculated stress;
instructing the tool to tighten the fastener in response to the determined parameter; and
terminating tightening in response to the determined parameter.]

16. The method of claim [15] *53* further comprising predicting the amount of tool overrun and wherein the instructing step comprises instructing the tool to tighten each fastener in response to the determined parameter and the amount of tool overrun, and the terminating step comprises terminating tightening in response to the determined parameter and the amount of tool overrun.

17. The method of claim [15] *53* comprising the step of empirically determining the value of FR_1, FR_2 and T_{os} where FR_1 is stress rate in a low stress range, FR_2 is stress rate in a higher stress range and T_{os} is offset torque, and the calculating step comprises calculating the stress from the empirically determined values of FR_1, FR_2 and T_{os} as well as from the sensed values of torque and angle.

[18. Apparatus for tightening a multiplicity of substantially identical joints having components including at least one threaded fastener to a final desired stress value below the yield point of any joint component that can be correlated with stress, comprising a powered instructable tool for tightening the fastener;

means for sensing torque at various angles of advance during tightening;

means for determining the torque rate of the fastener from the sensed values of torque and angle;

means for calculating the stress appearing in the fastener at least at one instant of tightening below the yield point of any joint component that can be correlated with stress from the determined torque rate and the sensed torque;

means for determining the value of a tightening parameter sufficient to tighten the fastener to the final desired stress value below the yield point of any joint component that can be correlated with stress; and

means for instructing the tool to tighten the fastener in response to the determined parameter.]

19. The apparatus of claim [18] *54* further comprising means for predicting the amount of tool overrun, and wherein the instructing means comprises means for instructing the tool to tighten the fastener in response to the determined parameter and the amount of tool overrun.

20. The apparatus of claim [18] *54* wherein the determining means comprises means for determining the torque value sufficient to tighten the fastener to the final desired stress value.

21. The apparatus of claim [18] *54* wherein the determining means comprises means for determining the angle of threading advance sufficient to tighten the fastener to the final desired stress value.

22. The apparatus of claim [18] *54* wherein the fastener is a bolt and the calculating means comprises means for calculating the tension in the bolt.

23. Apparatus for tightening a joint having components including at least one threaded fastener, comprising

a powered tool for tightening the fastener;

means for monitoring stress in the fastener including

means for sensing torque and angle while tightening; and

data processor means for calculating stress in the fastener below the yield point of [any] *all* joint [component] *components* that can be correlated with stress from sensed values of torque and angle; and

means for terminating tightening in response to a tightening parameter related to monitored stress.

24. The apparatus of claim 23 wherein the tightening parameter is torque.

25. The apparatus of claim 23 wherein the tightening parameter is angle.

26. The apparatus of claim 23 wherein the tightening parameter is a linear combination of torque and angle.

27. Apparatus for tightening substantially identical threaded fasteners in production lots to the same final desired stress value ±15%, comprising

a powered instructable tightening tool having a source of energy, means for connecting and disconnecting the tool to the energy source, a torque sensor and an angle sensor;

a data processor connected to the torque and angle sensors including

means for determining a mid-point stop of the fasteners at least about 0.4 elastic limit of the weakest joint component from a sensed value of torque and angle and means for instructing the tool to halt tightening at the mid-point stop;

means for calculating a torque rate in a region adjacent the mid-point stop from sensed values of torque and angle;

means for calculating the stress appearing in the fastener at a location between the onset of tightening and the mid-point stop from a sensed value of torque at the location, the calculated torque rate and an empirically determined stress rate for the region including 0.1–0.5 elastic limit;

means for calculating a value of a tightening parameter sufficient to tighten the fastener to a final desired stress value from an empirically determined stress rate above the region 0.1–0.5 elastic limit;

means controlled by the data processor for resuming tightening; and

means responsive to the value of the tightening parameter for terminating tightening adjacent the final desired value.

28. The apparatus of claim 27 further comprising means for calculating the amount of tool overrun adjacent the final desired stress value and wherein the tightening terminating means comprises means responsive to the value of the tightening parameter and the amount of tool overrun for terminating tightening adjacent the final desired stress value.

29. The apparatus of claim 27 wherein the means for calculating the tightening parameter value comprises means for dividing the difference between the final desired stress value and the stress calculated at the location by the empirically determined stress rate above the region 0.1–0.5 elastic limit.

30. The apparatus of claim 27 wherein the means for calculating the tightening parameter value comprises means for dividing the difference between the final desired stress value and the stress at an angular position adjacent the location by the empirically determined stress rate above the region 0.1–0.5 elastic limit.

31. The apparatus of claim 27 wherein the tightening parameter is in units of angle.

32. The apparatus of claim 27 wherein the tightening parameter is in units of torque.

33. The apparatus of claim 27 wherein the torque rate calculating means includes means for storing and recalling the sensed values of torque and angle and means for determining an average torque rate from the sensings.

34. A method of tightening a joint including a threaded fastener, comprising

tightening the fastener;

sensing torque applied to the fastener and the angle of threading advance;

determining, during tightening, the origin of stress in the fastener from the sensed values of torque and angle;

determining a shut off parameter based on the origin of stress; and

terminating tightening in response to the shut off parameter.

35. Apparatus for tightening a joint including a threaded fastener, comprising

a powered tool for tightening the fastener;

means for sensing the torque applied to the fastener and the angle of threading advance;

means for determining, during tightening, the origin of stress in the fastener pair from sensed values of torque and angle;

means for determining, during tightening, a shut off

parameter based on the origin of stress; and
means for terminating operation of the powered tool in response to the shut off parameter.

36. A method of tightening seriatim a multiplicity of substantially identical production joints including at least one threaded fastener, comprising
empirically determining, prior to tightening the production joints, at least one joint characteristic;
applying torque to the fastener for tightening the production joint;
determining, while tightening below the yield point of [any] *all* joint [component] *components* that can be correlated with stress, a tightening parameter based on the empirically determined joint characteristic, which tightening parameter varies from one joint to the next; and
terminating tightening in response to the tightening parameter.

37. The method of claim 36 wherein the empirically determined joint characteristic is the fastener tension rate.

38. The method of claim 36 wherein the empirically determined joint characteristic is the offset torque.

39. Apparatus for tightening seriatim a multiplicity of substantially identical production joints including at least one threaded fastener and having at least one empirically determinable joint characteristic, comprising
means for applying torque to the fastener;
means for determining, while tightening below the yield point of [any] *all* joint [component] *components* that can be correlated with stress, a tightening parameter based on the empirically determined joint characteristic, which tightening parameter varies from one joint to the next, including
means for delivering a signal to the determining means representative of the empirically determinable joint characteristic; and
means for terminating tightening in response to the tightening parameter.

40. A method of tightening seriatim a multiplicity of substantially identical production joints including at least one threaded fastener, comprising
determining, prior to tightening the production joints, at least one tightening tool characteristic;
applying torque to the fastener with the tightening tool for tightening the production joint;
determining, while tightening, a tightening parameter based on the determined tool characteristic, which tightening parameter varies from one joint to the next; and
terminating tightening in response to the tightening parameter.

41. The method of claim 40 wherein the determined tool characteristic is a function of tool overrun.

42. The method of claim 41 wherein the tightening tool characteristic is the stall torque of the tool.

43. The method of claim 41 wherein the tightening tool characteristic is the angle overrun of the tightening tool under no torque conditions.

44. Apparatus for tightening seriatim a multiplicity of substantially identical production joints including at least one threaded fastener, comprising
a tightening tool for applying torque to the fastener;
means for determining, while tightening, a tightening parameter based on a tool characteristic, which tightening parameter varies from one joint to the next, including
means for delivering a signal to the determining means representative of the determined tool characteristic; and
means for terminating tightening in response to the tightening parameter.

45. The method of claim 57 wherein said joint characteristic is determined from one or more actual, representative joints.

46. The method of claim 57 wherein the joint characteristic is proportional to the joint tension rate.

47. The apparatus of claim 58 wherein the joint characteristic is proportional to the joint tension rate.

48. The apparatus of claim 58 further comprising means for determining, after the onset of tightening, a parameter proportional to the torque rate of the fastener.

49. The apparatus of claim 58 wherein the determining means comprises means for combining the determinable joint characteristic and the torque rate proportional parameter.

50. The apparatus of claim 58 wherein the determinable joint characteristic is the joint tension rate, said apparatus further comprising means for determining, after the onset of tightening, the torque rate of the fastener and the determining means comprising means for combining the joint tension rate and the determined torque rate.

51. A method of tightening a multiplicity of substantially identical joints having components including at least one threaded fastener to a final desired atress value below the yield point of all joint components that can be correlated with stress, including:
tightening the fastener with an instructable tool;
sensing torque at various angles of advance during tightening below the yield point of all joint components that can be correlated with stress;
calculating, while tightening below the yield point of all joint components that can be correlated with stress, the stress appearing in the fastener at least at one instant of tightening below the yield point of all joint components that can be correlated with stress from the sensed values of torque and angle;
determining the value of a tightening parameter sufficient to tighten the fastener to the final desired stress value below the yield point of all joint components that can be correlated with stress from the calculated stress;
instructing the tool to tighten the fastener to the determined parameter; and
terminating tightening in response to the attainment of the determined parameter.

52. Apparatus for tightening seriatim a multiplicity of substantially identical joints having components including at least one threaded fastener to substantially the same final desired stress value below the yield point, comprising:
a powered instructable tool for tightening the fastener;
means for sensing torque at various angles of advance during tightening below the yield point of all joint components that can be correlated with stress;
means for calculating the stress appearing in the fastener at least at one instant of tightening below the yield point of all joint components that can be correlated with stress from the sensed values of torque and angle;
means for determining a tightening parameter value sufficient to tighten the fastener to the final desired stress value below the yield point of all joint components that can be correlated with stress from the calculated stress; and
means for instructing the tool to tighten the fastener to the determined parameter value.

53. A method of tightening a multiplicity of substantially identical joints having components including at least one threaded fastener to a final desired stress value below the yield point of all joint components that can be correlated with stress, comprising:

tightening the fastener with an instructable powered tool;

sensing torque at various angles of advance during tightening;

determining the torque rate of the fastener from the sensed values of torque and angle;

calculating the stress appearing in the fastener at least at one instant of tightening below the yield point of all joint components that can be correlated with stress from the determined torque rate and from sensed torque;

determining the value of a tightening parameter sufficient to tighten the fastener to the final desired stress value below the yield point of all joint components that can be correlated with stress from the calculated stress;

instructing the tool to tighten the fastener in response to the determined parameter; and

terminating tightening in response to the determined parameter.

54. Apparatus for tightening a multiplicity of substantially identical joints having components including at least one threaded fastener to a final desired stress value below the yield point of all joint components that can be correlated with stress, comprising:

a powered instructable tool for tightening the fastener;

means for sensing torque at various angles of advance during tightening;

means for determining the torque rate of the fastener from the sensed values of torque and angle;

means for calculating the stress appearing in the fastener at least at one instant of tightening below the yield point of all joint components that can be correlated with stress from the determined torque rate and the sensed torque;

means for determining the value of a tightening parameter sufficient to tighten the fastener to the final desired stress value below the yield point of all joint components that can be correlated with stress; and

means for instructing the tool to tighten the fastener in response to the determined parameter.

55. Apparatus for tightening a threaded fastener in a joint including the fastener, the apparatus comprising:

a tightening tool for imparting input characteristics including torque and rotation to the fastener to tighten the fastener, the tool being capable of terminating the tightening of the fastener in response to an instruction incorporating a directly measurable tightening related parameter which can vary from one to another of ostensibly alike joints in tightening fasteners therein to the same final tension;

means for sensing at least one of the input characteristics;

means for determining from the sensed input characteristics, after the onset of tightening and while below the yield point of all joint components that can be correlated with stress, that value of the tightening related parameter which is representative of the amount of tightening required to tighten the fastener to the selected final tension; and

means for transmitting to the tool an instruction that will cause the tool to terminate the tightening of the fastener in response to the reaching of the determined value of the tightening related parameter.

56. Apparatus for tightening a threaded fastener in a joint including the fastener, comprising:

a power instructable tool, capable of terminating tightening in response to an instruction which varies from one fastener to the next, for imparting input characteristics including torque and rotation to the fastener;

means for sensing at least one of the input characteristics;

means responsive to the sensing means for determining after the onset of tightening and while below the yield point of all joint components that can be correlated with stress, a tightening parameter value, variable from one fastener to the next, sufficient to tighten each fastener to the same final desired stress value; and

means for terminating tightening of the fastener in response to the determined tightening parameter value.

57. A method of tightening a threaded fastener in a joint including the threaded fastener, comprising:

determining, prior to tightening the fastener, at least one joint characteristic;

applying torque to the fastener for tightening the same;

determining, after the onset of tightening and while below the yield point of all joint components which can be correlated with stress, a tightening parameter based on the determined joint characteristic, which tightening parameter varies from one joint to the next; and

terminating tightening in response to the tightening parameter.

58. Apparatus for tightening a threaded fastener in a joint including the fastener and having a determinable joint characteristic, comprising:

means for applying torque to the fastener;

means for determining, after the onset of tightening and while below the yield point of all joint components that can be correlated with stress, a tightening parameter based on the joint characteristic, which tightening parameter varies from one joint to the next; and

means for terminating tightening in response to the tightening parameter.

59. Apparatus for tightening seriatim a multiplicity of substantially identical joints having components including at least one threaded fastener to substantially the same final desired stress value, below the yield point of all components that can be correlated with stress, appearing in the fastener, comprising a powered instructable tool, capable of terminating tightening in response to an instruction which varies from one fastener to the next, for applying torque to the fastener and tightening the same; means for sensing the torque applied to the fastener at various angles of advance; means responsive to the torque and angle sensings for determining, while tightening at a value below which any of the aforesaid joint components are alterable in configuration by the application of a load thereto, a tightening parameter value, variable from one fastener to the next, sufficient to tighten each fastener to the final desired stress value; and means for instructing the tool to terminate tightening of each fastener in response to the determined tightening parameter value.

* * * * *

Pages E-94 through E-105 are blank and are not used in this technical reference.

United States Patent [19]

Osterholm

[11] **4,445,500**

[45] * **May 1, 1984**

[54] **STROKE TREATMENT UTILIZING EXTRAVASCULAR CIRCULATION OF OXYGENATED SYNTHETIC NUTRIENTS TO TREAT TISSUE HYPOXIC AND ISCHEMIC DISORDERS**

[75] Inventor: **Jewell L. Osterholm**, Radnor Township, Delaware County, Pa.

[73] Assignee: **Thomas Jefferson University**, Philadelphia, Pa.

[*] Notice: The portion of the term of this patent subsequent to Jul. 19, 2000 has been disclaimed.

[21] Appl. No.: **428,850**

[22] Filed: **Sep. 30, 1982**

Related U.S. Application Data

[60] Division of Ser. No. 354,346, Mar. 3, 1982, which is a continuation-in-part of Ser. No. 275,117, Jun. 18, 1981, Ser. No. 275,116, Jun. 18, 1981, Pat. No. 4,393,863, and Ser. No. 139,886, Apr. 14, 1980, Pat. No. 4,378,797, said Ser. No. 275,117, and Ser. No. 275,116, each is a division of Ser. No. 139,886.

[51] **Int. Cl.**^{3} **A61K 31/00; A61M 5/14**

[52] **U.S. Cl.** .... **128/1 R; 424/355; 424/153; 604/52**

[58] **Field of Search** .... **128/1 R. ; 424/355, 424/153; 604/52**

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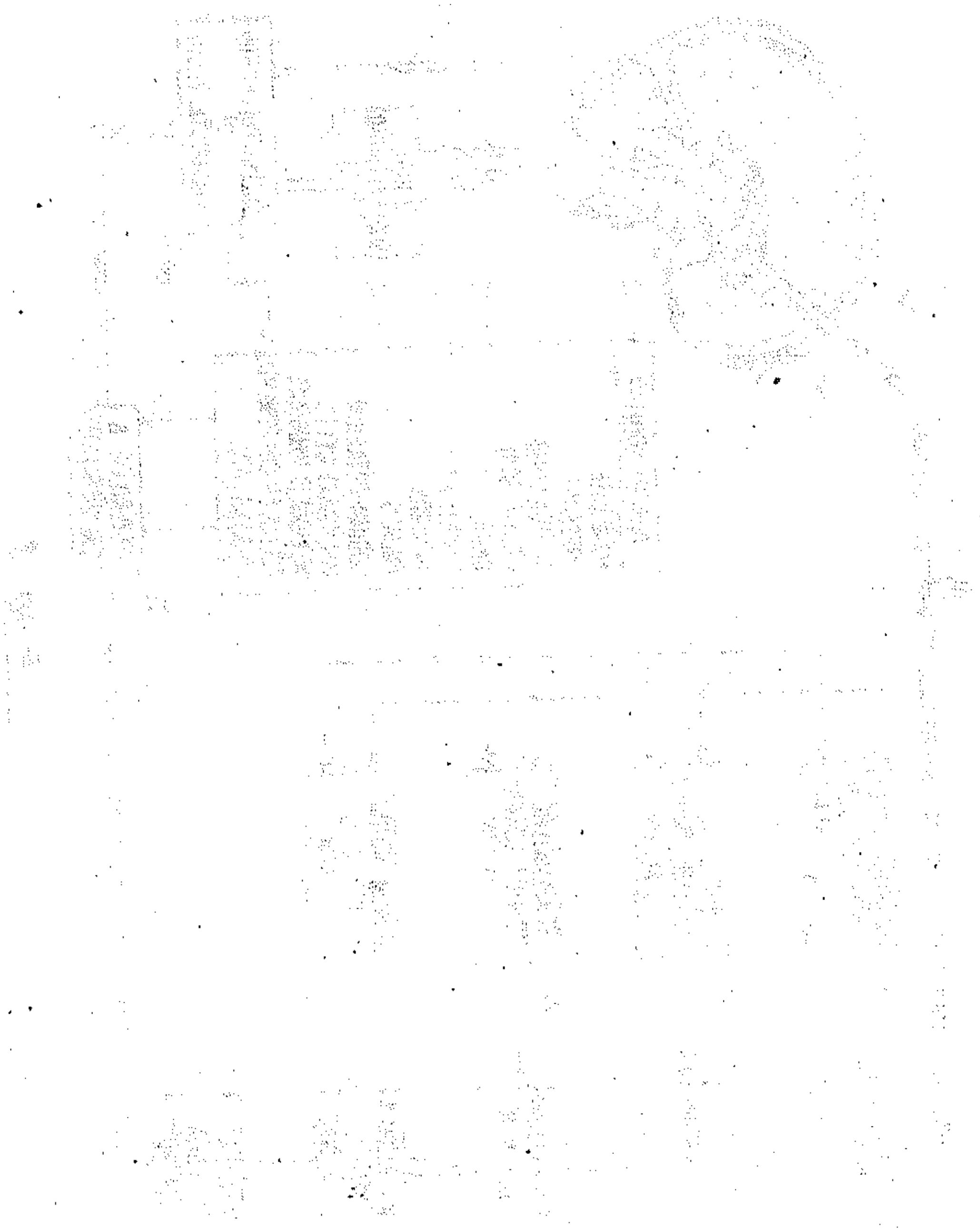
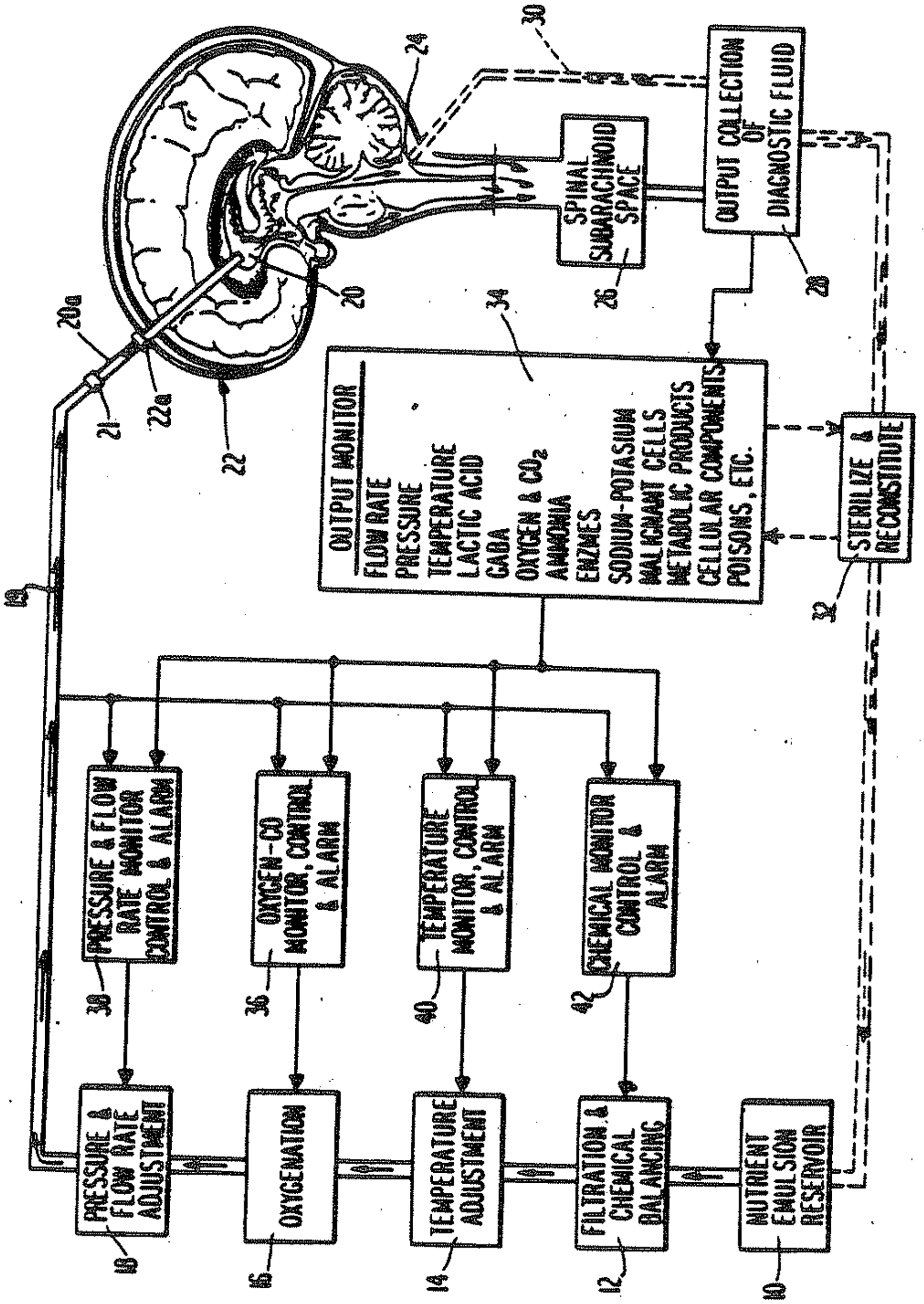
Primary Examiner—George F. Lesmes
Assistant Examiner—Nancy A. B. Swisher
Attorney, Agent, or Firm—Woodcock, Washburn, Kurtz, Mackiewicz & Norris

[57] ABSTRACT

A novel acute care cerebral support system and method for treating severly ischemic brains is disclosed wherein an oxygenated nutrient emulsion is circulated through at least a portion of the ventriculo-subarachnoid spaces. The nutrient emulsion contains an oxygenatable nonaqueous component, an aqueous nutrient component, an emulsification component, and other components which render physiologic acceptability to the nutrient emulsion. The disclosed system and method have been shown to effectively exchange oxygen, carbon dioxide, glucose, and other metabolites in severely stroked brains. Significant restoration of oxidative metabolism and electrographic activity result from the disclosed treatment. Methods for producing the nutrient emulsion and a system for delivering that emulsion to the cerebrospinal pathway are also disclosed. Additionally, novel diagnostic methods for diagnosing the physiologic state of hypoxic-ischmeic and other diseased neurologic tissue during treatment are provided.

6 Claims, 13 Drawing Figures

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OUTPUT COLLECTION OF DIAGNOSTIC FLUID
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OUTPUT MONITOR
FLOW RATE
PRESSURE
TEMPERATURE
LACTIC ACID
GABA
OXYGEN & CO2
AMMONIA
ENZIMES
SODIUM-POTASIUM
MALIGNANT CELLS
METABOLIC PRODUCTS
CELLULAR COMPONENTS
POISONS, ETC.
STERILIZE & RECONSTITUTE
32
18
PRESSURE & FLOW RATE MONITOR CONTROL & ALARM
38
OXYGEN-CO MONITOR, CONTROL & ALARM
36
TEMPERATURE MONITOR, CONTROL & ALARM
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CHEMICAL MONITOR CONTROL & ALARM
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PRESSURE & FLOW RATE ADJUSTMENT
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NUTRIENT EMULSION RESERVOIR
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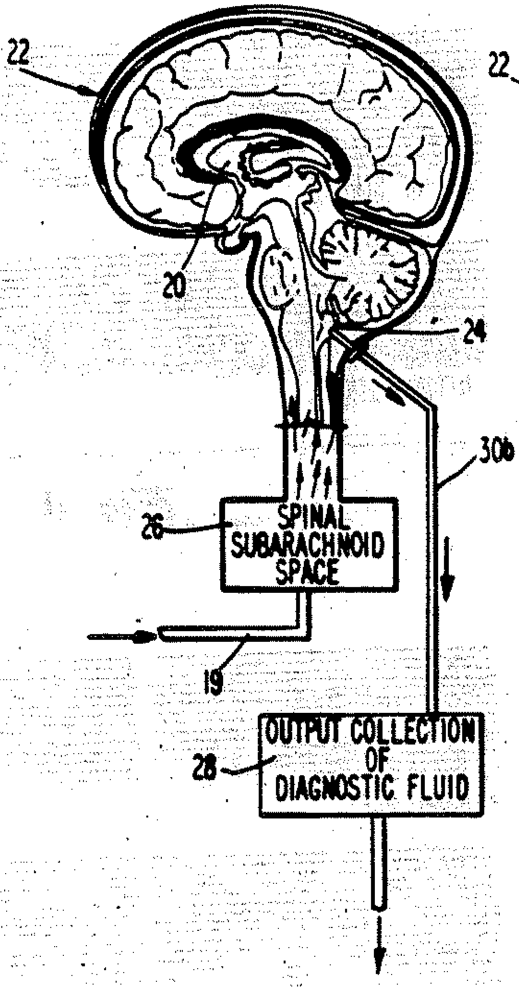
Fig. 1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OUTPUT COLLECTION OF DIAGNOSTIC FLUID

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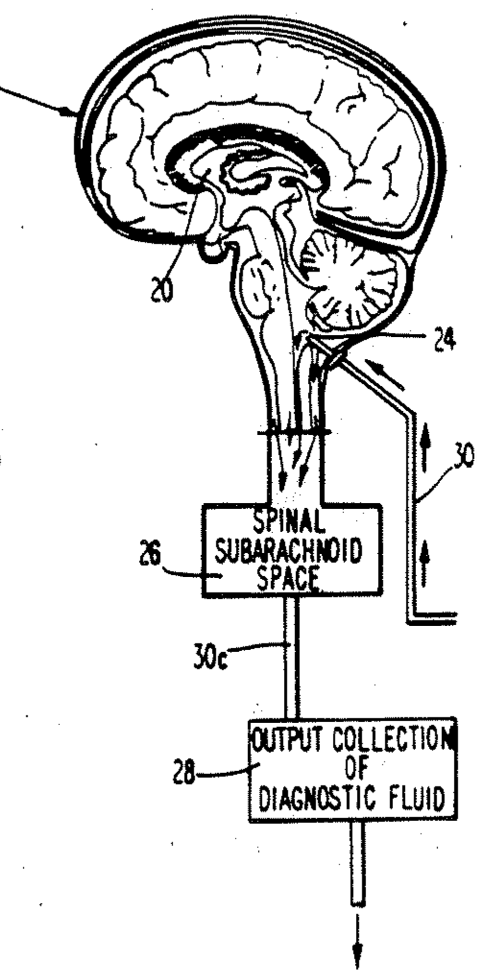
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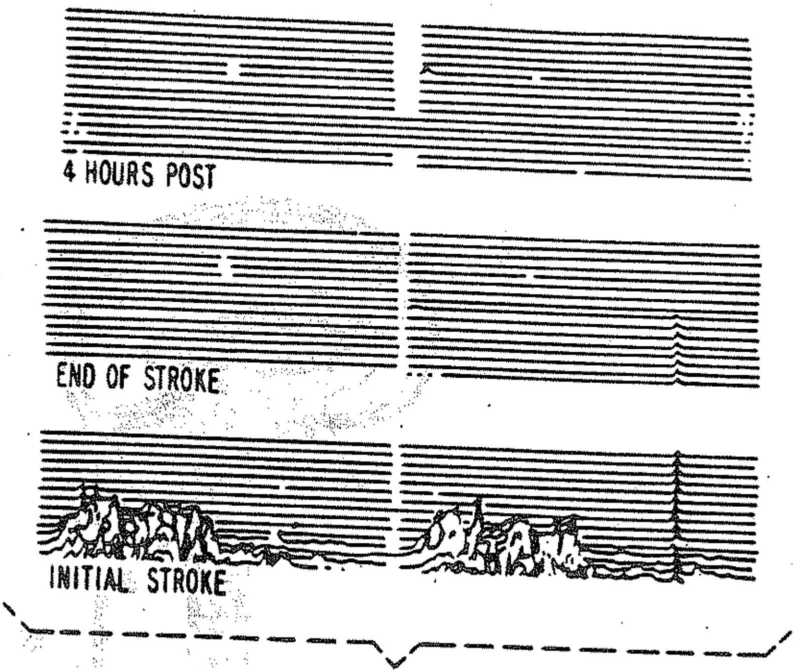
Fig. 3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INITIAL STROKE

Fig. 4

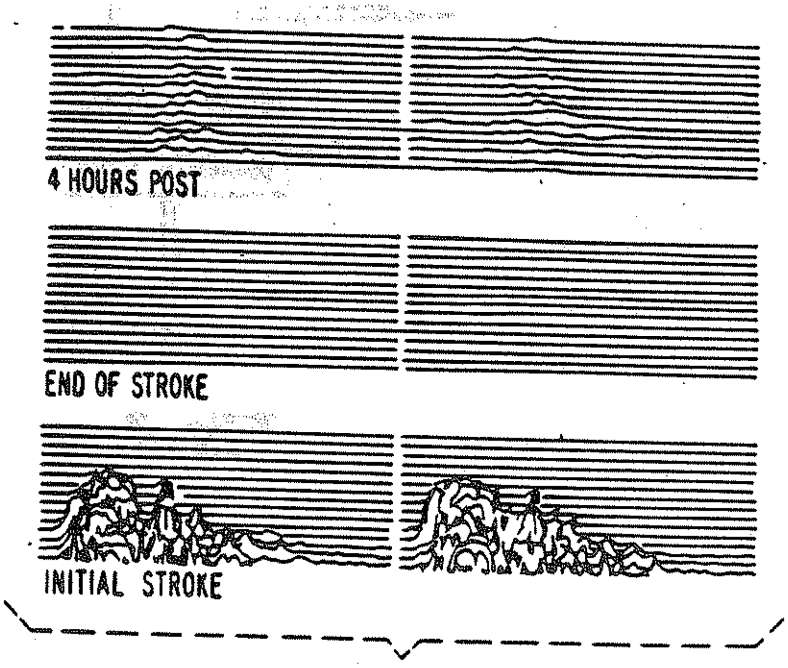
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Fig. 5

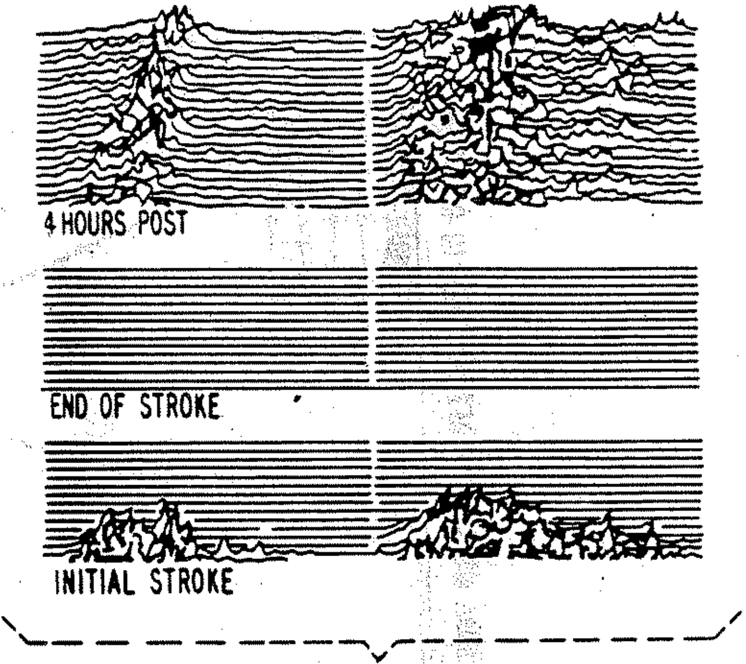


Fig. 6

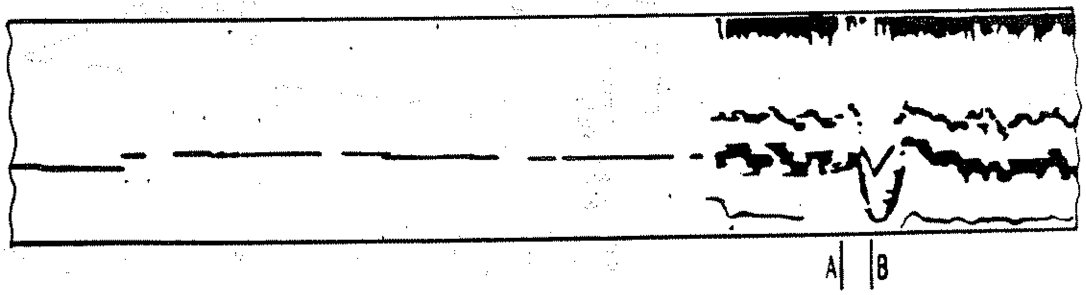
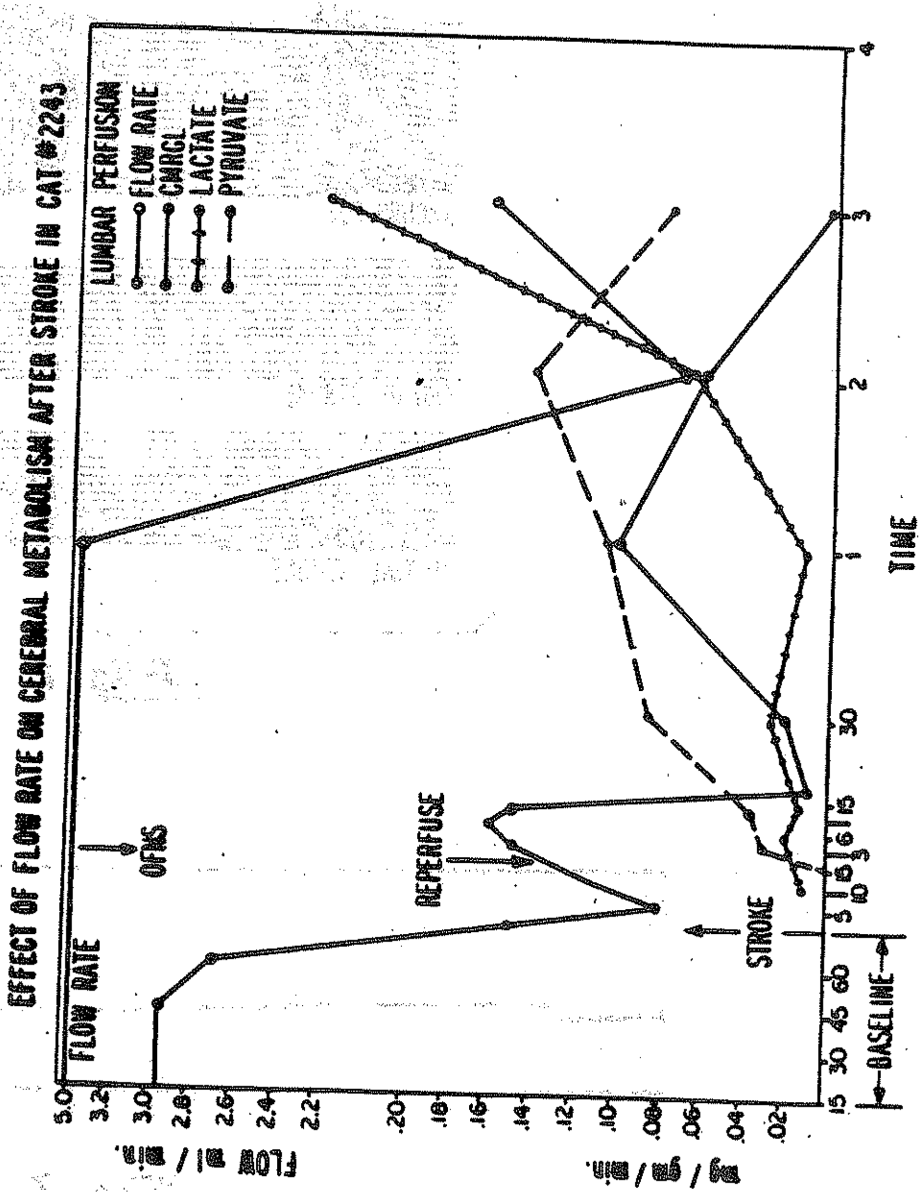


Fig. 7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CMRGL
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Fig. 8

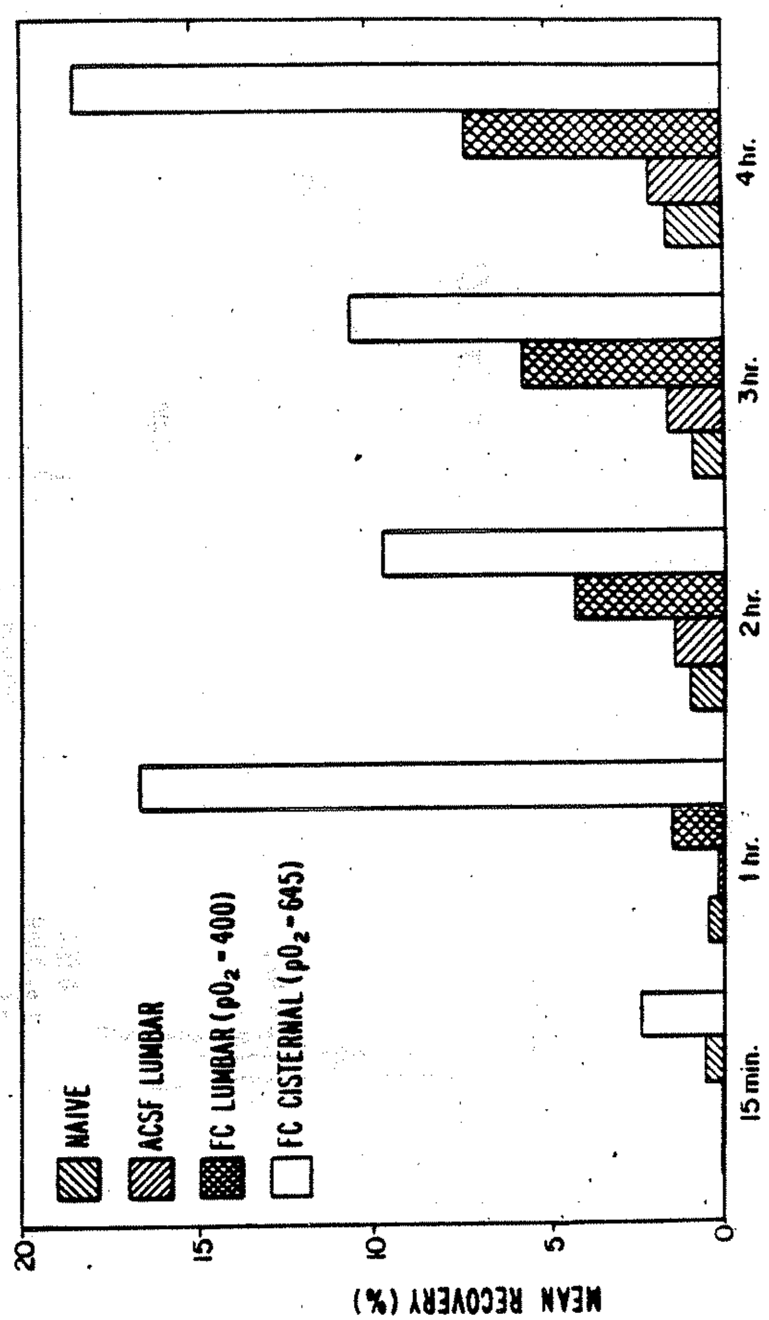

▨ NAIVE
▨ ACSF LUMBAR
▩ FC LUMBAR (pO_2 = 400)
☐ FC CISTERNAL (pO_2 = 645)
MEAN RECOVERY (%)
20
15
10
5
0
15 min.
1 hr.
2 hr.
3 hr.
4 hr.

Fig. 9

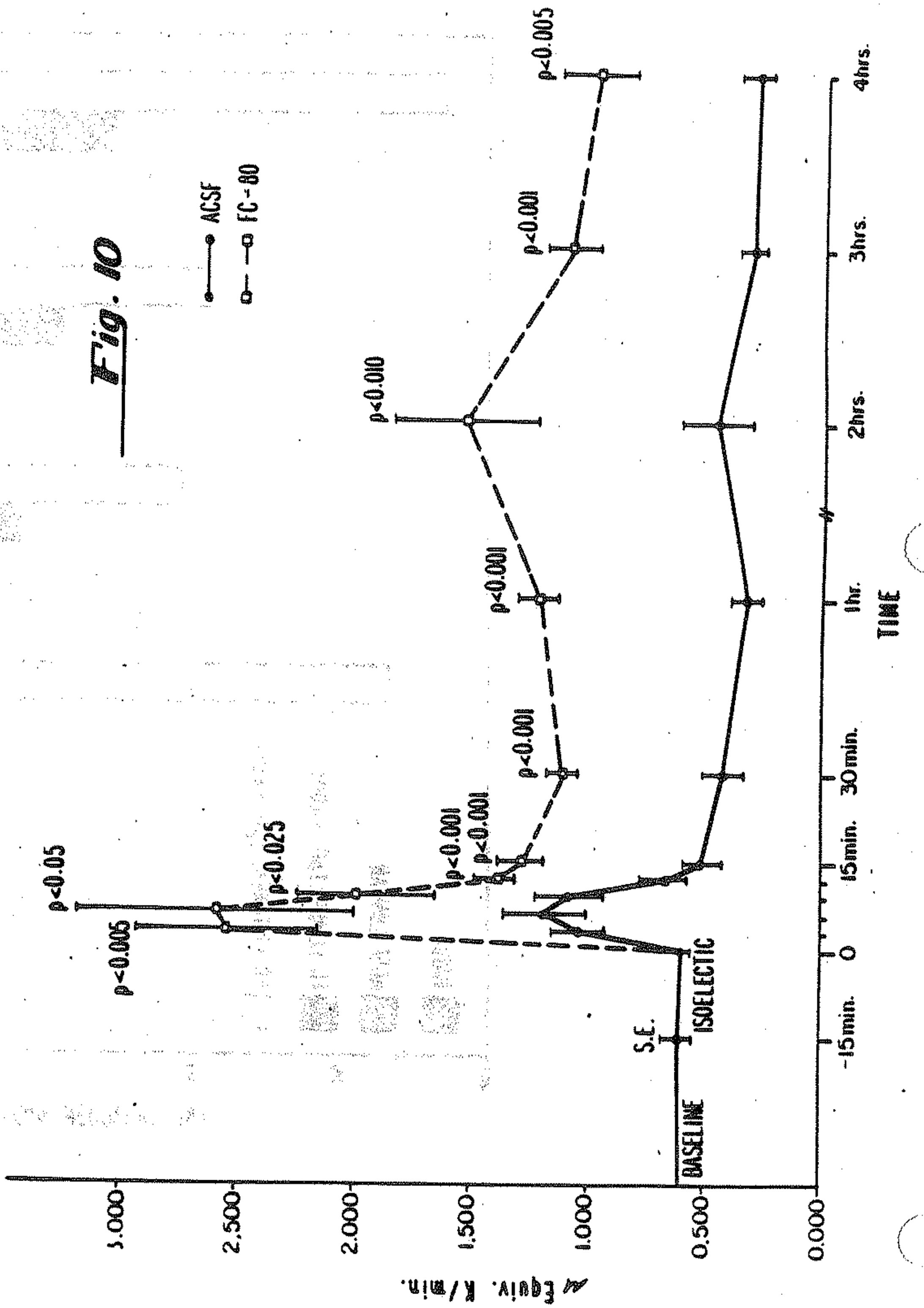
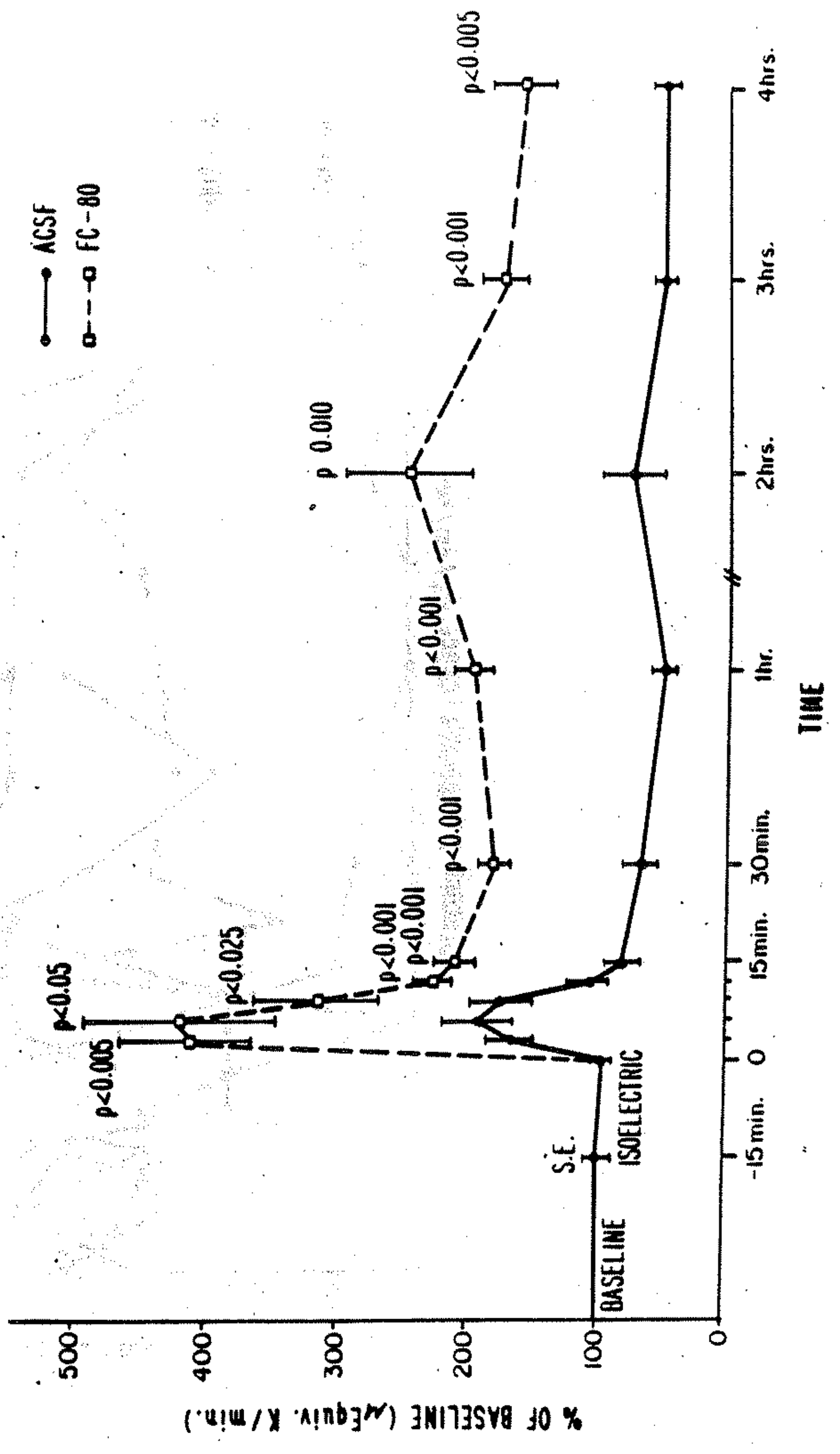

ACSF
FC-80
p<0.005
p<0.05
p<0.025
p<0.001
p<0.001
p<0.001
p<0.001
p<0.010
p<0.001
p<0.005
S.E.
BASELINE
ISOELECTIC
3.000
2.500
2.000
1.500
1.000
0.500
0.000
μ Equiv. K/min.
-15min.
0
15min.
30min.
1hr.
2hrs.
3hrs.
4hrs.
TIME

Fig. 10

Fig. 11


ACSF
FC-80
p<0.005
p<0.001
p 0.010
p<0.001
p<0.001
p<0.001
p<0.001
p<0.025
p<0.05
p<0.005
S.E.
ISOELECTRIC
BASELINE
500
400
300
200
100
0
% OF BASELINE (μEquiv. K/min.)
-15 min.
0
15min.
30min.
1hr.
2hrs.
3hrs.
4hrs.
TIME

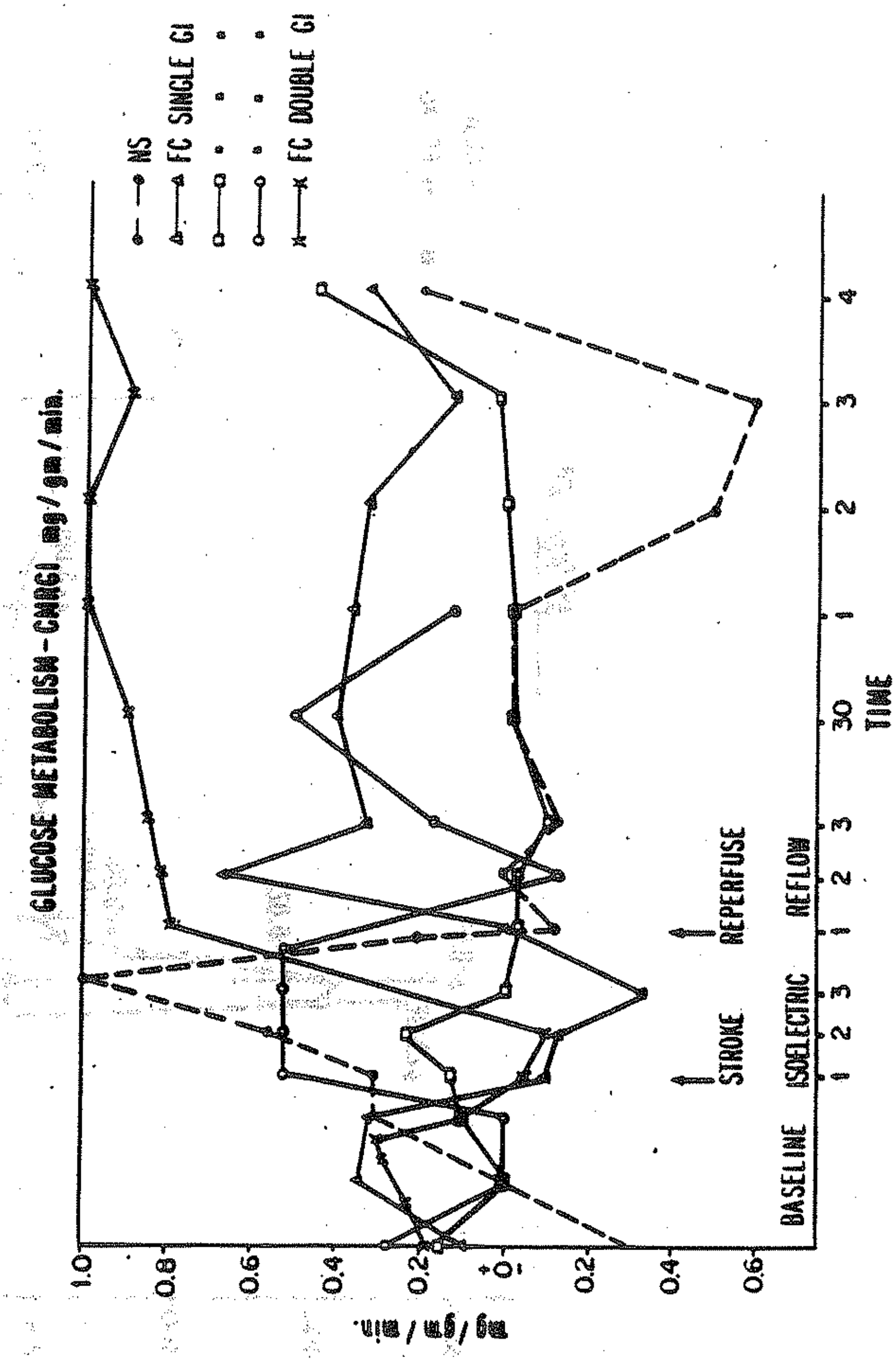

GLUCOSE METABOLISM-CMRGl mg/gm/min.
NS
FC SINGLE GI
" " "
" " "
FC DOUBLE GI
1.0
0.8
0.6
0.4
0.2
+0
0.2
0.4
0.6
mg/gm/min.
BASELINE
STROKE
ISOELECTRIC
REPERFUSE
REFLOW
1
2
3
1
2
3
30
1
2
3
4
TIME

Fig. 12

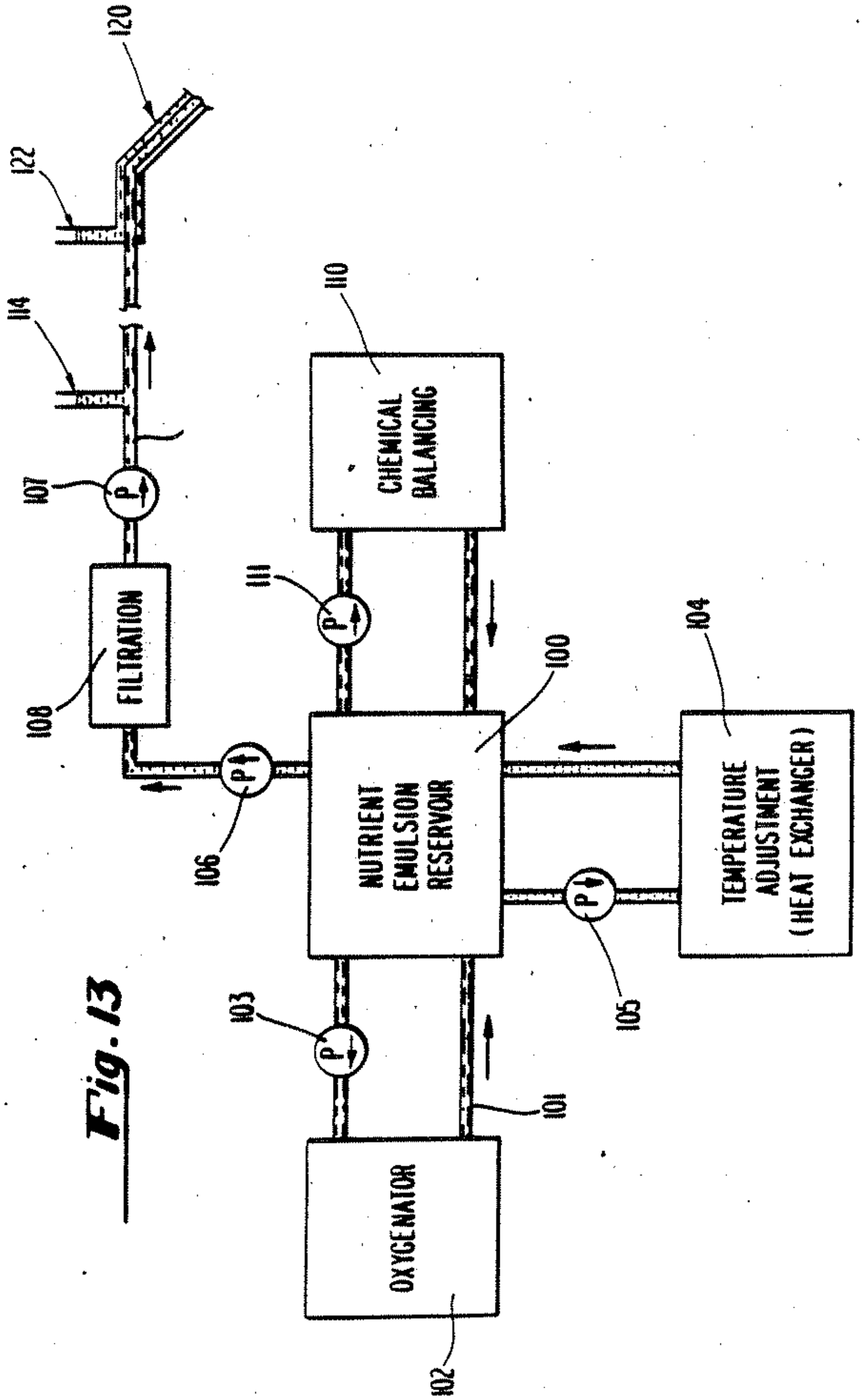

120
122
114
110
CHEMICAL BALANCING
107
P
111
P
FILTRATION
108
100
104
NUTRIENT EMULSION RESERVOIR
P
106
TEMPERATURE ADJUSTMENT (HEAT EXCHANGER)
P
105
103
P
101
OXYGENATOR
102

Fig. 13

STROKE TREATMENT UTILIZING EXTRAVASCULAR CIRCULATION OF OXYGENATED SYNTHETIC NUTRIENTS TO TREAT TISSUE HYPOXIC AND ISCHEMIC DISORDERS

CROSS REFERENCE TO RELATED APPLICATIONS

The present application is a divisional application of Ser. No. 354,346, filed Mar. 3, 1982, which is a continuation-in-part of U.S. patent application Ser. No. 139,886, filed Apr. 14, 1980, now U.S. Pat. No. 4,378,797, entitled "Extravascular Circulation Oxygenated Synthetic Nutrients to Treat Tissue Hypoxic and Ischemic Disorders", as well as Ser. No. 275,116, filed June 18, 1981, now U.S. Pat. No. 4,393,863 and Ser. No. 275,117, also filed June 18, 1981, which in turn are divisionals of Ser. No. 139,886.

BACKGROUND OF THE INVENTION

Cerebrovascular accident, a disease commonly known as "stroke", remains the third leading cause of death, and probably constitutes the single largest category of long term disability in this country. In spite of current medical knowledge and available treatments, a major central nervous system vascular occlusion is quickly attended by irreversible damage to the affected brain region(s). A "completed stroke" is manifest by a fixed and permanent neurological deficit. Millions of dollars have been expended in stroke research and care by Federal and private agencies without a single substantial gain in our present chemotherapeutic abilities for a completed stroke.

On a clinical level, once vascular flow in any portion of the central nervous system has ceased for longer than a few minutes, a permanent "stroke" invariably follows. It is not currently possible to recover substantial neural function with clinical ischemia of 5–7 minutes duration. An exquisite neuronal sensitivity to oxygen deprivation has been blamed for this ultra-short stroke irreversibility. Neurons do indeed have meager metabolic storage and are unable to meet energy needs by anerobic means. Well accepted concepts hold that such permissible cerebral ischemia times are critical and neurons must quickly be resupplied or metabolic infarction will result. While clinically true, recent laboratory investigations have addressed the problems of ischemic vascular and neuronal reactions separately with considerably different results. Recently reported studies indicate neurons are not as sensitive as previously believed. Indeed, it has been suggested that neurons can withstand global ischemia for 1 hour or longer. K. A. Hossman, P. Kleihues, *Arch. Neurol.* 29, 375–389 (1973). If the clinical and experimental observations are to be reconciled, one hypothesis is that long-term damage results from vascular rather than neuronal sensitivity to oxygen deprivation. It is known that secondary reactive changes appear within the microcirculation after sufficient stagnation. A. Ames III, R. L. Wright, M. Kowada, J. M. Thurston, G. Majno, *Am. J. Pathol.* 52, 437–448, (1968). J. Ching, M. Kowada, A. Ames III, *Am. J. Pathol.* 52, 455–476 (1968). E. G. Fischer, *Arch Neurol.* 29, 361–366, (1973). E. G. Fischer, A. Ames III, E. T. Hedly-Whyte, S. O'Gorman, *Stroke* 8, 36–39, (1977). Even if blood is represented to the local tree, the small vessels do not completely reopen. Under these circumstances ischemic, though potentially recoverable, neurons may be lethalized because they are not adequately resupplied with blood within their metabolically tolerable limits. This concept shifts the basic fault in stroke from "ultrasensitive" neurons to a protracted blood flood failure. Nonetheless, a long felt need exists to prevent permanent damage and/or reverse neurologic deficits resulting from interrupted vascular flow.

One experimental approach which has been used to investigate the effects of stroke on neurologic tissue is the perfusion of fluids of known composition through ventriculocisternal spaces. For example, E. Fritschka, J. L. Ferguson and J.J. Spitzer have reported increases in free fatty acid turnover in cerebral spinal fluid during hypotension in dogs. According to the Fritschka technique, a "mock" cerebral spinal fluid containing radiolabelled palmitate was perfused from the lateral ventricle to the cisterna magna of conscious dogs. Arteriovenous glucose and fatty acid concentrations, and "mock" CSF fatty acid concentrations were monitored over a period of 6 hours of perfusion. Estimates of the amount of palmitate recovered from the cisternal effluent and cerebral venous blood lead to the conclusion that a sizeable fraction of free fatty acids may be taken up by tissues "in the vicinity of the CSF space". See Fritschka et al, "Increased Free Fatty Acid Turnover in CSF During Hypotension in Dogs", *American Journal of Physiology*, 232:H802–H807. In "Bulk Flow and Diffusion in the Cerebral Spinal Fluid System of the Goat", by Heise, Held, and Pappenheimer, a ventriculo cisternal perfusion method was used on chronically prepared, unanaesthized goats. Measurements were made of steady-state rates at which inulin, fructose, creatinine, urea, potassium, sodium, and labelled water were removed from perfusion fluid at various hydrostatic and osmotic pressures. The subject perfusions were carried out on female goats provided with implanted ventricular and cisternal guide tubes or cannulas. Each clearance period involved perfusion of 70–120 mills of fluid through the ventricular cisternal system. Inflow rate was maintained constant in the range of 1.50–2.00 ml-min, and outflow was measured continuously. The data obtained was used to investigate the effects of hydrostatic pressure on inulin clearance, rate of formation of CSF, and the permeability of the ventricular system, particularly as compared with that of the toad bladder. This ventriculo cisternal perfusion method was first reported by Pappenheimer, Heise, Jordan and Downer in "Perfusion of the Cerebral Ventricular in Unanaestheized Goats", *American Journal of Physiology*, Vol. 203, pp. 763–774 (1962). Pappenheimer et al reported that goats are anatomically and tempermentally suited for ventricular cisternal perfusions and can tolerate such perfusions for many hours without showing signs of discomfort. The volume of the ventricular system and rate of production of CSF are at least double corresponding values reported for large dogs, and the thickness of the goat occipital bone and its shape facilitates retrograde placement of cannulas through the occipital bone into or above the cisterna magna without interfering with muscles in the neck. The goat's horns provide natural mechanical protection for the cannulas and "are almost indispensable" for operative procedures. In accordance with the Pappenheimer et al technique, guide tubes are implanted just above the dura over the cisterna magna and just above the ependymal linings of the lateral ventricules. Prior to each perfusion the cisterna and ventricle are punctured with sharp probe needles extending a few millimeters beyond the tips of the guide tubes. Alternatively, cannulas were implanted in the subarachnoid space over the parietal cortex, thus permitting perfusion of the entire ventriculo cisternal-subarachnoid system. Pappenheimer et al followed detailed protocols for implanting the guide tubes, and for preparing sterile, synthetic CSF. The Pappenheimer et al perfusion circuit is reported to comprise a bottle sealed with a rubber cap having two stainless steel tubes extending to the bottom of the bottle. One tube serves as a gas bubbler, the second as a liquid outlet. A third opening connects with atmosphere through a sterile cotton plug. The bottle is mounted on an indicating balance and the reservoir outflow is connected through tubing to a parastalic pump with a variable drive permitting pumping rates in the range of 0.5–5 ml/min. One pump output is lead to a male syringe joint which fits the ventricular probe needles and a second outlet on the joints connects to a strain gauge manometer. A 5 ml empty sterile syringe is placed in parallel with the output to damp pulsations of the pump. The cisternal outflow is connected to an enclosed drop counter and wing flask and the output is recorded cumulatively on a polygraph which also gives a vertical record proportional to outflow rate. Pappenheimer et al reports that perfusion with CSF of normal composition can usually be maintained for 4–8 hours before the animal becomes resistive, and if correctly performed, the animal will show no sign of knowing when the perfusion pump is on or off. No attempt is made to regulate the temperature of fluid entering the ventricular probe, however at flow rates of 1–2 ml/min it is theorized that the fluid reaches temperature equilibrium with the brain before reaching the hypothalmus. At higher flow rates (4–6 ml/min) the animals are reported to start to shiver. In this regard, see also F. H. Sklar and D. M. Long, *Neurosurgery* 1, 48–56 (1977).

Over the years, many experiments have been conducted with materials possessing high oxygen-dissolving properties, many of which have been incorporated as constituents in "artificial blood". The concept of utilizing materials possessing high oxygen-dissolving properties for the maintenance of tissue respiration was first reported by Rodnight in 1954. See Rodnight, R., *Biochemistry Journal*, Vol. 57, p. 661. Rodnight capitalized upon the considerable oxygen solubility found in silicone oils, and sustained tissue slices by incubation in these oxygen laden oils. Approximately 12 years later, Clark reported experiments involving the total immersion of small animals in silicone oils and fluorocarbon liquids. Rats totally immersed in oxygenated silicone oil survived for one hour with no apparent ill effects, but died several hours after removal, from unknown causes. Similar experiments using synthetic fluorocarbon liquids, which dissolve about 3 times more oxygen than do the silicone oils, were performed with some success. Under these conditions animals survived immersion in oxygenated synthetic fluorocarbon liquids and thereafter returned to apparent health. See Clark, L. C. Jr. and Gollon F., *Science*, Vol. 152, p. 1755, (1966); and Gollon, F., Clark, L. C. Jr., *Alabama Journal of Medical Science*, Vol. 4, p. 336, (1967). While arterial oxygenation was reported as excellent for Clark's studies in rats, coincident impairment of carbon dioxide elimination was also reported, as was pulmonary damage from breathing fluorocarbon liquids. One rat, which was observed for five days following liquid breathing, was described as being in respiratory distress and as succumbing within 15 minutes after the subcutaneous administration of hydrocortisone (50 mg), with copious loss of body fluid from the trachea. In this regard, Clark concluded:

> These organic liquids should prove to be of value in studies of gas exchange in living tissues in animals. Organic liquids, since they can support respiration with oxygen at atmospheric pressure and have other unique qualities, may find use in submarine escape, undersea oxygen support facilities, and medical application. The pulmonary damage caused by the breathing of the organic liquids available at the present time remains a major complication of their use in man. *Science*, Vol. 152., p. 1756.

See also K. K. Tremper, R. Lapin and E. Levine, *Critical Care Medicine* 8:738 (1980); S. A. Gould, A. L. Rosen, L. R. Sehgal, *Fed. Proc.* 40:2038 (1981).

Following these observations, fluorocarbon liquids were used as an incubation medium for isolated rat hearts. See Gollon and Clark, *The Physiologist*, Vol. 9, p. 191, (1966). In this work, myocardial oxygen requirements were apparently well met, however these hearts did not flourish without intermittent fluorocarbon removal and washing with oxygenated, diluted blood. This phenomenon has been explained in terms of aqueous phase lack in pure fluorocarbons such that necessary ionic exchange is impeded.

More recently, considerable attention has been directed to the use of fluorocarbons as constituents of artificial blood. Sloviter, in order to overcome the problem of aqueous-metabolite fluorocarbon insolubility, made an emulsion with fluorocarbon and albumin. Sloviter's emulsion sustained the isolated rat brain by a vascular perfusion as well as did an erythrocyte suspension. See Sloviter, H. A. and Kamimoto T., *Nature* (London), Vol. 216, p. 458 (1967). A better emulsion was later developed comprising a detergent, "Pluronic F 68" (manufactured by the Wyandotte Chemical Corp., Wyandotte, Mich.), and fluorocarbon liquids which were properly emulsified using sonic energy. This improved emulsion permitted the replacement of most of the blood of a rat which was then reported as surviving in an atmosphere of oxygen for five to six hours. See Geyer "Survival of Rats Totally Perfused with a Fluorocarbon-Detergent Preparation", *Organ Perfusion and Preservation*, edited by V. C. Normen, N.Y.: Appelton-Century-Crofts, pp. 85–96 (1968), Geyer, R. P., *Federation Proceedings*, Vol. 29, No. 5, September–October, 1970; and Geyer, R. P. *Med u Ernohn*, Vol. 11, p. 256 (1970).

Experiments have also been reported wherein fluorocarbons have been used to perfuse livers. Ten hours after in vitro fluorocarbon perfusion, the isolated liver ATP; AMP; lactate/pyruvate ratio; and a number of other metabolites were found to be as good or better than livers perfused in vitro with whole blood. See Krone W., Huttner, W. B., Kampf S. C. et al., *Biochemika et Biophysica Acta*, Vol. 372, pp. 55–71 (1974). These detailed metabolic studies indicated that the organs perfused with 100% fluorocarbon liquid were redeemed "intact"; while only 75% of the whole blood infused organs maintained a similar degree of metabolic integrity. The ability of fluorocarbon perfusion to maintain cellular integrity was confirmed by electron-microscopy studies. The cells had normal mitochondrial ultra structure after ten hours of fluorocarbon support, indicating the persistence of normal or adequate aerobic metabolism. In Brown and Hardison, "Fluorocarbon Sonicated as a Substitute for Erythocytes in Rat Liver Perfusion", *Surgery* 71, pp. 388–394 (1972) a fluorocarbon perfusate preserved organ function and integrity far better than perfusate with much lower oxygen carrying capacity, but was reported as resulting in a decreased rate of bile secretion which was probably the earliest sign of hepatic damage, tissue edema, and a reproducible rise of portal pressure over a period of 2½ to 3 hours. Both tissue edema and rising portal pressure with fluorocarbon perfusion were associated with progressive vascular occlusion as determined histogolically. A greatly diminished perfusion of fluorocarbon at the end of experiments was documented by injection of India ink twenty minutes before the end of the perfusion. Brown and Hardison hypothesized that the fluorocarbon perfusate may react with amino acids and proteins, that the oxygen concentration in the fluorocarbon perfusate may affect the perfusion results, and that filtration of the fluorocarbon emulsion through filter paper and differing instrumentation were responsible for the apparently conflicting results in the literature. Brown and Hardison hypothesize that phagocytosis of fluorocarbon particles might completely block reticticuloendotheilial cells in liver or that capillary endotheilial damage may be another reason for late fluorocarbon perfusion problems.

Fluorocarbons have also been used in experiments involving cerebral blood circulation. In Rosenblum's studies, mouse hematocrits were reduced to 10–15 by exchanging the animal's blood with a fluorocarbon solution. When the animals were respired with 100% oxygen after intravascular fluorocarbon infusions, the brains remained metabolically sound. These organs were able to reverse rising NADH levels and EEG abnormalities induced by short period nitrogen inhalation. The EEG's of fluorocarbon treated animals could be activated by the central nervous system stimulant metrazole. By these criteria, intravascular fluorocarbon does support the cerebral microcirculation and provides functions of oxygenation, metabolism and electrical activity which are normally associated with blood transport. Please refer to Rosenblum, W. I., "Fluorocarbon Emulsions and Cerebral Microcirculation", *Federation Proceedings*, Vol. 34, No. 6, p. 1493 (May 1975). See also S. J. Peerless, R. Ishikawa, I. G. Hunter, and M. J. Peerless, *Stroke* 12, pp. 558–563 (1981); B. Dirk, J. Creiglstein, H. H. Lind, H. Reiger, H. Schultz, *J. of Pharm. Method* 4, pp. 95–108 (1980); J. Suzuki, T. Y. Oshomoto, S. Tanaka, K. Moizoi, S. Kagawa, *Current Topics* 9, pp. 465–470 (1981).

As reported by Kontos et al, the marked vasodilation of small cerebral surface arteries which occurs in response to acute profound hypoxemia may be locally obviated by perfusing oxygen equilibrated fluorocarbon into the space under the cranial window. See Kontos, H. A., et al, "Role of Tissue Hypoxemia in Local Regulation of Cerebral Microcirculation", *American Journal of Physiology*, Vol. 363, pp. 582–591 (1978). Kontos et al described the effect of perfusions with fluorocarbon with 100% oxygen as resulting from increased supplies of oxygen to the neural cells and consequent partial or complete relief of hypoxia, rather than to a local increase in the oxygen tension in the immediate environment of the vascular smooth muscle of the pial arterioles. Two other potential explanations for the observed action are also suggested in the Kontos et al article.

In 1977, Doss, Kaufman and Bicher reported an experiment wherein a fluorocarbon emulsion was used to partially replace cerebrospinal fluid, with the intention of evaluating its protective effect against acute anoxia. Doss et al, *Microvascular Research* 13, pp. 253–260 (1977). According to this experiment, systemic hypoxia was produced through one minute of 100% nitrogen inhalation. A bolus of oxygenated fluorocarbon placed in the cisterna magna immediately prior to nitrogen breathing increased regional cerebrospinal fluid O_2 tension by a factor of 5. During the one minute experimental period, the fluorocarbon emulsion provided twice as much brain tissue oxygen as was found in saline injected controls. Doss et al found the anticipated regional tissue oxygenation decline attending nitrogen inhalation to be halved by the administration of the oxygen bearing fluorocarbon emulsion.

In spite of the above described experiments, there is yet to be reported any practical therapeutic approach to the treatment of ischemic neurologic tissue, and particularly human ischemic central nervous system tissue resulting from stroke, accident or disease.

SUMMARY OF THE INVENTION

The present invention provides a novel nutrient formulation for circulation through cerebrospinal fluid pathways, and systems and methods for using same, to treat central nervous tissue hypoxic-ischemic conditions. Through its use, a new diagnostic methodology is also disclosed.

Applicant has recognized that there is a therapeutic time window through which neuron can be reached and resuscitated. The method of the present invention is designed to bypass obstructed vascular circulation and deliver cerebral metabolic needs through an alternate cerebral spinal fluid (CSF) circulation portal. Since particle size exerts a major influence on brain penetration from CSF, the method of the present invention is hypothesized to permit diffusion of oxygen, glucose, electrolytes and essential amino acids into ischemic neural tissue when presented in abundance in the cerebral spinal pathway. Thus, a rapidly exchanging cerebral spinal fluid perfusion system is provided to amply supply these materials and, at the same time, remove metabolic waste.

The cerebrospinal fluid (CSF) pathway system, which intimately bathes and permeates brain and spinal cord tissues, constitutes a unique anatomical relationship within the body. Although it has some similarities to systemic lymphatics, its anatomical arrangement differs considerably from that of lymph. Indeed, this system has been named the "third circulation". Due to the extensive area of CSF-tissue contact over the cerebral and cord surfaces, in the miniature Virchow-Robins spaces, and cerebral ventricles, the cerebrospinal fluid system constitutes a vast, complex and intimate therapeutic avenue for access to central nervous tissue. Excepting certain infections and neoplasms where the cerebrospinal fluid is now utilized as a treatment conduit, the cerebrospinal fluid system has not been otherwise widely exploited as an easily accessible therapeutic route and has never been used as a continuous therapeutic diagnostic circulation system in man. The present invention is predicated on the recognition that, when regional cerebral blood flow is interrupted, such as after major stroke, or is otherwise seriously impeded by profound vaso-spastic states, the cerebrospinal fluid pathway actually represents the only practical and viable anatomical route by which these tissues may be readily treated. This results from the fact that the usual vascular delivery system is either occluded or non-functional, and thus tissues within affected territories cannot be properly served.

In accordance with the present invention, essential cellular substrates are delivered to beleaguered ischemic brain regions by utilizing the "back door" cerebrospinal fluid delivery route. Accordingly, the present invention provides a novel nutrient emulsion, circulatory method and system which provide necessary nutrient penetration into regions suffering vascular deprivation.

It has been found that the cerebrospinal fluid to brain relationship is not characterized by the rigid and highly selective barrier mechanism which are present at the blood-brain interface. Thus, the penetration rate of materials from cerebrospinal fluid regions to the brain relate largely to molecular size, that is, small substances penetrate deeply while large molecules move more slowly into brain substance. Although entry rates are generally inversely proportional to molecular weight, penetration is also influenced by lipid solubility and the molecular configuration of the penetrating substance. Accordingly, the present invention provides a nutrient emulsion containing essential brain nutrients including selected electrolytes, having a relatively low molecular size which, in accordance with the methods of the present invention, are caused to relatively freely diffuse from either the ventricular or subarachnoid fluid regions into the brain matter to be treated. Accordingly, the present invention provides a novel nutrient emulsion which has been purified, balanced, and perfected to fall within narrow physiologic limits while nonetheless providing the desired nutritional characteristics referred to above.

In accordance with the preferred embodiment of the present invention, this nutrient emulsion constitutes "synthetic cerebrospinal fluid" comprising preselected electrolytes, glucose, amino acids, at least one oxygen-carrying component, typically a fluorocarbon, and other components which impart to the composition a preselected pH, buffering capability, and osmolarity. This nutrient emulsion is prepared by controlling sonication time and by properly dialyzing the materials to achieve a toxic free emulsion. The resulting solution may be rapidly oxydated to O_2 pressures of 650 mm of mercury by using the herein disclosed modified recirculating pediatric oxygenator. As a result, a novel oxygenated nutrient emulsion is provided which is believed to exhibit exceptional therapeutic properties.

The present invention also provides a novel method and apparatus for circulating the oxygenated nutrient emulsion through cerebrospinal fluid pathways, particularly those pathways which contact brain and spinal cord tissue. According to these methods, treated tissues exhibit a substantially improved ability to resist and/or repair damage which would otherwise result from vascular occlusion. In accordance with the preferred method of the present invention, the novel oxygenated nutrient emulsion is circulated through this cerebrospinal fluid route by injecting it into brain ventricles and withdrawing it from the cisterna magna or the spinal subarachnoid space to nour . and to treat central nervous tissues. In other instances the fluid may be injected into the subarachnoid space and withdrawn from another subarachnoid position. The preferred embodiment oxygenated nutrient emulsion should be circulated to tissues to be treated in amounts sufficient to provide adequate gas exchange. Pure fluorocarbon may contain 50 ml O_2 per 100 ml at one atmosphere oxygen while normal blood contains only 20 ml O_2/100 ml under the same conditions. The oxygen carrying capability per ml of the final emulsion is considerably less than that of pure fluorocarbon by reason of its content of other constituents for normalizing osmotic pressure, buffering, electrolytes, and other physiologic balancing materials. Thus, the preferred embodiment nutrient emulsion may be charged with oxygen (100% O_2 at one atmosphere) to attain pO_2 tensions of 640–700 mm of mercury and an O_2 content of 20 ml per 100 ml. Under rapid circulation conditions, the integral O_2 exchange (fluorocarbon to tissue) has been found to be about 33%. Thus, an oxygen exchange value of about 6.6 ml O_2/100 ml nutrient emulsion per minute is provided by the present method.

In accordance with the preferred embodiment of the present invention, sufficient nutrient emulsion should be supplied to counteract oxygen deprivation to the affected tissue. For example, the entire supertentorial adult cat brain weighs 12 grams (±2) and the normal metabolic consumption of oxygen of mammalian brain tissue equals 3–4 ml per 100 grams per minute. This total metabolic need may be met with the circulation rate of 6–8 mls per minute. Metabolic needs necessary to simply sustain and/or salvage tissue may be achieved by perfusion rates of one half or less of this optimum. Within these constraints an easily achieved sustenance flow rate of at least 20–30 ml/minute, optimally 45–60 ml/minute, would be anticipated to salvage 100 gms of human brain tissue. It has been found experimentally that it is possible to supply sufficient oxygen to counteract the deprivation of the affected tissue through circulation of the nutrient emulsion through the cerebrospinal fluid route. In fact, under carefully controlled conditions, it is believed within the scope of the present invention to nourish the entire human brain using the preferred embodiment apparatus, method and substance of the present invention. In this manner, central nervous neurons deprived of major blood supply may be sustained without significant damage.

In accordance with the preferred embodiment of the present invention, a novel system is disclosed for administering and maintaining the oxygenated nutrient emulsion for delivery and circulation through the cerebrospinal route.

The preferred embodiment system of the present invention effectively carries out the circulation and equilibration of the nutrient emulsion during treatment. This system, which is diagrammatically illustrated in FIG. 1, generally comprises a reservoir containing nutrient emulsion; means for delivering the nutrient emulsion at preselected flow rates; an oxygenation means for equilibrating the nutrient emulsion to desired gaseous tension levels; heat exchanger and/or cooling unit means for selectively controlling the temperature of the nutrient emulsion; filtering means for cleansing the nutrient emulsion; and circulation monitoring means for insuring that desired circulation flows and pressures are maintained within the system.

The present invention also provides a method of diagnosing conditions of neurologic tissue in mammals. This novel method generally comprises providing an artificial spinal fluid of known composition, injecting that artificial spinal fluid into at least a first portion of the cerebrospinal pathway of a mammal, withdrawing a diagnostic fluid from a second portion of that pathway to create a circulation of fluid at least through a portion of said pathway, monitoring the composition of said diagnostic fluid, and comparing for at least a selected difference in the compositions of said artificial spinal and diagnostic fluids, whereby the detected differences in those compositions are at least diagnostic of neurologic tissue disposed along said portion of the cerebrospinal pathway. In accordance with the diagnostic methods of the present invention, the diagnostic fluids may be monitored for differences in oxygen content, lactic acid concentration, carbon dioxide concentration, potassium and/or sodium ion concentration, enzyme concentration, pH difference, ammonium concentrations, GABA (gamma-aminobutyric acid) and other amino acid(s) concentrations, microorganism content, bacterial count, myelin fragments, cellular fragments or organelles, malignant cells, and/or poisons.

It is also within the scope of the present invention to provide a novel nutrient liquid and/or diagnostic liquid for treating cerebrospinal tissue containing various novel specified components which is formulated using novel methodology.

It is additionally within the scope of the present invention to provide a novel apparatus for treating patients having ischemic-hypoxic tissues, including novel injection and withdrawal means comprising a novel catheter means which is particularly adapted for injecting oxygenated nutrient liquid into a cerebral ventricle without danger of substantially damaging neurologic tissue in the vicinity of that ventricle.

In addition to the methods described above, it is within the scope of the present invention to provide additional therapeutic agents to the nutrient emulsion, such as antineoplastic agents; antibiotics, and/or other therapeutic agents for use in treating the target tissue(s).

Accordingly, the primary object of the present is the provision of a method, substance, and system for providing early stroke treatment.

Other objects of the present invention are to provide treatments for brain and spinal cord injuries, cerebral hemorrhage, cerebral vasospasm, senility, after general hypoxia and other hypoxic-ischemic related neurological disorders.

It is a further object of the present invention to provide therapeutic treatment which may sustain the life of the brain and central nervous system tissues in case of profound shock and/or temporary cardio-respiratory failure.

It is a further object of the present invention to provide life-sustaining support to the brain and/or spinal cord tissues during the conduct of neurological or cardiovascular surgery.

Other objects of the present invention are the provision of methods which may compliment treatments of central nervous system neoplasms by either external radiation and chemotherapy by providing local tissue hyperoxygenation or drugs which may enhance drug or radiation tumorocidal effects.

Further objects of the present invention include the provision of methods which are useful in treating anoxic states attending birth injury. The present method will also assist in removal of central nervous system poisons.

These and other objects of the present invention will become apparent from the following more detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic view of the preferred embodiment treatment system of the present invention illustrating the circulation of nutrient emulsion from a reservoir, into a cerebral ventricle, such as a lateral ventricle, through a portion of the cerebrospinal fluid pathway for output from the spinal subarachnoid space or from the cisterna magna;

FIG. 2 is a diagrammatic view of a portion of the preferred embodiment treatment system of FIG. 1 illustrating an alternate circulation route wherein oxygenated nutrient emulsion is injected into the spinal subarachnoid space and is collected from the cisterna magna;

FIG. 3 is a diagrammatic view of portion of the preferred embodiment treatment system illustrated in FIG. 1 showing an alternate circulation route wherein oxygenated nutrient emulsion is injected into the cisterna magna for passage through the spinal subarachnoid space for withdrawal from a lumbar region;

FIG. 4 is an EEG power recording from the left and right hemispheres of a cat showing traces from the time of an initial stroke, at the end of the stroke, and four hours after the stroke;

FIG. 5 is an EEG recording of an animal perfused with oxygenated nutrient emulsion having a pO_2 level of 400 and showing a 5% return of EEG at 4 hours;

FIG. 6 is an EEG similar to FIG. 1 for an animal perfused with oxygenated nutrient emulsion having a pO_2 of 645 and showing an 88% return of electrocerebral power within 4 hours;

FIG. 7 is an EEG trace showing the effect on EEG activity of a temporary cessation in oxygenated nutrient emulsion circulation;

FIG. 8 is a graph showing the effect on glucose metabolism (CMRGl), lactate and pyruvate before and after stroke of a perfused animal particularly illustrating the effect of a reduction in perfusion rate to insubstantial levels;

FIG. 9 is a bar graph showing the mean EEG recovery (percent) for groups of cats subjected to strokes resulting in 15 minutes of EEG isoelectricity, and comparing naive animals to those perfused only with artificial cerebral spinal fluid (lumbar) and oxygenated nutrient emulsion through lumbar and cisternal routes;

FIG. 10 is a graph of microequivalents of potassium per minute versus time for two experimental groups of cats subjected to 15 minutes of a stroke induced isoelectric state;

FIG. 11 is a graph similar to FIG. 10 wherein the data in FIG. 10 is represented as a percent of the base line figure;

FIG. 12 is a glucose metabolism (CMRGl) graph plotting milligrams per grams per minute against time for three perfusions using a standard glucose concentration, one perfusion using twice that glucose concentration, and a control using artificial cerebral spinal fluid without fluorocarbon;

FIG. 13 is a diagrammatic view of an alternate embodiment oxygenated nutrient emulsion delivery system for use in performing the methods of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following more detailed description, numerous examples have been selected for the purposes of explanation and illustration of the preferred embodiments of the present invention. One of ordinary skill in the art will recognize that various changes may be made in the materials and methods disclosed herein without departing from the scope of the present invention, which is defined more particularly in the appended claims.

Referring now to FIG. 1, the preferred system for circulating nutrient emulsion through a cerebrospinal pathway is diagrammatically illustrated. As shown in FIG. 1, a nutrient emulsion reservoir 10 is provided for receiving and retaining nutrient emulsion, the preparation of which will be described more fully hereinafter. In accordance with the preferred system and method of the present invention, the nutrient emulsion is injected into a cerebrospinal pathway following pH adjustment and filtering, temperature adjustment, oxygenation, and adjustment of the pressure and flow rate of the nutrient input stream. In FIG. 1, these steps are illustrated diagrammatically at 12, 14, 16 and 18 respectively. Preferably, the nutrient input stream is delivered to a ventricle of the brain, and more particular to a lateral ventricle 20 of the human brain, designated generally 22. Injection of the nutrient input stream permits the oxygenated nutrient emulsion to come into contact with the subarachnoid spaces, miniature Virchow-Robins spaces, cerebral and cord surfaces, and cerebral ventricles. For the system illustrated in FIG. 1, the nutrient input stream is diagrammatically illustrated as being injected into a lateral ventricle 20. Since the lateral ventricle is in fluid communication with other portions of the cerebrospinal pathway, withdrawal of fluid from a portion of the pathway which is remote from that ventricle will create a circulation of fluid within the cerebrospinal pathway. More particularly circulation of the nutrient input stream though at least a portion of the cerebrospinal pathway may be accomplished by withdrawing fluid from the spinal subarachnoid space, diagrammatically illustrated as 26 in FIG. 1, or alternatively, from the cisterna magna 24.

It is not necessary to conduct steps 10–18 in the sequence illustrated in FIG. 1. In FIG. 13 the presently preferred apparatus for delivering oxygenated nutrient emulsion is diagrammatically illustrated. This apparatus, which may be easily constructed using a pediatric blood oxygenator such as an H-800 Pediatric Oxygenator available from The William Harvey Cardiopulmonary Division of C. R. Bard, Inc., Santa Ana, Calif. 92705, comprises a nutrient emulsion reservoir having oxygenation and temperature adjustment loops for constantly oxygenating and adjusting the temperature of the nutrient emulsion contained within the reservoir. In this manner the flow rates of nutrient emulsion provided from oxygenation by oxygenator 102 or for temperature adjustment 104 may be independently varied through adjusting the flow rate of delivery by variable speed pumps 103 or 105 to optimize the temperature and pO_2 characteristics of the oxygenated nutrient emulsion to be delivered for injection by variable speed delivery pumps 106 and 107. As normally used, pediatric blood oxygenators fail to provide a sufficient oxygen transfer rate to fluid flow rate to accommodate the emulsion of the present invention. The minimum blood flow rate of the H-800 oxygenator, for example, is 0.5 liters per minute, and the oxygen transfer rate (to blood) at this flow rate is less than about 25 ml/min. By routing the output 101 of the oxygenator to the reservoir, the oxygenator output pump 103 may operate at flow rates which easily achieve about 7 liters per minute of oxygen transfer to the fluorocarbon carbon emulsion contained in the 2000 ml reservoir. At the same time, delivery pumps 106 and 107 may provide much lower flow rates of nutrient emulsion to the animal undergoing treatment. In a similar manner, heat exchange may also be optimized. In order to maintain optimal pO_2 values, each conduit of this system should be composed of an oxygen impermeable material to prevent leakage of oxygen from the oxygenated nutrient emulsion during processing and delivery. The filtration and chemical balancing procedures followed in preparing the nutrient emulsion are not presently performed "on line", however it is anticipated that chemical balancing may be performed as a closed loop process, as illustrated in FIG. 13. Filtration 108 is performed on line under pressure from pump 106 using a millipore bacterial filter. Pump 107 establishes the final injection rate. The flow of nutrient emulsion to the chemical balancing system is adjusted using variable speed pump 111. In the embodiment of FIG. 13, pressure monitoring and control is accomplished using an open side arm 114 bearing indicia thereon which correspond to the hydraulic pressure of oxygenated nutrient emulsion within delivery line 19. The height of the side arm is adjusted so that overflow will occur when the maximum desired intracranial pressure has been obtained.

As shown in FIG. 1 the oxygenated nutrient emulsion input stream is carried through input stream conduit 19 to an injection cannula 20a which is coupled thereto by coupling 21. Injection cannula 20a is rigidly attached to skull 22 by fitting 22a which holds the cannula in its proper orientation to permit injection of the oxygenated nutrient emulsion into lateral ventricle 20.

If preferred, a double lumen catheter, such as catheter 120 (FIG. 13), may be utilized in place of input cannula 20a. One of the lumens of this catheter should be connected to a pressure monitoring means for monitoring the intracranial pressure within the lateral ventricle 20. This pressure monitoring means may comprise an open side arm, such as side arm 122 which functions similarly to side arm 114.

The preferred injection means of the present invention comprises a cerebral catheter means for insertion into a brain ventricle. This injection means comprises means for preventing a portion of the catheter located within a brain ventricle from damaging tissues surrounding the ventricle. In the preferred embodiment, an inflatable balloon tip may be provided for this purpose. The actual injection of nutrient emulsion into the brain ventricle is accomplished by providing an arrangement of outlet holes disposed as a series of slits radially spaced around the catheter tip. Both the injection means and withdrawal means also further comprise attachment means for attaching the catheter to the body in the vicinity of the injection or withdrawal sites. Thus the injection catheter may comprise a means for fixing at least a portion thereof with respect to the skull to insure catheter stability. The withdrawal catheter, which may have a tip with multiple perforations disposed therein, further comprises means for attaching at least a portion thereof to tissue in the region of the subarachnoid space. This attachment means may include a staple for attaching a non-collapsible portion of the catheter to a lumbar region of the skin.

In many applications, the oxygenated nutrient emulsion will be delivered under normothermic conditions, that is, at about 37° C. Under these conditions, and under hypothermic or hyperthermic conditions where the delivery temperature of oxygenated nutrient emulsion is higher than ambient temperature, temperature adjustment is easily accomplished by providing a thermostatically controlled heater coupled to a suitable heat exchanger for adjusting the temperature of oxygenated nutrient emulsion recirculated to the nutrient emulsion reservoir.

The circulation route illustrated in FIG. 1 permits the treatment of at least cerebral tissues. It is within the scope of the present invention, however, to focus treatment on selected neural tissue areas, in which case alternative points of injection and withdrawal of fluid may be selected by the attending physician. For example, in the case of spinal cord injury, it is anticipated that the point of injection of oxygenated nutrient emulsion may be the lumbar, spinal subarachnoid space, with the point of withdrawal being the cisterna magna. While the above mentioned cerebrospinal pathway injection and withdrawal points are preferred, it is within the scope of the present invention to utilize other injection and withdrawal locations, provided a substantial circulation of fluid through the area of affected neurologic tissue is established by utilizing the selected loci. Such alternate pathways are illustrated in FIGS. 1-3. In FIG. 1, withdrawal of the nutrient emulsion from the cisterna magna is illustrated via conduit 30 in dotted outline. In FIG. 2 input conduit 19 injects oxygenated nutrient emulsion into the diagrammatically illustrated subarachnoid space 26. Withdrawal from the cisterna magna is via conduit 30b. In FIG. 3 injection into the cisterna magna is accomplished via injection catheter 30a. Withdrawal is from the diagrammatically illustrated spinal subarachnoid space 26 via withdrawal catheter 30c.

The fluid which is withdrawn from the cerebrospinal pathway will not be of identical composition to the oxygenated nutrient emulsion which is injected at the injection point. By taking advantage of differences in composition which are detected in the withdrawn fluid, which may be considered to be a diagnostic fluid, the attending physician may easily monitor the physiologic condition of the neurologic tissue which is being treated. This diagnostic fluid may also be monitored to assure that treatment is proceeding according to plan. Accordingly, fluid which is withdrawn from the cerebrospinal pathway is directed to an output collection means 28 for collecting diagnostic fluid. Preferably, an output monitor 34 will continuously monitor various chemical and physical characteristics of the diagnostic fluid for such properties as flow rate, hydraulic pressure, potassium and sodium ion concentration, temperature, lactic acid concentration, gamma amino butyric acid and other amino acid concentrations, oxygen concentration, carbon dioxide concentration, enzymes, and ammonia concentration. The output of this output monitor will not only provide the attending physician with information concerning the state of the cerebrospinal tissue being treated, but also will be fed back to the monitor, control and alarm systems for at least pressure and flow rate, temperature, oxygen-carbon dioxide and chemical constituency, as described more fully hereinafter. This diagnostic system takes advantage of the fact that ischemic neurologic tissue produces higher concentrations of such materials as Gamma-aminobutyric acid (GABA), lactate ion (lactic acid), enzymes and/or LDH (lactic dehydrogenase), ammonia, and other constituents which have been determined by analyzing cerebrospinal fluid of patients subjected by disease to similar anoxic conditions.* In accordance with the system of the present invention, however, a continuous monitoring of the state of neurologic tissue is possible, since the circulation of oxygenated nutrient emulsion will produce a continuous flushing of the affected tissue regions, and thus will result in diagnostic fluid component variations which are rapidly reflective of the physiologic state of the tissues being treated. Due to the multipoint injection-withdrawal method of the present invention, dangers which are inherent in sampling natural cerebrospinal fluid at a single location are avoided by utilizing a double venting method wherein the cerebrospinal fluid pressure is at all times carefully controlled.

It is within the scope of the present invention to sterilize and reconstitute that diagnostic fluid as shown at step 32, whereupon that reconstituted diagnostic fluid may be provided as nutrient emulsion to the nutrient emulsion reservoir 10. As shown in FIG. 1, the output monitor 34 may monitor the diagnostic fluid during the sterilization and reconstitution processes and, if desired, ensure that the reconstituted fluid satisfies the requirements of the nutrient emulsion reservoir. As shown in FIG. 1, in order to ensure that appropriate degrees of oxygenation, filtration and chemical balancing, temperature adjustment, and pressure and flow rate are maintained, the nutrient input stream is monitored by various monitors, controls, and alarms, which are intended to provide a fail-safe nutrient input stream. In particular, a pressure and flow rate monitor, control and alarm 38 is provided for monitoring the pressure and flow rate of the nutrient input stream, for controlling the pressure and flow rate adjustment 18 to establish desired pressures and flow rates, and for sounding an alarm in the event that the nutrient input stream exceeds or falls below preselected pressures or flow rates. If desired, this alarm may additionally disable the pumping mechanism producing flow of the nutrient input stream such that the unit "shuts down" upon detection of unacceptable input stream conditions.

Referring now to the temperature monitor, control and alarm, the temperature characteristics of the nutrient input stream are similarly detected, at least to ensure that hyperthermic states, except when used as therapeutic modality, are avoided. While in most instances, the nutrient input stream will be adjusted to a 37° C. temperature, it may be desired to select hypothermic temperatures in order to establish certain treatment conditions. In either event, the temperature monitor will continuously detect the temperature of the input stream, will control the temperature adjustment 14 to establish a preselected temperature, and will sound an alarm and/or disable the system in the event that a preselected temperature range is not maintained in the nutrient input stream.

Referring now to the chemical monitor, control and alarm 42, the nutrient input stream will be continuously monitored for one or more chemical or physical characteristics of the nutrient input stream, and will control the chemical balancing, filtration, etc. which is performed by the filtration and chemical balancing unit 12. The chemical monitor, control and alarm may, for example, monitor the pH, osmolarity, electrolyte component, carbohydrate component, amino acid component, or other components of the nutrient emulsion to ensure that the nutrient input stream falls within preselected

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*See for example, "Rapid and Sensitive Ion-Exchange Fluorimetric Measurement of G-Aminobutyric Acid in Physiological Fluids", Hare et al. *Anal. Biochem.* Vol. 101, pp. 349-355 (1980) for a preferred GABA measurement method.

stream characteristics. In the event that these characteristics do not fall within the preselected range, the alarm for unit 42 may sound and/or may disable the system to thereby prevent further injection of nutrient input stream into the cerebrospinal pathway.

Finally, an oxygen/carbon dioxide monitor, control and alarm unit 36 is provided which continuously monitors the oxygen and carbon dioxide contents of the nutrient input stream, which controls the oxygenation unit 16, and which sounds an alarm in the event that the oxygen or carbon dioxide concentrations do not fall within preselected ranges. It is anticipated that each of units 36–42 may provide continuous displays of the information monitored from the nutrient input stream, and may, if desired, enable back-up units which either manually or automatically supplement or replace the functions of units 12–18 in the event that those units are not functioning to produce a nutrient input stream within the desired ranges. For example, it is anticipated that a manual or battery operated pump, oxygenator, filter, and pressure and flow rate adjustments be provided to enable emergency operation of the system, since continual nutrient flow is lifesaving for the devitalized portion of the treated organ.

The preferred nutrient emulsion of the present invention is comprised of carefully formulated components which, to the extent possible while maintaining desired therapeutic activity, mimic the physical and chemical characteristics of natural cerebrospinal fluid. Generally, tissues and cells will not fair well if exposed to large volumes of non-physiologic ionic solutions. Accordingly, it has been recognized that appropriate electrolyte compositions at the tissue level are indispensable when it is considered that the circulatory method of the present invention would otherwise result in the washing and the dilution of electrolytes from the region even after short terms of circulation, to the detriment of cell membrane functions. Accordingly, in accordance with the preferred embodiment of the present invention, sodium, potassium, calcium, magnesium, and chloride ions are carefully balanced in the nutrient emulsion of the present invention to thereby create, to the degree possible, normal extra-cellular compositions. The present invention also provides a non-aqueous oxygen transfer component for selectively combining with oxygen and for transferring oxygen to the tissues to be treated. Numerous compounds are known to the art which are characterized by having a high solvent property for oxygen, carbon dioxide, and other gases. The preferred non-aqueous oxygen transfer component of the preferred nutrient liquid should exhibit when so charged, oxygen vapor pressure ranges of above 400, and preferably 600, Torr. Such oxygen transfer components should similarly not have in themselves high vapor pressures which would boil at body temperatures, nor have viscosities which are difficult if not impossible to emulsify. Generally, the preferred compounds for use as non-aqueous oxygen transfer components are fluorocarbon polymers, such as perfluorocarbons, perfluorinated alkyl polyethers, fluoroethers, fluoramines, etc. While compounds within these groups range in molecular weight from 250 to 7000, their selection for use as non-aqueous transport components are based upon the combination of features of the proper vapor pressure, molecular weight, viscosity, and emulsifiability, emulsion-stability and tissue distribution. One such fluorocarbon which has been found to be particularly suited for the non-aqueous oxygen transport component of the preferred nutrient liquid is a reagent grade perfluorobutyltetrahydrofuran which has been sold by the 3-M Corporation under the trademark "FC-80". FC-80 has an oxygen solubility coefficient ScO_2 of 0.45 of ml O_2/ml at pO_2 of 760 Torr. See Navari et al., *Res. Exp. Med.* 170, pp. 169–180 (1977), which paper is specifically incorporated by reference as if fully set forth herein. It should be noted that whole blood under the same circumstances contains 0.23 ml O_2/ml. The FC-80 ScO_2 is linear from 760 to 200 Torr but declines quite rapidly below the lower level. The high oxygen diffusion coefficient (5.71×10^{-5} cm^2/sec per second) indicates more than adequate FC-gas in a physiologic sense. Similar studies concerning CO_2 solubility and diffusion indicate that absorption and release are described by a straight line function. From these observations, metabolic tissue CO_2 accumulations should theoretically be easily removed by fluorocarbon solutions administered through a circulatory method.

Not only do fluorocarbons possess these unique physical gaseous properties but they are for the most part non-toxic. The main acute toxicity has been found to reside in free fluoride ion accumulation which occurs mainly from sonication. See, Clark et al., *Fed. Proc.* 34, pp. 1468–1477 (1979). The free ion can, however, be removed by repetitive dialysis and the emulsion thereby rendered physiologically acceptable. Accordingly, the preferred embodiment nutrient liquid of the present invention, which has been dialysized and filtered through a millipore filter, has evidenced no toxicity either in short term or long term use during circulation through cerebrospinal pathways of animals. One chief advantage of the CSF circulation route is that most or all the nutrient liquid can be removed by washing at the time of treatment termination. In this way long term cellular retention as previously noted for liver and reticuloendothelial cells in vascular circulations of oxygenating liquids may be avoided.

In the preferred embodiment nutrient liquid of the present invention, an emulsification component is provided for permitting the emulsification of the nutrient component with the oxygen transfer component of that liquid. See Clark et al, *Triangle II*, pp. 115–122 (1972b); Clark et al, *Microvasc. Res.* 8, pp. 320–340 (1974). The best currently available material for this purpose is believed to be block polymer polyols, which are known to the art as "pluronics", of which, pluronic F68 has proven to be a most efficient emulsifying agent. As used in a nutrient liquid as described more fully hereinafter, the toxicity from such a pluronic detergent is negligible. At the present time, however, it is anticipated that other emulsification components which will permit the non-aqueous transfer component of the nutrient liquid to become soluble with respect to the aqueous nutrient component of the nutrient liquid may be utilized to provide solutions which have adequate physiologic perimeters. Such other means of solubilizing fluorocarbons includes the formation of micelles, etc.

In the preparation of the preferred nutrient liquid, an important factor in producing an acceptable nutrient liquid is the achievement of an acceptable final osmotic pressure. The osmotic pressure of the nutrient liquid will depend upon the amount of the emulsification component, the particle size of the fluorocarbon, and the ionic composition of the aqueous nutrient component. In accordance with the preferred method of preparing the nutrient liquid of the present invention, toxic emulsification components should be removed by dialysis.

Fluorocarbon particle size will be controlled by sonification time and filtering, while the ionic composition of the aqueous nutrient component will be carefully adjusted to produce a nutrient liquid possessing desired osmotic characteristics. If desired, a final osmotic tuning may be accomplished in accordance with the method of the present invention by adding ascorbic acid to the nutrient liquid.

In order to provide fully successful treatment of ischemic tissues, it is desirable to provide nutrient liquid for circulation around those tissues which will compensate for relative or complete deficiencies of blood transport metabolites. In addition to oxygen, other tissue metabolic requirements include glucose, amino acids, ions, hormones, vitamins, etc. While in temporary treatment conditions, it may be suitable to temporarily omit one or more vitamin, hormone, ion, or amino acid, for prolonged treatment and to produce the most desirable results, it is preferred to provide substantially all of the above mentioned metabolites in the preferred nutrient liquid. It is at least desirable to provide in the nutrient liquid all components necessary to support aerobic metabolism which will be available within the medium for use at cellular levels. Glucose deprivation of central nervous system tissue causes a serious cellular metabolic deficiency, as does the same degree of oxygen deficiency. Accordingly, by providing a total and finely adjusted mixture that has all the necessary components for total cell survival, an extremely efficient and therapeutic liquid material is provided which is ideal for circulation through the cerebrospinal pathways.

In order to illustrate the preferred method and composition of such an oxygen-nutrient material, the following example is provided.

EXAMPLE 1

Under conditions of replacing blood borne materials by perfusion all nutrients necessary for aerobic metabolism must be available within the medium for immediate use at cellular levels. As far as the central nervous system is concerned, glucose deprivation causes as serious a cellular metabolic deficiency as does the equivalency of oxygen lack. To achieve the desired ends all known essential nutrients have been added to the FC (fluorocarbon) emulsion. FC itself thereby serves the purpose of a gas transport system while the aqueous emulsion phase contains an array of cellular metabolic essentials. The total and finally adjusted mixture has all the necessary ingredients for total cell survival. The combination material is referred to as an oxygen-nutrient formula (Ox-N), or oxygenated nutrient emulsion.

Method and Composition Preparation of Oxygen-Nutrient Material

1. Reagents
   - (A) 5% Commercial grade Pluronic F68 (Basic Wyandotte).
   - (B) 20% W/V FC-80 (3M Corporation)
   - (C) Synthetic C.S.F.

Sodium Chloride	7.3 gm/L
Potassium Chloride	300 mg/L
Calcium Chloride (dehyd)	200 mg/L
Magnesium Sulfate	300 mg/L
Sodium Phosphate (hepta)	200 mg/L
Sodium Bicarbonate	190 mg/L

Adjust the pH to between 7.380–7.420 with 10% Ascorbic Acid

   - (D) Bacitracin Inj. 50,000 U/vial (Pharmacy) reconstitute with 10 ml saline to give a concentration of 5000 U/ml. Use 0.2 ml for each liter of perfusate to obtain a concentration of 1,000 units per liter of perfusate.
   - (E) Essential Amino Acids (Pool) (Sigma)

D-Glutamic Acid	11.8 mg
L-Glutamine	730.0 mg
DL-Serine	26.3 mg
D-Threonine	30.0 mg
D-Lysine	38.8 mg
D-Valine (optional)	19.0 mg
D-Leucine	14.0 mg
DL-Isoleucine	13.0 mg
D-Phenylalanine	15.0 mg
DL-Tyrosine	14.0 mg
D-Methionine	4.5 mg

Before oxygenating the fluorocarbon emulsion add 9.8[*]mg. amino acid and 200 mg dextrose for each 100 ml of emulsion.

   - (F) Steroid (Methylprednisolone sodium succinate) 125 mgs. (The Upjohn Company). Reconstitute the steroid with 2 ml of diluent to obtain a concentration of 62.5 mg/ml. Add 0.5 ml of this mixture to each liter of emulsion before oxygenation (31.2 mg/L).
   - (G) 1 N NaOH

2. Materials
   - (A) Sonifier Cell disrupter (Branson) Model W185D
   - (B) Waring Blender for mechanical dispension of Pluronic Acid.
   - (C) Dialyzer tubing ⅞ in. (22 mm) (Thomas). It is necessary to dialize the emulsion to remove fluoride ions as well as other low molecular weight contaminants.
   - (D) Whatman Filter Paper #1 (46×57) (Thomas). The emulsion should be filtered to remove particles originating from disrupted carbon skeletons of fluorocarbon during sonication.
   - (E) 0.8 micron filter unit (Thomas). Sterilization is accomplished by filtering the emulsion through a micro filter.
   - (F) CO_2 tank (Welders Supply Company). CO_2 is used as a defoaming agent while sonicating.
   - (G) 100% O_2 tank (Welders Supply Company). CO_2 is used as a defoaming agent while sonicating.
   - (H) 100% O_2 tank (Welders Supply Company) for saturating perfusate.
   - (I) Sterile Culture Flasks (Thomas) for storing perfusate.
   - (J) Gas Dispersion Tubes (Fisher Scientific Company) for equilibrating the emulsion with O_2.
   - (K) Aspiratory Bottle (Thomas)
     - a. 250 ml capacity-cut off 2⅛" from the neck with a glass cutter in order to accommodate the macrotip for sonification.
     - b. 500 ml capacity—for equilibration of the emulsion with 100 ml capacity—100% O_2.
   - (L) K50 Extension tubing. Capacity approximately 2.1 ml length 40.7 centimeters (20 in.).
   - (M) Circulating Pump
   - (N) Sonification Assembly

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[*] Siegel et al., *Basic Neurochemistry* (2nd edition), Little, Brown and Company, Boston, p. 297.

a. Fill a container with crushed ice; one that will allow drainage of the water as the ice melts (a fish tank will do).

b. On the serated outlet near the bottom of the aspiratory bottle connect seven lengths (140 in.) of K50 extension tubing. Place the bottle in the ice bath and connect the tubing to circulating pump.

c. Place the precooled Pluronic acid in the aspirator bottle. Drape and return extension tubing from the pump over the side of the bottle. Drape the tubes from the CO_2 tank over the side of the bottle and bubble slowly. Carefully lower the macrotip into the solution and start sonification.

3. Method 20% FC-80 (5% Pluronic (F68)) (w/v)

(A) Place 25 gms of F68+250 ml of artificial CSF in a Waring blender and blend at a high speed for 2 minutes. The solution will become very foamy. For best results the solution should be refrigerated overnight before using. This allows the head of foam to settle and precools the solution to the proper temperature for sonification.

(B) Place the precooled Pluronic acid solution in the aspirator bottle. Turn on Sonifier. With a Pasteur pipette add 58.8 mls (100 gm) of FC-80 over a 30 minute period sonifying throughout. Once added allow the mixture to sonicate for 45 minutes. Be sure that the temperature does not exceed 20° C.

(C) Cut dialyzer tubing that has been presoaked in artificial C.S.F. into 60 inch strips. Fill each strip half full with the mixture. Place strips in containers filled with approximately 1000 ml. of artificial C.S.F. Refrigerate and allow to dialize for 48 hours. The dialyzing solution should be changed every twelve hours, and the emulsion checked and transferred to additional tubing since the volume is considerably increased during dialysis.

(D) After dialysis filter the solution through Whatman #1 filter paper, then take the total volume. 25 gm of Pluronic acid and 58 750 ml of emulsion. The former volume represents 20% FC-80 and 5% F68 w/v ratio. The emulsion should be kept in an ice bath while processing.

(E) Add bacitracin to the emulsion. The pH at this point should be between 6.5 and 6.8.

(F) It is necessary to adjust the electrolytes at this stage.

Unadjusted electrolytes:		
Na	=	127
K	=	5
Cl	=	126
CO_2	=	1.5
Osmolarity	=	271

It is necessary to add 696 mg NaCl/L of emulsion in order to normalize the electrolytes.

Adjusted electrolytes:		
Na	=	131
K	=	3.8
Cl	=	130
CO_2	=	3
Osmolarity	=	303

(G) Using 1.0 N NaOH adjust the pH to between 7.380 and 7.420, then check the osmolarity (Range 298–317)

(H) Sterilize the emulsion by filtering through 0.8 micron filter. The emulsion can be frozen at −20° C. and is stable for several months.

4. Immediately Before Using Emulsion

(A) Add:	Glucose	0.8–2.5 gm/L
	Amino Acid	0.098 gm/L
	Steroid	31.2 mg/L (optional)

(B) Warm the emulsion to 37° C. and equilibrate with 100% O_2 using a gas dispersion tube for 30 minutes to obtain a pO_2 of between 580–660.

(C) A typical batch of FC-80 emulsion shows the following properties:

Na	=	131 meq/L
K	=	3.8 meq/L
Cl	=	130 meq/L
CO_2	=	3 meq/L
Glucose	=	186 mg. %
Osmolarity	=	311 mOsM

(D) A typical batch of oxygenated nutrient emulsion contains:

Fluorocarbon	=	78.6 ml/L
Pluronic Acid	=	213 ml/L
NaCl	=	7.3 gm/L
Potassium Cl	=	300 mg/L
Calcium Cl (dehydrated)	=	200 mg/L
Mg Sulfate	=	300 mg/L
Sodium Phosphate	=	200 mg/L
Sodium Bicarbonate	=	190 mg/L
Amino Acid Pool (added to fluorocarbon)	=	0.098 gm/L
Manitol Injection USP 259	=	50 ml/L
Bacitracin	=	5000 units/L
Gentamicin	=	80 mg/L
Dextrose	=	2 gm/L
Ascorbic Acid (10%)	=	0.5 ml/L
Sterile Water	=	remainder per liter

Gas Characteristics After Oxygen Equilibration

	Unsaturated	Saturated
pH	7.231	7.342
pCO_2	3.7	5.7
pO_2	190	640–5

In order to provide an indication of the efficacy of the preferred treatment methods, the following examples are provided:

EXAMPLE 2

For reasons of simplicity and reproducability a model continually in use in applicant's laboratory has been employed. Osterholm, J. L., *Pathophysiology of Spinal Cord Injury*, C. C. Thomas, Springfield, Ill. (1978). Extensive experience with spinal cord injury in terms of standardization, quantitative histological studies, regional blood flow and biochemical parameters suggested these procedures. A primary pathophysiologic event in that model has been determined to be discrete regional ischemia. A microcirculatory flow failure within the injured region has been documented by many study techniques including microangiography, distribution of intravascular particulate materials, hydrogen-platinum flow studies, regional istopic techniques and lactate accumulation. Recent C 14 antipyrine microregional blood flow studies conducted in applicant's laboratory have accurately delineated the magnitude of ischemia in the injured cord. Within one hour the regional grey matter flow drops from the control of 44 cc/100 gm/min to only 2 cc/100 gm/min. The white matter is also ischemic. Blood flows in these regions are depressed from 15 cc/100 gm/min to 1-2 cc/100 gm/min.

From these observations, standarized spinal cord injury causes a restricted ischemic lesion which can be easily studied and quantitated. In this rigid system therapeutic treatment effects are readily detected by comparison with our extensive untreated injury data. It should be noted here that the mechanical injury forces used in these experiments are substantially above saturation and all wounded animals are rendered permanently paraplegic.

Circulation Experiments

Experiments were carried out by continuously injecting either saline or Ox-N emulsion saturated with O_2 at 1 atm into the distal subarachnoid spinal space. The outflow (withdrawal) of the diagnostic fluid was at the cisterna magna. Infusions were begun immediately after severe wounding. An infusion rate of 3 ml/minute was easily achieved, and this rate was maintained for two hours.

Oxygen

Prior to lumbar spinal infusion we were able to develop pO_2 tensions of 535±89 mm O_2 in the Ox-N emulsion by simply bubbling 100% oxygen through the solution. Upon exit at the cisterna magna after traversing the entire spinal subarachnoid space the pO_2 had fallen to 243±63. The oxygen difference between entering and exit was 292±63, or a 55% decline, which is statistically significant at the $P<0.001$ level. This finding indicates a rapid pO_2 exchange during the thirty seconds or less transit time. For various technical reasons our initial pO_2 was lower than can be achieved under idealized circumstances. More recently it has been possible to regularly attain pO_2 of about 650 Torr. Even better experimental results might have now been obtained under conditions of higher O_2 tension.

Carbon Dioxide

FC-80 is an efficient CO_2 exchange and transport agent, and the emulsion therefore easily extracts tissue CO_2. This is indicated by an initial emulsion pCO_2 of 2.7 Torr which rose to 16.0 Torr after the tissue perfusion contact. This represents a 593% increase in FC-80 CO_2 ($P<0.001$). The emulsion also removes other acid metabolites since in some experiments the inherent buffering capacities were exceeded as the exit fluid pH exhibited a considerable depression toward the acid side (original pH 7.4, exit pH 7.0). This pH change exceeded any acid contribution by the collected CO_2, and amounted to 0.248 mole lactate/hour.

A. Cross Sectional Area (Edema)

Frozen tissues were sectioned and stained (H & E, and acid phosphatase). The sections were evaluated by projection to 25× magnification and preselected lesion parameters measured by means of a compensating polar planimeter. There was considerable increase in the untreated injury cord cross sectional area (1280 mm^2) which was significantly reduced in the Ox-N experiments, (896 mm^2). We have assumed that this substantial cross sectional cord area increase is caused by edema fluid. In the course of other experiments, the degree of edema appearance has been quantified. It was found that net water accumulation at those post injury times ranged from 25% to 40%. The absolute reduction in cross sectional area by the Ox-N treatment is significant at the $P=0.001$ level.

Lesion Size

Using our standard sampling methodology which includes skip serial sections throughout the injury region, and analysis by quantification techniques, the degree of injury induced hemorrhagic necrosis can be determined. With the perfected injury system the lesion size at any time point can be reliably predicted. The effects of saline and Ox-N circulations upon lesion size were compared to each other and to our established untreated values. The results are summarized in Table I:

TABLE I

LESION SIZE
2 Hour Injuries

	% Grey	% White	% Total
Standard Injury (No Infusion)	79.5±16% SD	30.1±9% SD	39.5±10% SD
Saline Circulation	78.3±15% SD	25.0±14% SD	34.4±12% SD
Ox—N Circulation	47.4*±17% SD	12.8*±2% SD	19.2*±10% SD

Percentages are expressed in terms of total tissue area lesioned by hemmorrhagic necross for grey, white or total cord area two hours after servere injury with the various treatments. (*Statistical Significance P = <0.01. The saline values are not significant).

The data indicates a highly significant degree of protection against injury lesions afforded by the Ox-N circulation treatments. The actual lesions are halved by the treatment and this remarkable stabilizing effect upon the important white matter tracts would be anticipated to substantially improve the final functional result attending severe spinal cord injury.

Anterior Horn Cells

A technique of counting the anterior horn cells which contain visible acid phosphatase histomchemical reaction product has been developed in this laboratory. The procedure has been previously used to assess ischemic cellular effects in terms of cellular survival and/or lysis time.

From Table II it can be seen that untreated injury has a highly lethal effect upon anterior horn neurones. Within the two hour experimental time period, more than 97% of all cells at the injury center undergo cytoplasic lysis. Ox-N infusions stabilized the injured cells as 60% of all neurones were protected from lysis.

TABLE II

ANTERIOR HORN CELLS	
Control	34 ± 2 (SD)
Injury	2 ± 1.73*
Injury + Ox—N circulation	21 ± 5.12**

Number of anterior horn cells containing acid phosphatase reaction product within well defined cytoplasmic borders. (*statistical difference from control $P < 0.001$. **Difference from injury alone $P < 0.001$).

Spinal Cord Adenosine Triphosphate (ATP)

Biochemical ATP tissue determinations were undertaken to determine the metabolic oxidative state of injured spinal tissues. This metabolite was selected for study since it reflects the progress of normal oxidative metabolism. ATP levels fall very rapidly under sufficient hypoxic-ischemic conditions. Untreated injured cords have a 200% ATP decline in one minute. In the current experiments ATP levels would be expected to reflect (1) the cellular oxidative capability and (2) functional cellular viability. The latter aspect is especially important in terms of cellular integrity which was discussed in the preceeding section.

From Table III it can be seen that 2 hour injury causes a four and three fold drop in grey matter and white matter ATP respectively. This information amply supports other observations about the degree of regional cord tissue ischemia after impaction. ATP was found in significantly higher concentration in the Ox-N experiments than noted after saline circulation alone. The high energy compound suffered only a 30% fall from normal in the oxygenated perfusion group which contrasts vividly with the 300–400% loss found with the saline treatments.

TABLE III

ATP LEVELS (μmol/gm) (2 hours post injury)

	Injury & Saline	Injury & Ox—N	Control
Grey Matter	0.46	1.24*	1.88
White Matter	0.40	0.87*	1.23

ATP tissue levels in control, saline and Ox—N injured cords. The difference between saline and Ox—N is significant *($P = 0.05$). Although not shown in the Table, the Ox—N treatments also statistically increase ATP in spinal cord regions directly above ($P < 0.001$) the injury site.

Comparison of the above results to those later reported by R. E. Hanseabout, R. H. C. Van Der Jagt, S. S. Sohal, and J. R. Little, *Journal of Neurosurgery* 55, pp. 725–732 (1981) is of interest. Hanseabout et al report the use of a commercial oxygenated fluorocarbon artificial blood perfusate to treat experimental spinal cord injuries. Treated dogs are reported as showing improved motor function more rapidly and as having a better final hind limb functional result than did controls. To some extent, this non-prior art report confirms the spinal cord injury findings reported here.

EXAMPLE 3

Cerebrovascular Ischemia

Initial studies have been conducted to determine the efficiency of Ox-N emulsions in protecting the brain against profound ischemia. We employed the cat brain and utilized right hemispheric regional vascular interruption so that the left cerebral hemisphere might serve as an internal control. The middle cerebral artery of cat is accessible through the bony orbit. It lies immediately above the optic nerve after the canal has been opened and can be identified with certainty in that position. Preliminary experiments determined that an inconstant cerebral field was devascularized by occluding the middle cerebral artery. It became apparent that collateral blood flow via the anterior and posterior cerebral arteries supplied some retrograde filling into the experimental region. This phenomenon could be largely prevented by concommittantly reducing the mean systemic blood pressure to 70 mmHg by external bleeding. Hemorrhagic hypotension plus middle cerebral artery occulsion yielded a reasonably constant ischemic cerebral lesion from animal to animal.

In that model either saline or Ox-N were circulated from the right cerebral ventricle to the cisterna magna at a rate of 3 ml/min. Cerebral tissues were harvested one hour after vascular occlusion by immediate immersion in liquid Freon. The tissues were sectioned in the frozen state and reacted with luciferin upon photographic film. A combination of high energy cellular metabolites plus luciferin react to emit visible light, which is recorded upon the film. Tissues removed from saline treated ischemic cerebral regions were uniquely devoid of phospholuminescence, while the opposite hemisphere demonstrated this reaction to a degree similiar to that found in normal animals. Middle cerebral ischemic tissue samples from Ox-N treated animals contained sufficient high energy materials to demonstrate a positive histochemical high energy reaction one hour after vascular arrest.

EXAMPLE 4

Profound Spinal Cord Ischemia

The combined evidence from spinal cord injury and middle cerebral artery occlusion models demonstrate that the preferred oxygenated nutrient emulsion can be circulated to maintain cellular integrity and aerobic metabolism under the stress of profound regional ischemia. A third model was utilized to determine if vascular deprived neurones perfused via cerebrospinal fluid pathways with oxygenated-nutrient would continue to perform a physiologic function. A transthoracic aortic ligation just distal to the left subclavian effectively devascularizes the cervical, thoracic and lumbar cat spinal cord. In some examples the lower brain stem was also found ischemic by regional flow studies. The mid and lower thoracic cord are universally and profoundly blood deprived by this vascular interruption. Animals under light Ketamine anesthesia were treated by circulating from the lumbar subarachnoid space to the cisterna magna with either saline or Ox-N solutions. Respiratory movements were evaluated in these experiments. The lungs were ventilated by positive presence respiration, but the mechanical movements are easily distinguished from neuromuscular respiratory contractions. This is especially so since for the most part the respiration and neuromuscular drive occur at separate times and are largely asynchronous. Following the aorta ligation all physiologic neuromuscular respiratory movements progressively diminished to total cessation after 5–10 minutes in the saline treated cats. The arrest obtains for intercostal muscles as well as diaphragmatic contractions. The Ox-N treated animals, on the other hand, continue to respire in an essentially normal neuromuscular sequence. The respirati ... under those conditions, were often of irregular rates, diminished in amplitude, and showed some individual magnitude variations. The singular difference between saline and Ox-N circulations is the universal persistence of respiration in the latter group. It is also true that Ox-N sustained sufficient chest bellow movements so that if the chest were closed the respirations were clinically adequate to support life.

EXAMPLE 5

Experiments have also been conducted to determine the efficacy of the herein disclosed methods on global cerebral ischemia induced in cats.

Although the Ox-N emulsions of the present invention are oxygenatable by bubbling gas through them, perfusate from stroke animals were initially found to have oxygen pressures (pO_2) below those known efficient oxygen exchange values (pO_2 less than 200) for the fluorocarbon component of the material. See Navari et al, supra. Accordingly, the pump oxygenation system described above in connection with FIG. 13 was developed to optimize fluorocarbon O_2 saturation. As mentioned above, this system comprises a heat exchange-oxygenator which was coupled to recirculating, warming and delivery pumps. This system rapidly oxygenates the emulsion (pO_2=645[mean] Torr) at 37° C. with oxygen gas delivered at 7 L/min.

Global cerebral ischemia experiments were conducted on cats after brevital induction and nitrous oxide oxygen (70-30%) anesthesia. A double lumen inflow cannula of the type described above was sterotactically placed into a lateral cerebral ventricle while an exit cannula was inserted either into the cisterna magna or lumbar theca. When the conduits are properly installed, the CSF pathways have little resistance and a mean flow perfursion rate of 6.0 cc/min. can be achieved through the animals without intracranial pressure alterations. Entry and exit fluid were collected for metabolic studies. Both gases were normalized by respiratory adjustment. Further experimental manipulations awaited electroencephalograph (EEG) normalization. Cerebral ischemia was produced by the combined insult of hemorrhagic hypotension (mean arterial blood pressure lowered to 30±3 mm Hg) plus simultaneous carotid artery clamping. This method caused a bihemispheric isoelectric EEG within 5-8 minutes. After sustained and total cerebral electro silience for 15 minutes, the carotid arteries were unclamped and the withdrawn blood reinfused.

A well accepted measure of cerebral function, the EEG, was used to assess both the degree of insult and subsequent discovery. A computer based EEG method, compressed spectral analysis, was used to determine brain activity. A Nicolet Instrument Corporation "MED-80" computer utilizing frequency analysis package "Super C" was used with the following setup parameters:

2 channels, 1024 SEC. EPOCH, 1024/PTS.EPOCH
2 sweep average/printout.

The total output is expressed in (microvolts^2) assuming a constant source impedence of 1 ohm. The data presented here is the total cerebral power 0.3-25 Hz in picowatts. Recordings were made from skull electrodes at maximum sensitivity of 1 picowatt. Since a steady state prestroke EEG was obtained, each animal served as its own control.

Ten animals had cannulas placed and the stroke accomplished without perfusion. A second control group of ten animals were treated similarly, but were also perfused through the ventriculo spinal (lumbar) route with nutrient solution without fluorocarbon. There were no apparent differences found for post-stroke electroencephalographic activity in these groups. As a measure of stroke severity, 13 animals (of 20) had persisting electrocerebral silience. Of the remaining animals, 5 gained only 2% of their base line power while two had 10% power return within the 4 hour experimental period. FIG. 4 is a representative EEG power tracing from the left and right cerebral hemispheres of a cat perfused only with nutrient solution without fluorocarbon and which exhibited persisting electro-cerebral silience during the 4 hour experimental period. The tracings are read from bottom upwards. Normal activity is seen in the lowest tracing and is totally arrested by the ischemic insult half way through the first grouping. There is electro-cerebral silience thereafter througout the experimental period.

Thirteen cats underwent the same experimental procedure, but were perfused immediately after ischemia with bubble oxygenated nutrient solution ($pO_2=400$). For these cats, the flow rate was 4 ml/min with withdrawal from the umbar theca. Five exhibited continued electro-silience whereas 8 demonstrated EEG recovery from 5% (6 animals) up to 34% (2 animals). FIG. 5 is a representative EEG tracing of one of the eight animals demonstrating 5% recovery after perfusion with oxygenated nutrient emulsion ($pO_2=400$).

A fourth group of 7 cats was perfused with pump oxygenated nutrient solution ($pO_2=645$) at 6 ml/min. with withdrawal from the cisterna magna. All cats in this group regained some electrocerebral activity. The final total power which returned ranged from 5 to 88% of the prestroke base line (average 22%; $p<0.01$ compared to all non-oxygen groups). The electroencephalographic activity recovered generally throughout the 4 hour recovery period with the returning total cerebral power exhibiting a first order relationship as a function of time. At the observed recovery rate all animals should achieve completely normal EEG power spectra within 8 hours. An oxygen dependent EEG response is seen when non-oxygenated, bubble oxygenated ($pO_2=400$), and pump oxygenated ($pO_2=645$) groups are compared as electrocerebral activity recovery greater than 5% was found in 10%, 62% and 100% respectively. FIG. 6 is an EEG tracing of the animal showing 88% return of electrocerebral activity within 4 hours after perfusion with oxygenated nutrient emulsion ($pO_2=645$). The asymmetry between hemispheres is an individual variation for this animal.

FIG. 7 is a portion of an EEG tracing showing the recorded effect on electro-cerbral activity of a temporary perfusion failure. This animal, which was perfused using the pump-oxygenated ($pO_2=645$) nutrient emulsion described above, experienced an interruption (pt. A) in perfusion for a time period of approximately 1 hour, whereupon perfusion was resumed (pt. B). As seen in this tracing a major deterioration of EEG activity occurred following cessation of perfusion, and resumed thereafter, confirming that the present method in fact sustains EEG activity.

In FIG. 8, the effect of a diminished perfusion flow rate of oxygenated nutrient emulsion is shown on the rate of glucose metabolism, and lactate and pyruvate concentration. In accordance with the above-described ventriculo-lumbar perfusion procedure using bubbled oxygenated ($pO_2=400$) nutrient emulsion, flow rate with nutrient emulsion without fluorocarbon was established at about 5.0 ml/min. A base line cerebral metabolic rate of glucose metabolism (CMRGl) was established prior to stroke, which was followed after 15 minutes with the perfusion of the oxygenated nutrient emulsion. CMRGl, which has recovered somewhat after 1 hour, is seen to decline rapidly as the flow rate of perfusate declines. Similarly, lactate levels rise precipitiously with flow rate decay. These results once again confirm that the flow of oxygenated nutrient emulsion through the cerebral spinal pathway should be maintained at acceptable rates in order to sustain neurologic tissue.

In FIG. 9, the mean recovery percent for the four groups of animals discussed above is presented in the form of a bar graph. It is presently preferred to insure that the pO_2 value of oxygenated nutrient emulsion upon input is great enough to insure that efficient oxygen transfer capabilities are maintained at the selected flow rate. For the FC lumbar group, exposure of oxygenated nutrient solution to certain tissue regions when its oxygen exchange value was below the known efficient oxygen exchange value (pO_2 less than 200) for the fluorocarbon component of this material may have occurred. This may be true even though the mean oxygen exchange value of the withdrawn emulsion is above 200. Accordingly, it is presently preferred to maintain the pO_2 value of withdrawn oxygenated nutrient emulsion at twice this minimum, or at above 400, either by raising the input pO_2 value to much higher levels, as with the ventriculo-cisternal animals described above, or by increasing the flow rate of oxygenated nutrient emulsion through the animal to maintain those values. In smaller animals, such as cats, the size of the cerebro spinal pathways creates hydraulic resistance which limits the flow rates which may be achieved at atmospheric pressures using certain pathways. In such animals, higher oxygen exchange values and shorter perfusion routes, such as the ventriculo-cisternal perfusion route, are preferred. In larger animals, such as humans, it is not anticipated that flow rates will be so limited. Nonetheless, high pO_2 values (at least 50% preferably 80+% of the maximum obtainable pO_2) are preferred to minimize the volume of perfusate necessary to perform a given treatment and to provide an additional margin of safety at the selected flow rate.

Samples of the perfusing fluids for the animals of this example were removed at predetermined times from entry and exit perfusion ports for analysis of lactate and pyruvate under a single blind condition. The results are summarzied in Table IV:

TABLE IV

Levels of lactate and pyruvate in cerebral spinal fluid perfusate before (baseline), during (isoelectric) and following (reflow) global ischemia in cats. Data are expressed in mg per 100 ml of perfusate and the values are means ± standard error. Six animals were perfused with NS[1] and 7 with OFNS[2] solution. After collecting the perfusate in tubes a 4#C, the samples were stored at −80° C. for analysis. Lactate and Pyruvate were assayed by a Sigma Method (Sigma Technical Bulletin #726, Oct. 1968 and #862, Oct. 1969) and conducted by Jefferson University Clinical Laboratories.

Experimental Period	Lactate		Pyruvate		Lactate/ Pyruvate Ratio	
Baseline +*	3.6±1.1°		0.5±0.1		7.2	
Isoelectric +	8.1±1.9°		0.5±0.1		16.2	
	NS	OFNS	NS	OFNS	NS	OFNS
Reflow (5 min)	21.9±11	10.0±1.0	0.5±0.1	1.2±0.6	43.8	8.3+

TABLE IV-continued

Reflow	8.9±3.3	10.4±3.8	0.5±0.1	1.7±0.7	17.8	6.1

*During baseline and isoelectric time periods all cats were perfused with NS

°$p < 0.01$ when compared to baseline lactate. $p < 0.025$ when compared to the ratio of reflow (5 min) perfused with NS.

[1] As used herein, NS refers to the nutrient solution of Example 1 without fluorocarbon component.

[2] As used herein, OFNS refers to the preferred oxygenated, fluorocarbon nutrient emulsion of Example 1.

In animals perfused with nutrient solution without fluorocarbon the concentration of lactate during the actual stroke (isoelectro) was of the normal CSF value. The lactate level rose percipitiously, an additional 440%, within 5 minutes of restoring the blood pressure and blood flow through the carotid arteries. Thereafter the level declined during the 4 hour period to 147% of base line. In contrast to the lactate data, the pyruvate concentration remained constant through the perfusion period.

When animals were perfused with oxygenated nutrient emulsion, on the other hand, the percipitious increase in lactate did not occur; instead there was a modest 52% rise during the initial 5 minute period, and the level thereafter remained stable. Significantly, in the oxygenated series the concentration of pyruvate more than doubled during the initial 5 minutes and continued to increase gradually during the remainder of the 4 hour period. The net production of lactate and pyruvate are often used as indicators of anarobic and aerobic glycolysis, respectively. Since these compounds change under different circumstances the expression of lactate/pyruvate (L/P) ratio best illustrates the net metabolic effects. A high L/P ratio indicates that anarobic glycolysis predominates. It is common practice, therefore, to use the L/P ratio as a sensitive indicator of the redox state of cells. Perfusion oxygenation in accordance with the present inventions significantly ($p \leqq 0.01$) lowered the L/P ratio when compared to non-oxygenation (8.3 vs. 43.8). It is further evident that the oxygenated 4 hour L/P ratio is additionally lowered, whereas the non-oxygenated values are still 5 times greater than the control.

Although the oxygenated nutrient perfusate transit time through the brain is only a few seconds, significant oxygen extraction does occur. It was determined by the pO_2 difference between inflow and outflow fluids that oxygenated nutrient emulsion lost $pO_2 = 210$ (mean) during its intracerebral passage. Also unique to the oxygenated nutrient emulsion studies was a rising carbon dioxide presence in the exit fluid which did not occur in non-oxygenated experiments. The pCO_2 rose 5 fold in these fluids over the four hour period ($pCO_2 = 6.0$ vs. 3.0). It is considered that the appearance of carbon dioxide is important since it is a normal product of aerobic metabolism.

In FIGS. 10 and 11 levels of potassium in perfusate before (base line), during (isoelectric) and following (reflow) global cerebral ischemia in cats are represented. Data are expressed in micro equivalents per minute, and the values are means ± standard error. Five animals were perfused with nutrient emulsion without fluorocarbon, and six with oxygenated fluorocarbon emulsion. After collecting the perfusate in tubes at 4° C., the samples were stored at −80° C. for analysis. Potassiums were assayed by atomic absorption spectrophotometry. During the base line and isoelectric time periods, all 11 cats were perfused with nutrient emulsion without fluorocarbon. There were no significant differences between isoelectric and base line levels of potassium in the perfusate. As seen from FIGS. 10 and 11, significant differences in the values of potassium were observed beginning almost immediately with perfusion (at time 0) and extending throughout the 4 hour experimental period.

FIG. 12 discloses the effects on glucose metabolism for ventriculo-cisterna perfused animals subjected to the stroke and reperfusion procedure of this example. In accordance with the invention of Dr. John Lewis Alderman, one of these animals was perfused with twice the glucose concentration (372 mg %) of that used for the remaining animals described herein. As seen from FIG. 12, the glucose metabolism of animals provided with oxygenated nutrient emulsion (glucose = 186 mg %) is generally superior following reperfusion to the metabolism rate of the control receiving that solution without fluorocarbon. In view of the substantial increase in glucose metabolism exhibited by the animal having a "double glucose" solution (372 mg %), it is presently preferred to include at least such elevated glucose concentrations in perfusions performed in accordance with the method of the present invention.

These experimental results demonstrate that extravascular perfusion of oxygenated nutrient emulsion affects a significant reversal of the adverse cerebral metabolic effects induced by the experimental stroke condition. Coincident with the improve metabolic state electrocerebral activity returned. These findings indicate that extravascularly supplied oxygen, glucose and other nutrients were taken up and metabolized in amounts sufficient to restore high energy compounds and thereby reactivate membrane ionic pumps and reinstitute electrocerebral activity.

Oxygenated-fluorocarbon-nutrient-emulsion caused no detrimental effects on vital physiologic functions such as heart rate, blood pressure or electrocerebral (EEG) activity when perfused through the ventricular system for four hours of cats not subjected to the stroke paradigm. These animals exhibited no ill effects after 5-8 months, and were killed for a double blind neuropathologic examination of the brain, spinal cord and subarachnoid spaces. No gross or microscopic changes were observed and the specimens were indistinguishable from non-perfused animals.

In view of the above, those of ordinary skill in the art will recognize that various modifications can be made to the methods and apparatus described above without departing from the scope of the present invention. For example, it should be understood that, the injection and withdrawal catheters used to perform the herein described method should be sealed with respect to the skull so that a water and bacteria tight seal is created between these catheter and skull. Although conventional bone wax has been used for creating this seal in the feline experiments described above, fitting 22(*a*) preferably comprises a double threaded sleeve which is threaded into a bone aperture, and in turn receives complimental threads formed on injection catheter 20*a*. Such attachment means, particularly when used with a ventricular injection catheter, should eliminate any need for total head immobilization during human treatment.

It should also be understood that the oxygenated nutrient emulsions of the present invention may contain various therapeutic agents including free fatty acids, prostaglandins, prostacyclins, cyclic nucleotides and hormones.

As seen from the above, it is desired to maintain the the pO_2 level in the withdrawn fluid at levels which are substantially above the minimum level of efficient oxygen exchange of the subject fluorocarbon. For the fluorocarbon nutrient emulsion described above, that minimum (unsaturated condition) occurs at a pO_2 equal to about 190, which is about 30% of the readily achieved maximum pO_2 level. ($pO_2=645$) As described above, it is preferred to perform the treatment method of this invention so as to maintain the pO_2 of the withdrawn oxygenated nutrient emulsion at a pO_2 above 400, that is, at a pO_2 level which is about twice the minimum level of efficient oxygen exchange for the subject fluorocarbon. It is presently anticipated that a similar differential should be maintained in practicing the present invention utilizing oxygenated nutrient emulsions having other oxygenatable components exhibiting different ranges of efficient oxygen exchange.

The methodology described requires the formulation of a physiochemical fluid which must be adequately oxygenated, temperature controlled and delivered under well controlled conditions. The perfusion system of the present invention may be routinely placed by trained animal surgeons. Neurosurgeons commonly possess skills necessary to implant treatment ports in accordance with the present invention in humans. The procedure is relatively simple and can be quickly accomplished with available instruments. The oxygenated nutrient emulsion treatment delivery system of the present invention has certain similarities to the arterial heart-lung machine. Major differences, however, include the use of a complex synthetic fluid for cerebral spinal perfusion, the route performed by cerebral spinal perfusion is an extravascular one, and there is no known limitation on perfusion time in accordance with the herein disclosed method. Oxygenated fluorocarbon nutrient emulsion tolerates pumping mechanics well and the exit fluid can either be discarded or recirculated. Formed blood elements, on the other hand, are fragile and lyse under prolonged recirculation conditions. It is presently contemplated that cerebral-spinal fluid perfusion support will need to be carried out until the vascular system can once again take over. Surgical revascularization or bypass procedures will in some cases be necessary to accomplish this end. The return of cerebral vascular compentency can be assessed by measurements of regional blood flow, electro cerebral activity, and the metabolic configuration of the exit perfusion fluid. One foreseeable complication of this technique is bacterial infection, and rigorous attention to ambient sterility, millipore filtering, and antibiotics should reduce this hazard to acceptable levels. Safeguards have been built into the pumping system to immediately stop delivery if either the inlet or outlet become obstructed.

Conclusion

As seen from the above examples, and the foregoing description, circulation of the preferred embodiment nutrient liquid is capable of sustaining cellular integrity, aerobic metabolism and ongoing neuronal function. Even for neurons deep within the spinal cord (grey matter) the process has been successful in nurturing the ischemic neurons. The ability to sustain the central nervous system in a lethally ischemic field which persists for longer than a few minutes has never been accomplished before. The extravascular pathway has not been employed as a global nutrient route prior to the present invention, nor has the combined use of oxygen rich emulsion which also contains the other disclosed novel components been know to the art.

As seen from the above experiments, the methods, compositions and system of the present invention are capable of providing substantial amounts of oxygen to neurologic tissues to be treated, while at the same time, removing the by-products of aerobic metabolism, including carbon dioxide, which have been found to exist in substantially higher concentrations in the exit, diagnostic fluid. Similarly, as discussed above, rapid, normally lethal, lyses of anterior horn cells is readily preventable through the treatment of the present invention, protecting at least 60% of the cells through this modality. Similarly, high energy phosphate metabolism utilizing both oxygen and glucose is maintained at substantial levels. Accordingly, the methodology of the present invention represents a substantial advance in the treatment of central nervous system tissue. Prior to this invention there was not a method available to sustain central nervous tissues after a few minutes of profound ischemic insult. This invention should revolutionize the therapeutic capabilities by providing therapeutic approaches for stroke, aneurysm, brain injury, vasospasm, senility, tumors, coma, spinal cord injury, ischemia, post shock, post cardiac arrest and central nervous system poisoning.

It is further anticipated that the treatment method of the present invention should make it possible to interrupt the cerebral blood supply with some impunity for surgical maneuvers not heretofore possible without great attendant risk of producing cerebral infarction. Those of ordinary skill in the art will recognize that future development may result in perfection of the oxygenated nutrient emulsion composition, delivery rates, treatment times, the width of the therapeutic window in which treatment may be instituted and the correlation of behavioral functions in surviving animals with normalization of cerebral chemistry and electrographic activity. Nonetheless, by any standard, the present invention provides a dramatic, yet clinically acceptable, therapeutic method for treating ischemic neurologic tissue.

What is claimed is:

1. A method of treating hypoxic-ischemic central nervous system tissue comprising:
   - (a) providing a physiologically acceptable oxygenated fluorocarbon emulsion as treatment fluid;
   - (b) establishing a circulation of said fluid through an oxygenator at a first preselected flow rate to oxygenate said fluid;
   - (c) injecting said oxygenated fluid into the cerebrospinal pathway at a first injecting point and at a second preselected rate;
   - (d) substantially continuously withdrawing fluid from said cerebrospinal fluid pathway at a second point which is selected to create a circulation of said oxygented fluid in the vicinity of said hypoxic-ischemic tissue sufficient to support significant aerobic respiration of a portion of said tissue,

whereby said portion of said tissue will be metabolically sustained during said treatment.

2. The method of claim 1 wherein step (b) further comprises establishing a circulation of said fluid through a heat exchanger to adjust the temperature of said fluid prior to injection.

3. The invention of claim 2 wherein step (a) further comprises providing a reservoir means for containing said fluid and step (b) further comprises establishing a separate circulation through said heat exchanger to said reservoir.

4. The method of claim 3 wherein said separate circulation is established at a third preselected flow rate.

5. The method of claim 1 wherein step (c) further comprises first forcing said fluid through a filter.

6. The method of claim 5 wherein said filter is a bacterial filter.

* * * * *

United States Patent [19]

Post et al.

[11] **4,445,970**

[45] **May 1, 1984**

[54] **HIGH MINERAL COMPOSITE FINE PAPER**

[75] Inventors: **Richard L. Post**, Ridgway; **Robert G. Fort**, St. Marys, both of Pa.

[73] Assignee: **Penntech Papers, Inc.**, White Plains, N.Y.

[21] Appl. No.: **267,941**

[22] Filed: **Jun. 1, 1981**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 199,165, Oct. 22, 1980, abandoned.

[51] **Int. Cl.**^{3} **D21F 11/00**

[52] **U.S. Cl.** **162/135**; 162/136; 162/164.6; 162/168.2; 162/168.3; 162/181.1; 162/181.2; 162/181.4; 162/181.6; 162/181.8

[58] **Field of Search** 162/169, 183, 181.1, 162/168.1, 181.2, 175, 181.4, 135, 181.8, 136, 158, 164.1, 164.6, 168.2, 168.3, 181.6

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Primary Examiner—Peter Chin

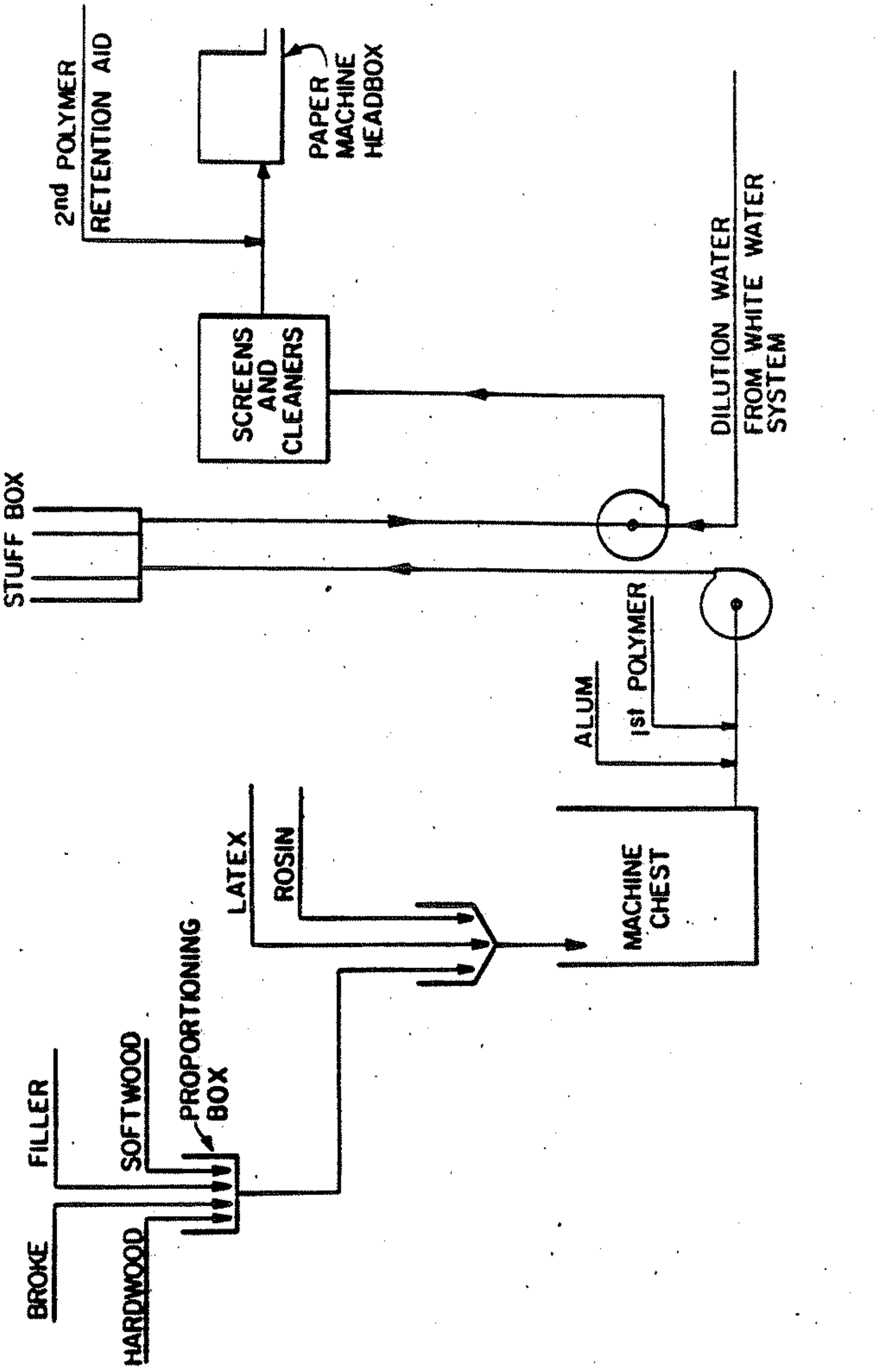
Attorney, Agent, or Firm—Karl W. Flocks; Sheridan Neimark

[57] **ABSTRACT**

Composite fine paper suitable for offset and gravure printing at high speeds and containing over 30% filler up to 70% filler for basis weights of 30–150 lbs/3300 ft^2, is produced on a high speed paper-making machine from a furnish containing large quantities of filler, preferably a mixture of clay and talc, and including 3–7% of an ionic latex which is selected to provide good retention and good strength without leaving a residue on the screen.

28 Claims, 1 Drawing Figure

Page E-137 is blank and is not used in this technical reference.


BROKE
HARDWOOD
FILLER
SOFTWOOD
PROPORTIONING BOX
LATEX
ROSIN
MACHINE CHEST
ALUM
1st POLYMER
STUFF BOX
DILUTION WATER FROM WHITE WATER SYSTEM
SCREENS AND CLEANERS
2nd POLYMER RETENTION AID
PAPER MACHINE HEADBOX

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HIGH MINERAL COMPOSITE FINE PAPER

DESCRIPTION

FIELD OF INVENTION

This application is a continuation-in-part of patent application Ser. No. 199,165, filed Oct. 22, 1980 by Richard L. Post and Robert G. Fort, entitled "HIGH MINERAL COMPOSITE FINE PAPER" and now abandoned.

The present invention relates to offset or gravure printable fine paper and, more particularly, to highly mineral filled fine paper weighing from 30 to 150 lbs/3300 ft^2 and having sufficient strength to be usable for offset or gravure printing.

BACKGROUND OF THE INVENTION

Normal fine paper contains internally some filler up to a maximum of about 30% mineral filler. As fine paper suitable for offset and gravure printing must have sufficient strength to resist the printing operation which is carried out under high speed, and this includes both tensile and Z-direction strength, it has been found that the use of high quantities of mineral filler are not suitable. Indeed, the normal offset printable fine paper has a very low mineral filler content, and this paper is normally surface sized after the paper web has been dried. The term "fine" paper is used in the conventional industry sense and includes tablet, bond, offset, coated printing papers, text and cover stock, coated publication paper, book paper and cotton paper; it does not include so-called "high-strength" paper products.

The use of filler internally in the manufacture of paper in general and fine paper in particular has been practiced for many years using common fillers such as kaolin clay, talc, titanium dioxide, calcium carbonate, hydrated aluminum silicate, diatomaceous earth and other insoluble inorganic compounds. The use of filler accomplishes two objectives: one is the extension of the paper-making fibers to reduce cost and the other is to obtain certain optical and physical properties such as brightness and opacity. In fine paper manufacture, fillers are normally added at a level of 4-20% by weight of the finished paper, although rarely as much as 30% filler has been used in Europe and 25% in the United States. Fine paper manufacture in part depends on hydrogen bonding and one problem which occurs in the use of more than 20% filler in fine paper manufacture is that too much filler reduces hydrogen bonding and causes the web to lose its strength. Using external methods of application, such as coating with pigment/adhesive mixture on the size press or coater, the total filler content can easily be increased.

Fine paper containing up to a maximum of 30% filler is normally made by adding 15-20 pounds of cationic starch or 1-5 pounds of guar gum per ton of dry furnish, as normal internal strength agents. Latices are sometimes used in paper manufacture as noted below, but not in fine paper manufacture because such latices are normally sticky and difficult to use on a Fourdrinier machine for making fine paper at high speed.

The U.S. Pat. No. 3,184,373 to Arledter discloses the production of paper having greater than normal quantities of mineral fiber, but no mention is made of the properties of the resultant paper. The Arledter process depends on what is referred to as a synergistic mixture of filler retention aids, including a water soluble mucilaginous material, such as guar gum, and a water-soluble

polyethylene imine resin. An earlier patent in the name of the same patentee, U.S. Pat. No. 2,943,013, contains similar subject matter, but the resultant paper is specified to be for use in the manufacture of decorative laminates, i.e. there is no requirement for the high strength necessary for fine papers which are to be printed by the offset method.

It has been common knowledge in the paper industry that the addition of an anionic latex to the wet end of a paper machine combined with a cationically charged chemical, such as alum, causes the latex to precipitate in the presence of the paper-making fibers and fillers and thereby gives the paper increased strength. This procedure is normally used in the manufacture of certain so-called "high-strength" products such as gasket material, saturated paperboard, roofing felt, flooring felt, etc. No similar technique has heretofore been suggested for the manufacture of fine paper having greater than normal quantities of mineral filler.

A number of prior patents disclose the general idea that a charged latex can be added to the paper-making furnish. Because of the basic electro-chemical reaction of an anionic paper-making system, a cationic latex precipitates easily and provides additional fiber bonding and, accordingly, strength to the resultant paper. These patents relate primarily to so-called "high-strength" papers which are largely devoid of fillers, or at best contain only very small quantities of fillers or pigments. For example, Wessling et al U.S. Pat. No. 4,178,205 discusses the use of a cationic latex, but pigment is not essential. Also the U.S. Pat. No. 4,187,142 to Pickleman et al discloses the use of an anionic polymer co-additive with a cationic latex, with the use of a sufficient amount of latex to make the entire paper-making system cationic; the use of fillers in any example is not mentioned. Foster et al U.S. Pat. No. 4,189,345 discusses extremely high levels of cationic latex.

It has been proposed noting the McReynolds U.S. Pat. No. 4,225,383, in the manufacture of relatively thick paper product, similarly to the manufacture of roofing and flooring felt papers, to use the combination of a cationic polymer with an anionic latex, and substantial quantities of mineral filler. Once again, however, the product is not designed for printing using the offset method, and its strength requirements are accordingly relatively low. Moreover, because of the substantial thickness of the products produced by such a technique, the product is given some additional strength merely by means of its mass.

The Riddell et al U.S. Pat. No. 4,181,567 is directed to the manufacture of paper using an agglomerate of ionic polymer and relatively large quantities of filler. The patentees indicate that either anionic or cationic polymers may be used, and fillers mentioned are calcium carbonate, clay, talc, titanium dioxide and mixtures. In example 1, an 80 basis weight paper having 29% ash is produced using calcium carbonate as the filler. This patent in essence discusses precipitation of the pigment with a retention aid system prior to its addition to the paper-making system.

Such Riddell et al patent mentions German Offenlegunschrift No. 25 16 097 near the bottom of column 1 thereof, the latter of which corresponds to U.K. Pat. No. 1,505,641 which discloses the pre-treatment of calcium carbonate with a styrene-butadiene latex to produce a protected pigment which can then be used in paper making preferably at the 20% by weight level, although the patent does state that there is little or no reduction in strength up to the 50% by weight level. In more detail, the U.K. patent discloses mixing an anionic latex with an aqueous suspension of the special filler having a cationic charge, e.g. made by mixing with positively charged starch. One to twenty parts of latex are used per 100 parts of filler, and the filler composition is added to the beater, pulper or elsewhere before the breast box. Example III shows the use of 400 parts of filler to 700 parts of wood fiber. A point to be emphasized, however, is that the technique of the U.K. patent requires extra equipment and extra processing, as the filler is first encapsulated and then only later added to the paper-making system; in other words, the technique of the U.K. patent is unduly complex. Moreover, the encapsulation provides inadequate protection to enable the calcium carbonate to be used in acidic medium without undesirable foaming.

SUMMARY OF THE INVENTION

It is, accordingly, an object of the instant invention to overcome deficiencies in the prior art, such as indicated above.

It is another object to provide fine paper suitable for use in offset printing, which paper contains more than normal quantities of mineral filler.

It is a further object to provide good quality, fine paper of thickness 1.5–15 mils, preferably 2–8 mils, and a weight of 0.009–0.945 lbs/ft^2, having adequate strength for offset printing and having a high mineral filler content ranging from about 30% filler for 30 pound paper (based on 3300 ft^2) to 70% filler for 70–150 pound paper.

It is yet another object of the invention to provide a process for making good-quality, fine printing paper containing large amounts of mineral filler, in an economical manner, at less cost, and at a higher production rate.

It is yet a further object to provide high mineral content paper of good quality containing a synergistic mixture of mineral fillers.

These and other objects and the nature and advantages of the instant invention will be more apparent from the following detailed description of various embodiments of the instant invention, taken in conjuction with the following drawing of an exemplary embodiment.

BRIEF DESCRIPTION OF THE DRAWING

The sole FIGURE is a schematic flow sheet showing a system, upstream of the paper-making machine, for preparing a paper-making furnish in accordance with the invention.

DETAILED DESCRIPTION OF EMBODIMENTS

Generally in accordance with the invention, fine paper of thickness 1.5–15 mils, preferably 2–8 mils, and weight $9–45\times10^{-3}$ lbs/ft^2, preferably $9–24\times10^{-3}$ lbs/ft^2, is produced containing from 30% mineral filler to 70% mineral filler, although it will be understood that the invention can be used in making other types of paper and that the filler range will depend on the ultimate use for which the paper is intended. However, for fine paper suitable for use in offset printing, 30% mineral filler will normally be used for 30 pound paper, 40% for 40 lbs, 50% for 50 lbs, 60% for 60 lbs and 70% mineral filler for 70–150, preferably 70–80, pound paper, all based on 3300 ft^2.

The fine paper is suitably produced on a conventiona Fourdrinier paper machine at increased speeds with major energy saving which permits production increases, although it will be understood that other types of paper-making equipment can also be used, e.g. cylinder machines, twin wires, etc. Because of the exceptional strength of the present paper-making system in relation to other high filler content fine paper systems, the paper machine runs better and the resultant fine paper can be used in general printing processes and functions as a bond paper.

The use of large quantities of mineral filler drastically reduces the cost of the fine paper manufacture. In the first place, there is provided a savings of $30–70 per ton in the materials from which the fine paper is made. This number will increase as fiber is much more costly than filler material and tends to increase in cost more rapidly. Moreover, the high mineral filled paper is much easier to dry than normal paper and therefore the machinery can be run more rapidly, e.g. 10–25% more rapidly, which reduces production costs. Furthermore, the amount of steam necessary to dry the paper is reduced, conservatively, at least 15% and, more realistically, as much as 30%.

In addition to the mineral filler, the fine paper is normally made from hardwood and softwood pulps prepared by various conventional pulping processes, as well as the conventional paper-making chemicals such as rosin size, alum and polymeric retention aids. It will be understood, however, that the invention can also be used in the manufacture of synthetic paper. With regard to the wood fibers used, any conventional stock may be used. Desirably, however, the wood fibers in the furnish will be from 50–100% hardwood kraft, with 0–50% softwood kraft, most desirably 25% softwood kraft and 75% hardwood kraft. Calculated on the basis of total solids in the furnish, it is preferred to have 15–30% by weight softwood kraft and 15–50% hardwood kraft.

The paper-making slurry in accordance with the invention is preferably at an acid pH, although an acid paper-making furnish is not essential. Alum and rosin size are preferably but not essentially present, and by term "rosin size" it is intended to encompass dispersed rosin size, synthetic rosin size and rosin derivatives. Other methods of internal sizing can also be used. Polymeric polyacrylamide (such as Accostrength) dry strength additives can also be used in this system to promote additional dry strength and some wet web strength on the paper-making machine.

The preferred furnishes all contain alum and rosin size, preferably in the ratio of approximately 3 parts of alum to one part of rosin size, although it will be understood that these ratios may be varied. Suitable quantities are 5–10 pounds of rosin size per ton of dry furnish, and an amount sufficient of alum, usually about 10–20 and preferably 15 pounds of alum per ton of dry furnish to provide a pH of 4.0–5.0.

An important aspect of the present invention is the use of a suitable latex. The latex can be a styrene-butadiene latex, an acrylic latex, a polyvinyl acetate latex, or another type of latex, but most latices which have been used for wet-end saturation are not necessarily suitable because they will not exhaust onto the fibers and fillers when precipitated. It has been found that the most satisfactory latex is an amphoteric latex which is cationic under the preferred conditions of use, e.g. cationic under acid conditions. Cationic latices may also be used. Even an anionic latex can be used, although it has been found that the anionic latex is less satisfactory. Cationic latex, compared to anionic latex, is easier to use, provides good strength and better retention.

The latex, preferably cationic (positive) under the preferred conditions of use, is of a charge opposite to and less than that of the anionic (negative) paper-making system, and thereby precipitates easily on the negatively charged paper fibers and filler (clay) particles thereby forming a paper floc nucleus which, however, remains anionic because the net charge of the fibers and clay filler is greater than that of the cationic latex. As is known, the normal paper-making slurry has an anionic charge because this is the normal charge of the cellulose fibers. In addition, most mineral fillers, i.e. clays, are also strongly anionic, and this adds to the negative charge of the system. Where the filler used is non-ionic or slightly cationic, precipitation of the latex occurs mostly on the cellulose fibers, but floc formation still occurs with the filler becoming entrained in the floc and thereby attaching to the fiber.

It will be understood that in order to reduce the anionic charge it is desirable to add to the system a cationic polymer. Indeed, in accordance with the preferred embodiment, two cationic polymers, alum (which is also cationic), rosin and latex, are added to the system. It will be understood that when an anionic latex is used, the quantity of cationic polymer used should be sufficient to precipitate the anionic latex.

The floc formed by the precipitated latex can either be anionic or cationic and is dependent upon the amount and charge density of the latex used, the pH of the paper-making system and the materials other than the latex used, e.g. type of fiber, type of filler, the charge density of the anionic materials used, etc. This is so because the quantity of latex used is small compared with amounts used to make paperboard or saturated felt, generally running between only 3 and 7% based on the dry furnish. Nevertheless, in spite of the small amount of latex used, which itself is an economic advantage, the characteristics of the floc formed provide excellent retention on the wire of the paper-making machine. Use of this system, as opposed to a standard wet-end saturation approach, gives better filler retention; and, of course, when filler retention is poor, filler is lost which is difficult to recover. In addition, lost filler tends to build up in the wet-end system which can cause runnability problems. At the 5% by weight latex addition levels and with the addition of cationic polymer, the systems allows approximately 87% total retention in the first pass.

As mineral filler, there can be used almost any material that is not water soluble. Most common paper-making filler materials may be used, e.g. kaolin clay, talc, titanium dioxide, aluminum hydrate, hydrated silica, calcium carbonate, etc., and these fillers are accordingly referred to as being "system compatible". Certain fillers have, however, been found to be undesirable when used by themselves; these include diatomaceous earth. Another filler found less satisfactory than others is porous calcined clay, such as high opaque clay and Ansilex. On the other hand, fillers which have been found particularly desirable are various forms of talc, including Mistron vapor talc which is a high brightness talc, and Yellowstone talc. Calcium carbonate is system compatible only in neutral or basic media, and not in paper-making slurrys below the pH of 7.0, as calcium carbonate reacts at acidic pH to generate carbon dioxide which causes foam problems, and therefore calcium carbonate cannot be used in the standard acidic paper-making system where the pH is between 4 and 5.

A particular blend of fillers has been shown to provide superior results, i.e. the two components of the blend act synergistically to provide improved results, primarily increased strength at given filler contents. Thus a mixture of talc, which is neutral in charge, and kaolin clay, which is strongly anionic, act together synergistically to give a stronger product, it being theorized that the talc particles have a physical affinity for the latex and therefore sequester and absorb the latex and act as nuclei for the flocculation. The talc does not disrupt the fiber bonding as much as the kaolin clay. The blend of kaolin clay and talc may range from 95:5 to 5:95 parts by weight, although the preferred range is 5–75% talc for 95–25% kaolin clay. Calculated on the basis of total solids in the furnish, the preferred filler content is 10–30% talc and 10–30% kaolin clay.

The clay, preferably kaolin clay, ranges in particle size from very fine, e.g. about 0.5 microns, to relatively coarse, e.g. maximum size about 15 microns. A highly suitable clay is Astraplate (Georgia kaolin) which is a kaolin clay composed of thin hexagonal plates, 80–82% of which are finer than 2 microns and only 0.005% of which are retained on a 325 mesh screen. Suitable special kaolin clays are disclosed in U.S. Pat. Nos. 2,904,267; 3,477,809; and 4,030,941. The talc is desirably ground to 325 mesh, although its size also is subject to considerable variation.

The synergistic filler system of talc and kaolin clay can be used in high filler content fine papers containing up to 70% by weight filler. When used with the preferred amphoteric latex system, as described above, or even with the next-preferred cationic latex system, the resultant sheet has excellent strength. Even if anionic latex is used instead of the cationic latex, the system will still have good strength because of the filler synergism, although there are operating problems using the anionic latex because it is more difficult to control the precipitation and insure adequate paper floc strength in an acid furnish with the anionic latex due to its charge compatibility with the other components of the furnish. Another problem with the anionic latex system is that the fillers are normally dispersed in water and the dispersion agents normally used are anionic; as the filler must be flocculated with the cationic polymer, excessive polymer usage is required which creates problems in standard paper-making systems and in the handling of the filler.

With reference to the attached drawing, it is seen that hardwood pulp, broke, softwood pulp and filler are all added to a proportioning box (if plural fillers are used they may be pre-blended together) and the slurry then fed to a funnel where latex and rosin are then added, with the mixture flowing into the machine chest; or the latex and rosin may be added directly to the machine chest. From the machine chest the slurry is pumped to a stuff box and on the way alum and a first cationic polymer, e.g. Dow XD-30440.01, are added. From the stuff box the slurry is diluted with water from the white water system, then pumped to the conventional cleaners and screens. Finally the furnish is pumped to a paper machine head box, and on the way a second cationic polymer, e.g. Betz 1260, which also serves as a retention aid, is added.

With reference to the FIGURE, it will be seen that cationic polymer is added at two different points. These polymers are each added to the furnish in an amount of about 0.25 to 3 pounds per ton of dry furnish, preferably about 0.5 pounds per ton. As the stock leaves the machine chest, e.g. at a solid consistency of about 3%, a first cationic polymer is added to the system, preferably Dow XD-30440.01. This cationic polymer is a high M. W. polyacrylamide polymer of pH 4.6, density of 1.1, solids content of 8% and a bulk viscosity of 15,000–20,000 cps.

After the furnish has left the screens and cleaners and before it reaches the paper machine head box, e.g. head box approach piping, a second cationic polymer, preferably Betz 1260, is added to the furnish normally in an amount of 0.25 to 1 pound per ton based on the dry furnish. The second cationic polymer acts in concert with the other components as indicated above to insure maximum flocculation, and also serves as a conventional retention aid. The Betz 1260 cationic polymer is an extremely high M. W. acrylamide copolymer and is sold as a white, free-flowing, water-soluble powder of density approximately 28 lbs/ft^3. It will be understood that the first cationic polymer addition may be at any location upstream of the second cationic polymer addition, the latter of which should be at any location downstream of the first addition, the precise addition points depending on the paper machine system.

As indicated above, selection of a proper latex is an important consideration in the successful operation of the present process in order to achieve maximum strength for a given high load of mineral filler. As indicated above and shown in the FIGURE, the latex is preferably added at the machine chest, most desirably in an amount between 3 and 7% based on the dry furnish. It is presently unknown why some latices work well and others do not, but it is believed that possibly important characteristics include particle size, charge, charge density and glass transition temperature. Successful operation has been carried out with the following three latices, listed in the order of their desirability.

(1) Rhoplex P-57 Amphoteric Acrylic Latex (Rohm and Haas). This acrylic latex is characterized by being non-ionic under neutral conditions, but becoming cationic under acid conditions. It is sold in the form of milky-white liquid of 50% solid content having a density of 8.8 lbs per gallon and a specific gravity of 1.06 and a Brookfield LVF Viscosity at 25° C. (No. 2 Spindle 60 rpm) of 200 CPS.

(2) Dow XD-30288.00 Cationic Latex (Dow Chemical Co.). This is a carboxylated styrene-butadiene latex.

(3) Dow XD-30374.01 Anionic Latex (Dow Chemical Co.). This is a carboxylated styrene-butadiene latex of pH 8.0, solids content of 45–47%, particle size of approximately 1600 Å and a specific gravity of 1.01. It is disclosed in the McReynolds U.S. Pat. No. 4,225,383.

Also satisfactory are a cross-linkable styrene-butadiene latex of 60% styrene and 40% butadiene; and a styrene-butadiene latex of 90% styrene and 10% butadiene.

Other successful latices can, in view of the present disclosure, be determined by routine testing, key requirements of the latex being that it must precipitate on the fibers and filler to exhaustion or near exhaustion, that it provide good retention, and that it give adequate strength at high filler contents to enable offset or gravure printing when used at levels not substantially exceeding 7%. Such routine testing may be carried out using a furnish of 3–7% of the test latex and a 50:50 mixture of clay filler and wood pulp on a Noble and Wood hand-sheet machine or equivalent laboratory paper-former with white water recirculation using a standard screen of 100 mesh, the paper sheet being pressed once through a felted Noble and Wood or equivalent presser, and then contact dried. A suitable ionic latex is capable of exhaustion or near exhaustion if, in the test, the paper sheet leaves the wire without a latex residue being left behind; provides good retention if in such test about 75% or more, preferably at least 88%, of the filler and fiber is retained; and provides good strength if in such test the resultant paper sheet has at least 10%, preferably at least 16%, mullen.

With all the furnish combinations discussed above, treatment on the paper machine at the size press position or later for external treatment, e.g. coating or sizing, is desirable to produce the best results, as is also true in the production of normal paper. The material used at e.g. the size press may be selected from those normally used including starch size or polyvinyl alcohol, polyvinyl acetate, styrene-butadiene latex, acrylic latices, clay, titanium dioxide, calcium carbonate, talc, and other commonly used material in the coating of paper and any combination thereof which provides the proper functional surface for printing or other functional end use. By "starch size" it is intended to encompass unmodified potato starch, tapioca starch, corn starch, anionic starch and derivatives of such starches. A particularly suitable material is ethylated corn starch having a solids content of 8–12%, and one example of such a material is Penford Gum 280 (Penick and Ford) which is an 80 fluidity, 2% substituted hydroxyethyl corn starch. It may be applied at the rate of between 30–200 pounds, preferably 60 to 150 pounds per ton.

The following examples are offered illustratively. As adequate strength is a most important function of the resultant paper, strength is set forth in percent mullen, defined as mullen in pounds per square inch (psi) divided by the weight of the paper at 3300 square feet.

EXAMPLE 1

Two series of runs of hand sheets were prepared in a Noble and Wood sheet machine. The filler system was 50% kaolin clay and 50% talc. Both furnishes contained 5% latex and 0.39 lbs/ton of cationic polymer. The latex in the first furnish was Dow anionic XD-30374.01, and in the second furnish was Rohm & Haas P-57 amphoteric latex, the pH of the furnish being adjusted to 4.5 making the latex cationic.

Retention was good, strength was adequate, and no residue was left on the screen for both series of trials. However, the filler in the resultant paper was more concentrated in the paper made with the cationic latex, thereby indicating a larger and more stable floc.

EXAMPLE 2

Using a Noble and Wood laboratory sheet machine, samples were prepared with a furnish of 55% kaolin clay, 45% wood pulp comprising a mixture of 75% hardwood and 25% softwood, 5% Dow XD-30374.01 anionic latex, 0.3 lbs/ton of Dow cationic polymer XD-30440.01, 2.5 lbs/ton of dispersed rosin size (Neuphor 100), and 10 lbs/ton of alum.

The quantity of filler retained was 88%, and the quantity of clay in the paper sheet was 48.9%. The strength of the paper was 10.9% mullen.

EXAMPLE 3

Example 2 was repeated except that the anionic latex of Example 2 was replaced with Rhoplex P-57 amphoteric acrylic latex, the pH of the system being on the acid side so that the latex was in effect cationic. All other variables were maintained the same as in Example 2. The quantity of filler retained was 89.6% and the quantity of clay in the paper product was 49.3%. The strength of the paper was 16.6% mullen.

A comparison between Examples 2 and 3 demonstrate the difference in percent mullen at approximately the same filler content. These examples indicate that cationic latex produces a significantly stronger sheet, expressed in percent mullen, than the anionic latex.

EXAMPLE 4

A pilot paper machine trial was conducted on a standard Fourdrinier machine used for testing purposes (the machine is smaller in width and slower in speed than a normal fine paper machine). The furnish comprised 46% wood pulp, 54% acid flocced kaolin coating clay, 0.5 lbs/ton of Dow XD-30440.01 cationic polymer, 12 lbs/ton of alum, and 5 lbs/ton of dispersed rosin size (Neuphor 100), in addition to 5% of Dow XD-30374.01 anionic latex. The resultant paper of basis weight 83 lbs/3300 ft^2 was size press treated at about 100–120 lbs/ton with ethylated corn starch.

First pass retention was 73.9%, the resultant paper having a filler content of 44.7% and a strength of 21.7% mullen. The total ash retention efficiency was 66.2%.

EXAMPLE 5

Example 4 was repeated to make paper at a basis weight of 47.3 lbs compared with the Example 4 basis weight of 83 lbs. The total ash retention efficiency was 61.3% with first pass retention of 64.5%. The resultant paper contained 41.4% of the clay filler and had a strength of 14.8% mullen.

EXAMPLE 6

Example 4 was repeated using the same furnish, except that the anionic styrene-butadiene latex was replaced by Dow XD-30288.00 cationic carboxylated styrene-butadiene latex, used at the same rate of 5% based on the total dry solids of clay and wood fiber. The total ash retention efficiency was 68.2% and the first pass retention was 81.4%. The resultant paper sheet contained 47% filler and had a strength of 19% mullen. Comparing Example 6 with Examples 4 and 5, it is seen that the cationic latex gives better retention and is easier to use than the anionic latex. In addition, the Example 6 paper is stronger than the paper of Example 5.

EXAMPLE 7

Example 6 was repeated except that the Dow cationic latex was replaced with an equal amount of Rhoplex P-57 amphoteric acrylic latex. The total ash retention efficiency was 83.1% and the first pass retention was 81.6%. The resultant paper sheet contained 49.2% filler and had a strength of 19.6% mullen.

The process of Example 7 was carried out at an acidic pH so that the amphoteric latex was actually cationic. Comparing Example 7 to Example 4, it is seen that the quantity of filler retained in Example 7 was higher, and the strength was only slightly lower. Compared with Example 5, both the retention and strength was improved. Examples 4–7 demonstrate the higher first pass retentions and ash efficiencies of the cationic and amphoteric latices, thereby indicating that these latices work better in the acid paper-making process.

EXAMPLE 8

Using the pilot Fourdrinier machine, paper was formed from a furnish comprising 50% wood pulp, 50% coating grade kaolin clay, 5% Dow XD-30374.01 anionic carboxylated styrene-butadiene latex, 5 lbs/ton of Neuphor 100 and 12 lbs/ton of alum. The ash efficiency was 74.9% and the first pass retention was 74.5%. The paper was not sized externally. The resultant paper contained 42.8% filler and had a strength of 15.3% mullen.

EXAMPLE 9

Example 8 was repeated except that the quantity of paper pulp in the furnish was reduced to 46% and the quantity of coating grade kaolin clay was increased to 54%, and also the latex used was Rhoplex P-57 amphoteric acrylic latex, cationic under the conditions of use. The ash efficiency was 73.19% and the first pass retention was 76.7%. The resultant product contained 46.6% filler and had a strength of 13.5% mullen.

EXAMPLE 10

Example 8 was repeated except that the relative quantities of kaolin clay and wood pulp were adjusted to provide 55% clay and 45% wood pulp. The ash efficiency was 66% and the first pass retention was 66.1%. The resultant product contained 44.7% filler and had a strength of only 9.8% mullen.

Examples 8–10 demonstrate that while the anionic latex approaches the cationic latex in efficiency when the furnish contains no more than about 50% filler, its efficiency drops off considerably, particularly relative to the strength of the product, when the quantity of filler in the slurry reaches 55%.

EXAMPLE 11

Using the pilot paper machine, paper was made from a furnish comprising 46% wood pulp and 54% filler, of which 50% was talc and 50% clay. Also present in the furnish was 5% Dow XD-30374.01 anionic carboxylated styrene-butadiene latex, 5 lbs/ton of Neuphor 100 rosin, 12 lbs/ton of alum and 0.5 lbs/ton of Dow XD-30440.01 cationic polyacrylamide. The ash efficiency was 73.9% and the first pass retention was 79.5%.

The resultant paper was size press treated with starch. It had a filler content of 50.9% and a strength of 20.9% mullen.

EXAMPLE 12

Example 11 was repeated except that the filler comprised 46% talc and 54% clay. The basis weight of the paper produced was 48.8 lbs/3300 ft^2. The ash efficiency was 67.8% and the first pass retention 83.6%. The resultant paper contained 46.9% filler and had a strength of 20% mullen.

EXAMPLE 13

Example 12 was repeated except that the 5% anionic styrene-butadiene latex was replaced with 5% Rhoplex P-57 amphoteric acrylic latex. The ash efficiency was 78.2% and the first pass retention was 87.9%. The product contained 49.3% filler and had a strength of 22.1% mullen.

A comparison between Examples 13 and 12 again shows the superiority of the amphoteric acrylic latex, cationic in use, compared with the anionic latex, other variables remaining constant.

EXAMPLE 14

Example 13 was repeated except that the quantity of filler was increased to 54%, and the relative quantities of talc and clay were changed to provide 21.5% talc and 78.5% clay. The ash efficiency was 72.6% and the first pass retention 87.8%. The resultant paper contained 50.9% filler and had a strength of 17.1% mullen.

Comparing Example 14 to Example 13, it is seen that the strength is reduced, although the retention remains very high.

EXAMPLE 15

Example 12 was repeated except that the basis weight of the paper produced was 96.8 lbs/3300 ft², approximately double the weight of the paper of Example 12. The ash efficiency was 83.4% and the first pass retention was 83.6%. The resultant paper contained 49.8% filler and had a strength of 26.5% mullen.

A comparison of Examples 15 and 12 shows that an increase in basis weight, all other factors remaining constant, provides a significant increase in strength for high filler content, fine paper containing a mixture of talc and clay as the filler. Examples 11-15 demonstrate the synergism of the combination of clay and talc, these examples showing that talc at the 50% level is synergistic using all satisfactory latex systems, but is particularly effective with the amphoteric latex where it produces a stronger composite paper.

EXAMPLE 16

Paper sheets of Examples 4, 7 and 14 were printed on a full size Mhiele 1000, four-color offset press, with no problems, with inks designed for coated paper. All of these papers had sufficient strength to withstand the printing process, the press running at 600 ft/min.

EXAMPLE 17

A comparative test was conducted to determine the economics of producing fine paper according to the present invention. Four paper furnishes were prepared from which paper was formed.

The first furnish, the blank or comparative test, comprised 90% wood fiber (75% hardwood, 25% softwood), 12 lbs/ton alum, 5 lbs/ton of rosin and 10% kaolin clay.

Samples 1, 2 and 3 in accordance with the invention comprised similar furnishes except that each of these samples contained 5% of Rhoplex P-57 amphoteric acrylic latex, as well as increased amounts of kaolin clay, Sample 1 comprising 40% clay, Sample 2 comprising 50% clay, and Sample 3 comprising 60% clay.

The four samples were dried to a 5% moisture level at the reel. The results are shown in Table I below:

TABLE I

Laboratory Dryness Evaluation - Based on 5% Moisture at the Reel

Sample	Filler in Furnish	% Filler in Paper	% Dryness	Lbs. Steam to Dry to 5% Moisture	Lbs. Steam Saved Compared to Blank	Cost Saving	% Production Increase
Blank	10%	6.70%	29.34%	5370 lbs.			
1	40%	41.24%	37.39%	3698 lbs.	1672 lbs.	$4.18	31.1%
2	50%	48.49%	38.45%	3530 lbs.	1840 lbs.	$4.60	34.3%
3	60%	59.16%	40.36%	3249 lbs.	2121 lbs.	$5.30	39.5%

As shown in the table above, the comparative paper containing 10% clay and no latex after pressing had a dryness of 29.34% while an identically formed and pressed 60% clay and 5% latex paper had a 40.36% dryness after pressing. Consequently, the high filler paper required far less steam heat to dry to a 5% moisture level, and consequently there resulted an important energy savings as indicated in the table. Also, because less drying is required, the production speed is increased as shown.

EXAMPLE 18

A series of hand sheet comparisons were made using different latices and different filler contents. All furnishes were the same except for the differences shown in Tables II and III, which tables also give the comparative results.

TABLE II

Clay/Talc Series

Latex	Target % Filler	Basis Wt. lbs/3300 ft² Product	Caliper Mils	Caliper/wt.	Mullen psi	% Mullen	gms Elmendorf Tear	Scott Bond Units	% Ash	Actual % Filler	% Filler Retention
BLANK (no latex)	20	60.2	7.4	1.23	14.0	23.26	64	84	16.5	18.3	.92
Cross-linkable											
60% styrene-40% butadiene*	20	57.7	6.9	1.20	18.0	31.2	74	134	17.6	19.5	.98
90% styrene-40% butadiene**	20	59.1	7.1	1.20	18.2	30.8	76	108	15.3	17.0	.85
P-57	20	55.0	6.5	1.18	21.3	38.7	60	162	16.0	17.8	.89
BLANK (no latex)	30	60.4	7.3	1.21	7.7	12.75	48	50	24.5	27.2	.91
Cross-linkable											
60% styrene-40% butadiene	30	57.3	6.8	1.19	14.3	25.0	62	141	25.5	28.3	.94
90% styrene-40% butadiene	30	55.6	6.7	1.21	12.7	22.8	58	87	21.4	23.8	.79
P-57	30	50.1	6.3	1.26	15.4	30.7	48	136	21.9	24.3	.81
BLANK (no latex)	40	57.5	7.2	1.25	4.2	7.3	30	40	32.4	36.0	.90
latex (i)	40	56.8	6.6	1.16	10.2	18.0	44	85	31.7	35.2	.88
latex (ii)	40	50.6	6.3	1.25	8.0	15.8	44	80	28.5	31.6	.79
P-57	40	48.5	6.1	1.26	10.7	22.1	42	114	27.9	31.0	.78
BLANK (no latex)	50	52.6	6.7	1.27	2.3	4.37	24	32	35.9	39.9	.80
latex (i)	50	55.9	6.9	1.23	8.0	14.3	42	101	39.7	44.1	.88
latex (ii)	50	46.7	6.0	1.29	4.7	10.1	34	63	34.9	38.7	.77
P-57	50	44.8	5.8	1.30	7.1	15.9	28	91	35.4	39.3	79

*latex (i)
**latex (ii)

TABLE III

Clay Series

Latex	Target % Filler	Basis Wt. lbs/3300 ft² Product	Caliper Mils	Caliper/ wt.	Mullen psi	% Mullen	gms Elmendorf Tear	Scott Bond Units	% Ash	Actual % Filler	% Filler Retention
BLANK (no latex)	20	60.2	7.7	1.28	10.6	17.61	72	62	15.5	17.5	88
latex (i)	20	62.6	7.2	1.15	20.1	32.1	84	126	15.4	17.4	87
latex (ii)	20	61.7	7.4	1.20	16.0	25.9	78	81	13.9	15.7	79
P-57	20	59.1	6.9	1.17	18.7	31.6	50	140	15.7	17.7	89
BLANK (no latex)	30	58.7	7.3	1.24	6.1	10.39	46	42	21.9	24.8	83
latex (i)	30	61.2	7.0	1.14	17.0	27.8	74	113	21.9	24.8	83
latex (ii)	30	58.5	7.0	1.20	12.4	21.2	64	70	20.2	22.8	76
P-57	30	55.4	6.5	1.17	12.3	22.2	62	95	22.4	25.3	84
BLANK (no latex)	40	56.5	6.9	1.22	2.95	5.22	32	35	29.9	33.8	85
latex (i)	40	57.2	6.6	1.15	13.1	22.9	58	108	29.3	33.1	83
latex (ii)	40	56.1	6.9	1.23	8.2	14.6	50	58	25.0	28.8	72
P-57	40	50.3	6.3	1.25	9.5	18.9	46	93	26.1	29.5	74
BLANK (no latex)	50	48.4	6.3	1.30	1.1	2.27	18	29	32.3	36.5	73
latex (i)	50	56.9	6.3	1.11	8.0	14.1	44	101	36.9	41.7	83
latex (ii)	50	50.7	6.2	1.22	5.2	10.3	42	54	30.7	34.7	69
P-57	50	44.7	5.7	1.28	6.1	13.7	34	80	30.3	34.2	68

EXAMPLE 19

To compare the process U.K. Pat. No. 1,505,641 with the present invention, a series of comparative tests were carried out. Consistent with Example 1 of the U.K. patent, the furnish comprised 50 parts of cellulose fibers, 48 parts of filler and 5% latex, based on the total quantity of cellulose fibers and filler. In the trials according to the U.K. patent, the filler was calcium carbonate and such calcium carbonate was pretreated with the latex. In the trials according to the invention, the filler was clay or an equal mixture of clay and talc. Where an anionic latex was used it was Dow XD-30374.01 carboxylated styrene-butadiene anionic latex. Where the latex was cationic, it was Rhoplex P-57. The paper was formed on a laboratory hand-former. The results are given below in Table IV.

TABLE IV

Filler	Latex	pH	Basis Wt. lbs/3300 ft²	Actual % Filler	% Mullen	% Filler Retention
U.K. Patent 1505641	Anionic	7.5	42.8	39.1	8.2	81.5
U.K. Patent 1505641	Anionic	5.5	43.8	31.1	10.2	64.8
Clay	Anionic	4.6	53.2	41.5	12.5	86.5
Clay Talc 1:1	Anionic	4.7	53.1	39.9	8.5	83.1
Clay	Cationic	4.8	52.5	41.0	13.3	85.4
Clay Talc 1:1	Cationic	4.6	51.6	40.9	14.0	85.2

From the second trial given in Table IV above, it is clear that the system of the U.K. patent is not suitable for use at an acid pH, as the latex did not adequately protect the calcium carbonate which, to some extent, reacted with the acid and caused foaming; 8% of the filler was lost due to reaction with the alum and it can be seen that the calcium carbonate buffered the system to a pH of 5.5. In the trials carried out in an acid pH the target pH was 4.5, achieved by the addition of alum.

The strength of the hand sheets made using the cationic amphoteric latex exceeded the strength obtained by the U.K. patent system at the selected filler level. The U.K. patent system at alkaline pH 7.5 retained 39.1% filler with an 8.2% mullen. The cationic amphoteric latex system with clay and talc retained 40.9% filler with a 14% mullen, and thus was superior to the U.K. system.

EXAMPLE 20

A series of runs were made on a full-size Fourdrinier paper-making machine. The furnish to the machine consisted of 50% wood fiber, 25% kaolin clay (Kaopaque 10) and 25% Yellowstone talc, the fiber constituting 35–40% hardwood kraft and 10–15% softwood kraft based on the total solid content of the furnish. Amphoteric latex P-57 was added at the machine chest in an amount of 4.4% based on the total solids in the furnish. Rosin size was also added in the machine chest at the rate of 7.6 lbs/ton. Alum at the rate of 20 lbs/ton and Dow XD-30440.01 at the rate of 3.2 lbs/ton were added at the suction side of the machine chest pump. Betz 1260 cationic polymer was added prior to the machine head box at the rate of about 0.4 lbs/ton. After paper formation, a size of 10% solids Penford Gum 280 was applied at the size press at a pickup rate of 111–117 lbs/ton. The machine speed was 600 ft/min with a production rate of 4.5–5.0 tons/hr.

Table V shows the average results on the eight runs conducted. Table VI shows the average results on the eight runs conducted after sizing. Table VI shows the average base sheet results.

Results were, generally excellent, with very high strength at 40% filler levels. First pass retention levels ranged from 60–80%. The sheets were easily dried, allowing an increase in the production rate. Several rolls were printed successfully with no noticeable buildup on the printing presses.

The tensile properties of the papers so produced are shown in Table VII.

TABLE V

AVERAGE RESULTS AFTER SIZING

	Sets 201-205	Sets 206-208
Basis Weight in lbs/3300 ft^2	75.9	76.7
Moisture %	3.6	3.1
Caliper in mils	6.0	5.3
Smoothness (Sheffield units)		
FS (felt side)	239	136
WS (wire side)	267	156
Gurley Density (seconds/100 ml. air passage)	8.8	15.0
Mullen (psi)	24.2	22.7
GE Brightness	82.9	82.9
% Opacity	95.9	96.1
% Ash	34.7	36.7
Scott Bond (10^{-3} ft-lbs)	128	126
Taber Stiffness	3.36	3.40
Bulk/Weight Ratio	0.79	0.69
% Mullen	31.9	29.6
% Filler	38.5	40.5

TABLE VI

AVERAGE BASE SHEET RESULTS

Basis Weight in lbs/3300 ft^2	75.2
Caliper in mils	7.5
B/W Ratio	1.00
Smoothness (Sheffield units)	
FS	340
WS	357
Gurley Density (seconds/100 ml. air passage)	9
Mullen (psi)	12.9
% Mullen	17.2
GE Brightness	83.4
% Opacity	97.1
% Ash	39.6

TABLE VI-continued

AVERAGE BASE SHEET RESULTS

% Filler	43.9
Scott Bond (10^{-3} ft-lbs)	63
Taber Stiffness	3.16

NOTE:
Sample taken before size press at the end of the trial.

TABLE VII

				TENSILE PROPERTIES						
Set	Basis Weight (lb/3300 ft^2	% Filler	Caliper (in)	Peak Load (lb)	Peak Elongation (in)	% Strain	Breaking Length (km)	Tensile Strength (lb/in^2)	Tensile Energy (ft-lb)	TEA (ft-lb) ft^2
201	59.6	19.8	.00511	31.97	.0621	2.24	1.270	6.26×10^3	0.1080	5.65
202	74.4	34.0	.00578	29.75	.0523	1.89	0.835	5.15×10^3	0.0873	4.56
203	77.2	38.2	.00585	27.31	.0479	1.73	0.730	4.67×10^3	0.0743	3.83
204	79.1	44.7	.00603	23.63	.0496	1.79	0.598	3.92×10^3	0.0682	3.56
205	81.1	45.8	.00563	25.15	.0440	1.59	0.665	4.47×10^3	0.0630	3.29
206	62.9	38.4	.00444	20.51	.0465	1.64	0.887	4.62×10^3	0.0549	2.87
207	78.6	44.8	.00491	25.17	.0502	1.81	0.787	5.13×10^3	0.0716	3.74
208	75.3	41.6	.00491	27.85	.0517	1.86	0.909	5.67×10^3	0.0817	4.27
Pen Web Offset	66.9	16.0	.00539	34.00	.0423	1.52	1.138	6.31×10^3	0.0800	4.18

EXAMPLE 21

Using the same machine as used in Example 20, a series of runs were conducted to make 60 lb, 50 lb, and 45 lb paper containing 32–42% filler. Essentially the same procedure was followed as in Example 20, although relatively larger quantities of softwood in relation to hardwood were used in the production of the 50 lb and 60 lb paper. Once again, results were excellent, with the paper drying rapidly and having excellent printability. Results are shown in Tables VIII through XI.

TABLE VIII

AVERAGE TEST RESULTS

	Set # 534-544	Set # 545-547	Set # 548-551	Set # 552
Basis Weight	58.6	56.4	50.6	45.7
Moisture %	3.7	4.2	3.0	—
Caliper	4.2	3.7	3.4	3.9
Smoothness-FS	130	125	115	105
WS	145	140	135	125
Gurley Density	11	13	12	9
Mullen (psi)	23.2	17.5	16.2	18.0
% Mullen	39.6	31.0	32.1	39.4
Brightness	82.6	83.2	83.3	82.3
% Opacity	93.0	93.6	91.5	89.5
% Ash	28.6	35.7	36.0	33.6
% Filler	31.7	39.6	40.0	37.3
Scott Bond (10^{-3} ft-lbs)	110	98	107	150
Taber Stiffness	1.82	1.50	1.09	0.75
Bulk/Weight Ratio	0.72	0.66	0.66	0.68

TABLE IX

DRY END CONDITIONS

	Set 543	Set 544	Set 545	Set 546	Set 547	Set 548	Set 549	Set 550	Set 551	Set 552	Common Offset Paper		
Basis Weight	58.0	59.3	57.6	56.4	55.3	50.8	50.7	50.5	50.5	45.7	60	50	40
Speed (fpm)	800	825	825	900	900	900	900	900	900	900	725	775	—
Production (tons/hr)	4.92	5.19	5.04	5.38	5.28	4.85	4.85	4.85	4.85	4.36	3.83	3.83	3.75
Dryer Steam Pressure:													
Main Section (psi)	13.5	16.0	16.0	14.5	13.5	10.5	10.5	10.5	10.5	9.0	20	20	20
After Section (psi)	21.0	24.0	18.0	20.5	19.0	15.0	15.0	16.0	17.0	17.0	30	30	30

TABLE X

I.G.T. PRINTING TEST RESULTS
Westvaco Rod Applicator: #7 Ink;
A-spring tension; 50 kg pressure

Set #	Felt Side (fpm)	Wire side (fpm)
543	190	400
544	190	420
545	110	290
546	90	260
547	100	290
548	110	340
549	130	330
550	130	310
551	90	310
552	190	420

NOTE: 420 denotes no picking

TABLE XI

MATERIAL ANALYSIS

Set #	% Hardwood	% Softwood	% Latex	% Starch	% Moisture	% Filler
543	38.1	15.5	3.9	7.7	3.7	31.1
544	39.6	13.2	3.9	7.3	3.7	32.3
545	28.6	12.8	4.1	7.6	4.2	42.7
546	29.0	18.5	4.1	7.0	4.2	37.2
547	22.9	22.8	4.1	7.2	4.2	38.8
548	26.8	17.8	4.6	7.8	3.0	40.0
549	27.5	17.6	4.6	7.8	3.0	39.5
550	27.0	18.7	3.0	7.8	3.0	40.5
551	24.0	22.2	3.0	7.8	3.0	40.0
552	32.7	15.4	3.3	8.3	3.0	37.3

It will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is shown in the drawings and described in the specification.

What is claimed is:

1. A method of manufacturing fine paper containing mineral filler at a high speed comprising:

preparing an acidic paper furnish including papermaking fibers; an amount sufficient of mineral filler to retain internally in the fine paper web formed of 30-70% mineral filler, and wherein said mineral filler is system compatible; at least one retention aid agent which comprises a water soluble cationic polymer; and 3-7%, based on the dry furnish, of a cationic latex or amphoteric latex which is cationic at acid pH, said cationic or amphoteric latex being selected from latices which provide good mineral filler retention without substantial reduction in strength, which have a charge opposite to and less than the sum of the charges of the other ingredients of said furnish, and which precipitate on the fibers and fillers to exhaustion or near exhaustion;

forming a wet paper web from said furnish such as to produce fine paper of thickness 1.5-15 mils and weight 30-150 lbs/3300 ft^2 containing internally greater than 30% mineral filler up to 70% mineral filler, and having tensile and Z-directional strength sufficient to withstand high-speed offset or gravure printing;

drying said web; and surface treating the dried web to improve the printability thereof.

2. A method according to claim 1 wherein said wet paper web is formed on a Fourdrinier paper machine.

3. A method according to claim 1 wherein said furnish also comprises alum.

4. A method according to claim 3 wherein said furnish comprises approximately 5-10 lbs of rosin size per ton of dry furnish and sufficient of said alum to provide a pH of 4.0-5.0.

5. A method according to claim 1 wherein said papermaking fibers are cellulose fibers and comprise 50-100% hardwood kraft and 0-50% softwood kraft.

6. A method according to claim 5 wherein said cellulose fibers comprise approximately 25% softwood kraft and 75% hardwood kraft.

7. A method according to claim 1 wherein said latex is selected from styrene-butadiene latex, acrylic latex, and polyvinyl acetate latex.

8. A method according to claim 1 wherein said latex is amphoteric at a pH of 7.0, and is cationic under acidic conditions.

9. A method according to claim 1 wherein said retention aid agent comprises two said cationic polymers, each of which is added to the furnish at a different stage during the preparation of said furnish.

10. A method according to claim 1 wherein said mineral filler is selected from the group consisting of kaolin clay, talc, titanium dioxide, aluminum hydrate, hydrated silica and mixtures thereof.

11. A method according to claim 1 wherein said filler comprises a mixture of talc and kaolin clay.

12. A method according to claim 11 wherein said mixture of kaolin clay and talc is in the ratio of 95:5 to 5:95 parts by weight.

13. A method according to claim 11 wherein said mixture comprises 5-75% talc and 95-25% kaolin clay.

14. A method according to claim 10 or 11 or 12 or 13 wherein the particle size of said filler ranges from 0.5 to 15 microns.

15. A method according to claim 1 wherein said preparation of the paper furnish comprises mixing hardwood pulp, broke, softwood pulp and filler, feeding the resultant slurry to a funnel where latex and rosin are added, passing the resultant mixture into a machine chest, adding alum and a first cationic polymer, adding dilution water, and adding a second cationic polymer.

16. A method according to claim 15 wherein each of said cationic polymers is added in an amount of about 0.25 to 3 lbs per ton of dry furnish.

17. A method according to claim 1 wherein said surface treating of the dried web comprises surface sizing of the dried web comprising coating the dried web with starch size at the rate of 30-200 lbs of said starch size per ton of paper.

18. Method according to claim 1 wherein said surface treating of the dried web comprises coating the dried web with starch, polyvinyl alcohol, styrene-butadiene latex, polyvinyl acetate latex, clay, titanium, calcium carbonate, talc, or any combination thereof to improve the surface of printing or other functional end use.

19. Method according to claim 1 wherein the thickness of the said paper ranges from 2.0-8.0 mils.

20. Method according to claim 1 wherein said papermaking fibers are cellulose fibers comprised of bleached and unbleached hardwood and softwood fibers pulped by various pulping methods, i.e. groundwood, sulfite and kraft pulping including thermomechanical, semichemical and soda pulping process.

21. Method according to claim 1 wherein said papermaking fibers contain 1-100% synthetic fibers.

22. A method according to claim 1 wherein said fine paper produced has a filler content no greater than 50% by weight.

23. Fine paper of 2-13 mils thickness produced according to the method of claim 1 and containing about

40% mineral filler for a basis weight of about 40 lbs/3300 ft^2, about 50% mineral filler for a basis weight of about 50 lbs/3300 ft^2, about 60% mineral filler for a basis weight of about 60 lbs/3300 ft^2, or about 70% mineral filler for a basis weight of about 70–150 lbs/3300 ft^2.

24. Fine paper of 3–10 mils thickness having sufficient tensile and Z-directional strength to withstand high-speed offset or gravure printing, of weight 30–150 lbs/3300 ft^2, containing 30–70% mineral filler, produced according to the method of claim 1.

25. Fine paper of 3–10 mils thickness having sufficient tensile and Z-directional strength to withstand high-speed offset or gravure printing, of weight 30–150 lbs/3300 ft^2, containing 30–70% mineral filler, produced according to the method of claim 14.

26. Fine paper according to claim 23 having a fill content no greater than 50% by weight.

27. Fine paper according to claim 25 or 26 wherein said filler has a particle size no greater than about 325 mesh.

28. Fine paper of 2–13 mils thickness produced according to the method of claim 3 and containing about 40% mineral filler for a basis weight of about 40 lbs/3300 ft^2, about 50% mineral filler for a basis weight of about 50 lbs/3300 ft^2, about 60% mineral filler for a basis weight of about 60 lbs/3300 ft^2, or about 70% mineral filler for a basis weight of about 70–150 lbs/3300 ft^2, said fine paper having sufficient tensile and Z-directional strength to withstand high-speed offset or gravure printing.

* * * * *

United States Patent [19]

Sprecker et al.

[11] **4,446,060**

[45] **May 1, 1984**

[54] **MONO-OXOMETHYL SUBSTITUTED POLYHYDRODIMETHANONAPHTHALENE DERIVATIVES, ORGANOLEPTIC USES THEREOF AND PROCESSES FOR PREPARING SAME**

[75] Inventors: **Mark A. Sprecker**, Sea Bright; **Marie R. Hanna**, Hazlet; **Richard J. Tokarzewski**, Keyport; **Robert P. Belko**, Woodbridge; **Hugh Watkins**, Lincroft; **Manfred H. Vock**, Locust, all of N.J.

[73] Assignee: **International Flavors & Fragrances Inc.**, New York, N.Y.

[21] Appl. No.: **478,353**

[22] Filed: **Mar. 24, 1983**

Related U.S. Application Data

[62] Division of Ser. No. 354,387, Mar. 2, 1982, Pat. No. 4,391,284.

[51] **Int. Cl.**^{3} **A61K 7/46**; C11B 9/00

[52] **U.S. Cl.** .... **252/522 R**

[58] **Field of Search** .... 252/522 R

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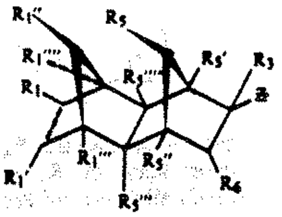
Primary Examiner—Helen M. S. Sneed

Attorney, Agent, or Firm—Arthur L. Liberman

[57] **ABSTRACT**

Described are mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives having the generic structure:

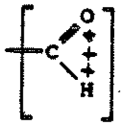


wherein the dashed line represents a carbon-carbon single bond or a carbon-carbon double bond; wherein R_1, R_1', R_1'', R_1''', R_1'''', R_3, R_5, R_5', R_5'', R_5''', R_5'''' and R_4 represent hydrogen or methyl with the provisos:

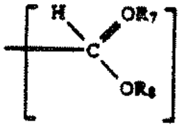
(i) at least four of R_1, R_1', R_1'', R_1''' and R_1'''' are hydrogen; and (ii) at least four of R_5, R_5', R_5'', R_5''' and R_5'''' represent hydrogen;

and wherein Z represents one of the moieties:

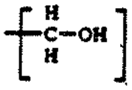
(i) carboxaldehyde having the structure:



(ii) alkylene dioxy or dialkoxy methyl having the structure:

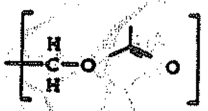


(iii) hydroxy methyl having the structure:



$\left[-\underset{H}{\overset{H}{C}}-OH\right]$ or

(iv) acetoxymethyl having the structure:


;

and wherein R_7 and R_8 take separately represent C_1–C_4 lower alkyl or R_7 and R_8 taken together represent C_2–C_4 alkylene; wherein the line represented by:

[++++]

is either (i) a carbon-carbon single bond when R_7 and R_8 taken together are C_2–C_4 alkylene or (ii) no bond at all when R_7 and R_8 taken separately represent C_1–C_4 lower alkyl. Also described are processes for preparing such mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives, and processes for using the above defined mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives for their organoleptic properties and compositions containing said mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives including perfumes, perfumed articles (such as solid or liquid anionic, cationic, nonionic or zwitterionic detergents, perfumed polymers, fabric softeners and cosmetic powders), foodstuffs, chewing gums, toothpastes, medicinal products, chewing tobaccos, smoking tobaccos and smoking tobacco articles.

12 Claims, 29 Drawing Figures

FIG.1

GLC PROFILE FOR EXAMPLE I.

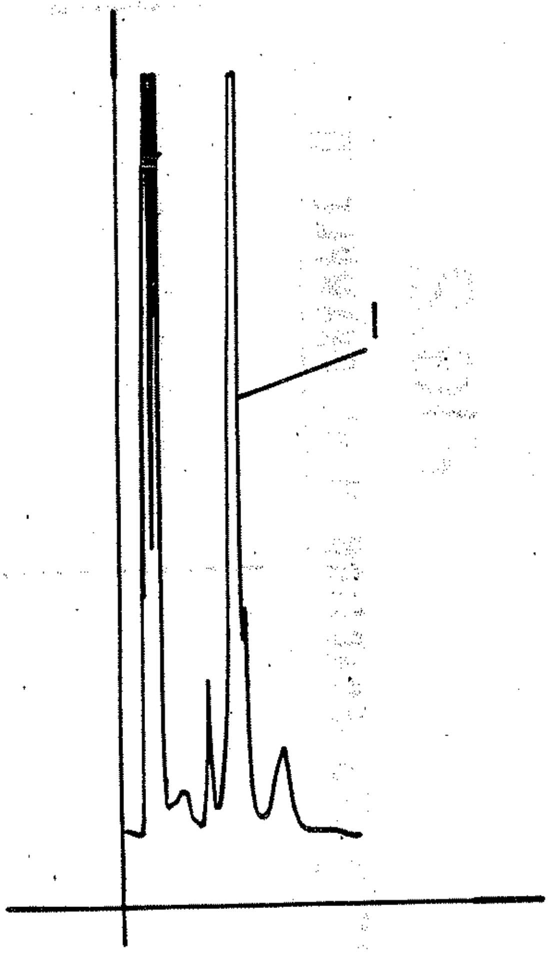


FIG.2

NMR SPECTRUM FOR FRACTION II OF EXAMPLE II.

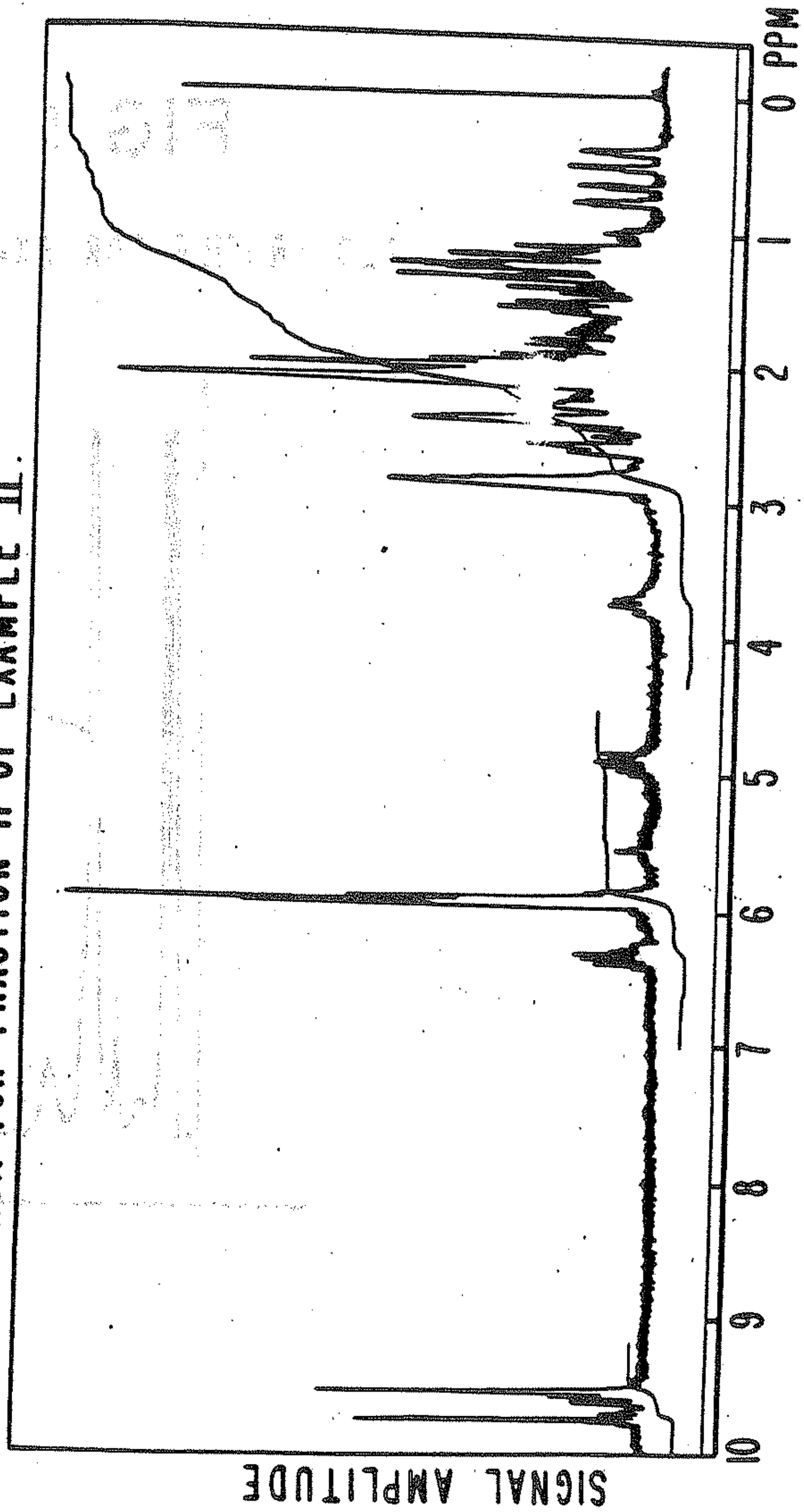
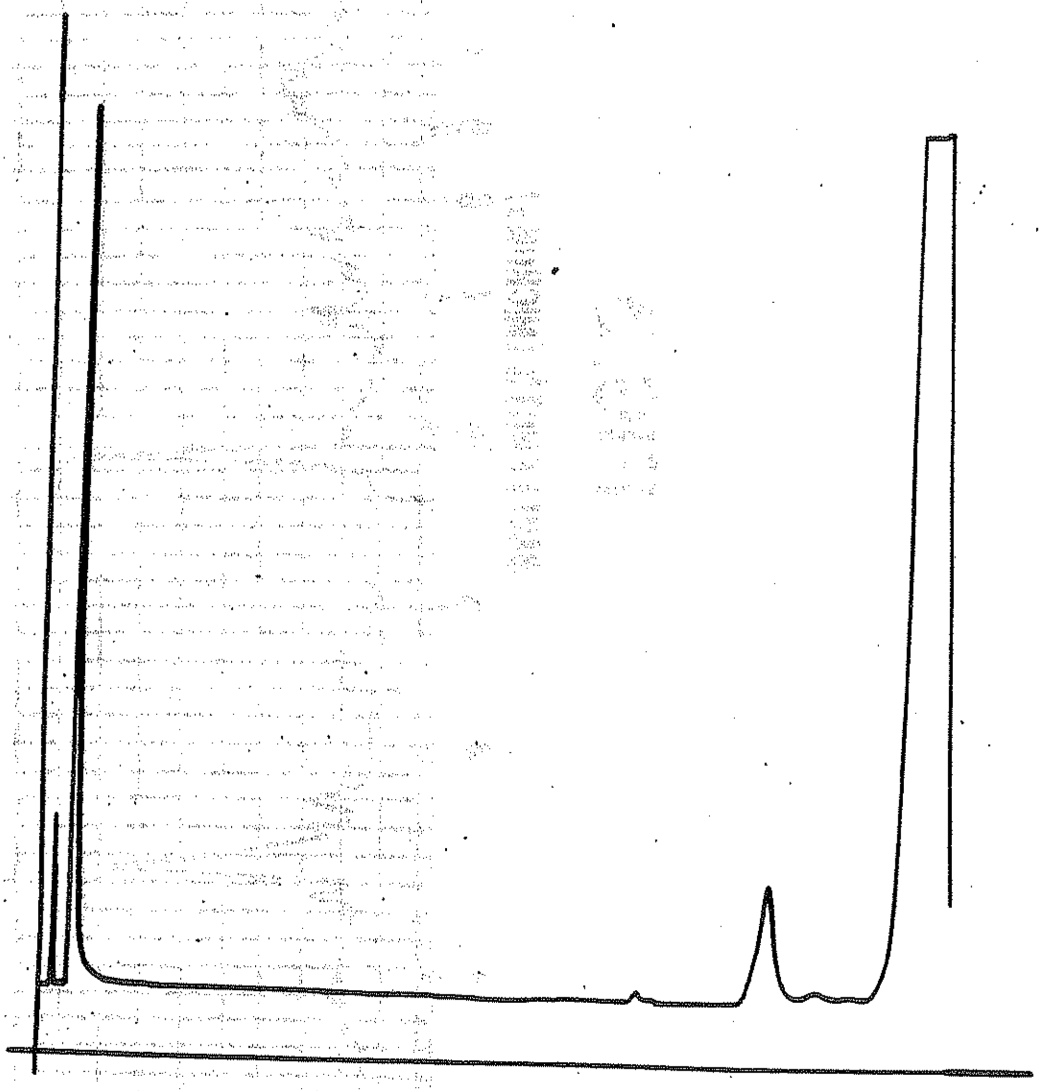


FIG. 4



GLC PROFILE FOR EXAMPLE II.

FIG.5

NMR SPECTRUM FOR FRACTION II OF EXAMPLE II

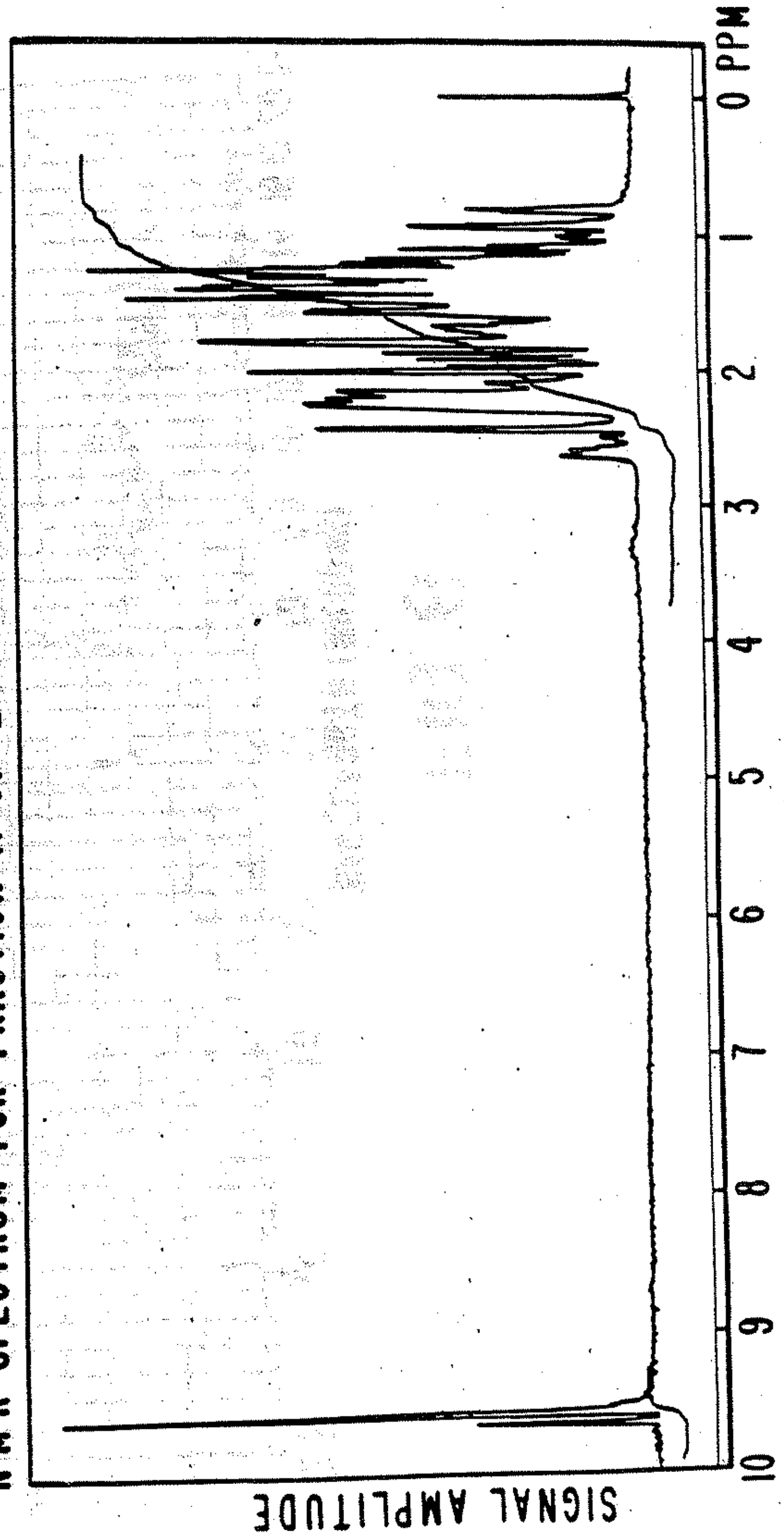
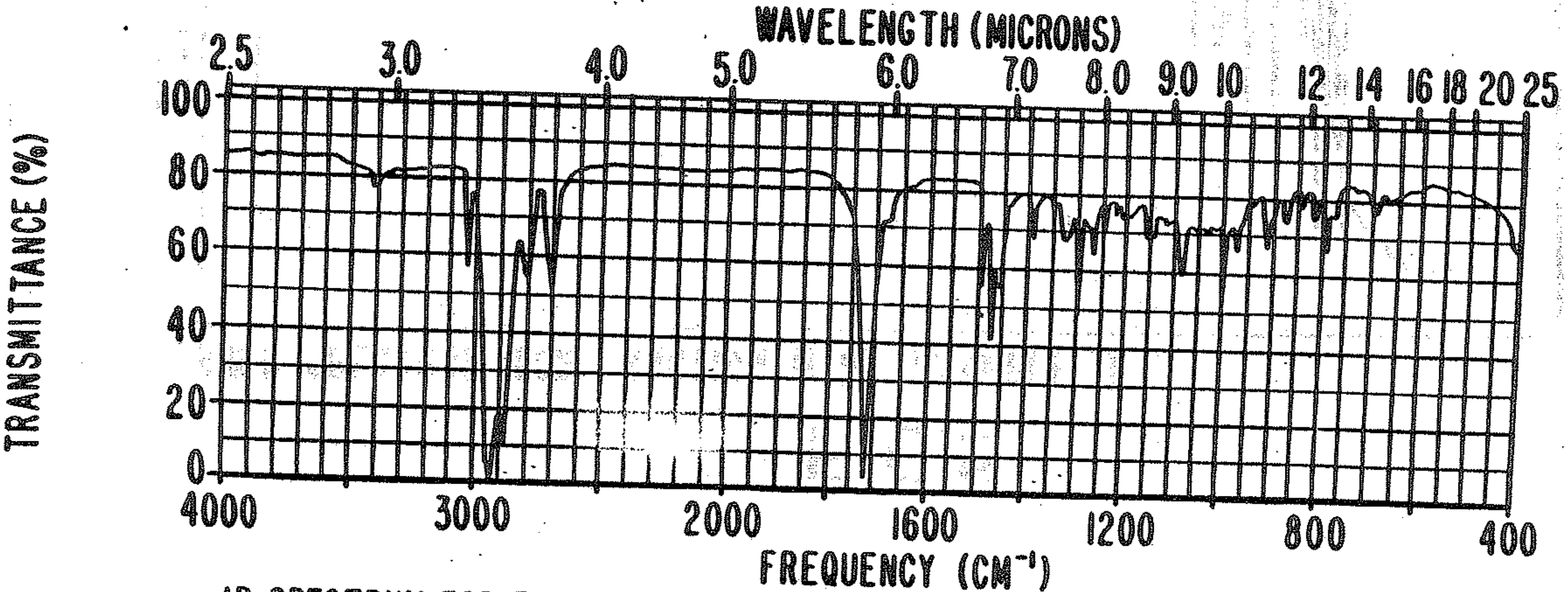
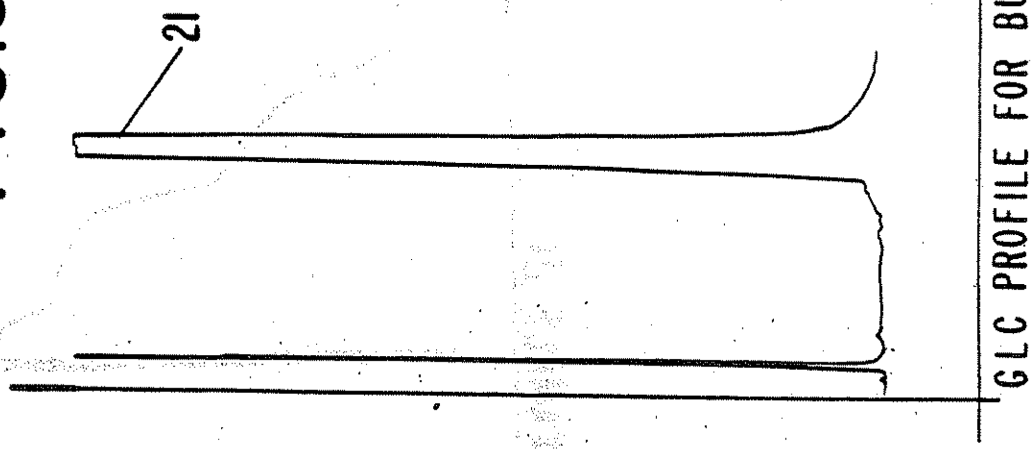


FIG. 6



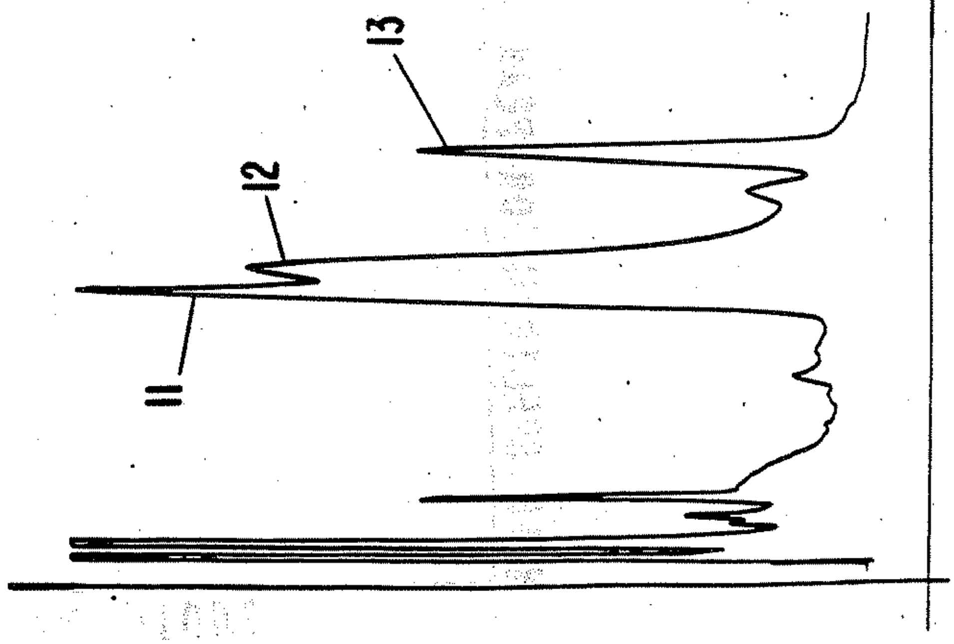
IR SPECTRUM FOR FRACTION 2 OF EXAMPLE II.

FIG.9



GLC PROFILE FOR BULKED FRACTIONS FOR EXAMPLE IV

FIG.7



GLC PROFILE FOR EXAMPLE III

FIG.8

NMR SPECTRUM FOR PEAK 13 OF FIG. 7, EXAMPLE III

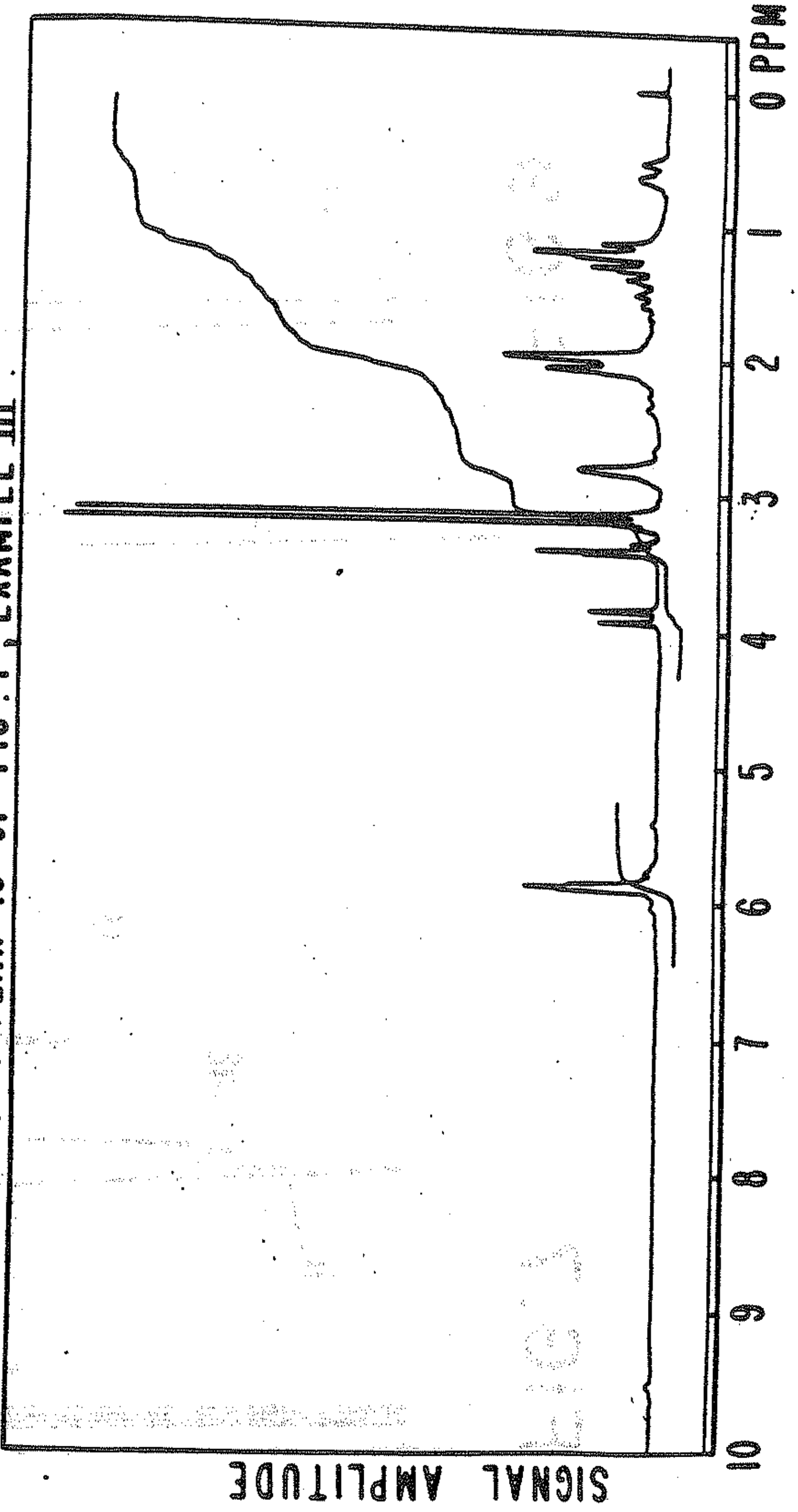


FIG. 10

NMR SPECTRUM FOR BULKED FRACTIONS 3-11 OF EXAMPLE IV.

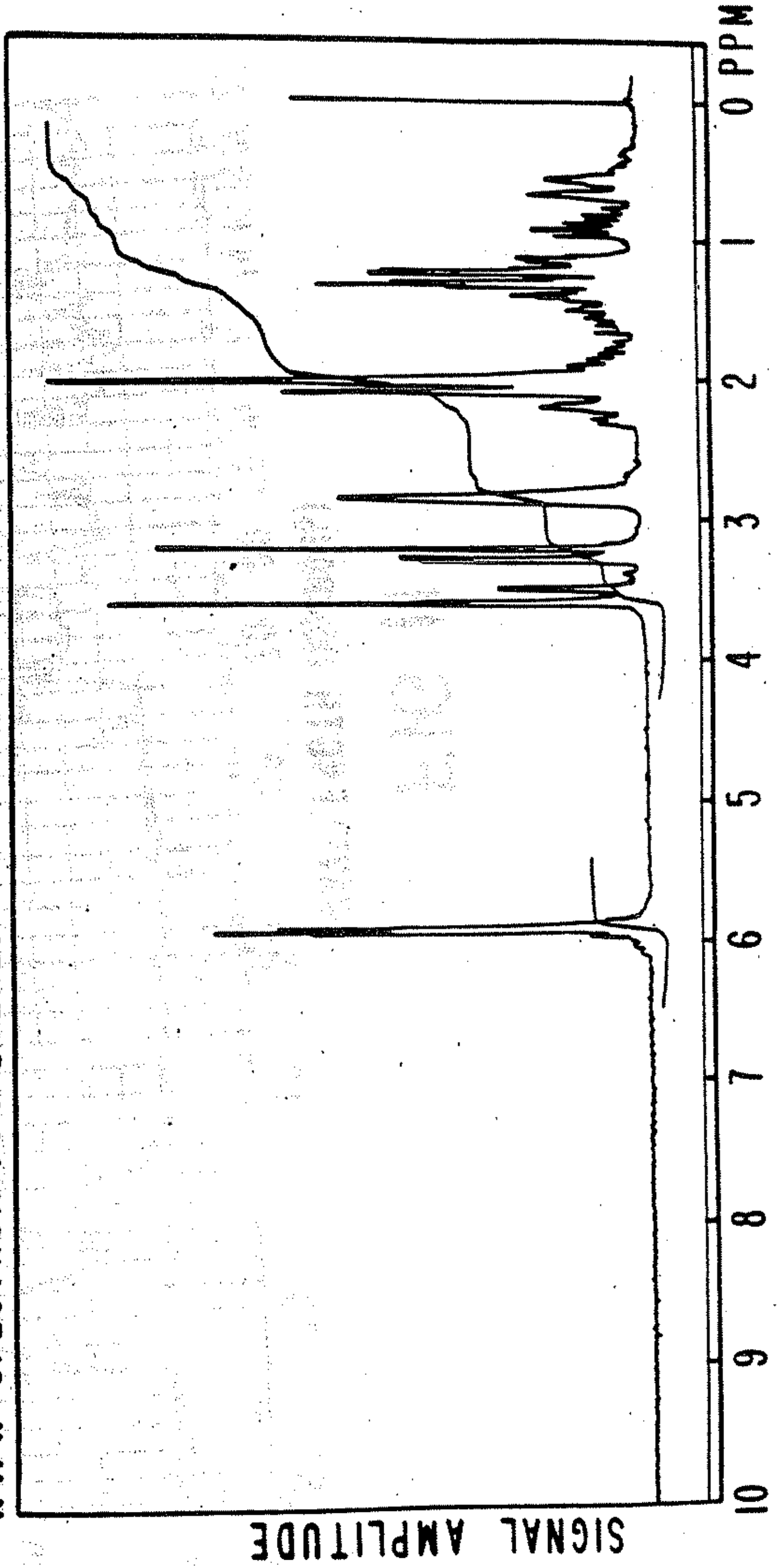
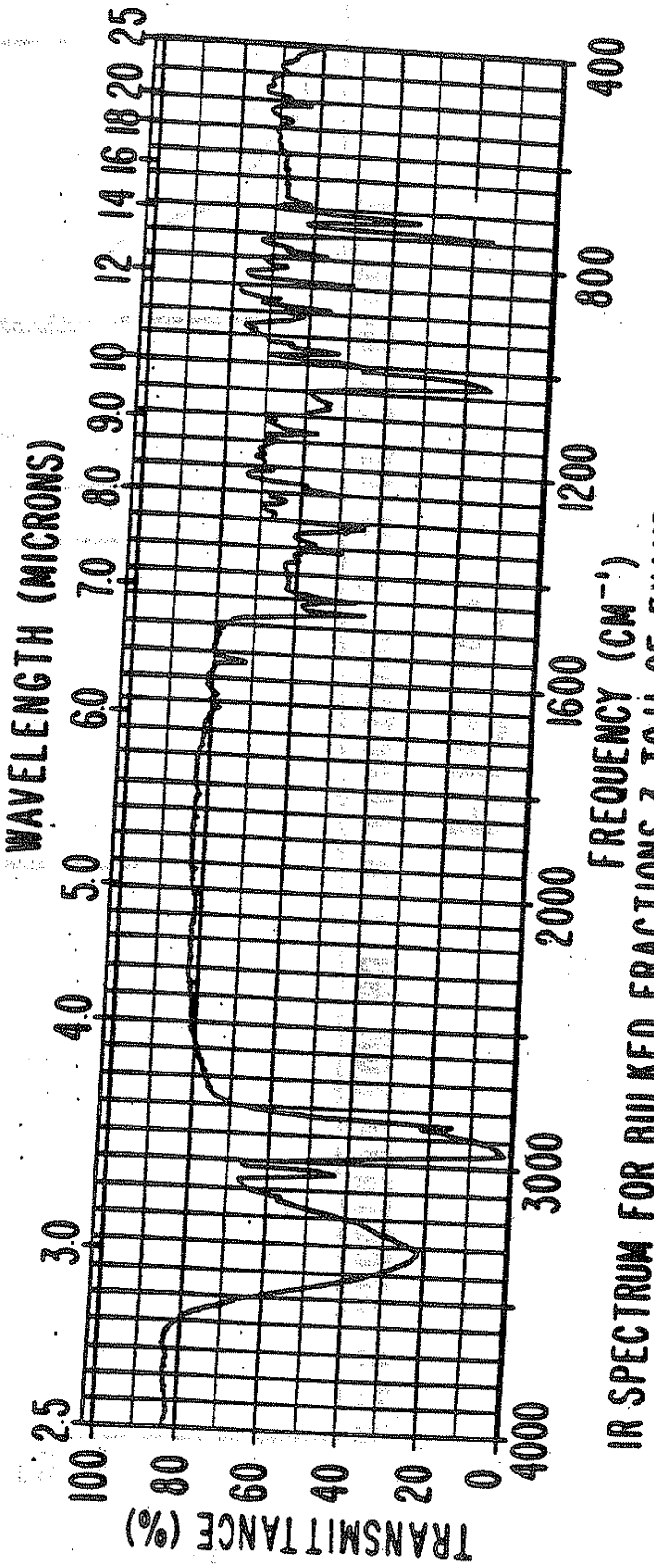
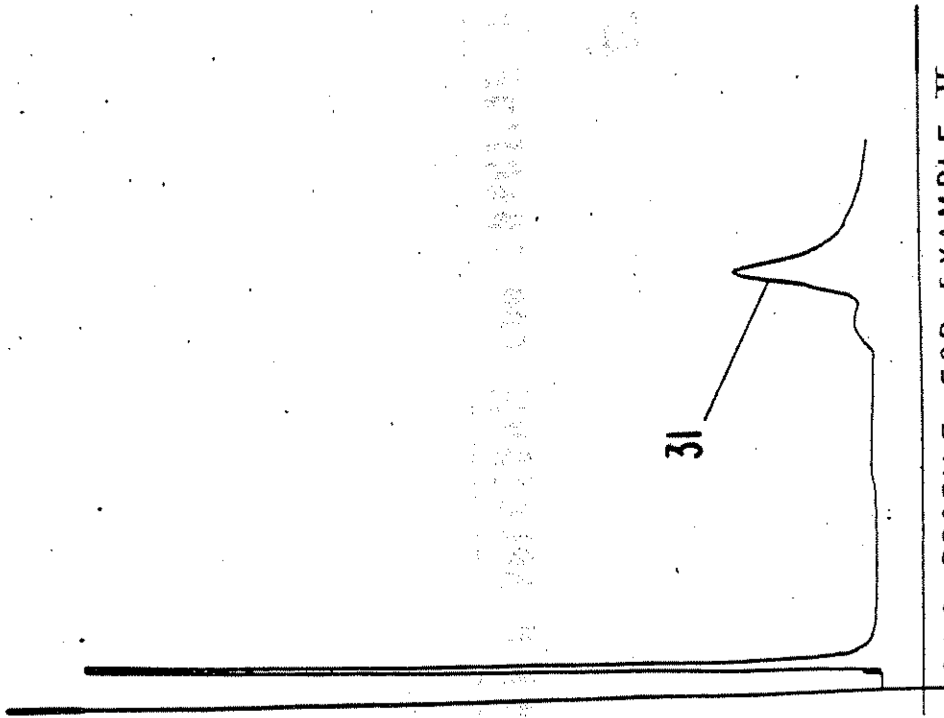


FIG. 11



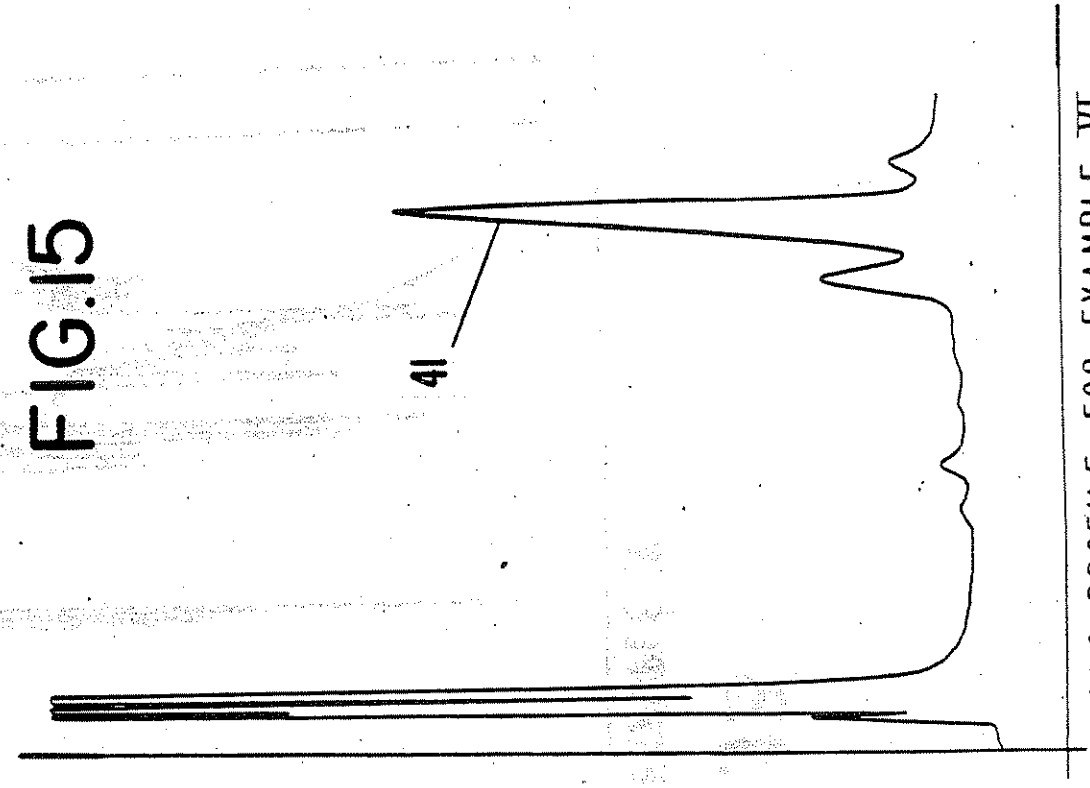
IR SPECTRUM FOR BULKED FRACTIONS 3 TO 11 OF EXAMPLE IV

FIG.12



GLC PROFILE FOR EXAMPLE V

FIG.15



GLC PROFILE FOR EXAMPLE VI

FIG.13

NMR SPECTRUM FOR FRACTION 8 OF EXAMPLE V.

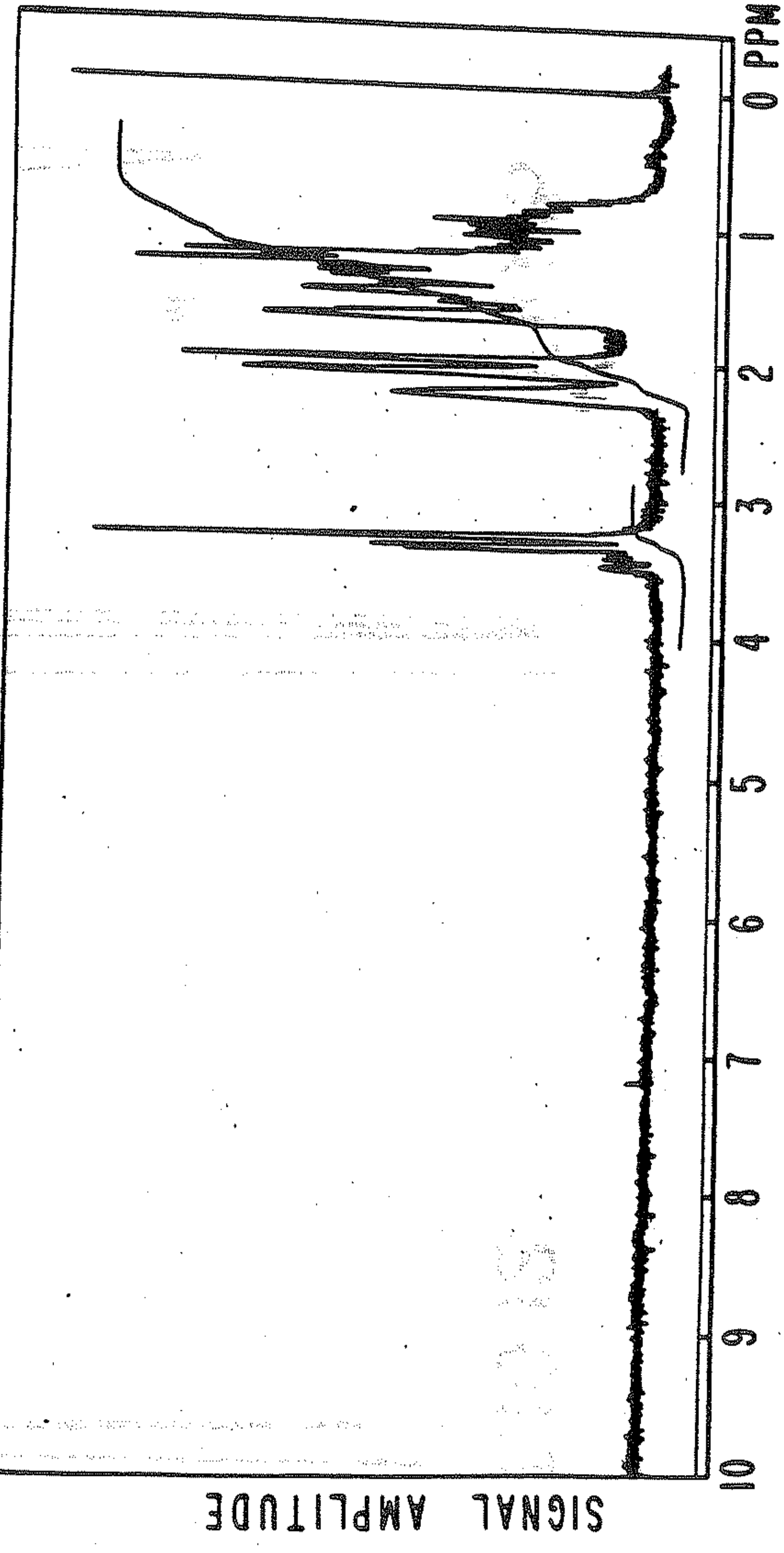
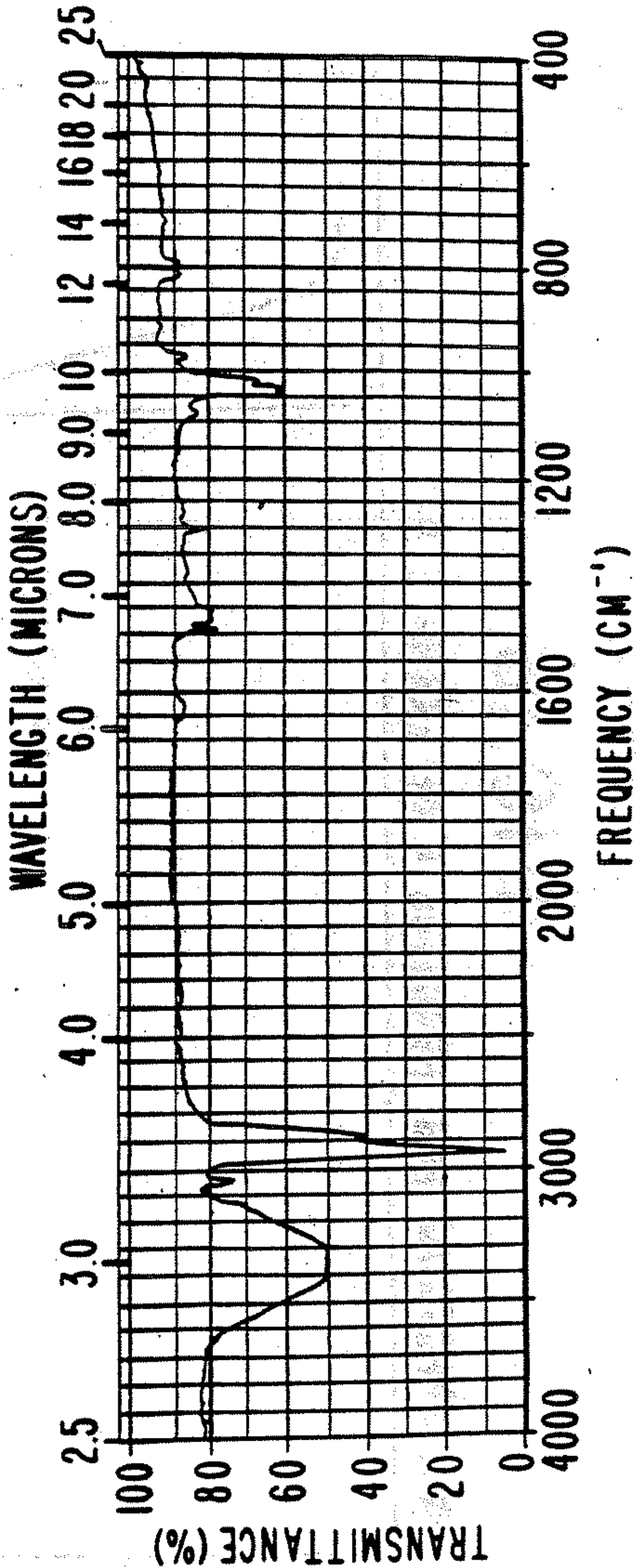


FIG. 14



IR SPECTRUM FOR FRACTION 8 OF EXAMPLE V

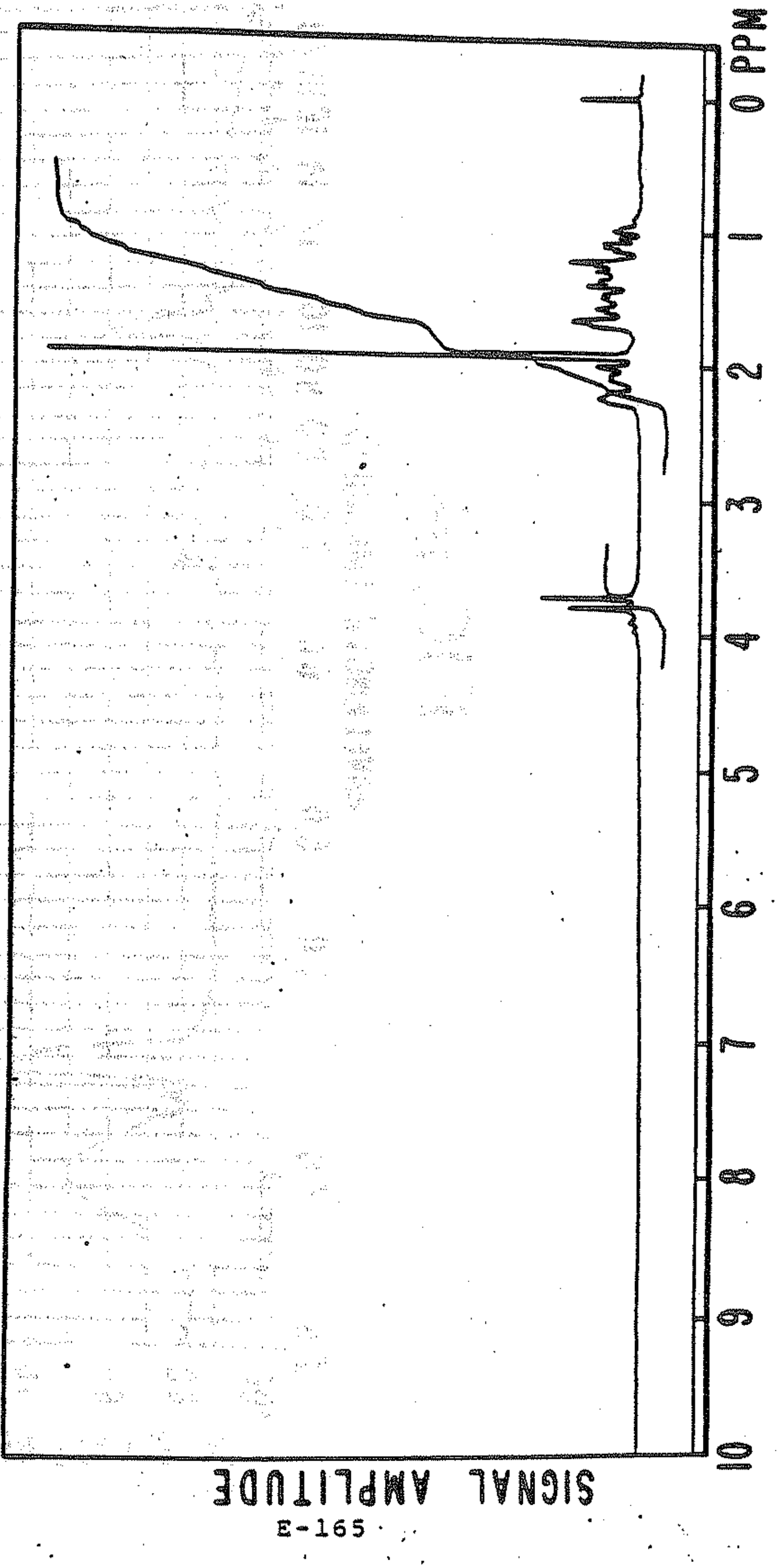
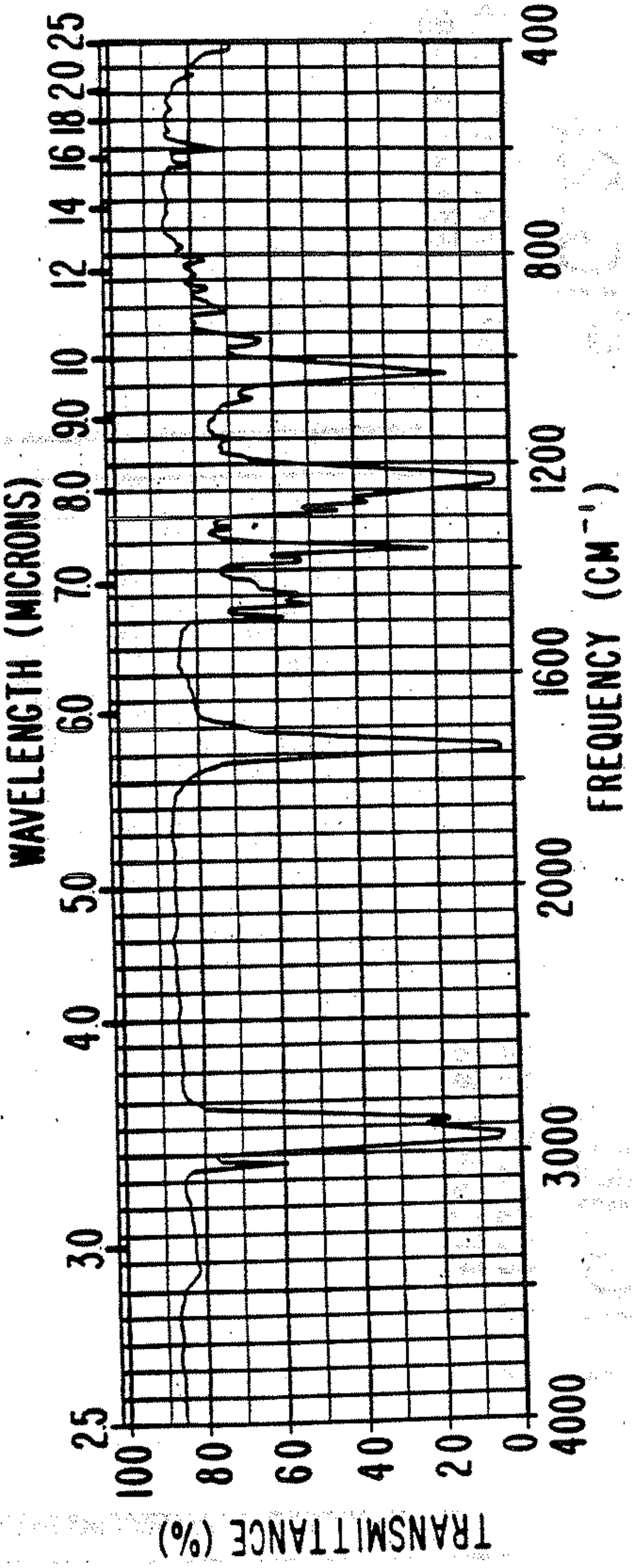


FIG. 16

NMR SPECTRUM FOR FRACTION 6 OF EXAMPLE VI.

FIG. 17



IR SPECTRUM FOR FRACTION 6 OF EXAMPLE VI

FIG.18

GLC PROFILE FOR
EXAMPLE VII.

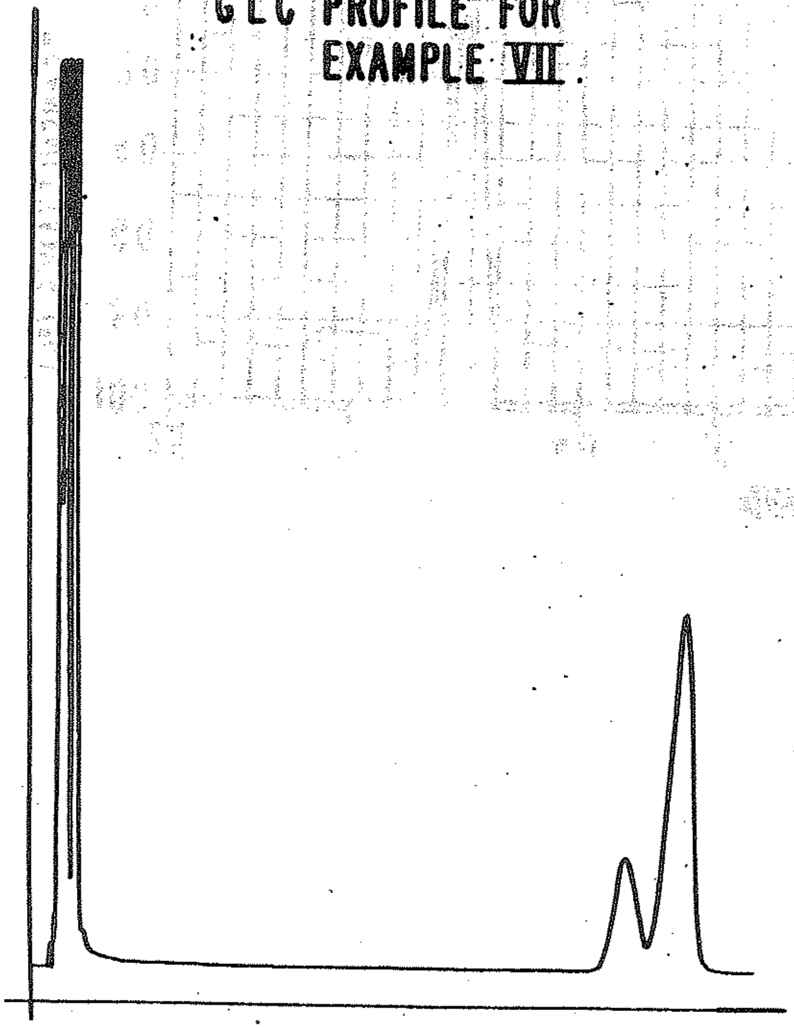


FIG.21

GLC PROFILE FOR
EXAMPLE VIII.

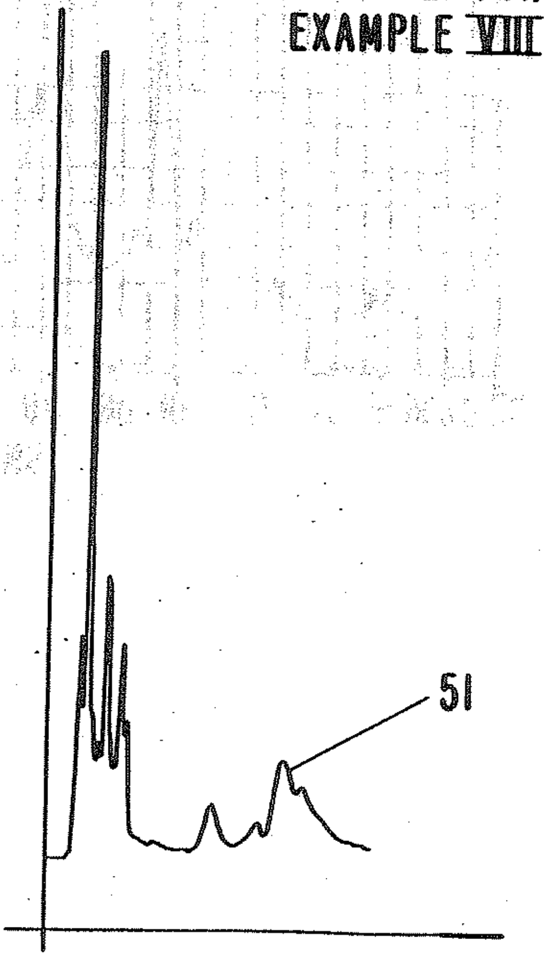


FIG.19

NMR SPECTRUM FOR FRACTION 4 OF EXAMPLE VII.

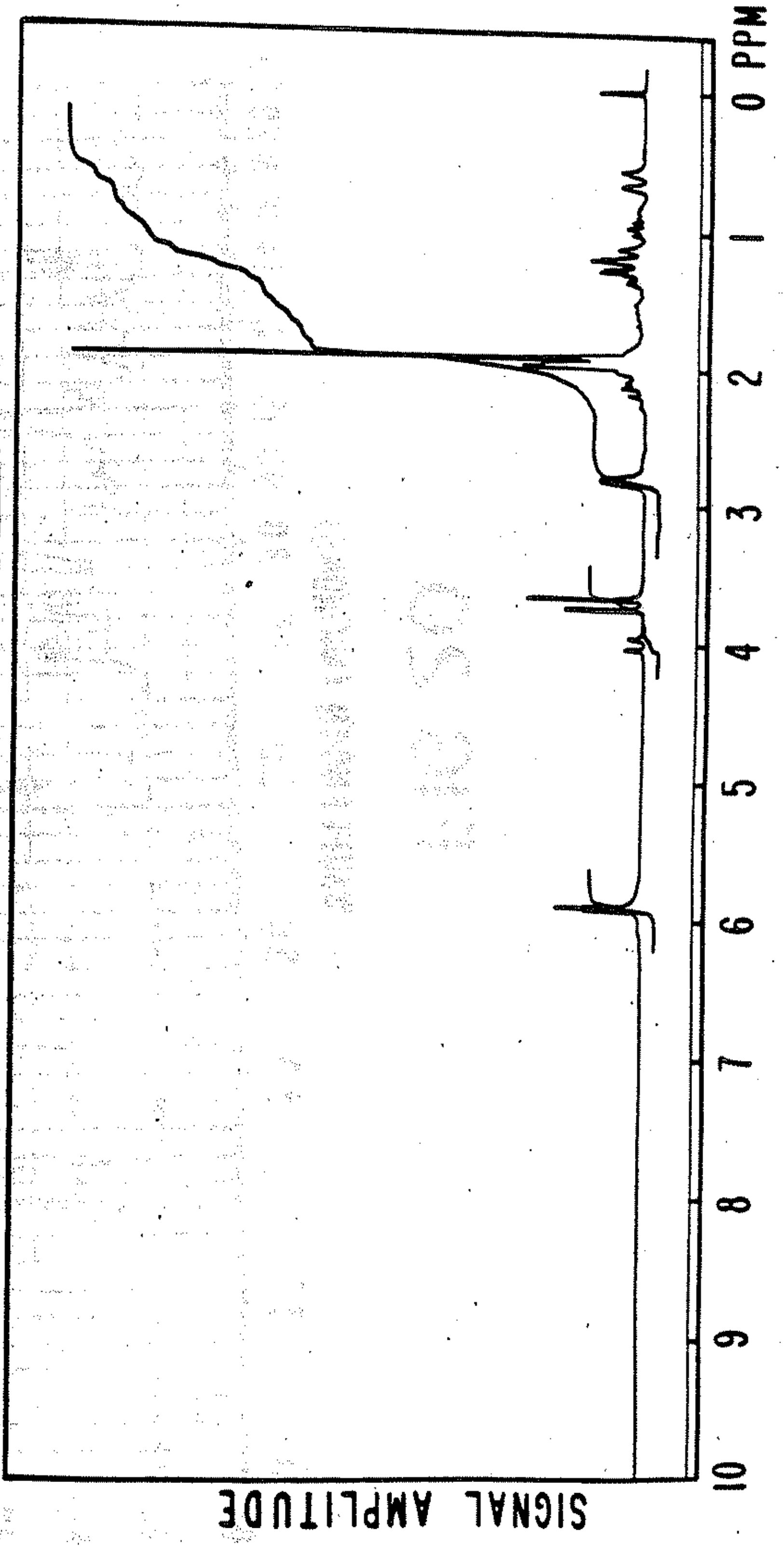
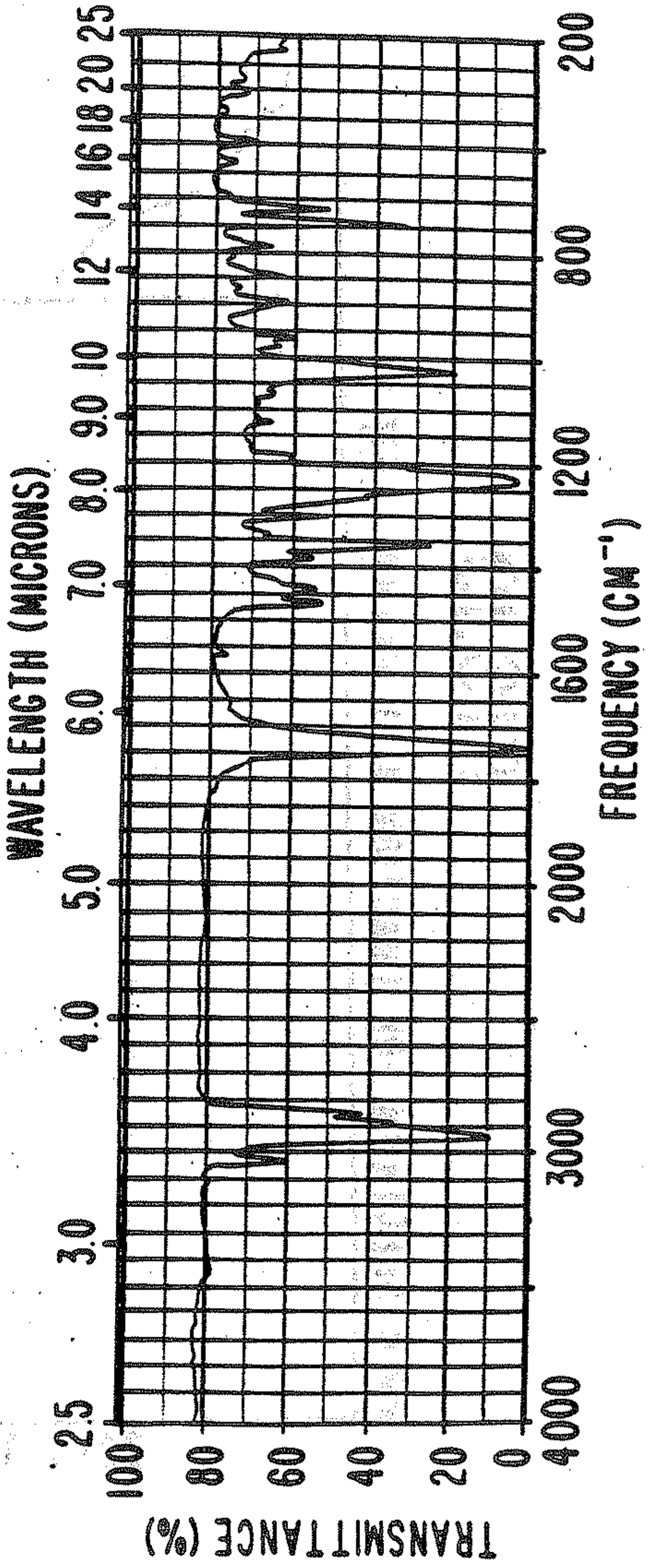


FIG. 20



IR SPECTRUM FOR FRACTION 4 OF EXAMPLE VII

FIG.22

N M R SPECTRUM FOR PEAK 51 OF FIG. 21, EXAMPLE VIII.

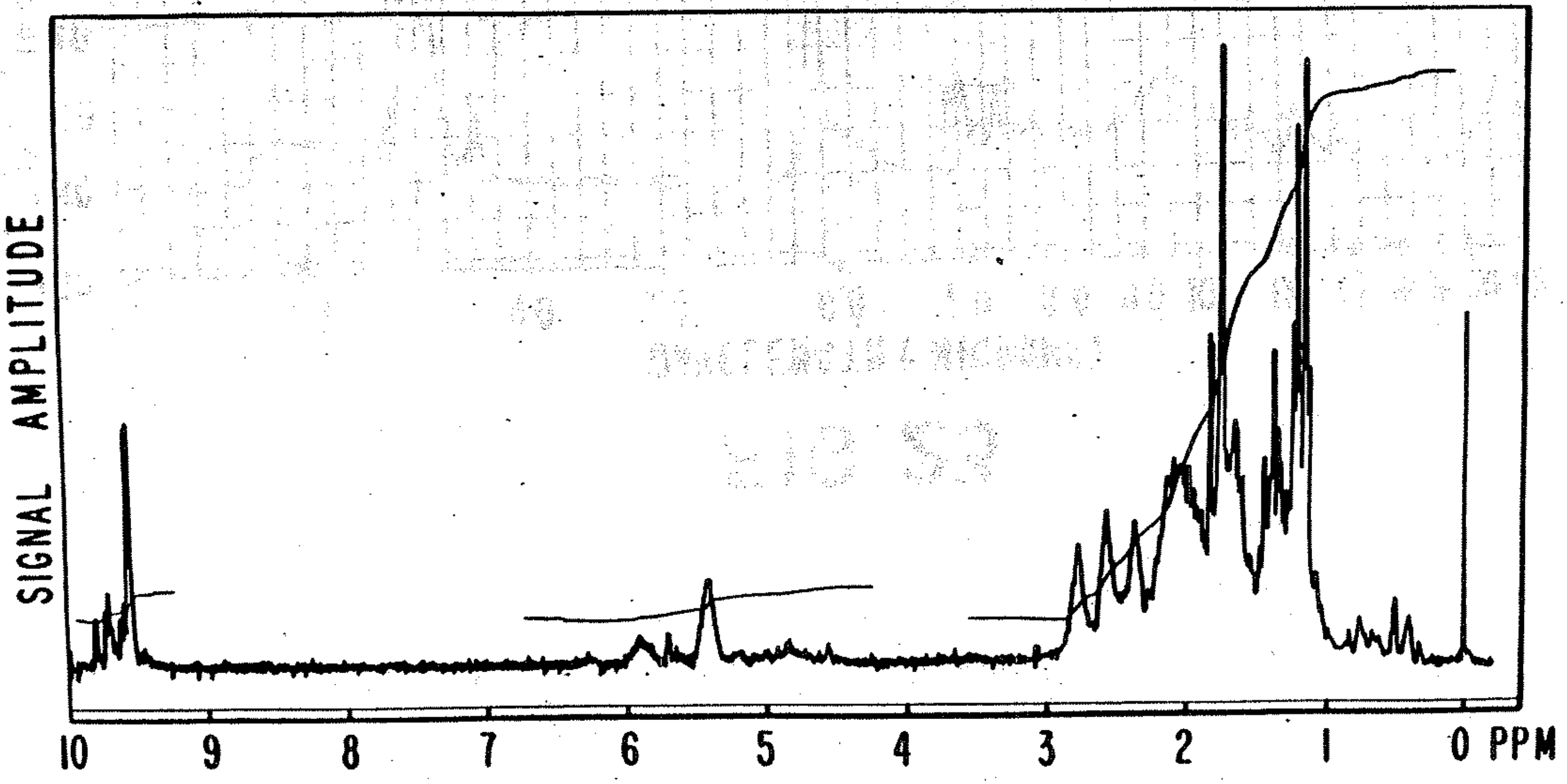
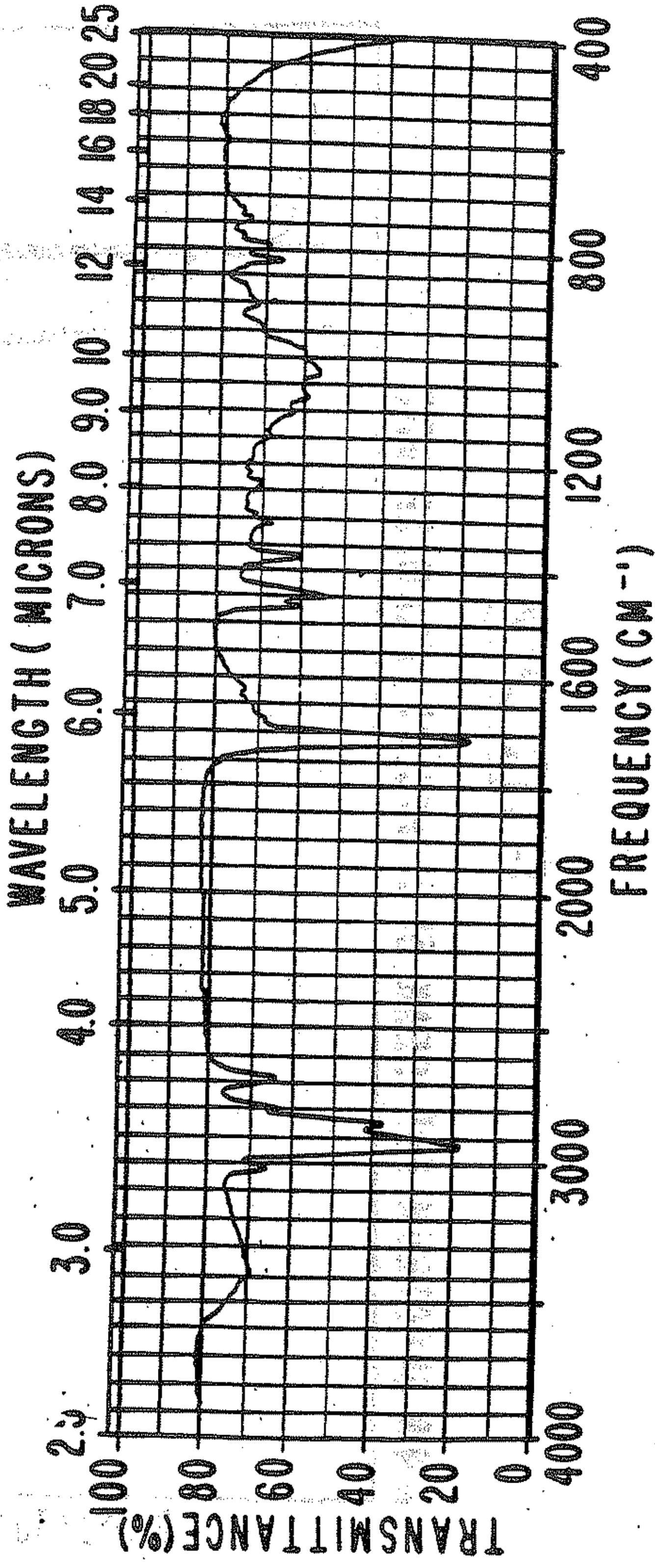


FIG. 23



IR SPECTRUM FOR PEAK 51 OF FIG. 21, EXAMPLE VIII

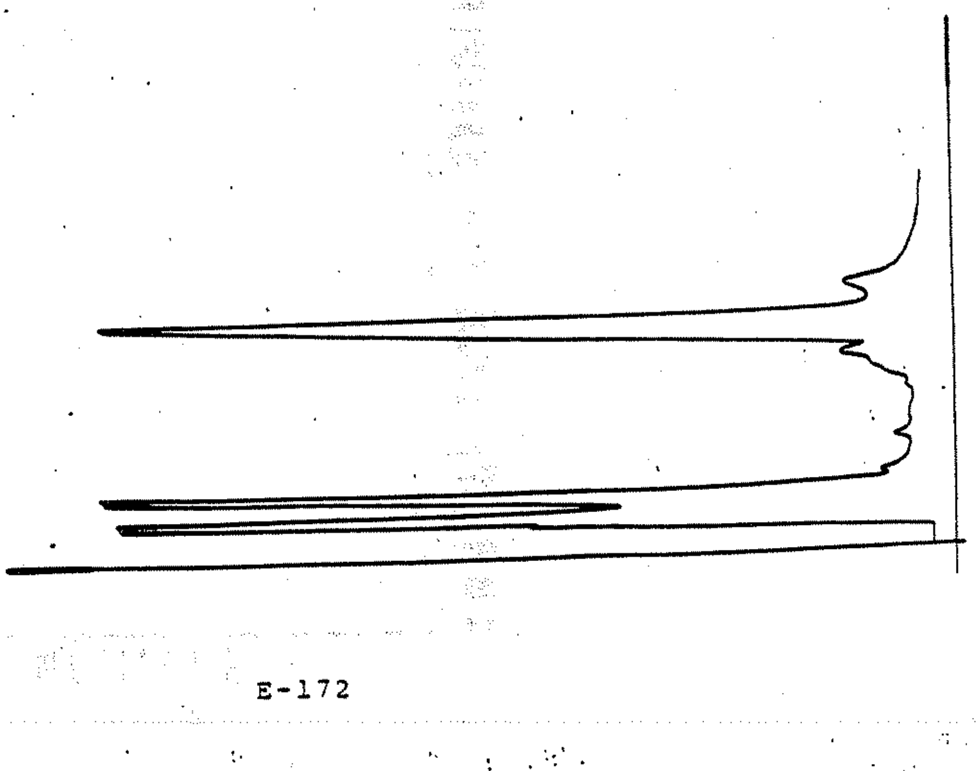


FIG. 24
GLC PROFILE FOR EXAMPLE IX

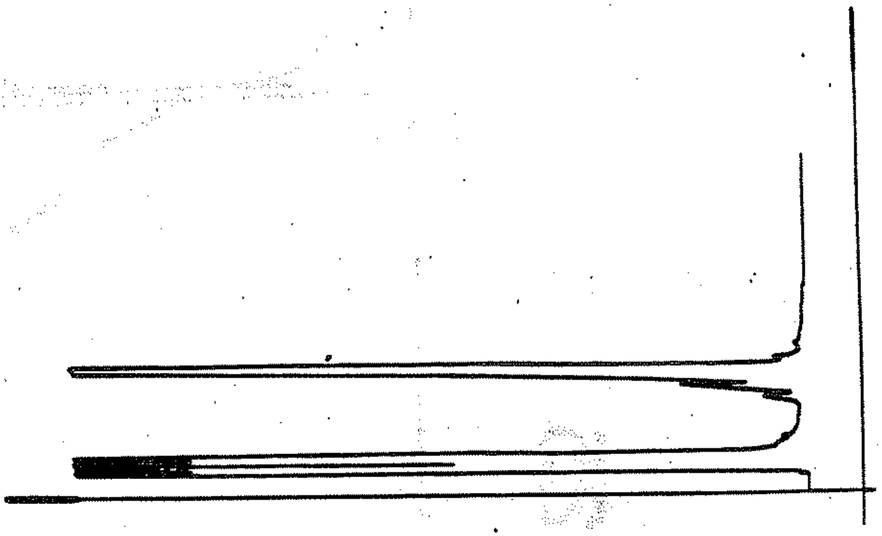


FIG. 27
GLC PROFILE FOR EXAMPLE X.

FIG.25

NMR SPECTRUM FOR EXAMPLE IX

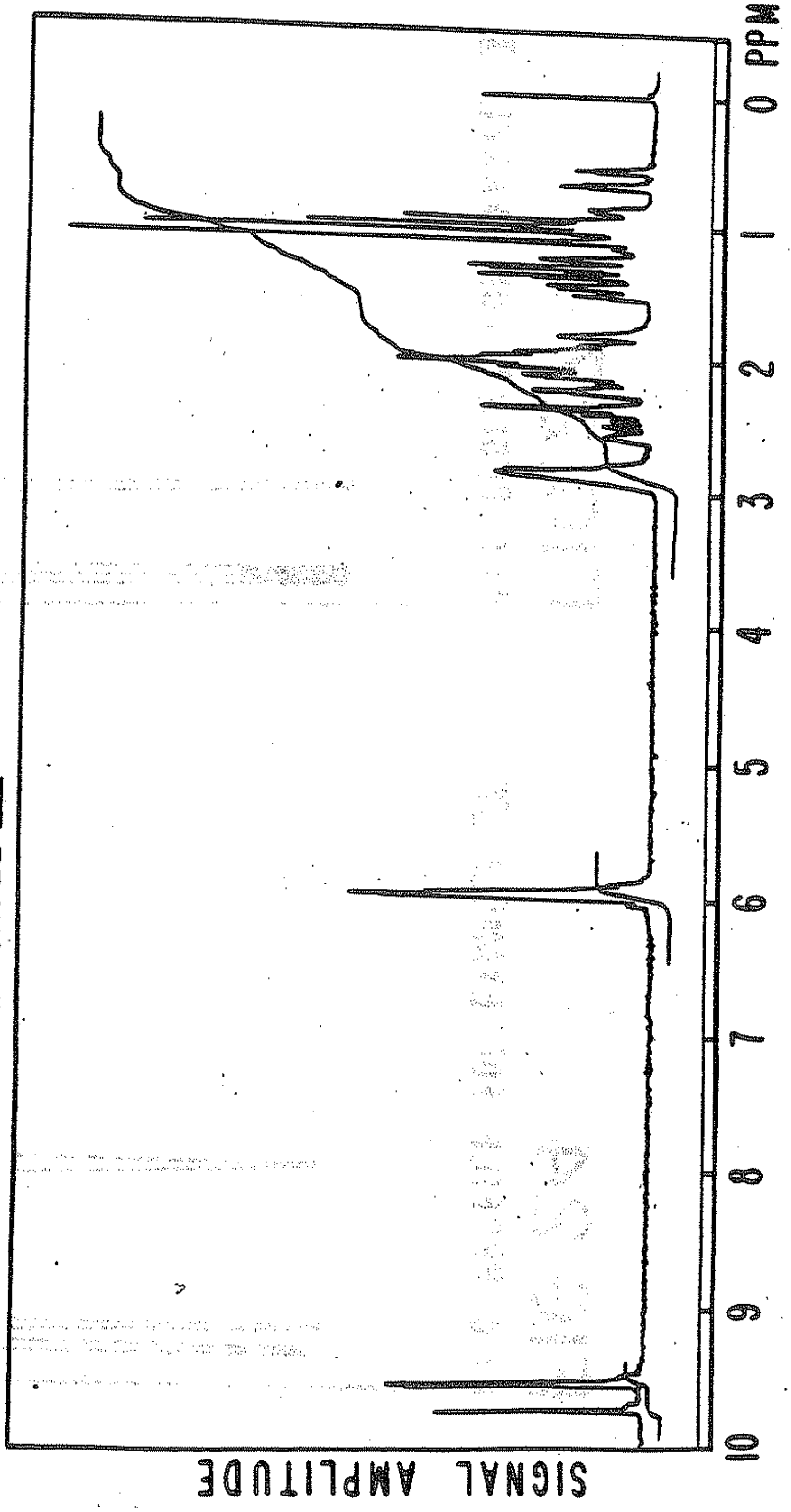
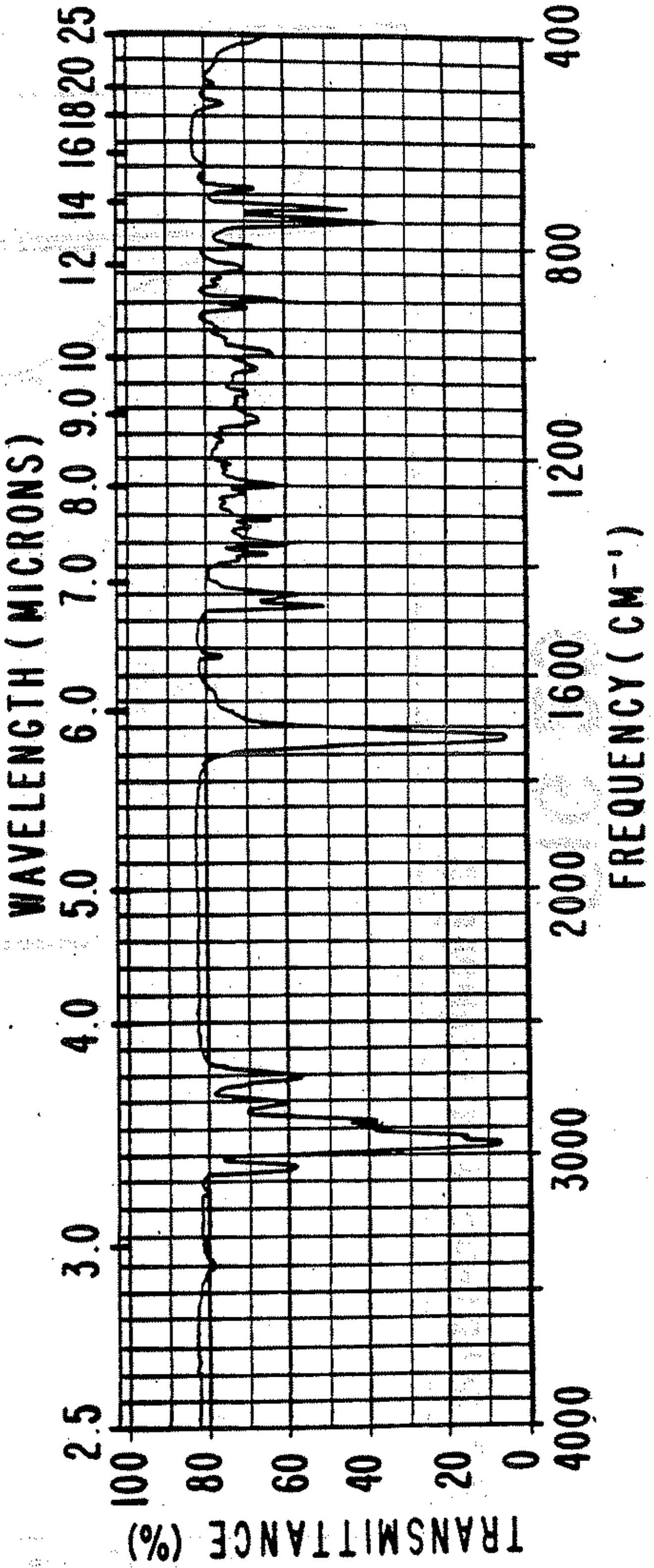


FIG.26



I R SPECTRUM FOR EXAMPLE IX

FIG. 28

NMR SPECTRUM FOR EXAMPLE X.

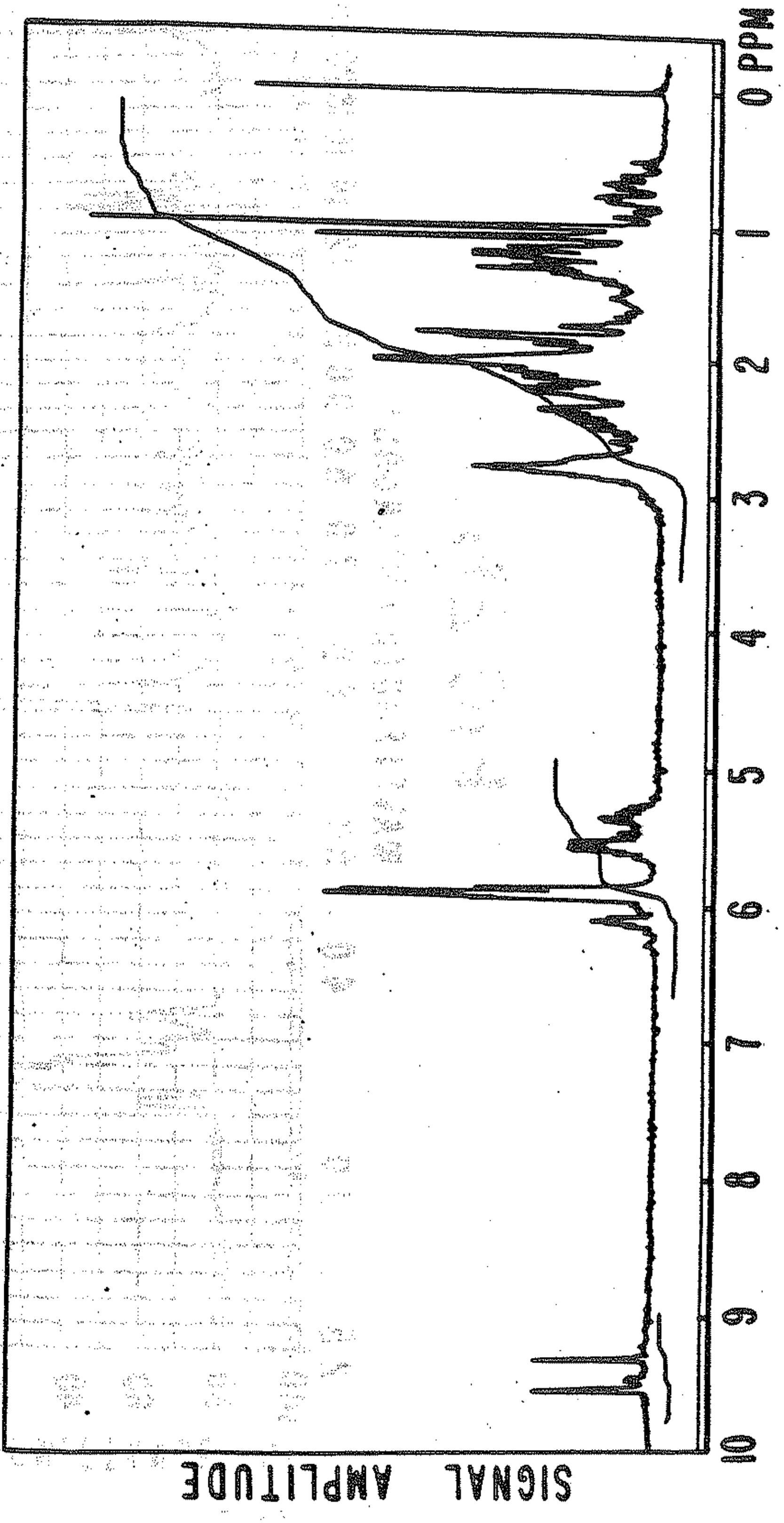
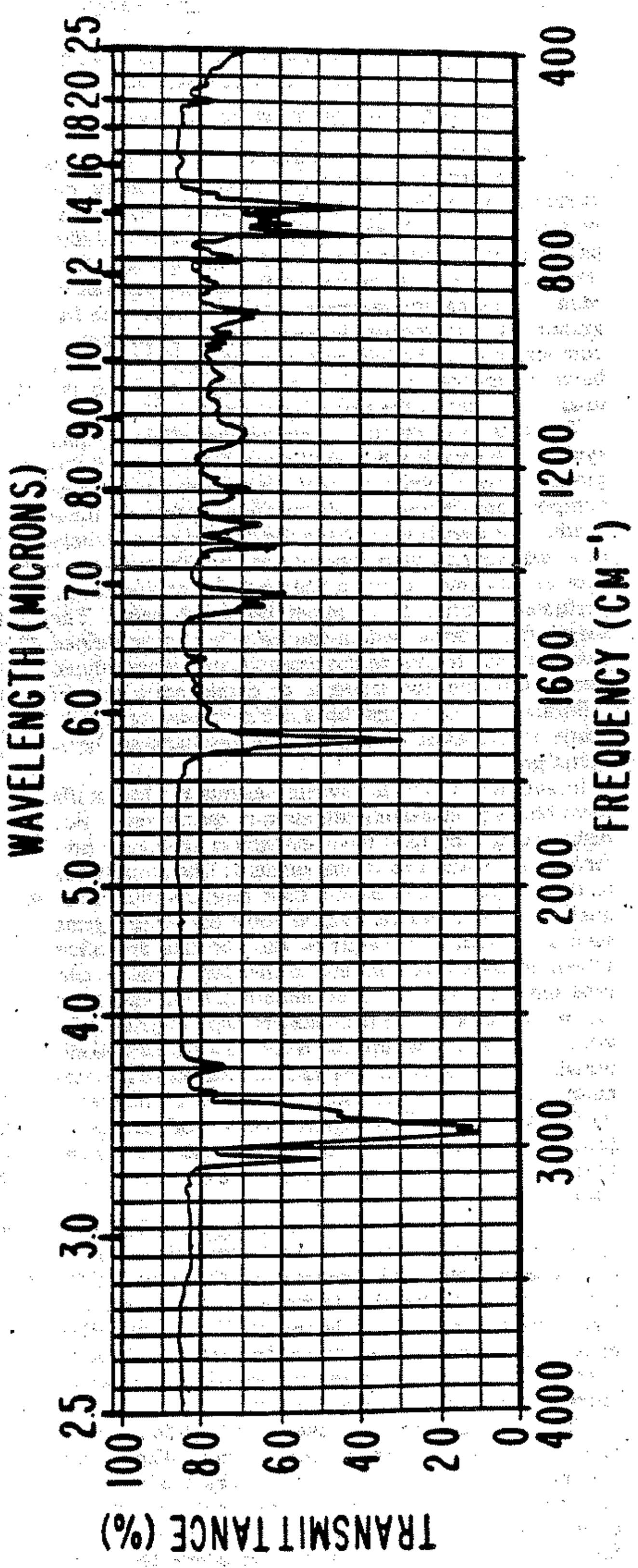


FIG. 29



IR SPECTRUM FOR EXAMPLE X

MONO-OXOMETHYL SUBSTITUTED POLYHYDRODIMETHANONAPHTHALENE DERIVATIVES, ORGANOLEPTIC USES THEREOF AND PROCESSES FOR PREPARING SAME

This is a divisional of application Ser. No. 354,387, filed Mar. 2, 1982 now U.S. Pat. No. 4,391,284.

BACKGROUND OF THE INVENTION

Materials including mixtures of natural products which can provide, augment or enhance melony, cucumber, violet-like, green, leafy green, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic and spicy fragrance notes are known in the art of perfumery. Many of the natural materials which provide such fragrances and contribute desired nuances to perfumery compositions are high in cost, vary in quality from one batch to another and/or are generally subject to the usual variations in the natural products.

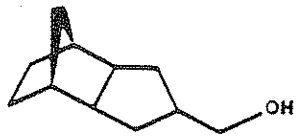
There is, accordingly, a continuing effort to find synthetic materials which will replace the essential fragrance notes provided by such natural essential oils or compositions thereof. Unfortunately, many of these synthetic materials either have the desired nuances only to a relatively small degree or else contribute undesirable or unwanted odor to the perfume compositions, perfumed articles or colognes using the same. The search for materials which can provide a more refined patchouli-like fragrance, for example, or a more refined floral fragrance, for example, or combination thereof ("floral/patchouli") has been difficult and relatively costly in the areas of both natural products and synthetic products.

In addition, artificial flavoring agents for foodstuffs have received increasing attention in recent years. For many years, such food flavoring agents have been preferred over natural flavoring agents at least in part due to their diminished costs and their reproducible flavor qualities. For example, natural food flavoring agents such as extracts, concentrates and the like are often subject to wide variations due to changes in quality, and type and treatment of the raw materials. Such variations can be reflected in the end product and result in unfavorable flavor characteristics in said end product. Additionally, the presence of the natural product in the ultimate food may be undesirable because of increased tendency to spoil. This is particularly troublesome in food and food uses where such products as dips, soups, chips, saugages, gravies and the like are apt to be stored prior to use.

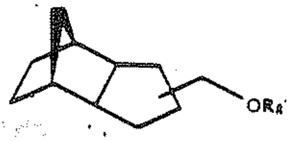
The fundamental problem in creating artificial flavor agents is that the artificial flavor to be achieved be as natural as possible. This generally proves to be a difficult task since the mechanism for flavor development in many foods is not completely known. This is noticeable in products which have orange flavors, mint flavors, peppermint flavors, and even artichoke-like flavors and corresponding aroma characteristics.

Thus, reproduction of sweet, aldehydic, floral, melony, herbaceous, green, and artichoke-like aroma and taste characteristics has been the subject of long and continuing searches by those engaged in the production of foodstuffs and beverages. The severe shortage of food in many parts of the world has given rise to the development of previously unused sources of protein which have heretofore been unpalatable. Accordingly, the need has arisen for the use of flavoring materials which will make such sources of protein palatable to human sensory organs.

The use of tricyclohydrocarbyl oxomethyl derivatives is known in the art of perfumery. Thus, U.S. Pat. No. 4,123,394 issued on Oct. 31, 1978 discloses specifically the compound having the structure:



and generically the compound having the structure:



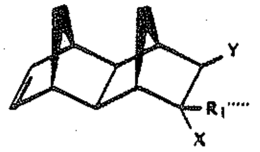
wherein R$_8$' is hydrogen, acyl, alkyl or alkenyl.

French Pat. No. 2,424,244 (corresponding to British patent application No. 2,019,841) discloses 8-exo-hydroxymethyl-endo-tricyclodecanes useful as perfumery agents in soaps, shampoos, cosmetics and waxes wherein the fragrances range from green, green grass-like, fruit-like to wood-like. The generic structure of the compounds disclosed in French Pat. No. 2,424,244 (assigned to the Kao Soap Company of Japan) is:

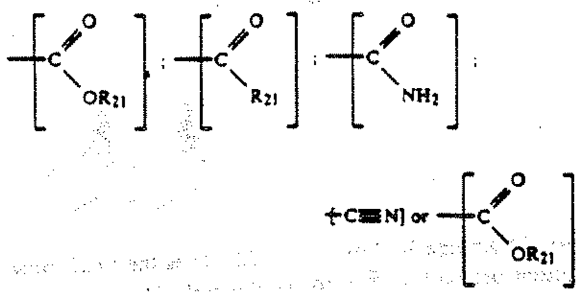
wherein R is unsaturated C_1–C_5 alkyl, C_1–C_5 acyl or glycidyl and the esters are prepared from the compound wherein R is hydrogen by means of esterification with a carboxylic acid and a mineral acid catalyst and ethers are prepared from the compound wherein R equals H using a sodium hydride/alkyl iodide compound and the glycidyl ethers are prepared from allyl ethers by treatment with peracids.

A number of the aldehydes found to be useful in our invention are known in the prior art.

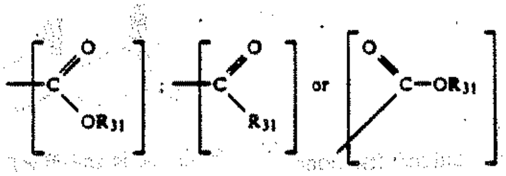
Thus, Japanese Pat. No. J76-011625 of April 1976 (assigned to Nado Research Institute Company) discloses a genus of compounds defined according to the structure:



wherein R$_1$''''' represents hydrogen, alkyl, or one of the moieties:



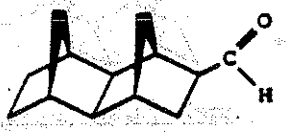
and R_{21} is hydrogen or alkyl; and wherein Y represents hydrogen, alkyl or one of the moieties:



wherein R_{31} represents hydrogen or alkyl.

In addition, Japanese Pat. No. J75-135071 abstracted at Vol. 84, Chem. Abstracts 43466h discloses the compound having the structure:

and Chem. Abstract Vol. 60, 4026g (1964) Abstract of Compt. Rend. 257 (20) 2995-8 (1963) discloses the compound having the structure:



None of the references disclosing the foregoing tetracyclic carboxaldehydes discloses their utilization for augmenting or enhancing the aroma or taste of consumable materials.

In addition, nothing in the prior art discloses the other compounds of our invention or organoleptic utilities of any mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is the GLC profile for the reaction product of Example I containing the compound having the structure:

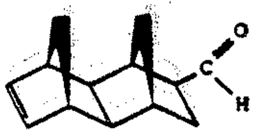


FIG. 2 is the NMR spectrum for the reaction product of Example I containing the compound having the structure:

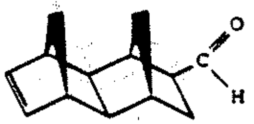


FIG. 3 is the infra-red spectrum for the reaction product of Example I containing the compound having the structure:

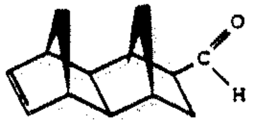


FIG. 4 is the GLC profile for the reaction product of Example II containing the compound having the structure:

FIG. 5 is the NMR spectrum for fraction 11 of the distillation product of the reaction product of Example II containing the compound having the structure:

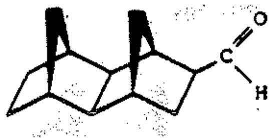


FIG. 6 is the infra-red spectrum for fraction 11 of the distillation product of the reaction product of Example II containing the compound having the structure:

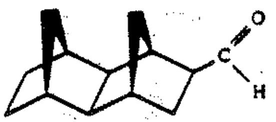


FIG. 7 is the GLC profile for the reaction product of Example III containing the compound having the structure:

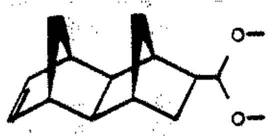


FIG. 8 is the NMR spectrum for Peak 13 of the GLC profile of FIG. 7 for the reaction product of Example III containing the compound having the structure:

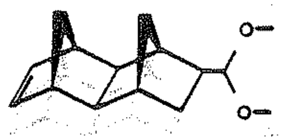


FIG. 9 is the GLC profile for bulked fractions 3-11 of the distillation product of the reaction product of Example IV containing the compound having the structure:

FIG. 10 is the NMR spectrum for bulked fractions 3-11 of the distillation product of the reaction product of Example IV containing the compound having the structure:

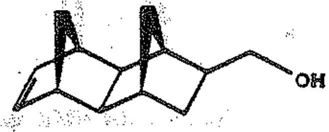


FIG. 11 is the infra-red spectrum for bulked fractions 3-11 of the distillation product of the reaction product of Example IV containing the compound having the structure:

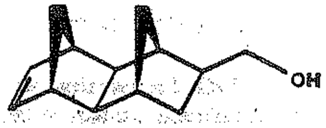


FIG. 12 is the GLC profile for the reaction product of Example V containing the compound having the structure:

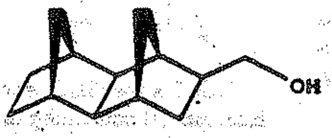


FIG. 13 is the NMR spectrum for fraction 8 of the distillation product of the reaction product of Example V containing the compound having the structure:

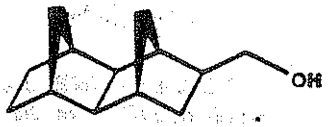


FIG. 14 is the infra-red spectrum for fraction 8 of the distillation product of the reaction product of Example V containing the compound having the structure:

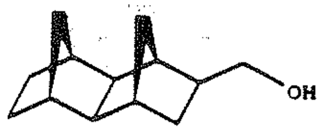


FIG. 15 is the GLC profile for the reaction product of Example VI containing the compound having the structure:

FIG. 16 is the NMR spectrum for fraction 6 of the distillation product of the reaction product of Example VI containing the compound having the structure:

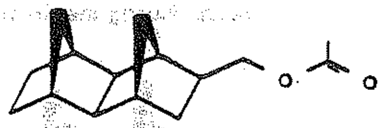


FIG. 17 is the infra-red spectrum for fraction 6 of the distillation product of the reaction product of Example VI containing the compound having the structure:

FIG. 18 is the GLC profile for the reaction product of Example VII containing the compound having the structure:

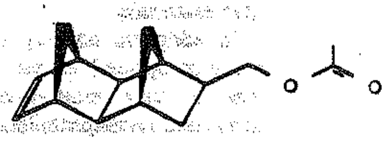


FIG. 19 is the NMR spectrum for fraction 9 of the distillation product of the reaction product of Example VII containing the compound having the structure:

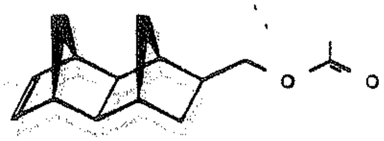


FIG. 20 is the infra-red spectrum for fraction 9 of the distillation product of the reaction product of Example VII containing the compound having the structure:

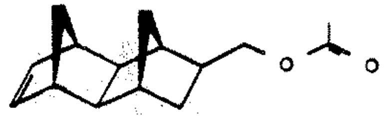
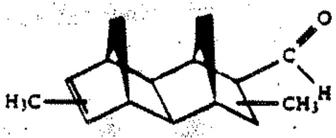


FIG. 21 is the GLC profile for the reaction product of Example VIII containing a mixture of compounds defined according to the structures:



and

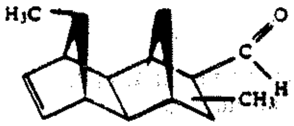
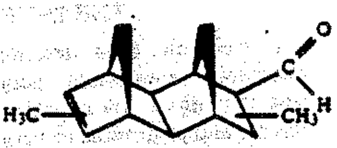


FIG. 22 is the NMR spectrum for Peak 51 of the GLC profile of FIG. 21 for the mixture of compounds defined according to the structures:



and

FIG. 23 is the infra-red spectrum for Peak 51 of the GLC profile of FIG. 21 for the reaction product of Example VIII containing a mixture of compounds defined according to the structures:

and

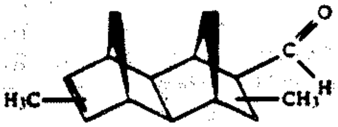


FIG. 24 is the GLC profile for the reaction product of Example IX containing the compound defined according to the structure:

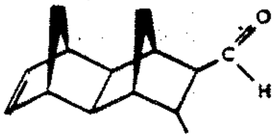


FIG. 25 is the NMR spectrum for the distillation product of the reaction product of Example IX containing the compound having the structure:

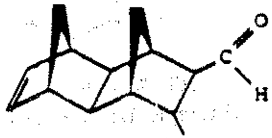


FIG. 26 is the infra-red spectrum for the distillation product of the reaction product of Example IX containing the compound having the structure:

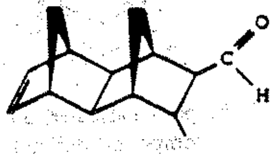


FIG. 27 is the GLC profile for the reaction product of Example X containing the compound having the structure:

FIG. 28 is the NMR spectrum for the distillation product of the reaction product of Example X containing the compound having the structure:

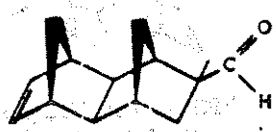
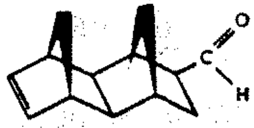


FIG. 29 is the infra-red spectrum for the distillation product of the reaction product of Example X containing the compound having the structure:

DETAILED DESCRIPTION OF THE DRAWINGS

FIG. 1 is the GLC profile for the reaction product of Example I containing the compound having the structure:



The peak indicated by the reference numeral 1 is the peak for the compound having the structure:

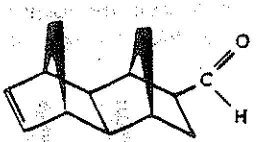
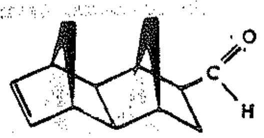
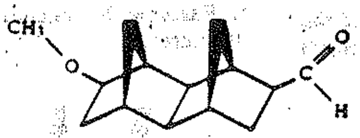


FIG. 7 is the GLC profile for reaction product of Example III. The peak indicated by the reference numeral 11 is for the compound defined according to the structure:



The peak indicated by the reference numeral 12 is for the compound defined according to the structure:



The peak indicated by the reference numeral 13 is for the reaction product defined according to the structure:

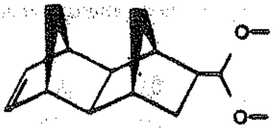


FIG. 9 is the GLC profile for the reaction product of Example IV, bulked distillation fractions 3–11. The peak indicated by the reference numeral 21 is for the reaction product having the structure:

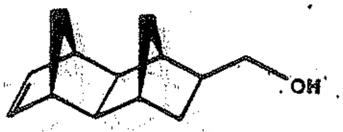


FIG. 12 is the GLC profile for the reaction product of Example V. The peak indicated by the reference numeral 31 is for the reaction product having the structure:

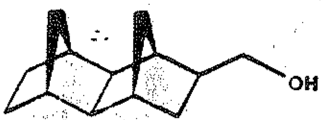


FIG. 15 is the GLC profile for the reaction product of Example VI. The peak indicated by the reference numeral 41 is for the reaction product having the structure:

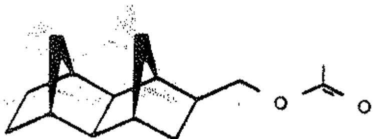
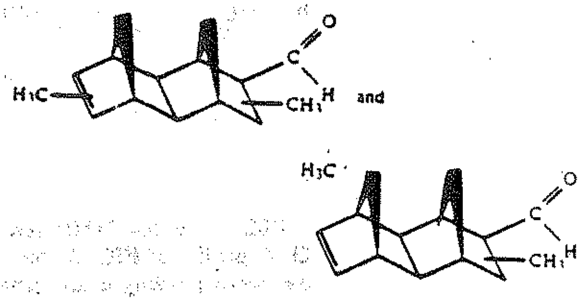


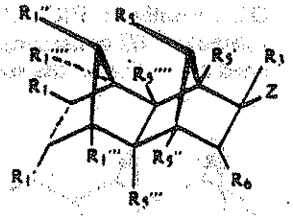
FIG. 21 is the GLC profile for the reaction product of Example VIII. The peak indicated by the reference numeral 51 is for the reaction product which is a mixture of compounds defined according to the structures:



THE INVENTION

It has now been determined that certain mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives are capable of imparting a variety of flavors and fragrances to various consumable materials.

Briefly, our invention contemplates augmenting or enhancing the flavors and/or fragrances of such consumable materials by adding thereto a small but effective amount of at least one such mono-oxomethyl substituted polyhydrodimethanonaphthalene derivative defined according to the generic structure:



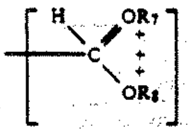
wherein the dashed line represents a carbon-carbon single bond or a carbon-carbon double bond; wherein R_1, R_1', R_1'', R_1''', R_1'''', R_3, R_5, R_5', R_5'', R_5''', R_5'''' and R_6 represent hydrogen or methyl with the provisos:

(i) at least four of R_1, R_1', R_1'', R_1''' and R_1'''' are hydrogen and (ii) at least four of R_5, R_5', R_5'', R_5''' and R_5'''' represent hydrogen;

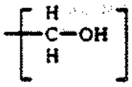
and wherein Z represents one of the moieties:

(i) carboxaldehyde having the structure:

(ii) alkylene dioxy or dialkoxy methyl having the structure:



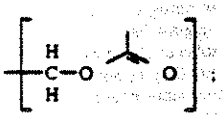
(iii) hydroxymethyl having the structure:



$$\left[-\overset{H}{\underset{H}{C}}-OH\right]$$

; or

(iv) acetoxymethyl having the structure:



;

and wherein R_7 and R_8 taken separately represent C_1–C_4 lower alkyl or R_7 and R_8 taken together represent C_2–C_4 aklylene; wherein the line represented by:

[++++]

is either a carbon-carbon single body when R_7 and R_8 taken together are C_2–C_4 alkylene or no bond at all when R_7 and R_8 taken separately represent C_1–C_4 lower alkyl.

Also described are processes for preparing such monooxomethyl substituted polyhydrodimethanonaphthalene derivatives, and processes for using the above defined mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives for their organoleptic properties and compositions containing said mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives including perfumes, perfumed articles such as solid or liquid anionic, cationic, nonionic or zwitterionic detergents, perfumed polymers, fabric softeners and cosmetic powders; and foodstuffs, chewing gums, toothpastes, medicinal products, chewing tobaccos, smoking tobaccos and smoking tobacco articles; and flavoring compositions (e.g., for foodstuffs, chewing gums, chewing tobaccos, medicinal products, toothpastes and smoking tobaccos) and fragrance compositions (e.g., for perfume compositions and compositions for augmenting or enhancing the aroma of perfumed articles such as solid or liquid anionic, cationic, nonionic or zwitterionic detergents or fabric softeners or fabric softener articles or cosmetic powders or perfumed polymers) containing such mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives.

The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives produced according to the processes of our invention which are used in practicing that part of our invention concerning flavoring and fragrance compositions are actually racemic mixtures rather than individual optical isomers such as is the case concerning isomers of patchouli alcohol which are obtained from patchouli oil.

The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention insofar as their fragrance profiles are concerned have intense and long lasting melony, cucumber, violet-like, green, leafy, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic and spicy aromas. Insofar as their flavor uses are concerned (e.g., foodstuffs, chewing gums, medicinal products, chewing tobaccos and toothpastes) the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention have sweet, aldehydic, floral, melony, herbaceous, green and artichoke-like aroma and taste profiles.

Insofar as smoking tobacco flavors are concerned the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention have sweet, floral and green aroma profiles prior to smoking and sweet, floral and aramatic aroma and taste nuances on smoking both in the main stream and in the side stream.

The following table sets forth the structure and organoleptic property profiles for specific compounds according to the examples listed herein and located infra:

TABLE I

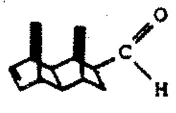
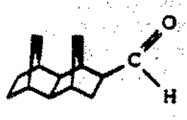
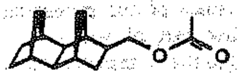
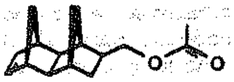
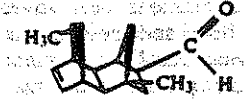
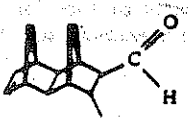
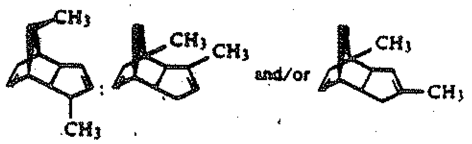
Structure of Compound	Fragrance Profile	Food Flavor Profile	Tobacco Flavor Profile
 Produced according to Example I.	A melony, cucumber-like, violet-like, green, herbaceous, wormwood-like, and floral aroma.	Sweet, aldehydic, floral, melony and herbaceous aroma at 0.0001 ppm.	A sweet, floral, herbaceous aroma prior to smoking and a sweet, floral and aramatic flavor and taste on smoking in both the main stream and the side stream.
 Produced according to Example II.	A floral, fruity (melony) cinnamic aroma.	A sweet, melony, cinnamon-like, aroma and taste profile.	A cinnamon/floral aroma prior to smoking and intense cinnamon-like nuances and aramatic tobacco notes on smoking in both the main stream and the side stream.

TABLE I-continued

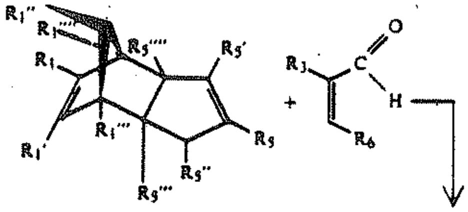
Structure of Compound	Fragrance Profile	Food Flavor Profile	Tobacco Flavor Profile
 Produced according to Example IV.	A sandalwood-like-patchouli-like and vetiver-like aroma profile.	A walnut-like aroma and taste profile.	A nutty/tobacco nuances prior to smoking and woody aroma and taste nuances on smoking in the main stream and the side stream.
 Produced according to Example VI.	A floral, fruit (pineapple) aroma profile.	An intense pineapple aroma and taste profile.	A sweet, floral, fruity aroma and taste prior to smoking and fruity virginia-like tobacco notes on smoking in both the main stream and the side stream.
 Produced according to Example VII.	A sweaty, musk-like aroma profile.	A green, artichoke-like aroma and taste profile.	—
 and  Produced according to Example VIII, infra.	An animalic, leafy, green, herbaceous, floral and violet-like aroma profile with cinnamic and cucumber-like undertones.	A green, melony, minty, herbaceous and floral aroma and taste profile at 2 ppm.	A minty tobacco nuance prior to smoking and minty cooling-like notes on smoking in both the main stream and the side stream.
 Produced according to Example X.	A spicy cinnamic-like aroma.	A spicy, cinnamon-like aroma and taste profile.	A spicy, cinnamon-like aroma and taste profile prior to smoking and spicy turkish oriental-like tobacco nuances on smoking in the main stream and the side stream.

The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives produced according to the process of our invention which are used in practicing that part of our invention concerning flavor and fragrance compositions may be mixtures of isomers or they may be substantially pure forms of exo or endo isomers or specific stereoisomers such as in the case concerning isomers of patchouli alcohol which are obtained from patchouli oil.

The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives prepared according to our invention can be obtained by reacting bicyclopentadiene or dimethyl bicyclopentadiene having the structures:



with an acrolein derivative according to the reaction:



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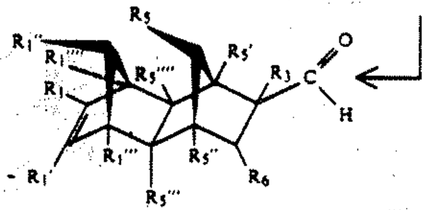
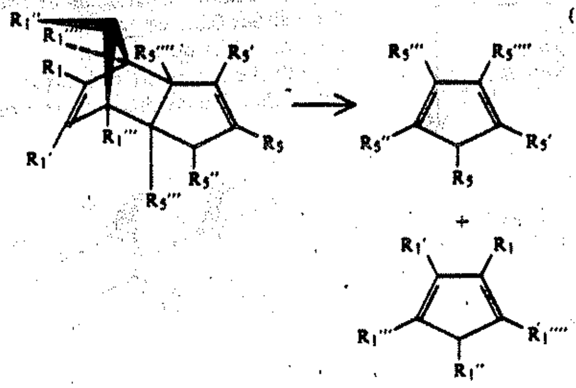


wherein R_1, R_1', R_1'', R_1''', R_1'''', R_3, R_5, R_5', R_5'', R_5''', and R_5'''' are defined, supra. The reaction is carried out at pressures in the range of from about 150 psig up to about 500 psig and at temperatures in the range of from about 150° C. up to about 250° C. in the presence of or in the absence of an inert solvent. When the solvent is used it is preferred to use a solvent such as toluene or xylene which can easily be separated from the reaction mass after the completion of the reaction. The ratio of bicyclopentadiene derivative-acrolein derivative may vary from about 0.5:1 up to about 1:0.5 with the preferred mole ratio being about 1:1. The concentration of reactant in the reaction mass may vary from about 100 grams per liter up to about 500 grams per liter. At the end of the reaction the pressure vessel is opened and the contents are distilled preferably by means of fractional distillation. The reaction product can be used "as is" for its organoleptic properties or it may be further reacted as set forth, infra.

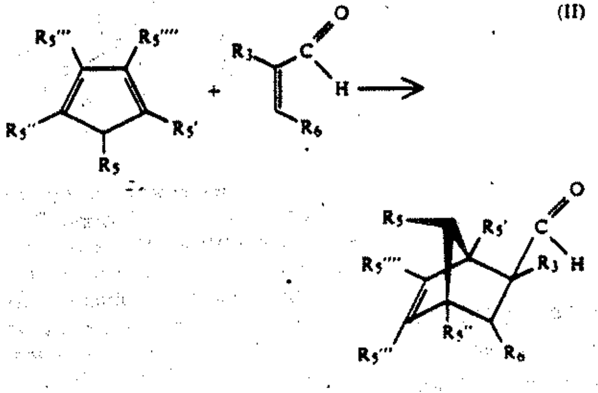
The mechanism for this reaction is as follows:

(I)



followed by:

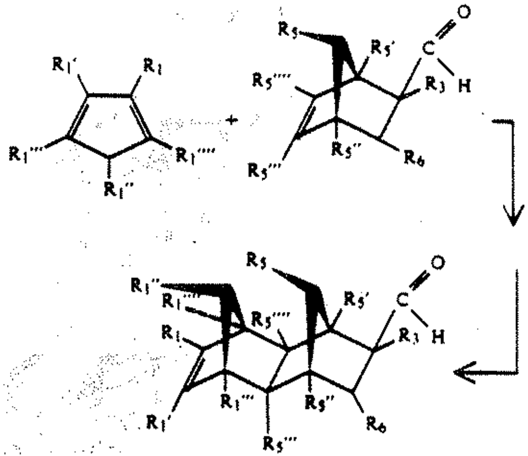
(II)



followed by:

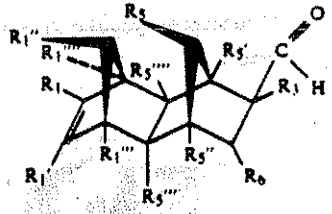
-continued

(III)



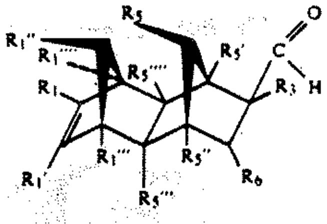
wherein R_1, R_1', R_1'', R_1''', and R_1'''' and R_3, R_5, R_5', R_5'' R_5''', R_5'''' and R_6 are defined, supra.

The resulting aldehyde defined according to the structure:

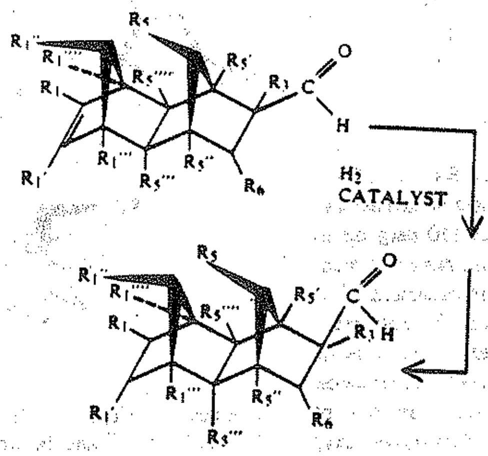


may then be reduced to form the corresponding saturated polycyclic carboxaldehydes or unsaturated polycyclic carboxaldehydes or saturated polycyclic carbinols or unsaturated polycyclic carbinols or the resulting aldehyde may be then reacted with an alkanol or alkanediol to form polycyclic carbinyl acetals, or cyclic acetals. In turn, the resulting carbinols may be acylated as with acetic anhydride or acetyl chloride or acetyl bromide to form the corresponding saturated polycyclic carbinol acetates or unsaturated polycyclic carbinol acetates.

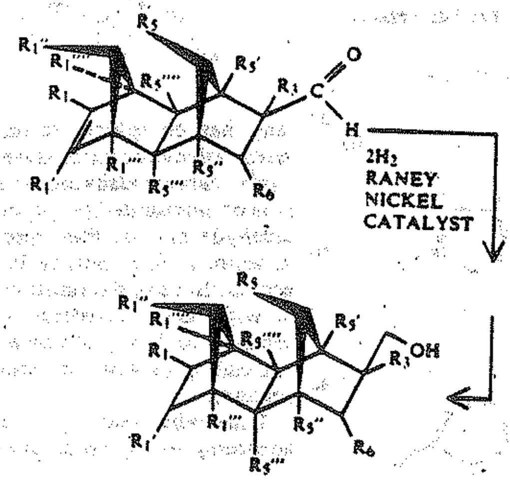
Thus, when reacting the aldehyde derivative defined according to the genus having the structure:



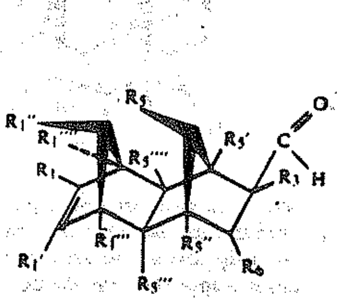
with one mole of hydrogen per mole of aldehyde at a pressure in the range of from about 50 psig up to about 200 psig and in the presence of a catalyst such as palladium supported on carbon, palladium supported on barium sulfate, palladium supported on calcium sulfate or palladium supported on calcium carbonate (for example: 5% palladium supported on calcium sulfate, 5% palladium supported on calcium carbonate or 10% palladium on carbon) at a temperature in the range of from about 10° C. up to 140° C., the aldehyde will be reduced to the saturated polycyclic carboxaldehyde according to the reaction:



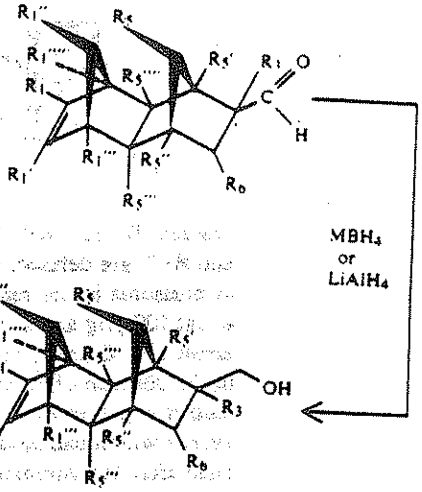
On the other hand when two moles of hydrogen are used per mole of aldehyde, the reduction is such that a saturated polycyclic carbinol is formed according to the reaction:



The aldehyde genus defined according to the structure:



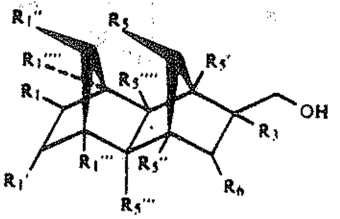
may be reduced with an alkali metal borohydride or lithium aluminum hydride in the presence of an inert solvent to form the unsaturated polycyclic carbinol according to the reaction:



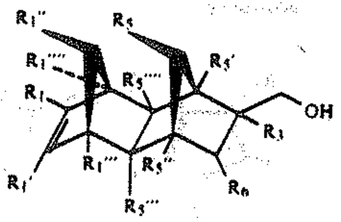
wherein M represents alkali metal such as lithium, sodium or potassium.

The reaction is carried out in the presence of an inert solvent such as isopropyl alcohol, n-propyl alcohol, ethyl alcohol or methyl alcohol or diethyl ether or tetrahydrofuran. The reaction is carried out at a temperature in the range of from about 20° C. up to reflux conditions (depending upon the solvent used) and is most conveniently and preferably carried out at atmospheric pressures since higher pressures do not give rise to higher yields or higher conversions. The mole ratio of alkali metal borohydride:aldehyde reactant or lithium aluminum hydride:aldehyde reactant may vary from about 0.2:1 up to about 1:1 with a preferred mole ratio of 0.25:1 up to 0.5:1.

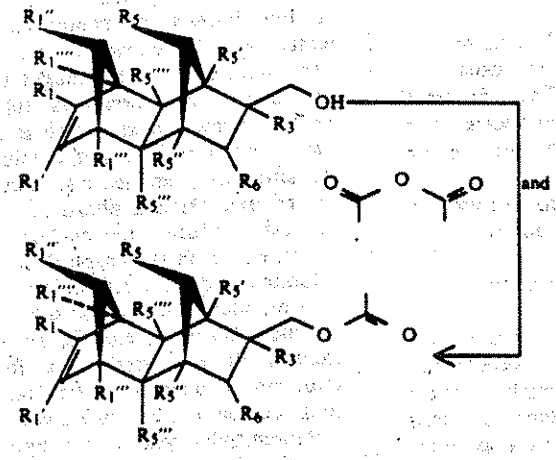
Both the saturated and unsaturated polycyclic carbinols defined according to the structures:

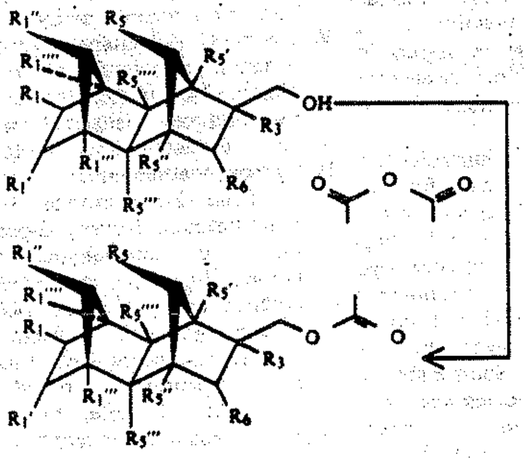


and

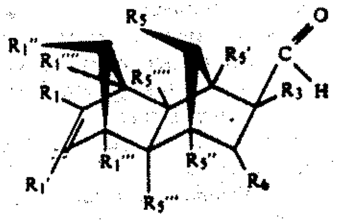


may be further reacted as by acetylation using acetic anhydride or acetyl chloride. The reaction with acetic anhydride is preferably carried out in the presence of an inert solvent at reflux conditions at atmospheric pressure. Such an inert solvent is toluene or xylene, the solvents being inert and having boiling points such that the reaction may proceed efficiently and in a minimum amount of time. Preferably the mole ratio of acetic anhydride:carbinol reactant is from about 0.5:1.5 up to about 1.5:0.5 with a most preferred ratio of acetic anhydride:carbinol reactant being 1-1.5:1. Each of these reactions is set forth as follows:

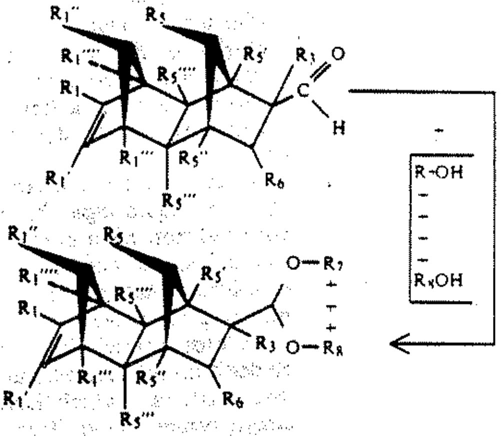




In addition, the aldehyde derivatives defined according to the structure:



may be converted into cyclic or acyclic acetals by means of reaction of the aldehyde with a C_1–C_4 alkanol or a C_2–C_4 alkanediol according to the reaction:



wherein R_1, R_1', R_1'', R_1''', R_1'''', R_3, R_5, R_5', R_5'', R_5''', R_5'''', R_6, R_7, R_8 and the line [++++] are defined, supra.

The reaction is carried out in the presence of a protonic acid catalyst or a Lewis acid catalyst at a temperature in the range of from about 30° C. up to about 90° C. Preferred catalysts are boron trifluoride etherate, 20% sulfuric acid, saturated aqueous, ammonium chloride and stannic chloride.

The preferred mole ratio of alkane diol:aldehyde reactant may vary from about 1:1 up to aboue 2:1 and the preferred mole ratio of alkylenediol:aldehyde reactant may vary from about 2:1 up to about 4:1.

At the end of each of the foregoing reactions the reaction product may, if desired, be separated from the resultant reaction mass by fractional distillation or preparative GLC (vapor phase, chromotography). However, if the desired reaction product is to be utilized as a reaction intermediate, the necessity of careful rectification of the reaction product in order to achieve odor acceptable substances or flavor acceptable substances is not usually necessary since the resultant reaction product will be further reacted.

Thus, the individual mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be obtained in pure form or in substantially pure form by conventional purification techniques. The products can be purified and/or isolated not only by distillation (as mentioned, supra), but also using extraction, crystallization, preparative chromatographic techniques and the like. It has been found desirable to purify the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention by fractional distillation in vacuo.

When the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention are used as food flavor adjuvants, the nature of the co-ingredients included with said mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives in formulating the product composition will also serve to alter, modify, augment or enhance the organoleptic characteristics of the ultimate foodstuff treated therewith.

As used herein in regard to flavors, the terms "alter", "modify" and "augment" in their various forms mean "supplying or imparting flavor character or note to otherwise bland, relatively tasteless substances or augmenting the existing flavor characteristic where a natural flavor is deficient in some regard or supplementing the existing flavor impression to modify its quality, character or taste."

The term "enhance" is used herein to mean the intensification of a flavor or aroma characteristic or note without the modification of the quality thereof. Thus, "enhancement" of a flavor or aroma means that the enhancement agents does not add any additional flavor note.

As used herein, the term "foodstuff" includes both solid and liquid ingestible materials which usually do, but need not, have nutritional value. Thus, foodstuffs include soups, convenience foods, beverages, dairy products, candies, vegetables, cereals, soft drinks, snacks and the like.

As used herein, the term "medicinal product" includes both solids and liquids which are ingestible, non-toxic materials which have medicinal value such as cough syrups, cough drops, aspirin and chewable medicinal tablets.

The term "chewing gum" is intended to mean a composition which comprises a substantially water insoluble, chewable, plastic gum base such as chicle, or substitutes therefor, including guttakay rubber or certain comestible natural or synthetic resins or waxes. Incorporated with the gum base in admixture therewith may be plasticizers or softening agents, e.g., glycerine, and a flavoring composition which incorporates one or more of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention, and in addition, sweetening agents which may be sugars, including sucrose or dextrose and/or artificial sweeteners such as cyclamates or saccharin. Other optional ingredients may also be present.

Substances suitable for use herein as co-ingredients or flavoring adjuvants are well known in the art for such use, being extensively described in the relevant literature. It is a requirement that any such material be "ingestibly" acceptable and thus non-toxic and otherwise non-deleterious particularly from an organoleptic standpoint whereby the ultimate flavor and/or aroma of the consumable material used is not caused to have unacceptable aroma and taste nuances. Such materials may in general be characterized as flavoring adjuvants or vehicles comprising, broadly, stablizers, thickeners, surface active agents, conditioners, other flavorants and flavor intensifiers.

Stabilizer compounds include preservatives, e.g., sodium chloride; antioxidants, e.g., calcium and sodium ascorbate, ascorbic acid, butylated hydroxyanisole (mixture of 2- and 3-tertiary-butyl-4-hydroxy-anisole), butylated hydroxytoluene (2,6-di-tertiary-butyl-4-methyl phenol), propyl gallate and the like, and sequestrants, e.g., citric acid.

Thickener compounds include carriers, binders, protective colloids, suspending agents, emulsifiers and the like, e.g., agar agar, carrageenan; cellulose and cellulose derivatives such as carboxymethyl cellulose and methyl cellulose; natural and synthetic gums such as gum arabic, gum tragacanth, gelatin, proteinaceous materials; lipids, carbohydrates; starches, pectins, and emulsifiers, e.g., mono- and diglycerides of fatty acids, skim milk powder, hexoses, pentoses, disaccharides, e.g., sucrose corn syrup and the like.

Surface active agents include emulsifying agents, e.g., fatty acids such as capric acid, caprylic acid, palmitic acid, myristic acid and the like, mono- and diglycerides of fatty acids, lecithin, defoaming and flavor-dispersing agents such as sorbitan monostearate, potassium stearate, hydrogenated tallow alcohol and the like.

Conditioners include compounds such as bleaching and maturing agents, e.g., benzoyl peroxide, calcium peroxide, hydrogen peroxide and the like; starch modifiers such as peracetic acid, sodium chlorite, sodium hypochlorite, propylene oxide, succinic anhydride and the like, buffers and neutralizing agents, e.g., sodium acetate, ammonium bicarbonate, ammonium phosphate, citric acid, lactic acid, vinegar and the like; colorants, e.g., carminic acid, cochineal, tumeric and curcuma and the like; firming agents such as aluminum sodium sulfate, calcium chloride and calcium gluconate; texturizers, anti-caking agents, e.g., aluminum calcium sulfate and tribasic calcium phosphate; enzymes; yeast foods, e.g., calcium lactate and calcium sulfate; nitrient supplements, e.g., iron salts such as ferric phosphate, ferrous gluconate and the like, riboflavin, vitamins, zinc sources such as zinc chloride, zinc sulfate and the like.

Other flavorants and flavor intensifiers include organic acids, e.g., acetic acid, formic acid, 2-hexenoic acid, benzoic acid, n-butyric acid, caproic acid, caprylic acid, cinnamic acid, isobutyric acid, isovaleric acid, alpha-methylbutyric acid, propionic acid, valeric acid, 2-methyl-2-pentenoic acid, and 2-methyl-3-pentenoic acid; ketones and aldehydes, e.g., acetaldehyde, acetophenone, acetone, acetyl methyl carbinol, acrolein, n-butanal, crotonal, diacetyl, 2-methylbutanal, beta-dimethylacrolein, methyl n-amyl ketone, n-hexanal, 2-hexenal, isopentanal, hydrocinnamic aldehyde, cis-3-hexenal, 2-heptenal, nonyl aldehyde, 4-(p-hydroxyphenyl)-2-butanone, alpha-ionone, beta-ionone, 2-methyl-3-butanone, benzaldehyde, β-damascone, α-damascone, β-damascenone, acetophenone, 2-heptanone, o-hydroxyacetophenone, 2-methyl-2-hepten-6-one, 2-octanone, 2-undecanone, 3-phenyl-4-pentenal, 2-phenyl-2-hexenal, 2-phenyl-2-pentenal, furfural, 5-methylfurfural, cinnamaldehyde, beta-cyclohomocitral, 2-pentanone, 2-pentenal and propanal; alcohols such as 1-butanol, benzyl alcohol, 1-borneol, trans-2-buten-1-ol, ethanol, geraniol, 1-hexanol, 2-heptanol, trans-2-hexenol-1, cis-3-hexen-1-ol, 3-methyl-3-buten-1-ol, 1-pentanol, 1-penten-3-ol, p-hydroxyphenyl-2-ethanol, isoamyl alcohol, isofenchyl alcohol, phenyl-2-ethanol, alpha-terpineol, cis-terpin hydrate, eugenol, linalool, 2-heptanol, acetoin; esters, such as butyl acetate, ethyl acetate, ethyl acetoacetate, ethyl benzoate, ethyl butyrate, ethyl caprate, ethyl caproate, ethyl carpylate, ethyl cinnamate, ethyl crotonate, ethyl formate, ethyl isobutyrate, ethyl isovalerate, ethyl laurate, ethyl myristate, ethyl α-methyl-butyrate, ethyl propionate, ethyl salicylate, trans-2-hexenyl acetate, hexyl acetate, 2-hexenyl butyrate, hexyl butyrate, isoamyl acetate, isopropyl butyrate, methyl acetate, methyl butyrate, methyl caproate, methyl isobutyrate, alpha-methylphenylglycidate, ethyl succinate, isobutyl cinnamate; cinnamyl formate, methyl cinnamate and terpenyl acetate; hydrocarbons such as dimethyl naphthalene, dodecane, methyldiphenyl, methyl naphthalene, myrcene, naphthalene, octadecane, tetradecane, tetramethylnaphthalene, tridecane, trimethylnaphthalene, undecane, caryophyllene, α-phellandrene, β-phellandrene, p-cymene 1-α-pinene, beta-pinene, dihydrocarveol; pyrazines such as 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 2-ethyl-3,5,6-trimethylpyrazine, 3-isoamyl-2,5-dimethylpyrazine, 5-isoamyl-2,3-dimethylpyrazine, 2-isoamyl-3,5,6-trimethylpyrazine, isopropyl dimethylpyrazine, methyl ethylpyrazine, tetramethylpyrazine, trimethylpyrazine; essential oils such as jasmine absolute, cassia oil, cinnamon bark oil, black pepper oleoresin, oil of black pepper, rose absolute, orris absolute, oil of cubeb, oil of coriander, oil of pimento leaf, oil of patchouli, oil of nutmeg, lemon essential oil, safran oil, Bulgarian rose, capsicum, yara yara and vanilla; lactones such as γ-nonalactone; Δ-decalactone; γ&Δ-undecalactone; γ&Δ-dodecalactone; sulfides, e.g., methyl sulfide and other materials such as maltol, and acetals (e.g., 1,1-diethoxyethane, 1-1-dimethoxyethane and dimethoxymethane), piperine, chavicine, and piperidine.

The specific flavoring adjuvant selected for use may be either solid or liquid depending upon the desired physical form of the ultimate product, i.e., foodstuff, whether simulated or natural, and should, in any event, (i) be organoleptically compatible with the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention by not covering or spoiling the organoleptic properties (aroma and/or taste thereof); (ii) be non-reactive with the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention; and (iii) be capable of providing an environment in which the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be dispersed or admixed to provide a homogeneous medium. In addition, selection of one or more flavoring adjuvants, as well as the quantities thereof will depend upon the precise organoleptic character desired in the finished product. Thus, in the case of flavoring compositions, ingredient selection will vary in accordance with the foodstuff, chewing gum, medicinal product or toothpaste to which the flavor and/or aroma are to be imparted, modified, altered or enhanced. In contradistinction, in the preparation of solid products, e.g., simulated foodstuffs, ingredients capable of providing normally solid compositions should be selected such as various cellulose derivatives.

As will be appreciated by those skilled in the art, the amount of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivative(s) of our invention employed in a particular instance can vary over a relatively wide range, depending upon the desired organoleptic effects to be achieved. Thus, correspondingly greater amounts would be necessary in those instances wherein the ultimate food composition to be flavored (e.g., with a peppermint flavor, or a specific vegetable flavor such as an artichoke flavor) is relatively bland to the taste, whereas relatively minor quantities may suffice for purposes of enhancing a composition merely deficient in natural flavor or aroma. The primary requirement is that the amount selected be effective, i.e., sufficient to alter, modify or enhance the organoleptic characteristics of the parent composition, whether foodstuff per se, chewing gum per se, medicinal product per se, toothpaste per se, of flavoring composition.

The use of insufficient quantities of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention will, of course, substantially vitiate any possibility of obtaining the desired results while excess quantities prove needlessly costly and in extreme cases may disrupt the flavoraroma balance, thus proving self-defeating. Accordingly, the terminology "effective amount" and "sufficient amount" is to be accorded a significance in the context of the present invention consistent with the obtention of desired flavoring effects.

Thus, and with respect to ultimate food compositions, chewing gum compositions, medicinal product compositions and toothpaste compositions, it is found that quantities of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention ranging from a small but effective amount, e.g., 0.00001 parts per million up to about 100 parts per million based on total composition, are suitable. Concentrations in excess of the maximum quantity stated are not normally recommended since they fail to provide commensurate enhancement of organoleptic properties. In those instances wherein the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention are added to the foodstuff as an integral component of a flavoring composition, it is of course essential that the total quantity of flavoring composition employed be sufficient to yield an effective mono-oxomethyl substituted polyhydrodimethanonaphthalene derivative concentration in the foodstuff product.

Food flavoring compositions prepared in accordance with the present invention preferably contain the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention in concentrations ranging from about 0.01% up to about 15% by weight based on the total weight of the said flavoring composition.

The composition described herein can be prepared according to conventional techniques well known as typified by cake batters and fruit drinks and can be formulated by merely admixing the involved ingredients within the proportions stated in a suitable blender to obtain the desired consistency, homogeneity of dispersion, etc. Alternatively, flavoring compositions in the form of particulate solids can be conveniently prepared by mixing the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention with, for example, gum arabic, gum tragacanth, carrageenan, xanthangum, guargum, mixtures of same and the like, and thereafter spray-drying the resultant mixture whereby to obtain the particular solid product. Prepared flavor mixes in powder form, e.g., a fruit flavored powder mix, are obtained by mixing the dried solid components, e.g., starch, sugar and the like, and one or more mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention in a dry blender until the requisite degree of uniformity is achieved.

It is presently preferred to combine with the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention, the following adjuvants:

Oil of Cubeb;
α-phellandrene;
β-phellandrene;
Oil of Coriander;
Oil of Pimento Leaf;
Oil of Patchouli;
Alpha Pinene;
Beta Pinene;
Beta-caryophyllene;
Dihydrocarveol;
Piperonal;
Piperine;
Chavicine;
Piperidine;
Oil of Black Pepper;
Black Pepper Oleoresin;
Capsicum;
Oil of Nutmeg.

Cardamom Oil;
Clove Oil;
Spearmint Oil;
Oil of Peppermint;
Ethyl-2-methyl butyrate;
Vanillin;
Butyl valerate;
2,3-Diethyl pyrazine;
Methyl cyclopentenolone;
Benzaldehyde;
Valerian Oil Indian;
Propylene glycol;
Acetaldehyde;
Isobutyraldehyde;
Isovaleraldehyde;
Dimethyl sulfide;
Isobutyl acetate;
Isoamyl acetate;
Phenylethyl acetate;
Diacetyl;
Acetophenone;
Furfural
Phenylacetaldehyde
Isoamyl alcohol;
β-Phenylethyl alcohol;
α-Phenyl ethyl alcohol
γ-Butyrolactone;
γ-Butyrolactone;
3-Phenyl-4-pentenal;
3-Phenyl-3-pentenal;
3-Phenyl-2-pentenal;
2-Methyl pyrazine;
2,6-Dimethyl pyrazine;
2,3,5,6-Tetramethyl pyrazine;
2,3,5-Trimethylpyrazine;
2-Ethyl-3-methylpyrazine;
2-Ethyl-3,5-dimethylpyrazine;
2-Ethyl-3,6-dimethylpyrazine;
2-Ethyl-5-methylpyrazine;
2(n-pentyl) thiazole;
2(i-butyl) thiazole;
2(i-propyl) thiazole;
2(n-propyl) thriazole;
2-phenyl-4-pentenal;
2-phenyl-4-pentenaldimethylacetal;
Methional;
4-methylthiobutanal;
2-ethyl-3-acetylpyrazine
trans-2-hexenal;
Hydrolyzed vegetable protein;
Monosodium glutamate;
Celery Oil;
Lemon Oil:
Mustard Oil;
2,4-dimethyl-Δ^3-thiazoline;
4,5-dimethyl-Δ^3-thiazoline;
2,4,5-trimethyl-Δ^3-thiazoline;
2-propyl-2,4,5-trimethyl-Δ^3-thiazoline;
2-ethyl-2,4,5-trimethyl-Δ^3-thiazoline;
2-(2'butyl)-4-methyl-Δ^3-thiazoline;
2-n-butyl-4,5-dimethyl-Δ^3 thiazoline;
2-benzeyl-4-methyl-Δ^3-thiazoline;
2,5-dimethyl-2-benzyl-Δ^3-thiazoline;
2-(2'-methyl-n-propyl)-4,5-dimethyl-Δ^3 thiazoline;
β-Damascone
β-Damascenone; and
trans,transΔ^3-Damascone

The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be used to contribute melony, cucumber, violet-like, green, leafy, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic and spicy aroma nuances to perfume compositions, perfumed articles (such as solid or liquid anionic, cationic, nonionic or zwitterionic detergents, fabric softeners, fabric softener articles and perfumed polymers) and colognes. As olfactory agents the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be formulated into or used as components of a "perfume composition".

The term "perfume composition" is used herein to mean a mixture of organic compounds including, for example, alcohols (other than the alcohols of our invention), aldehydes (other than the aldehydes of our invention), ketones, nitriles, ethers, lactones, acetals (other than the acetals of our invention), esters (other than the esters of our invention), and frequently hydrocarbons which are admixed so that the combined odors of the individual components produce a pleasant or desired fragrance. Such perfume compositions usually contain: (a) the main note or the "bouquet" or foundation-stone of the composition; (b) modifiers which round-off and accompany the main note; (c) fixatives which include odorous substances which lend a particular note to the perfume throughout all stages of evaporation, and substances which retard evaporation; and (d) top-notes which are usually low-boiling, fresh-smelling materials.

In perfume compositions the individual component will contribute its particular olfactory characteristics, but the overall effect of the perfume composition will be the sum of the effects of each ingredient. Thus, the individual compounds of this invention, or mixtures thereof, can be used to alter the aroma characteristics of a perfume composition, for example, by highlighting or moderating the olfactory reaction contributed by another ingredient in the composition.

The amount of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention which will be effective in perfume compositions depends on many factors, including the other ingredients, their amounts and the effects which are desired. It has been found that perfume compositions containing as little as 0.2% of one or more of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention, or even less, can be used to impart melony, cucumber-like, violet-like, green, leafy, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic, and spicy aroma nuances to soaps, cosmetics, solid or liquid anionic, cationic, nonionic, or zwitterionic detergents, fabric softeners, fabric softener articles, perfumed polymers, cosmetic powders, hair preparations and other products. The amount employed can range up to 50% or higher and will depend on considerations of cost, nature of the end product, the effect desired on the finished product and a particular fragrance sought.

The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention can be used alone or in a perfume composition as an olfactory component in solid or liquid anionic, cationic, nonionic or zwitterionic detergents, fabric softeners, and soaps, space odorants and deodorants; perfumes; colognes, toilet waters; bath salts; hair preparations such as lacquers, brilliantines, pomades, and shampoos; cosmetic preparations such as creams, deodorants, hand lotions, and sun screens; powders such as talcs, dusting powders, face powder and the like. When used as an olfactory component of a perfumed article, as little as 0.005% of one or more of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention will suffice to impart an interesting melony, cucumber, violet-like, green, leafy, herbaceous, wormwood-like, floral, cinnamic, sandalwood-like, patchouli-like, vetiver-like, sweaty, animalic and spicy aromas. Generally, no more than 0.8% is required in the perfumed article. Thus, to be specific, the range of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention useful in perfumed articles varies from about 0.005% up to about 0.8%.

In addition, the perfume composition of our invention can contain a vehicle or carrier for the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention. The vehicle can be a liquid such as an alcohol such as ethanol, a glycol such as propylene glycol, or the like. The carrier can be an absorbent solid such as a gum or components for encapsulating the composition by coacervation such as gelatin or for encapsulating the composition by forming polymers around a central liquid core such as a urea formaldehyde capsule.

It is the further object of our invention to provide a smoking tobacco product treated with an additive which will enhance the tobacco aroma, as well as the flavor characteristics of the tobacco product made therefrom. Also, it is an object of the present invention to provide a smoking tobacco product having a material added to the tobacco which will readily transfer to the tobacco smoke and pass through a filter element (even of a high filtration type) so that the natural flavor qualities of the tobacco smoke are enhanced.

Another object of our invention is the provision of smoking tobacco products, such as cigarettes, cigars, pipe tobacco, or tobacco smoke filters, having added thereto a releasable flavor additive which will impart a desirable fresh natural taste to the smoking product when smoked.

Thus, in general, our invention further contemplates providing an organoleptically improved tobacco product having added thereto one or more mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention which imparts to the product the enhanced and desirable fresh flavor and aroma of natural tobacco. The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention are individually and in combination readily transferred either from the filter section or the tobacco section into the smoke stream when the tobacco product is smoked. The organoleptic qualities of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention particularly when transferred to the tobacco smoke, impart desirable fresh, oriental, spicy, floral, citrusy flavor and aroma nuances to tobacco causing the tobacco to be more desirable and causing a change from the "Virginia" and "Burley" types to the "imported", "Turkish" types.

The mono-oxomethyl substituted polyhydrodimethanonaphthalene of our invention employed to improve the organoleptic qualities of a tobacco product have odor characteristics which can be described as floral, spicy, woody, and cinnamon-like as well as citrusy. The amount of mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention taken alone or in combination added to a tobacco product may vary greatly; however a sufficient amount should be used to achieve the desired organoleptic properties for the smoking tobacco product when smoked. We have found that the levels of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention (taken alone or in combination) added to a tobacco product, either to the filter or to the tobacco section, may be as low as 0.001% based on the weight of the tobacco. The amount of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives added to the tobacco product may be from about 0.001% up to about 0.1% based on the weight of the tobacco, preferably from about 0.005% up to about 0.05%, and more preferably from about 0.01% up to about 0.015%.

The mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention may be incorporated at any step into the treatment of the tobacco but it is preferred that they be added either separately or in admixture after the tobacco has been cured, aged and shredded and just prior to the manufacture of the desired tobacco product, for example, cigarettes, cigars, pipe tobacco, or other smoking products. Also, it may be added to tobacco smoke filter material prior to forming the filter rod. The additive is conveniently dissolved in a solvent, such as ethyl alcohol, and applied to the tobacco by spraying, dipping or other methods of application generally employed for treating tobacco. Also, it may be sprayed onto the filter material. Although solutions of this compound are preferred, suspensions thereof may be utilized. Other suitable solvents are, for example, acetone, diethyl ether, n-hexane, or the like. After treatment of the tobacco or the filter with at least one of the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention, substantially all of the solvent is evaporated therefrom prior to its manufacture into tobacco products.

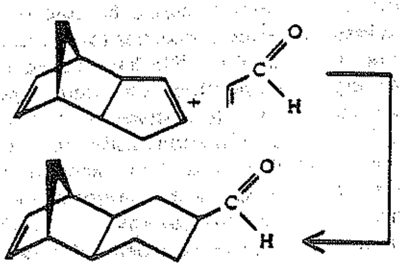
The term "tobacco" will be understood herein to mean the natural products such as, for example, Burley, Turkish tobacco, Maryland tobacco, flue-cured tobacco and the like including tobacco-like or tobacco-based products such as reconstituted or homogenized leaf and the like, as well as tobacco substitutes intended to replace natural tobacco, such as lettuce and cabbage leaves and the like. The tobaccos and tobacco products in which the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention are useful include those designed or used for smoking such as in cigarette, cigar and pipe tobacco, as well as products such as snuff, chewing tobacco, and the like.

The following examples I-X are given to illustrate methods for producing the mono-oxomethyl substituted polyhydrodimethanonaphthalene derivatives of our invention. The examples following Example X are given to illustrate embodiments of the utilization of the mono-oxymethyl substituted polyhydrodimethanonaphthalene derivatives of our invention. It will be understood that these examples are illustrative and that the invention is not to be considered as restrictive to these examples except as indicated in the appended claims.

EXAMPLE I

Preparation of 1,2,3,4,4A,5,5A,8 Octahydro-1,4:5,8 Dimethanonaphthalene-2-Carboxaldehyde

Reaction



Into a high pressure autoclave are placed the following ingredients:

396 dicyclopentadiene;
252 grams acrolein; and
500 ml toluene

The autoclave is sealed, and with stirring, heated at 225° C. at 200 psig for a period of three hours. At the end of the reaction, the autoclave is opened and a portion of the product is distilled in a "Rushover" apparatus yielding the following fractions:

Fraction No.	Vapor Temp. (°C.)	Liquid Temp. (°C.)	Vacuum mm.Hg. Pressure	Weight of Fractions (mg)	
1	23/50	23/70	50/52	911.0	
2	56	77	50	802.0	
3	68	100	40	1031.0	
4	75	100	30	902.0	
5	83	115	15	200.0	
6	86	128	15	125.1	
7	100	133	10	91.6	
8	108	137	10	105.5	
9	120	143	8	96.0	
10	125	147	8	96.5	
11	135	168	2		1588.0
12	139	186	2		
13	156	220	2	339.0	

Fractions 11 and 12 of this distillation are bulked and the resulting bulked fractions are distilled on a fractionation column yielding the following fractions:

Fraction No.	Vapor Temp. (°C.)	Liquid Temp. (°C.)	Vacuum mm.Hg. Pressure	Reflux Ratio	Weight of Fractions (mg)
1	23/77	23/122	2/2	9:1	20.8
2	78	125	2	9:1	17.3
3	78	126	2	9:1	18.9
4	78	125	2	9:1	21.3
5	79	126	2	9:1	27.8
6	80	127	2	9:1	23.5
7	80	128	2	9:1	106.5
8	80	127	2	9:1	122.4
9	80	129	2	9:1	44.0
10	80	129	2	9:1	31.1
11	83	130	2	9:1	39.0
12	83	130	2	9:1	42.4
13	83	130	2	1:1	106.4
14	83	130	2	1:1	102.3
15	83	130	2	1:1	106.9
16	83	133	2	1:1	128.1
17	83	134	2	1:1	130.1
18	84	136	2	1:1	128.7
19	86	170	2	1:1	132.0
20	78	187	2	1:1	64.2
21	50	220	2	1:1	44.1

Fractions 14–19 are bulked and have an herbal, strong, green, aldehydic, wormwood-like, floral aroma profile. Bulked fractions 4–14 has a melony, cucumber-like, violet, green, aldehydic aroma profile.

From a flavor standpoint fraction 14 has a sweet, aldehydic, floral, melony, herbaceous aroma and taste profile at 0.0001 ppm. In addition, it is an excellent vanilla flavor enhancer and orange oil flavor enhancer.

FIG. 1 is the GLC profile of the reaction production prior to distillation (conditions: SE-30 packed column, programmed at 220° C. isothermal (⅛"×10 feet). The peak indicated on FIG. 1 by the reference "1" is for the reaction product having the structure:

FIG. 2 is the NMR spectrum for the bulked fractions 4–20 of the foregoing distillation product containing the compound having the structure:

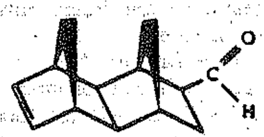
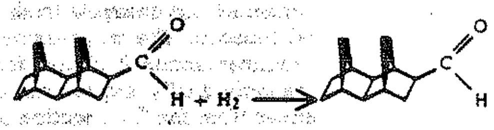


FIG. 3 is the infra-red spectrum for bulked fractions 4–20 of the foregoing distillation product containing the compound having the structure:

EXAMPLE II

Preparation of Decahydro-1,4:5,8-Dimethanonaphthalene-2-Carboxaldehyde

Reaction:



Into a Parr shaker apparatus is placed the following ingredients:

Ingredients	Parts by Weight
Bulked fractions 22-26 of the distillation product of the reaction product of Example I containing the compound having the structure 	260 grams (1.3 moles)
1% Palladium on carbon	3 grams

-continued

Ingredients	Parts by Weight
Anhydrous isopropyl alcohol	80 ml

The Parr shaker is pressurized with hydrogen to a pressure of between 87 and 109 psig while maintaining the reaction temperature at 48°-54° C. for a period of 14 hours. At the end of this period, the Parr shaker is depressurized, opened and the contents are filtered. The resulting product is then distilled on a fractionation column yielding the following fractions:

Fraction No.	Vapor Temp. (° C.)	Liquid Temp. (° C.)	Vacuum mm.Hg. Pressure	Weight of Fraction (gm)
1	35	37	20/20	13.6
2	119	120	1	10.6
3	122	122	1	15.6
4	127	127	1	15.1
5	127	140	1	16.7
6	127	140	1	16.7
7	127	140	1	18.1
8	127	140	1	19.5
9	127	140	1	16.0
10	127	140	1	15.6
11	127	147	1	17.3
12	127	147	1	21.2
13	127	147	1	22.5
14	130	200	1	22.7

Fraction 7-13 of the foregoing distillation are bulked for subsequent evaluation and for subsequent reaction. Fractions 7-13, bulked, from a fragrance standpoint, have a floral, cinnamon-like and melony aroma profile.

FIG. 4 is the GLC profile for the reaction product prior to distillation. (Conditions: SE-30 column programmed at 130°-220° C. at 8° C. per minute).

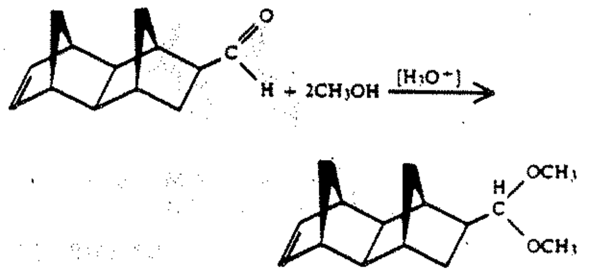
FIG. 5 is the NMR spectrum for fraction 11 of the foregoing distillation containing the compound having the structure:

FIG. 6 is the infra-red spectrum for fraction 11 of the foregoing distillation containing the compound having the structure:

EXAMPLE III

Preparation of Dimethyl Acetal of 1,2,3,4,4A,5,5A,8 Octahydro-1,4:5,8 Dimethanonaphthalene-2-Carboxaldehyde

Reaction:



Into a 100 ml reaction flask equipped with stirrer, thermometer, reflux condenser and heating mantle is placed the following:

10.0 grams of the reaction product of Example I. bulked fractions 22-26 containing the compound having the structure:

4.0 grams borontrifluoride etherate

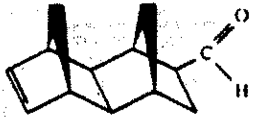
25.0 grams anhydrous methyl alcohol

The reaction mass is heated to 60° C. and maintained at 60° C. for a period of three hours.

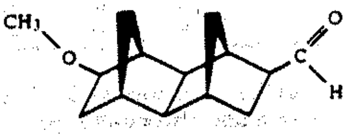
The reaction product having the structure:

(as confirmed by NMR, IR mass spectral analyses) is trapped via preparative GLC. (Conditions: SE-30 column programmed at 220° C., isothermal)

FIG. 7 is the GLC profile for the reaction product of this example. The peak indicated by the reference "11" is the peak for the staring material, the aldehyde having the structure:



The peak indicated by the reference numeral "12" is for a side-product having the structure:



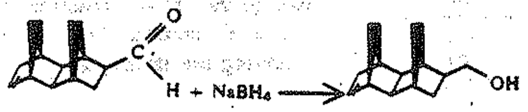
The peak indicated by the reference numeral "13" is the peak for the reaction product having the structure:

FIG. 8 is the NMR spectrum for the peak "13" of the GLC profile of FIG. 7.

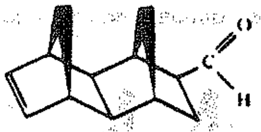
EXAMPLE IV

Preparation of 1,2,3,4,4A,5,8,8A-Octahydro 1,4:5,8-Dimethanonaphthalene-2-Methanol

Reaction:



Into a 1 liter reaction flask equipped with stirrer, thermometer, reflux condenser and heating mantle is placed 500 grams of isopropyl alcohol and 60 grams of sodium borohydride. The resulting mixture is heated to 50° C. While maintaining this mixture at 50° C., over a period of one hour 300 grams of the aldehyde produced according to Example I, bulked fractions 22–26 having the structure:



is added to the reaction mass. The reaction mass is then maintained at 60° C. for a period of 0.5 hours.

The reaction mass is then cooled and washed with 2 liters of water. An aqueous 10% solution of hydrochloric acid is then added until the solution is clear. The reaction mass is then washed and neutralized with sodium carbonate.

The reaction mass is then distilled on a 1"×12" Goodloe column yielding the following fractions:

Fraction No.	Vapor Temp. (° C.)	Liquid Temp. (° C.)	Vacuum mm.Hg. Pressure	Ratio Reflux	Weight of Fraction (gm)
1	23/110	27/147	1/1	9:1	14.0
2	111	147	0.8	9:1	15.3
3	111	147	0.65	9:1	20.1
4	111	147	0.65	9:1	24.3
5	116	153	0.65	1:1	26.1
6	122	157	0.65	1:1	27.1
7	122	158	0.65	1:1	25.0
8	122	161	0.65	1:1	27.4
9	121	168	0.65	1:1	26.3
10	119	196	0.65	1:1	25.8
11	115	230	0.65	1:1	17.6
12	100	235	—	—	—

Bulked fraction 6–10 of the foregoing distillation have a sandalwood-like, patchouli-like and vetiver-like aroma profile.

FIG. 9 is the GLC profile for bulked fractions 3–11 of of the distillation product of the foregoing reaction product. The peak indicated by the reference numeral "21" is the peak indicating the product having the structure:

The conditions for the GLC operation are: SE-30 column operated at 220° C. isothermal.

FIG. 10 is the NMR spectrum for bulked fractions 3–11 of foregoing distillation containing the compound having the structure:

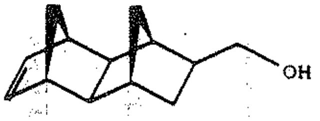
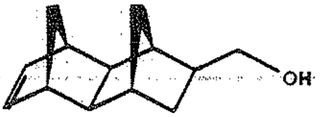


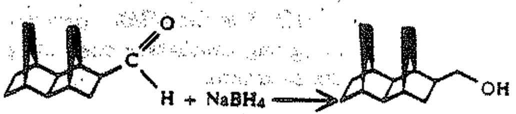
FIG. 11 is the infra-red spectrum for bulked fractions 3–11 of the foregoing distillation containing the compound having the structure:



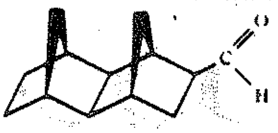
EXAMPLE V

Preparation of 1,4:5,8-Dimethanonaphthalene-2-Methanol Decahydro

Reaction:



Into a 1 liter reaction vessel equipped with reflux condenser, thermometer, addition funnel, heating mantle and stirrer is placed 500 grams of isopropyl alcohol and 40 grams of sodium borohydride. Over a period of 20 minutes, 280 grams (1.3 moles) of bulked fractions 4–11 of the distillation product of Example II containing the compound having the structure:

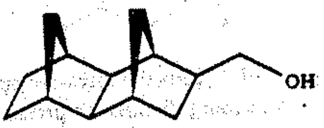


is added to the reaction mass, with refluxing. The reaction mass is maintained at a temperature of 70°–80° C. for a period of 20 hours.

At the end of the 20 hour period 200 ml acetone is added to the reaction mass. Then, 1.5 liters of water is added to the reaction mass and the aqueous phase is separated from the organic phase. The organic phase crystallizes, at room temperature. The organic phase is distilled on a fractionation column yielding the following fractions:

Fraction No.	Vapor Temp. (° C.)	Liquid Temp. (° C.)	Weight of Fraction (gm)
1	130	140	16.1
2	130	140	21.5
3	130	140	17.3
4	130	140	22.7
5	130	140	20.0
6	130	140	29.9
7	130	147	28.4
8	130	220	23.0

FIG. 12 is the GLC profile for the reaction product prior to distillation. The peak indicated by the reference numeral "31" is for the reaction product, the compound having the structure:



(Conditions: SE-30 column operated at 220° C. isothermal).

FIG. 13 is the NMR spectrum for fraction 8 of the foregoing distillation containing the compound having the structure:

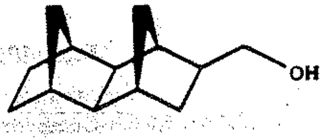
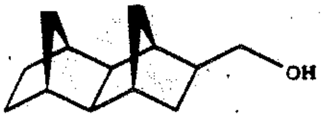


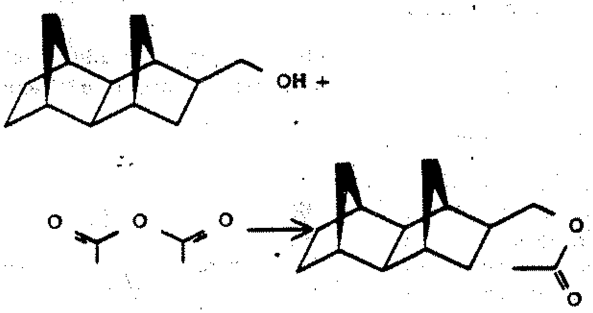
FIG. 14 is the infra-red spectrum for fraction 8 of the foregoing distillation containing the compound having the structure:



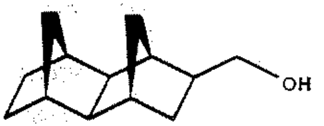
EXAMPLE VI

Preparation of 1,4:5,8-Dimethanonaphthalene-2-Methanol-Decahydro Acetate

Reaction:



Into a 1 liter reaction flask equipped with stirrer, thermometer, and reflux condenser is placed 160.0 grams of acetic anhydride, 200.0 ml toluene and 178.9 grams of the alcohol reaction product produced according to Example V, bulked fractions 3-8 having the structure:



The reaction mass is heated to 116° C. and maintained at 116° C. for a period of 2 hours. At the end of the reaction, 1 liter of water is added to the reaction mass and the organic phase is separated from the aqueous phase. The organic phase is washed with saturated sodium carbonate and the resulting product is fractionally distilled yielding the following fractions:

Fraction No.	Vapor Temp. (° C.)	Liquid Temp. (° C.)	Vacuum mm.Hg. Pressure	Weight of Fraction (gm)
2	147	152	2	19.4
3	137	150$	1	14.1
4	135	140	1	14.1
5	120	130	1	17.2
6	117	135	1	21.0
7	117	140	1	24.3
8	120	140	1	18 5
9	127	148	1	15.8
10	128	152	1	23 0
11	131	163	1	10.9
12	134	270	1	11 9

Fraction 8-10 are bulked for subsequent evaluation. Fractions 8-10 have a floral, pineapple-like aroma from a perfumery standpoint and a pineapple taste.

FIG. 15 is the GLC profile for the reaction product prior to distillation (Conditions: SE-30 column, programmed at 220° C. isothermal). The peak indicated by the reference numeral "41" is the peak for the reaction product having the structure:

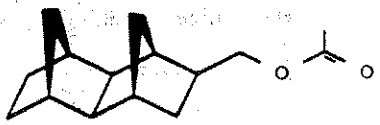


FIG. 16 is the NMR spectrum for fraction 6 of the foregoing distillation containing the compound having the structure:

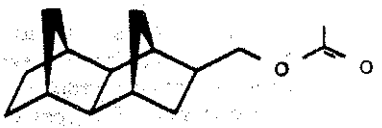
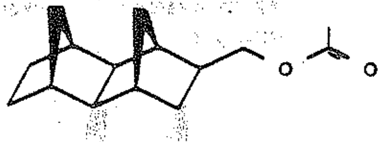


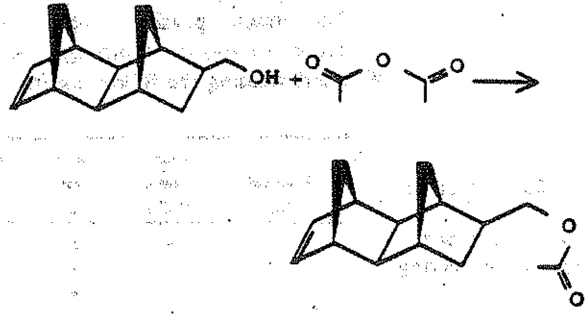
FIG. 17 is the infra-red spectrum for fraction 6 of the foregoing distillation containing the compound having the structure:



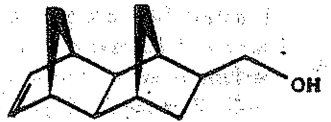
EXAMPLE VII

Preparation of 1,2,3,4,4A,5,8,8A-Octahydro-1,4:5,8-Dimethanonaphthalene-2-Methanol Acetate

Reaction:



Into a 1 liter reaction flask equipped with stirrer, thermometer and reflux condenser are placed 102 grams of acetic anhydride, 500.0 ml toluene and 72.0 grams of the alcohol reaction product produced according to Example IV, bulked fractions 6–10 having the structure:



The reaction mass is heated to 117° C. and maintained at 117° C. for a period of 1.5 hours. At the end of the reaction, the toluene solvent is stripped and the reaction mass is washed with concentrated aqueous sodium carbonate. The reaction mass is then distilled on a fractionation column yielding the following fractions:

Fraction No.	Vapor Temp. (° C.)	Liquid Temp. (° C.)	Weight of Fraction (gm)
1	126	180	1.9
2	128	190	6.2
3	130	195	4.7
4	130	200	9.2
5	130	205	3.5

Fractions 2–4 are bulked. The bulked fractions from a perfumery standpoint have a sweaty aroma nuance. From a flavor standpoint, bulked fractions 2–4 at a concentration of 1 ppm have a green, artichoke-like aroma and taste profile making it useful for augmenting or enhancing the aroma and taste of salad dressings.

FIG. 18 is the GLC profile of the reaction product of this example containing the compound having the structure:

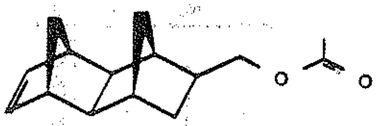


FIG. 19 is the NMR spectrum for fraction 4 of the foregoing distillation containing the compound having the structure:

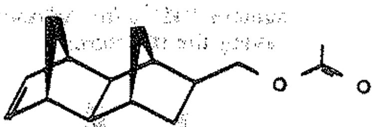
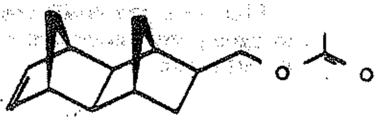


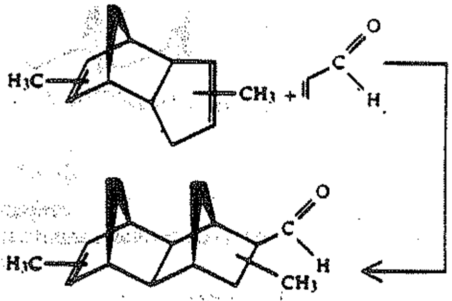
FIG. 20 is the infra-red spectrum for fraction 4 of the foregoing distillation product containing the compound having the structure:



EXAMPLE VIII

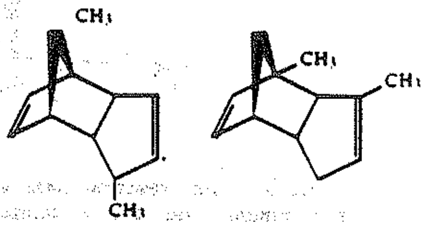
Preparation of Dimethyl 1,2,3,4,4A,5,8,8A-Octahydro-1,4:5,8-Dimethanonaphthalene-2-Carboxaldehyde

Reaction:



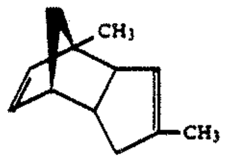
Into a 2 liter autoclave is placed the following materials:

(a) 400 grams of methyl cyclopentadiene dimer, a mixture of compounds defined according to the structures:



and

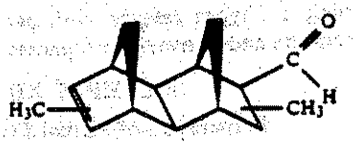
-continued



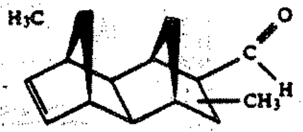
(b) 200 grams acrolein; and
(c) 300 ml toluene.

The autoclave is sealed and heated to 225° C. (180 psig) and maintained at that temperature and pressure for a period of two hours. At the end of the two hour period, the autoclave is depressurized and opened. The reaction product is analyzed via GLC, NMR, IR and mass spectral analyses. The resulting product has an animalic, leafy, green, herbaceous, floral (violet-like) aroma with cinnamon-like and cucumber undertones from a fragrance standpoint. The resulting substance has a green, melony, minty, herbaceous and floral aroma and taste profile at 2 ppm making it useful for mint and peppermint flavors.

FIG. 21 is the GLC profile for the reaction product. The peak indicated by the reference numeral "51" is the peak for the reaction product defined according to the structures:

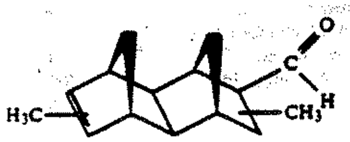


and



(mixtures of compounds).

FIG. 22 is the NMR spectrum for peak "51" of the GLC profile of FIG. 21 for the mixture of compounds defined according to the structures:



and

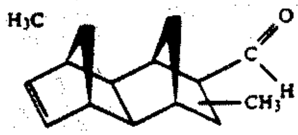
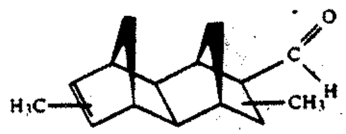
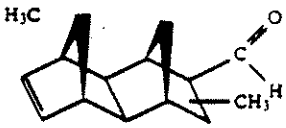


FIG. 23 is the infra-red spectrum for peak "51" of the GLC profile of FIG. 21 for the mixture of compounds defined according to the structures:



and

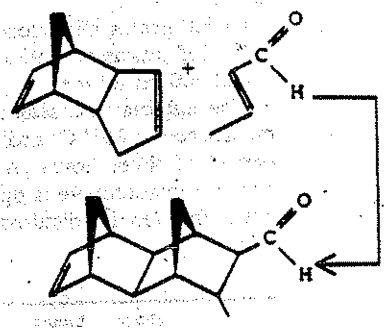
-continued



EXAMPLE IX

Preparation of 1,2,3,4,4A,5,8,8A-Octahydro-3-Methyl-1,4:5,8 Dimethanonaphthalene-2-Carboxaldehyde

Reaction:



Into a 2 liter autoclave is placed the following materials:

(a) Dicyclopentadiene	400 grams
(b) Crotonaldehyde	255 grams
(c) Toluene	500 ml

The autoclave is sealed and heated to 225° C. at a pressure of 200–320 psig and maintained at a temperature of 25° C. at a pressure in the range of 200–320 psig for a period of three hours. At the end of the three hour period, the autoclave is depressurized and opened. The reaction mass is then distilled on a fractionation column yielding a product boiling at a temperature in the range of 92°–96° C. (vapor temperature) and a liquid temperature in the range of 126°–140° C. at 1.0 mm/Hg pressure.

The reaction product at that boiling point has a spicy, cinnamon-like aroma.

FIG. 24 is the GLC profile for the reaction product (conditions: SE-30 column programmed at 220° C. isothermal).

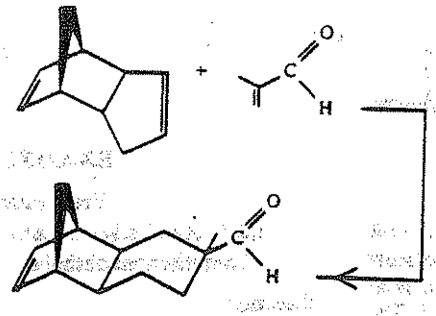
FIG. 25 is the NMR spectrum for the resulting reaction product at the foregoing boiling range.

FIG. 26 is the infra-red spectrum for the resulting reaction product at the above boiling range.

EXAMPLE X

Preparation of 1,2,3,4,4A,5,8,8A-Octahydro-2-Methyl-1,4:5,8-Dimethanonaphthalene-2-Carboxaldehyde

Reaction:



Into a 200 ml autoclave is placed the following ingredients:

(i) 400 grams Dicyclopentadiene;
(ii) 255 grams of methacrolein; and
(iii) 500 ml toluene

The autoclave is sealed and heated to 225° C. and maintained at 225° C. and at a pressure of 200 psig for a period of three hours. At the end of the three hour period the autoclave is opened and the resulting product is fractionally distilled yielding the following fractions:

Fraction No.	Vapor Temp. (°C.)	Liquid Temp. (°C.)	Vacuum mm.Hg. Pressure	Reflux Ratio	Weight of Fraction (gm)
1	27/57	23/90	2/2	9:1	21.1
2	70	126	2	9:1	11.5
3	75	132	2	9:1	13.7
4	83	135	2	9:1	17.2
5	83	135	2	9:1	13.5
6	85	136	2	9:1	23.5
7	85	136	2	9:1	24.8
8	85	136	2	9:1	26.1
9	85	176	2	9:1	18.7
10	86	136	2	9:1	17.8
11	86	136	2	1:1	33.1
12	86	137	2	1:1	30.6
13	86	137	2	1:1	29.8
14	86	137	2	1:1	31.3
15	86	137	2	1:1	32.0
16	86	140	2	1:1	33.1
17	86	140	2	1:1	29.6
18	86	140	2	1:1	29.0
19	87	140	2	—	32.1
20	85	143	2	—	33.3
21	80	186	2	—	30.1

Fractions 4–15 are bulked for subsequent evaluation for tobacco, food flavoring and fragrance properties.

EXAMPLE XI

Chypre Perfume Formulations

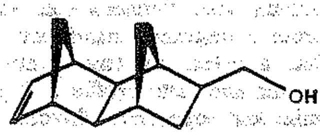
The following formulation is prepared:

Ingredients	Parts by Weight
Texas Cedarwood Oil	200
Patchouli Oil	50
Vetiver Oil	30
Bergamot Oil	150
African Geranium Oil	50
Coumarin	60
Natural Oak Moss	80
Tolu Balsam Peru	200
Labdanum	150
Musk Xylene	10

-continued

Ingredients	Parts by Weight
Product of Example IV, bulked fractions 6-10 consisting of the compound having the structure: 	135

The addition of the compound having the structure:



to this Chypre essence causes said Chypre to have an interesting sandalwood-like, patchouli-like and vetiver-like series of topnotes.

Accordingly, this formulation can be described as having a Chypre essence with patchouli-like, sandalwood-like and vetiver-like topnotes.

EXAMPLE XII

Preparation of Herbal Fragrances

The following mixtures are prepared:

TABLE I

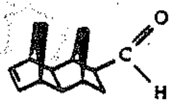
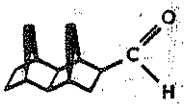
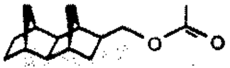
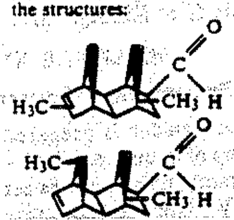
Ingredients	Parts by Weight XIIA	XIIB	XIIC	XIID
Amyl Cinnamic Aldehyde	20%	20%	20%	20%
Phenyl Acetaldehyde Dimethyl Acetal	4%	4%	4%	4%
Thyme Oil, White	8%	8%	8%	8%
Sauge Sclaree French	8%	8%	8%	8%
Galbanum Oil	4%	4%	4%	4%
Geranyl Acetate	10%	10%	10%	10%
Juniper Berry Oil	4%	4%	4%	4%
Methyl Octin Carbonate	2%	2%	2%	2%
Linalyl Acetate	10%	10%	10%	10%
Dihydro Methyl Jasmonate	20%	20%	20%	20%
Fenchyl Ethyl Ether	10%	10%	10%	10%
Aldehyde produced according to Example I having the structure:  (bulked fractions 8-19)	3%	0%	0%	0%
Reaction product of Example II having structure:  (bulked fractions 7-13)	0%	6%	0%	0%

TABLE I-continued

Ingredients	Parts by Weight XIIA	XIIB	XIIC	XIID
Product produced according to Example VI having the structure:  (bulked fractions 8-10)	0%	0%	6%	0%
Product produced according to Example VIII, a mixture of compounds defined according to the structures: 	0%	0%	0%	5%

When added to this herbal formulation the product of Example I imparts to the herbal formulation a melony, cucumber, violet-like, wormwood-like and generally pleasant floral undertone.

The product of Example II when added to this herbal formulation imparts to it, a floral, melony and cinnamon-like undertones.

When the product of Example VI is added to this herbal formulation a pineapple-like, pleasant floral undertone is added to the herbal essence profile.

When the reaction product of Example VIII is added to this herbal formulation, animalic, leafy, floral, violet-like, cinnamon-like and cucumber-like undertones are imparted to this formulation.

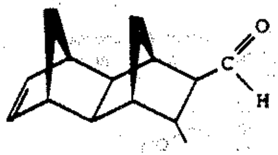
EXAMPLE XIII

Patchouli/Spicy Perfume Formulation

The following mixture is prepared:

Ingredients	Parts by Weight
Orange Oil	50
Beramot Oil	20
Lime Oil	100
1-Hydroxy-methyl-2,4,6 Trimethyl cyclohexane	45
Neroli Oil	5
4-(4-Methyl-4-Hydroxyamyl) Δ^3-cyclohexene carboxaldehyde	10
2,3,3A,4,5,7A-Hexahydro-6,7A,8,8-Tetramethyl-1,5-methano-[1H]-inden-1-ol	100
1',2',3',4',5',6',7',8'-octahydro 2',3',8',8'-tetramethyl-2'-aceto-naphthone isomer mixture produced according to the process of Example VII of the U.S. Letters Pat. No. 3,911,018 issued on October 7, 1975	20
Gamma Methyl Ionone	20
1-acetyl-2,5,5-trimethylcycloheptane	100

-continued

Ingredients	Parts by Weight
Substituted tricyclodecane derivatives prepared according to Example XII of U.S. Pat. No. 4,275,251 issued on June 23, 1981	100
Product of Example IX, supra, having the structure: 	85

The compound produced according to Example IX having the structure:

imparts to this patchouli/spicy formulation an intense, cinnamon-like, long lasting, oriental, spicy characteristic.

EXAMPLE XIV

Preparation of Soap Composition

A total of 100 grams of soap chips produced from unperfumed sodium base toilet soap made from talo and coconut oil is admixed with 1 gram of each of the perfume compositions set forth in Table II, below until a substantially homogeneous composition is obtained. The mixture is melted under 8 atmospheres pressure at 190° C. and maintained at 190° C. with mixing for a period of five hours at 8 atmospheres pressure. At the end of the five hour period, the resulting mixture is cooled and cut into soap bars. Each of the soap bars manifest an excellent aroma as set forth in Table II, supra:

TABLE II

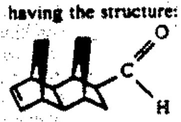
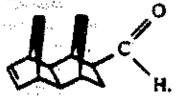
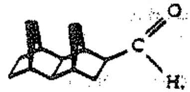
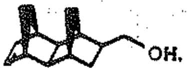
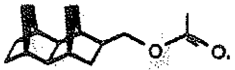
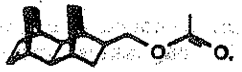
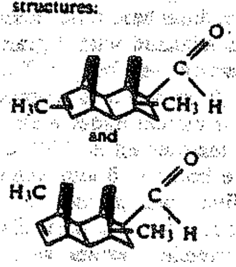
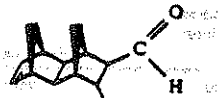
Structure of Compound and example by which produced	Perfumery Profile
Aldehyde produced according to Example I, bulked fractions 14-19, having the structure: 	An herbal, strong, green, aldehydic, wormwood-like and floral aroma profile.
Compound produced according to Example I, having the structure:  bulked fractions 8-12.	A melony, cucumber-like, violet-like, green, aldehydic aroma profile.
Compound produced according to Example II, having the structure:	A floral, melony, cinnamon-like aroma.

TABLE II-continued

Structure of Compound and example by which produced	Perfumery Profile
 bulked fractions 7-13.	
Compound produced according to Example IV, having the structure:  bulked fractions 6-10.	A sandalwood, patchouli, vetiver aroma profile.
Compound produced according to Example VI, having the structure:  bulked fractions 8-10.	A floral, pineapple-like aroma profile.
Compound produced according to Example VII, having the structure:  bulked fractions 1-5.	A sweaty, animal-like, musk-like aroma profile.
A mixture of compounds produced according to Example VIII, containing the compounds having structures: 	An animalic, leafy, green, herbaceous, floral, violet-like aroma with cinnamon-like and cucumber-like undertones.
Compound produced according to Example IX having the structure: 	A spicy, cinnamon-like aroma profile.
Perfume composition of Example XI.	A chypre aroma with patchouli-like, vetiver-like and sandalwood-like topnotes.
Perfume composition of Example XIIA.	A herbal aroma with melony, cucumber, violet-like, wormwood-like and pleasant floral undertones.
Perfume composition of Example XIIB.	A herbal aroma with floral, melony and cinnamon-like undertones.
Perfume composition of Example XIIC.	A herbal aroma with floral and pineapple-like undertones.
Perfume composition of Example XIID.	A herbal essence with animal-like, leafy, floral, violet-like, cinnamon-like and cucumber undertones.
Perfume composition of Example XIII.	A patchouli/spicy formulation an intense, cinnamon-like, long lasting, oriental, spicy characteristic.

EXAMPLE XV

Preparation of a Detergent Composition

A total of 100 grams of a detergent powder sold under the trademark "RINSO ®" are mixed with 0.15 grams of each of the perfumery substances as set forth in Table II of Example XIV, supra, until a substantially homogeneous composition is obtained. Each of the detergent powders manifest an excellent aroma as set forth in Table II of Example XIV.

EXAMPLE XVI

Preparation of Cosmetic Bases

A cosmetic powder is prepared by mixing in a ball mill 100 grams of talcum powder with 0.25 grams of one of the perfumery substances as set forth in Table II of Example XIV. The cosmetic powders produced using the materials of Table II of Example XIV have aroma characteristics as set forth in Table II of Example XIV.

EXAMPLE XVII

Liquid Detergent Composition

Concentrated liquid detergents with aromas as set forth in Table II of Example XIV containing 0.2%, 0.5% and 1.2% of one of the substances set forth in Table II of Example XIV are prepared by adding appropriate quantities of perfumery substances as set forth in Table II of Example XIV to a liquid detergent known as P-87. The aroma intensity of each of the liquid detergents so prepared increases with increasing concentration of each of the substances as set forth in Table II of Example XIV, each of the detergents manifesting aromas as set forth in Table II of Example XIV.

EXAMPLE XVIII

Preparation of Colognes and Handkerchief Perfumes

Each of the perfume substances of Table II of Example XIV are incorporated into 80%, 85%, 90% and 95% foodgrade ethanol solutions at the rates of 2.0%, 2.5%, 3.0%, 3.5% and 4.0%; and into handkerchief perfumes at concentrations of 15%, 20%, 25%, 30% and 40% (in 80%, 85%, 90% and 95% aqueous foodgrade ethanol). These of each of the substances of Table II of Example XIV are for distinct and definitive aroma nuances in each of the handkerchief perfumes and colognes as indicated in Table II of Example XIV.

EXAMPLE XIX

Preparation of Detergent Composition

A total of 100 pounds of a detergent powder prepared according to U.S. Pat. No. 4,058,472 (the disclosure of which is incorporated by reference herein) and containing 5% by weight of the sodium salts of a mixture of sulfonated C_{14}-C_{18} alkyl catechol as a surface active component, the mixture being 60 parts by weight of mono-C_{14}-C_{18} alkyl catechol and 40 parts by weight of di-C_{14}-C_{18} alkyl catechol, 35% of sodium tetrapyrophosphate, 30% of sodium silicate, 20% of sodium carbonate, 3% of sodium carboxymethyl cellulose and 7% of starch is mixed with 0.15 grams of one of the perfumery substances set forth in Table II of Example XIV, supra, until substantially homogeneous compositions are obtained. Each of the compositions have excellent aromas as set forth in Table II of Example XIV.

EXAMPLE XX

Scented polyethylene pellets having pronounced aromas as set forth in Table II of Example XIV are prepared as follows:

75 Pounds of polyethylene of a melting point of about 220° F. are heated to about 230° C. under 5 atmospheres pressure in a pressure vessel. 25 Pounds of each of the substances set forth in Table II of Example XIV, separately, are then quickly added to the liquified polyethylene. The temperature is maintained at 230° C. under high pressure and the mixing is continued for about 15 minutes in each case. The pressure vessel is then depressurized and the molten polyethylene enriched with each of the perfumery substances is permitted to exit from the vessel by gravity. The liquid falling through orifices (in the apparatus) in droplets solidifies almost instantaneously on impact with a moving cooled conveyor operating immediately below the pressure vessel. Solid polyethylene pellets having pronounced aromas as set forth in Table II of Example XIV are thus formed. In each case 50 pounds of thus-formed master pellets are then added to 1000 pounds of unscented polyethylene powder and the mass is heated to the liquid state. The liquid is molded into thin sheets, films and container shapes. The thin sheets, films and container shapes have pronounced aromas as set forth in Table II of Example XIV.

EXAMPLE XXI

Utilizing the procedure of Example I at column 15 of U.S. Pat. No. 3,632,396 (the specification for which is incorporated by reference herein), a non-woven cloth substrate useful as a drier-added fabric softening article of manufacture is prepared wherein the substrate, the substrate coating and the outer coating and the perfuming material are as follows:

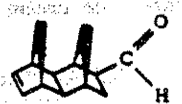
1. a water dissolvable paper as the substrate ("Dissolvo Paper");
2. Adogen 448 (melting point 140° F.) as the substrate coating; and
3. an outer coating having the following formulation (melting point about 150° F.):
    57% C_{20-22} HAPS
    22% isopropyl alcohol
    20% antistatic agent
    1% of one of the perfumery substances as set forth in Table II of Example XIV.

A fabric softening composition prepared as set forth above having aroma characteristics as set forth in Table II of Example XIV consists of a substrate having a weight of about 3 grams per 100 square inches, a substrate coating weighing about 1.85 grams per 100 square inches of substrate and an outer coating weighing about 1.4 grams per 100 square inches of substrate is created, thereby providing a total aromatized substrate and outer coating weight ratio of about 1:1 by weight of the substrate. The aromas as set forth in Table II of Example XIV is imparted in pleasant manners to head spaces in the dryers on operation thereof using the drier-added fabric softening non-woven fabric articles.

EXAMPLE XXII

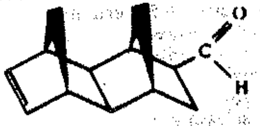
Vanilla Flavor

The following formulation is prepared:

Vanillin	10.0 grams
Ethyl Vanillin	3.0 grams
Benzodihydropyrone	3.0 grams
Heliotropin	1.0 gram
Propenyl Guiacol	0.5 grams
Gamma Nonyl Lactone	0.25 grams
Gamma Undecalactone	0.25 grams
Delta-Dodecalactone	0.25 grams
The aldehyde compound of Example I, having the structure:  bulked fractions 8-19	0.001 grams

The compound having the structure:

enhances the foregoing vanillin formulation (a) making it more natural-like; and (b) making it three times (3×) as powerful as the formulation without this compound added thereto. In addition, the formulation is rendered much more outstanding in a standard creme-de-Kahlua formulation causing the creme-de-Kahlua formulation to be more natural-like and preferred by a bench panel of five members, unanimously. The resulting formulation containing the compound having the structure:



is added to the following liqueur formulation:

Ingredients	Parts by Weight
Clove essential oils	780
Lemon essential oils	400
Orange essential oils	300
Cinnamon essential oils	250
Mace essential oils	180
Vanillin formulation (as set forth above)	150
Neroli essential oil	10
Citronellol	2
Rose absolute	1
Food grade ethanol	927

The resulting liqueur is added to the following mixture in order to produce a consumable material:

Ingredients	Parts by Weight
96% Food grade ethanol	301 kg
Sugar	40 kg
Distilled water	46.8 liters
Flavor (as set forth above) (0.5% in food grade ethanol)	0.5 kg

The resulting liquer has an interesting, bitter almond taste and aroma making it useful as such or as a "Bagne" for a sauce used for soaking pound cakes such as "Rum BaBa".

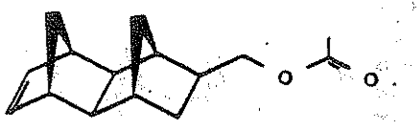
EXAMPLE XXIII

The vanilla flavor of Example XII is placed into an ice cream mix at the rate of 0.05%. The resulting previously-unflavored ice cream has an excellent vanilla flavor.

EXAMPLE XXIV

Salad Dressing

To a portion of essentially flavorless salad dressing, the compound of Example VII, having the structure:



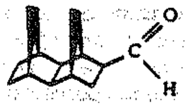
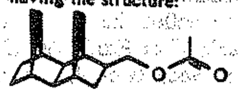
(bulked fractions 1-5) is added at the rate of 1 ppm and also at the rate of 2 ppm. The resulting mixtures have characteristic artichoke notes. The salad dressing is a mixture of the following:

Ingredient	Parts by Weight
Black pepper oil	3
Nutmeg oil	3
Celery Oil	3
Lemon oil	3
Mustard oil	1
Vinegar-citric acid (50-50 mixture)	120
Starch paste prepared from tapioca flour-water (50-50 mixture)	300
Liquid egg yolks	210
Sodium chloride	7
Sucrose	10
Mustard	20
Locust Bean gum	6

EXAMPLE XXV(A), (B)

Lemon/Fruity Flavor Formulation

The following lemony, fruity flavor formulations are prepared:

Ingredient	Parts by Weight XXV(A)	Parts by Weight XXV(B)
Natural Lemon Oil, Terpeneless	10.0	10.0
Acetaldehyde	0.6	0.6
Alpha-terpineol	2.1	2.1
Citral	1.8	1.8
Carvone	0.24	0.24
Terpinolene	1.2	1.2
Alpha-terpinene	0.25	0.25
Diphenyl	0.25	0.25
Alpha Fenchyl Alcohol	0.25	0.25
Limonene	0.35	0.35
Linalool	0.25	0.25
Geranyl Acetate	0.25	0.25
Nootkatone	0.25	0.25
Neryl Acetate	0.25	0.25
Geranyl nitrile	0.55	0.55
Citronellol nitrile	0.60	0.60
Fenchyl ethyl ether	0.05	0.05
The compound of Example II having the structure:  bulked fractions 7-13	0.50	0.0
The compound of Example VI having the structure:  bulked fractions 8-10	0.0	0.75

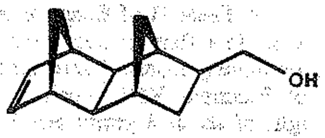
The compound of Example II adds to this lemon flavor formulation an excellent melony flavor causing the overall formulation to have a "lemon/melon" aroma and taste causing it to be useful in enhancing the taste of fresh papaya fruit when three or four drops of this flavor diluted at the rate of 1% in 50% aqueous foodgrade ethanol is placed on the open papaya fruit.

The compound of Example VI adds an excellent pineapple aroma and taste nuance to this lemon flavor. When the flavor (in 2% dilution and 50% foodgrade ethanol) is added to cooking chicken, the resultant cooked chicken has an excellent "lemony nuance" which is enhanced by use of the compound of Example VI.

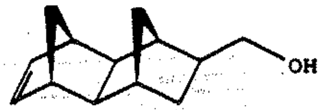
EXAMPLE XXVI

Root Beer Beverage

The compound having the structure:



produced according to Example IV, bulked fractions 6-10 is added to root beer (Barrelhead, produced by Canada Dry Corporation of Maspeth, N.Y., a division of the Norton Simon Corporation) at the rate of 1.5 ppm and submitted to a bench panel. The tetracyclic carbinol improves the woody rooty notes insofar as the aroma and taste of the rootbeer are concerned. Therefore, the beverage containing the compound defined according to the structure:

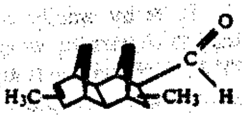


is preferred by a bench panel (of five members) unanimously over the beverage which does not contain the tetracyclic carbinol derivative produced according to Example IV.

EXAMPLE XXVII

Amaretto Flavor

The following formulation is prepared:

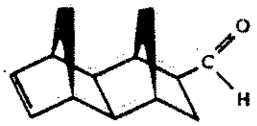
Ingredients	Parts by Weight
Lavender essential oil	105.0
Clary sage essential oil	100.0
Rosemary essential oil	100.0
Thyme essential oil	90.0
Fennel essential oil	40.0
Mint essential oil	20.0
Mixture of compounds prepared according to Example VIII having the structures:  and 	5.9
Angelica essential oil	5.0
Anise essential oil	5.0
Lemon essential oil	4.0
Wormwood essential oil	2.0
Cinnamon essential oil (10% in alcohol solution)	0.1
Aqueous 95%, foodgrade ethanol	523.0

The mixture of compounds produced according to Example VIII enhances this amaretto flavor in view of the green, melony, minty, herbaceous and floral aroma and taste nuances which particularly enhance the mint oil aroma and taste portion of this formulation.

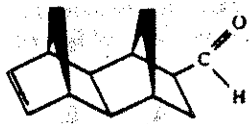
A liqueur is produced by using the foregoing formulation as follows:

Ingredient	Parts by Weight
96% alcohol	46.1 l
Sugar	1.0 kg
Distilled Water	55.1 l
Amaretto flavor produced, supra (diluted at the rate of 0.8% in 95% aqueous foodgrade ethanol)	0.5 kg

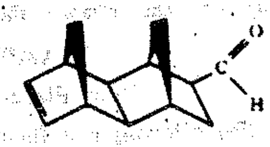
In addition, the wormwood essential oil component of the foregoing amaretto flavor can be replaced totally by the use of the compound of Example I having the structure:



bulked fractions 8–19. Actually the aldehyde having the structure:



can replace the 2 parts by weight of wormwood essential oil by using only 0.02 parts by weight of the aldehyde having the structure:



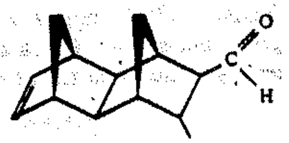
EXAMPLE XXVIII

Toothpaste Flavor Formulation

The following basic toothpaste flavor formulation is prepared:

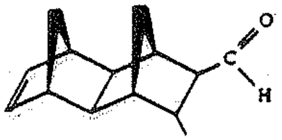
Ingredients	Parts by Weight
Cardamon Oil	0.2
Clove Oil	1.0
Spearmint Oil	2.0
Peppermint Oil	96.8

This flavor formulation is divided into three portions. To the first portion, nothing is added. To the second portion, 8 parts by weight of the first portion is combined with 2 parts by weight of anethole. Eight parts by weight of the third portion of this flavor is then combined with 2 parts by weight of the compound of Example IX having the structure:

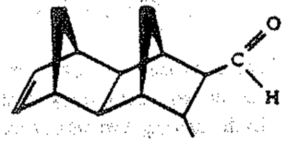


prepared according to Example IX and 2 parts by weight of anethole.

Each of the three flavors are compared in water at the rate of 10 ppm and evaluated by a bench panel. Each of the second and third flavors has sweet anise-like characteristics, but the flavor containing the compound defined according to the structure:



also has cinnamic and spicy aroma and taste nuances. Therefore, the flavor containing the aldehyde produced according to Example IX is preferred over flavors not containing the aldehyde of Example IX and, in addition, the aldehyde of Example IX having the structure:

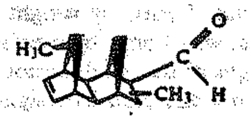


augments and enhances the anise-like flavor.

EXAMPLE XXIX

Mint Flavor Formulation

The following mint flavor formulation is prepared:

Ingredients	Parts by Weight
Peppermint Oil	60.0
Spearmint Oil	38.0
Mixture of compounds produced according to Example VIII having the structures:  and 	2.0

The mixture of compounds produced according to Example VIII imparts a minty, herbaceous, floral, green and melony aroma and taste nuance of great intensity to this mint flavor formulation.

EXAMPLE XXX

A. Powder Flavor Formulation.

20 Grams of the flavor composition of Example XXIX is emulsified in a solution containing 300 gm gum acacia and 700 gm water. The emulsion is spray-dried with a Bowen Lab Model Drier utilizing 260 c.f.m. of air with an inlet temperature of 500° F., an outlet temperature of 200° F. and a wheel speed of 50,000 rpm.

B. Sustained Release Flavor

The following mixture is prepared:

Ingredients	Parts by Weight
Liquid mint Flavor Composition of Example XXIX	20.0
Propylene glycol	9.0
Cab-O-Sil ® M-5 (Brand of Silica produced by the Cabot Corporation of 125 High Street, Boston, Mass. 02110; Physical Properties: Surface Area: 200 m^2gm Nominal particle size: 0.012 microns Density: 2.3 lbs/cu. ft.)	5.00

The Cab-O-Sil is dispersed in the liquid mint flavor composition of Example XXIX with vigorous stirring, thereby resulting in a viscous liquid. 71 Parts by weight of the powder flavor composition of Part A of this example, supra, is then blended into the said viscous liquid, with stirring, at 25° C. for a period of 30 minutes resulting in a dry, free flowing sustained release flavor powder.

EXAMPLE XXXI

10 Parts by weight of 50 Bloom pigskin gelatin is added to 90 parts by weight of water at a temperature of 150° F. The mixture is agitated until the gelatin is completely dissolved and the solution is cooled to 120° F. 20 Parts by weight of the liquid flavor composition of Example XXIX is added to the solution which is then homogenized to form an emulsion having particle size typically in the range of 5–40 microns. This material is kept at 120° F. under which conditions the gelatin will not jell.

Coacervation is induced by adding slowly and uniformly 40 parts by weight of a 20% aqueous solution of sodium sulphate. During coacervation the gelatin molecules are deposited uniformly about each oil droplet as a nucleus.

Gelation is effected by pouring the heated coacervate mixture into 1,000 parts by weight of 7% aqueous solution of sodium sulphate at 65° F. The resulting jelled coacervate may be filtered and washed with water at temperatures below the melting point of gelatin, to remove the salt.

Hardening of the filtered cake, in this example, is effected by washing with 200 parts by weight of 37% solution of formaldehyde in water. The cake is then washed to remove residual formaldehyde.

EXAMPLE XXXII

Chewing Gum

100 Parts by weight of chicle are mixed with 4 parts by weight of the flavor prepared in accordance with Example XXIX. 300 Parts of sucrose and 100 parts of corn syrup are added. Mixing is effected in a ribbon blender with jacketed side walls of the type manufactured by the Baker Perkins Co.

The resultant chewing gum blend is then manufactured into strips 1 inch in width and 0.1 inches in thickness. The strips are cut into lengths of 3 inches each. On chewing, the chewing gum has a pleasant, long lasting mint flavors.

EXAMPLE XXXIII

Chewing Gum

100 Parts by weight of chicle are mixed with 18 parts by weight of the flavor prepared in accordance with Example XXX(B). 300 Parts of sucrose and 100 parts of corn syrup are then added. Mixing is effected in a ribbon blender with jacketed side walls of the type manufactured by the Baker Perkins Co.

The resultant chewing gum blend is then manufactured into strips 1 inch in width and 0.1 inches in thickness. The strips are cut into lengths of 3 inches each. On chewing, the chewing gum has a pleasant, long lasting mint flavor.

EXAMPLE XXXIV

Toothpaste Formulation

The following separate groups of ingredients are prepared:

Parts by Weight	Ingredients
Group "A"	
30.200	Glycerine
15.325	Distilled Water
.100	Sodium Benzoate
.125	Saccharin Sodium
.400	Stannous Fluoride
Group "B"	
12.500	Calcium Carbonate
37.200	Dicalsium Phosphate (Dihydrate)
Group "C"	
2.000	Sodium N—Lauroyl Sarcosinate (foaming agent)
Group "D"	
1.200	Flavor Material of Example XXX(B)
100.00 TOTAL	

PROCEDURE:

1. The ingredients in Group "A" are stirred and heated in a steam jacketed kettle to 160° F.;
2. Stirring is continued for an additional three to five minutes to form a homogeneous gel;
3. The powders of Group "B" are added to the gel, while mixing, until a homogeneous paste is formed;
4. With stirring, the flavor of "D" is added and lastly the sodium-n-lauroyl sarcosinate; and
5. The resultant slurry is then blended for one hour. The completed paste is then transferred to a three roller mill and then homogenized, and finally tubed.

The resulting toothpaste when used in a normal toothbrushing procedure yields a pleasant mint flavor, of constant strong intensity throughout said procedure (1-1.5 minutes).

EXAMPLE XXXV

Chewable Vitamin Tablets

The flavor material produced according to the process of Example XXX(B) is added to a Chewable Vitamin Tablet. Formulation at a rate of 10 gm/Kg which Chewable Vitamin Tablet formulation is prepared as follows:

In a Hobart mixer, the following materials are blended to homogeneity:

	Gms/1000 Tablets
Vitamin C (ascorbic acid) as	70.11
Ascorbic acid-sodium ascorbate	4.0
mixture 1:1	
Vitamin B_1 (thiamine mononitrate) as	
Rocoat ® thiamine mononitrate	5.0
33⅓% (Hoffman LaRoche)	
Vitamin B_2 (riboflavin) as	
Rocoat ® riboflavin 33⅓%	4.0
Vitamin B_6 (pyridoxine hydrochloride) as	
Rocoat ® pyridoxine hydrochloride	33.0
33⅓%	
Niacinamide as Rocoat ® niacinamide	
33⅓%	
Calcium pantothenate	11.5
Vitamin B_{12} (cyanocobalamin) as	3.5
Merck 0.1% in gelatin	
Vitamin E (dl-alpha tocopheryl	6.6
acetate) as dry Vitamin E acetate 33⅓%	
d-Biotin	0.044
Flavor of Example XXX(B)	(as indicated above)
Certified lake color	5.0
Sweetener - sodium saccharin	1.0
Magnesium stearate lubricant	10.0
Mannitol q.s. to make	500.0

Preliminary tablets are prepared by slugging with flat-faced punches and grinding the slugs to 14 mesh. 13.5 gm dry Vitamin A Acetate and 0.6 gm Vitamin D are then added as beadlets. The entire blend is then compressed using concave punches at 0.5 gm each.

Chewing of the resultant tablets yields a pleasant, longlasting mint flavor for a period of 15 minutes.

EXAMPLE XXVI

Chewing Tobacco

Onto 100 pounds of tobacco for chewing (85% Wisconsin leaf and 15% Pennsylvania leaf) the following casing is sprayed at a rate of 30%:

Ingredients	Parts by Weight
Corn Syrup	60.0
Licorice	10.0
Glycerine	20.0
Fig Juice	4.6
Prune Juice	5.0
Mint flavor of Example XXX(I)	0.08

The resultant product is redried to a moisture content of 20%. On chewing, this tobacco has an excellent cooling mint flavor nuance in conjunction with the tobacco notes.

EXAMPLE XXXVI

Tobacco Formulation

A tobacco blend is made up by mixing the following materials:

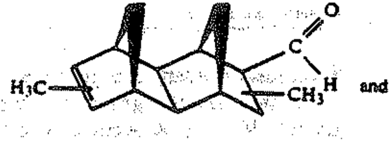
Ingredient	Parts by Weight
Bright	40.1
Burley	24.9
Maryland	1.1
Turkish	11.6
Stem (flue cured)	14.2
Glycerine	2.8
Water	5.3

The above tobacco is used in producing cigarettes, and the following formulation is compounded and incorporated into each of these cigarettes:

Ingredient	Parts by Weight
Ethyl butyrate	0.05
Ethyl valerate	0.05
Maltol	2.00
Cocoa extract	26.00
Coffee extract	10.00
Ethyl alcohol	20.00
Water	41.90

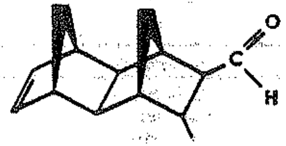
The above flavor is incorporated into model "filter" cigarettes at the rate of 0.1%.

One-fourth of these model cigaretts are treated in the tobacco section with the mixture of aldehydes produced according to Example VIII having the structures:



and

One-fourth of these model cigarettes are treated in the tobacco section with the compound defined according to the structure:



produced according to Example IX.

Each of the foregoing aldehydes is added at rates of 100, 200 and 300 ppm per cigarette.

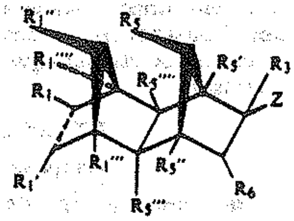
Another one-fourth of these model cigarettes are treated in the filter with either the mixture of aldehydes of Example VIII or the aldehyde of Example IX at the rate of 2×10^{-5} gm per gm of filter.

When evaluated by paired comparison, the cigarettes treated both in the tobacco and the filter with the mixture of compounds produced according to Example VIII are found, in smoke flavor, to have sweet, floral, green, herbaceous, minty and cooling aroma and taste nuances, and also cause the tobacco to be more natural-like. Also an excellent hay tobacco aroma and taste is imparted prior to and on smoking in both the main stream and the side stream by the product of Example VIII.

When evaluated by a paired comparison, these cigarettes are treated in both the tobacco and the filter with the compound of Example IX are found in smoked flavored to have oriental, spicy, cinnamon-like aroma and taste nuances causing the tobacco to be "oriental" and also natural in its "oriental" character. In general, an excellent "Turkish" tobacco aroma and taste is imparted prior to and on smoking in the main stream and in the side stream by the product produced according to Example IX, supra.

What is claimed is:

1. A process for augmenting or enhancing the aroma or taste of a consumable material selected from the group consisting of perfume compositions and colognes, comprising the step of adding to said consumable material an aroma augmenting or enhancing quantity of at least one compound defined according to the structure:

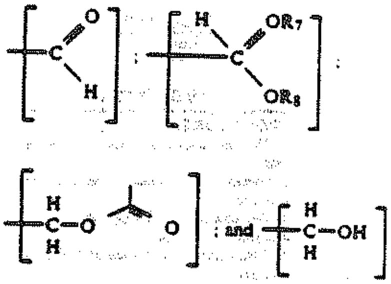


wherein the dashed line represents a carbon-carbon double bond or a carbon-carbon single bond; wherein R_1, R_1', R_1'', R_1''', R_1'''', R_3, R_5, R_5', R_5'', R_5''', R_5'''' and R_6 represent hydrogen or methyl; with the provisos:

(i) at least four of R_1, R_1', R_1'', R_1''' and R_1'''' represents hydrogen; and

(ii) at leat four of R_5, R_5', R_5'', R_5''', R_5'''' represent hydrogen;

with Z being a moiety selected from the group consisting of:



with the line:

(++++]

representing a carbon-carbon single bond or no bond at all; and R_7 and R_8 being separately C_1–C_4 lower alkyl or, taken together, being C_2–C_4 alkylene.

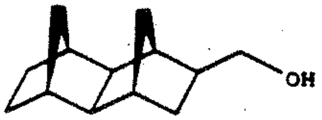
2. The process of claim 1 wherein the consumable material is a perfume composition.

3. The process of claim 1 wherein the consumable material is a cologne.

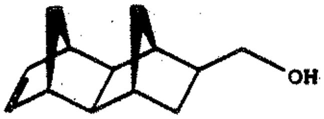
4. The process of claim 1 wherein the compound added to the consumable material has the structure:

5. The process of claim 1 wherein the compound added to the consumable material has the structure:

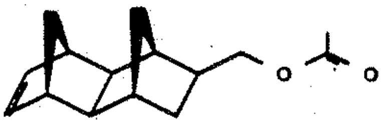
6. The process of claim 1 wherein the compound added to the consumable material has the structure:



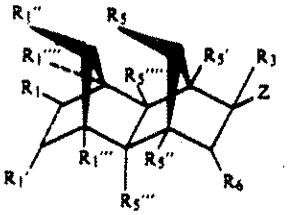
7. The process of claim 1 wherein the compound added to the consumable material has the structure:



8. The process of claim 1 wherein the compound added to the consumable material has the structure:

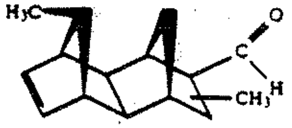


9. The process of claim 1 wherein the substance added to the consumable material which substance is defined according to the structure:



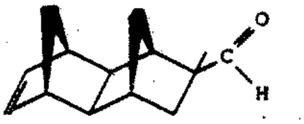
is a mixture having the structures:

and

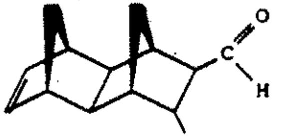


10. The process of claim 1 wherein the compound added to the consumable material has the structure:

11. The process of claim 1 wherein the compound added to the consumable material has the structure:



12. The process of claim 1 wherein the compound added to the consumable material has the structure:



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United States Patent [19]

Yamashita et al.

[11] **4,446,226**

[45] **May 1, 1984**

[54] **LIGHT-SENSITIVE COLOR PHOTOGRAPHIC MATERIAL**

[75] Inventors: **Kiyoshi Yamashita; Toshifumi Iijima,** both of Hino, Japan

[73] Assignee: **Konishiroku Photo Industry Co., Ltd.,** Tokyo, Japan

[21] Appl. No.: **397,083**

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[51] **Int. Cl.^{3}** **G03C 1/46; G03C 7/26**

[52] **U.S. Cl.** **430/506;** 430/502; 430/503; 430/509; 430/567

[58] **Field of Search** 430/502, 503, 505, 506, 430/509, 567, 569

[56] **References Cited**

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Primary Examiner—Mary F. Downey

Attorney, Agent, or Firm—Frishauf, Holtz, Goodman & Woodward

[57] **ABSTRACT**

A light-sensitive color photographic material having a support and, coated thereon, at least two light-sensitive silver halide emulsion layers respectively sensitive to lights of different spectral regions, characterized in that each of the light-sensitive emulsion layers comprises at least two emulsion layers having different light-sensitivities and containing negative type light-sensitive silver halide crystals essentially consisting of silver iodobromide containing silver iodide at a proportion not higher than 4 mole %.

This invention provides a silver halide color photographic material, in which the proportion of the silver halide utilized for the information of a color image to the total silver halide used is enhanced remarkably.

9 Claims, No Drawings

LIGHT-SENSITIVE COLOR PHOTOGRAPHIC MATERIAL

This invention relates to a light-sensitive color photographic material, and particularly to a light-sensitive color photographic material for use of photographing an object in a camera. More particularly, this invention relates to a multi-layer silver halide light-sensitive color photographic material for high-sensitivity photographing, in which the efficiency of utilizing the silver halide in a negative type silver halide emulsion for the formation of a dye image is improved.

Generally, light-sensitive color photographic materials used for the photographing purposes are required to exhibit a high sensitivity and a high image quality. Sensitivity of a silver halide depends on the size of silver halide crystals, and it is necessary to use relatively coarse silver halide crystals in order to obtain a high sensitivity. However, graininess of a dye image is decisively affected by the size of silver halide crystals. Therefore, it has been proposed to use a multi-layer light-sensitive color photographic material comprising two or more layers exhibiting sensitivity of light in the same spectral region and forming a dye of the same hue. Light-sensitive color photographic materials of this type are described for example in West German Patent No. 1121470, British Pat. No. 923,045, Japanese Patent Publication No. 15495/1974, Japanese Provisional Patent Publication Nos. 49027/1976, 143016/1977, 97831/1978 and 97424/1978. It is also known to form a light-sensitive photographic material comprising only one layer by using a mixture of a high-sensitivity emulsion containing relatively coarse crystals sensitive to light in a particular visible spectral region and a low-sensitivity emulsion containing relatively fine crystals. However, the material of this type is not popular because of its inferior graininess.

The present invention relates to a multi-layer light-sensitive color photographic material comprising at least two layers exhibiting different spectral sensitivities, and each layer exhibiting the same spectral sensitivity i.e. each layer exhibiting sensitivity to light in the same visible spectral region and forming a dye of the same hue is further constituted by two or more layers.

In silver halide light-sensitive color photographic materials, silver is used as the raw material for light-sensitive substance. In spite of small amount of silver deposits, silver is widely used for industrial, trinketry and medical purposes and the like. Thus, need exists for reduction in the amount of silver used in silver halide light-sensitive photographic materials for the purpose of preserving resources and also reducing the cost of silver halide light-sensitive photographic materials because of recent remarkable rise in the price of silver.

Usually, in silver halide light-sensitive color photographic materials for high-sensitivity photographing, negative type silver iodobromide containing silver iodide at a high molar percentage is used as the light-sensitive silver halide. However, with a light-sensitive material in which negative silver iodobromide containing silver iodide at a high molar percentage is used as the light-sensitive silver halide, the number of silver halide crystals not utilized for the image formation (hereinafter referred to as the dead grains) increases at the portion of maximum density in an image obtained upon exposure through an optical wedge. Thus, only about 40% of the exposed silver iodobromide crystals is utilized for the image formation. Although the mechanism of this phenomenon has not been completely clarified, it is assumed attributable to the occurrence of latent image bleaching during the development processing. In the color development, the proportion of the developed silver utilized for the formation of a color image is at most about 60% at the portion of maximum density because an oxidized product of the color developing agent is subjected not only to the reaction with a coupler but also to various reactions as described for example by T. H. James in "The Theory of the Photographic Process", Chapter 12, Section II, Macmillan Co., 1977. Therefore, because of the above-mentioned two factors affecting the utilization efficiency, the portion of the silver halide actually utilized for the formation of a color image is 25% or less of the silver amount used.

On the other hand, in a multi-layer light-sensitive color photographic material comprising at least two layers exhibiting different spectral sensitivities, and each layer exhibiting the same spectral sensitivity is further constituted by two or more layers, it is known to adjust the maximum color density of the high sensitivity layer by lowering the concentration of a coupler in the high sensitivity emulsion layer so as to improve graininess of the high sensitivity layer using relatively coarse silver halide crystals. However, if the concentration of the coupler is lowered, there is a serious drawback in that, many dead grains occur, resulting in low efficiency of silver halide utilization and low apparent sensitivity of the silver halide crystals.

Silver halide light-sensitive color photographic materials are generally subjected to color development after the imagewise exposure. Recently, the temperature of the color development is gradually raised for the purpose of meeting the need for quick processing. In many cases, the color development is conducted at a temperature between 35° and 40° C. for 3 to 3.5 minutes. However, to maintain such high processing temperatures, it is necessary to use much energy and to keep the concentration of the processing solution at a constant level as the solvent evaporates. Further, the processing solution deteriorates quickly as the processing temperature rises. Thus, need exists for a silver halide light-sensitive color photographic material capable of being developed at as low temperatures as possible.

The primary object of the present invention is to provide a silver halide light-sensitive color photographic material for high-sensitivity photographing which eliminates the disadvantages of the conventional techniques described above, and particularly a silver halide light-sensitive color photographic material for high-sensitivity photographing in which the proportion of the silver halide amount utilized for the formation of a color image to the amount of silver halide used is enhanced remarkably.

Another object of the present invention is to provide a silver halide light-sensitive color photographic material for high-sensitivity photographing, in which a negative type silver iodobromide emulsion having few dead grains is used.

A further object of the present invention is to provide a silver halide light-sensitive color photographic material for high-sensitivity photographing, in which the degree of color formation is increased with respect to the unit amount of developed silver.

A still further object of the present invention is to provide a silver halide light-sensitive color photographic material for high-sensitivity photographing, which is suitable for a low-temperature quick color development system.

The present invention provides a light-sensitive color photographic material having a support and, coated thereon, at least two light-sensitive silver halide emulsion layers respectively sensitive to lights of different spectral regions, each of which emulsion layers comprises at least two emulsion layers having different light-sensitivities and containing negative type light-sensitive silver halide crystals essentially consisting of silver iodobromide containing silver iodide at a proportion not higher than 4 mol %. The light-sensitive color photographic material characterized as described above is hereinafter referred to as the light-sensitive color photographic material in accordance with the present invention.

The above objects can be accomplished by the light-sensitive color photographic material described below in detail.

Namely, in the light-sensitive color photographic material in accordance with the present invention, a negative type silver halide emulsion having the sensitivity speck mainly at the surfaces of the silver halide crystals is used as the silver halide emulsion. The emulsion is of the surface latent image type, which means reversely from the so-called internal latent image type direct positive emulsion, namely means an emulsion which yields a blackened silver image in inverse proportion to the lightness of the object when developed with a surface developing solution after the exposure.

In the silver iodobromide emulsion, it is well known that more rapid development characteristics can be obtained as the molar percentage of silver iodide decreases. The inventors further studied this phenomenon and found that, although dead grains decrease as the molar percentage of silver iodide decreases in the case of a single layer, this feature does not occur remarkably if such a layer is stacked on or sandwiched between silver iodobromide emulsion layers containing a large molar percentage of silver iodide. Further studies revealed that, even in stacked layers, dead grains can be reduced if all of the negative type silver halide light-sensitive emulsions in the multi-layer silver halide light-sensitive material comprise silver iodobromide of low molar percentage of silver iodide. It was also revealed that the amount of dye formed per unit amount of developed silver increases considerably. The inventors presumes that dead grains occur because a small size latent image is bleached by an oxidized product of the developing agent. It is assumed that dead grains decrease in the case of low-iodine silver iodobromide because, if the development speed is high, the latent image quickly grows to a stable development nucleus, and that a relatively large amount of iodine occurring in a layer containing a large molar percentage of silver iodide restricts the development when a layer containing a small molar percentage of silver iodide is stacked on a silver iodobromide layer containing a large molar percentage of silver iodide.

It is not clear why the amount of a dye formed per unit amount of developed silver increases.

The silver halide used in the light-sensitive color photographic material in accordance with the present invention substantially consists of a negative type silver iodobromide containing 4 mole % or less of silver iodide. This means that the average content of silver iodide in the silver iodobromide crystals should be 4 mole % or less, and there may partially exist silver iodobromide crystals which contain more than 4 mole % of silver iodide and which are generated during the production process of silver halide. In the present invention, silver iodobromide preferably means the silver iodobromide containing 0.1 mole % or more of silver iodide. The preferable molar percentage of silver iodide in the present invention is between 1 and 3 mole %. The silver iodobromide may contain silver chloride, silver bromide, silver chlorobromide and/or a mixture thereof insofar as the effect of the present invention is not adversely affected. The silver iodobromide emulsion may contain large or small crystals, and may be monodispersed or polydispersed. However, the effect of the present invention is particularly remarkable when the emulsion is monodisperse. It is particularly preferable that the coefficient of variation obtained by dividing the standard deviation S (defined below) by the average crystal size $\bar{r}$ is 0.15 or less.

$$S = \frac{\sqrt{\Sigma(\bar{r} - r_i)^2 n_i^2}}{\Sigma n_i}$$

$$\frac{S}{\bar{r}} \leqq 0.15$$

The average crystal size as used herein means the average value of the diameters of silver halide crystals when they are spherical. When the crystals are cubic or not spherical, their projected images are converted to circular images of the same area, and the average of the diameters of the circular images is taken as the average crystal size. The average crystal size is defined by:

$$\bar{r} = \frac{\Sigma n_i r_i}{\Sigma n_i}$$

where r_i designates the crystal sizes of individual grains, and n_i designates the number of the crystals.

In the silver halide light-sensitive color photographic material according to the present invention, each emulsion layer containing negative type silver halide crystals having the same spectral sensitivity is constituted by at least two negative type silver halide emulsion layers having different light sensitivities.

It is preferable that the upper layer, viewed from the support, has a light sensitivity higher than that of the lower layer. Further, in the present invention, it is preferable that the at least two layers each having the same spectral sensitivity have the average crystal sizes of the silver halide crystals different from each other. For example, it is preferable that the average grain size of the silver halide grains contained in the emulsion layer having a higher light sensitivity is in the range between 0.5μ and 1.5μ, while that in the emulsion layer having a lower light sensitivity is in the range between 0.3μ and 0.8μ.

The light-sensitive color photographic material in accordance with the present invention comprises at least two kinds of emulsion layers which contain negative type silver halide crystals exhibiting different spectral sensitivities and which respectively consist of a plurality of layers. In the case of a light-sensitive natural color photographic material, three emulsion layers exhibiting different spectral sensitivities are generally used, and these layers are positioned in the order of for example red-sensitive, green-sensitive, and blue-sensitive emulsion layers from the side of the support towards the outermost layer. In this case, the proportion of silver iodide to the silver iodobromide in each layer should be 4 mole % or less. It is more preferable that the difference between the contents of silver iodide in the silver iodobromide emulsion layer containing the maximum molar percentage of silver iodide and that containing the minimum molar percentage of silver iodide is 2 mole % or less whereby the occurrence of dead grains is reduced much more. The molar percentage of silver iodide in the silver iodobromide contained in each layer is not limited in sofar as the silver halide light-sensitive emulsion contained in each of the two or more layers each exhibiting the same spectral sensitivity substantially consists of silver iodobromide containing 4 mole % or less of silver iodide. However, because of little occurrence of dead grains, it is preferable that the difference between the molar percentage of silver iodide in the silver iodobromide in the respective layers is small. Further, it is preferable that the difference between the molar percentage of silver iodide in the layer containing the maximum molar percentage of silver iodide and the layer containing the minimum molar percentage of silver iodide is 2 mole % or less.

The silver halide crystals used in the light-sensitive color photographic material in accordance with the present invention may be the so-called twinned crystals having irregular shapes such as sherical or plate-like shape, or may be of a regular shape such as cube, octahedron and tetradecahedron. Preferably, they are octahedral or tetradecahedral since lesser dead grains are generated. It is also possible to be a mixture of grains having a regular shape and an irregular shape.

The silver halide crystals used in the light-sensitive color photographic material in accordance with the present invention may be prepared by the acid process, neutral process or ammonia process. It is also possible to prepare seed crystals by the acid process, and grow them up to the predetermined size by the ammonia process which gives a high growth rate. When growing the silver halide crystals, it is desirable that the pH, pAg or the like in the reactor are controlled, and silver ions and halide ions are both poured sequentially and simultaneously and mixed in quantities matching the growth rate of silver halide grains, that is so called double jet method as described for example in Japanese Provisional Patent Publication No. 48521/1979.

The silver halides may be chemically sensitized with active gelatin; a sulfur sensitizer e.g. allylthiocarbamide, thiourea or cystine; a selenium sensitizer; a reduction sensitizer e.g. tin (II) salt, thiourea dioxide and polyamine; a noble metal sensitizer, e.g. gold sensitizer such as potassium aurithiocyanate, potassium chloroaurate, water-soluble gold salts or a water-soluble salt of ruthenium, platinum, rhodium or iridium, e.g. potassium chloroplatinate (some of these serve as sensitizers or fog restrainers depending on the amount used). These sensitizers may be used alone or in combination (e.g. a combination of the gold sensitizer with the sulfur sensitizer, or a combination of the gold sensitizer with selenium sensitizer).

Further, the silver halides may be optically sensitized (in which so-called super-sensitization may be obtained) to a desired wavelength region for example by using an optical sensitizer e.g. a cyanine dye such as zeromethine dye, monomethine dye, dimethine dye or trimethine dye, or a merocyanine dye singly or in combination of two or more.

As for the coupler used in the light-sensitive color photographic material in accordance with the present invention, i.e. the compound forming a dye by the reaction with an oxidized product of the color developing agent, it is sufficient only if it exists substantially at the time of color development. The coupler may be contained in the color developing solution or in the light-sensitive color photographic material. When the coupler is non-diffusion type, it is preferably contained in the light-sensitive color photographic material.

Generally, the coupler is contained in the light-sensitive layer of the light-sensitive color photographic material.

The coupler can be incorporated in the light-sensitive color photographic material in various ways in accordance with the present invention. When the coupler is soluble in an alkali, it may be added in the form of an alkaline solution. When it is soluble in an oil, it is preferably dissolved in a high boiling solvent optionally in combination with a low boiling solvent and finely dispersed in the silver halide emulsion according to the procedures described in U.S. Pat. Nos. 2,322,027 2,801,170, 2,801,171, 2,272,191 and 2,304,940. In this case, it is also possible to additionally add a hydroquinone derivative, an ultra violet ray absorber, a discoloration preventing agent or the like as required. It is also possible to use a mixture of two or more couplers. In the incorporation of the coupler into the light-sensitive material, one or more couplers may be dissolved optionally together with another coupler, a hydroquinone derivative, a discoloration preventing agent, an ultra violet ray absorber or the like as required in a high boiling solvent such as an organic acid amide, a carbamate, an ester, a ketone, a urea derivative or the like, particularly di-n-butyl phthalate, tri-cresyl phosphate, triphenyl phosphate, di-isooctyl azelate, di-n-butyl sebacate, tri-n-hexyl phosphate, N,N-diethyl-caprylamide butyl, N,N-diethyllaurylamide, n-pentadecyl phenyl ether, dioctyl phthalate, n-nonyl phenol, 3-pentadecylphenyl ethyl ether, 2,5-di-sec.-amylphenyl butyl ether, monophenyl-di-o-chlorophenyl phosphate, or a fluoroparaffin, or if necessary in a low boiling solvent such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, butyl propionate, cyclohexanol, diethylene glycol monoacetate, nitromethane, carbon tetrachloride, chloroform, cyclohexane, tetrahydrofuran, methyl alcohol, acetonitrile, dimethylformamide, dioxane or ethyl methyl ketone. The solution thus formed may be mixed with an aqueous solution containing a hydrophilic binder such as gelatin and an anionic surface active agent such as alkylbenzenesulfonate or alkylnaphthalenesulfonate and/or a nonionic surface active agent such as sorbitan sesquioleate or sorbitan monolaurate. The mixture thus obtained may then be emulsified and dispersed in a high-speed rotating mixer, colloid mill, supersonic dispersing unit or the like, and added to a constituent of the light-sensitive color photographic material in accordance with the present invention, preferably the silver halide emulsion.

Further, the coupler may be dispersed in the photosensitive material by a latex dispersing method.

The latex dispersing method and its effect are described for example in Japanese Provisional Patent Publication Nos. 74538/1974, 59943/1976 and 32552/1979, and "Research Disclosure", August 1976, No. 14850, pages 77–79.

Examples of suitable lateces are homopolymers, copolymers and terpolymers of monomers such as styrene, ethyl acrylate, n-butyl acrylate, n-buty methacrylate, 2-acetoacetoxyethyl methacrylate, 2-(methacryloyloxy) ethyltrimethylammonium sulfate, sodium 3-(methacryloyloxy) propane-1-sulfonate, N-isopropylacrylamide, N-[2-(2-methyl-4-oxopentyl)]acrylamide, and 2-acrylamido-2-methylpropane sulfonate.

The amount of the coupler used is not critical. However, when it is added to the light-sensitive color photographic material, it is preferably used in an amount between 10 g and 100 g per one mole of silver halide. When it is added to the color developing solution, it is used preferably in an amount between about 0.1 g and 3 g per liter of the color developing solution.

For the purpose of preventing the dye from discolorating due to active rays having a short wavelength, it is advantageous to use ultraviolet ray absorbers such as thiazolidone, benzotriazole, acrylonitrile and benzophenone compounds together with the coupler in the light-sensitive color photographic material in accordance with the present invention. It is particularly advantageous to use *Tinuvin* P's, 320, 326, 327 and 328 (available from Ciba-Geigy AG) alone or in combination.

The hydroquinone derivatives used together with the coupler in the light-sensitive color photographic material in accordance with the present invention also include their precursors. The precursors as used herein mean the compounds releasing hydroquinone derivatives by hydrolysis.

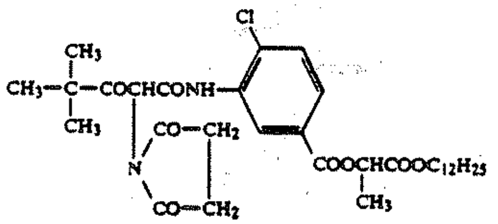
Examples of the discoloration preventing agents used together with the coupler in the present invention preferably include coumarone, coumaran and spirochroman compounds and the like.

The coupler used in the light-sensitive color photographic material in accordance with the present invention may be of either two or four equivalent type of an optional combination thereof.

Further, the coupler may be a low molecular coupler or the so-called polymeric coupler.

The coupler used in the light-sensitive color photographic material in accordance with the present invention may be any of the known photographic couplers, preferably α-acylacetamide yellow coupler (α-benzoylacetanilide yellow coupler, α-pivaloylacetanilide yellow coupler or the like), 5-pyrazolone magneta coupler, pyrazolinobenzoimidazole magenta coupler, phenol cyan coupler or naphthol cyan coupler.

Typical examples of the α-acylacetamide yellow couplers used in the present invention are:



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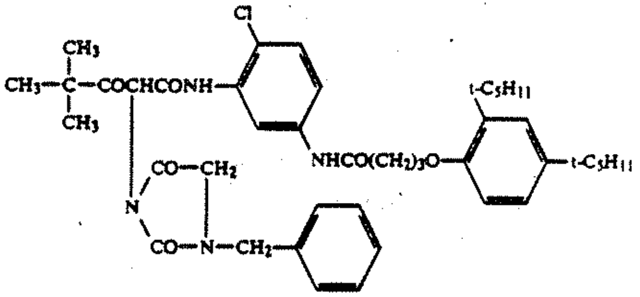

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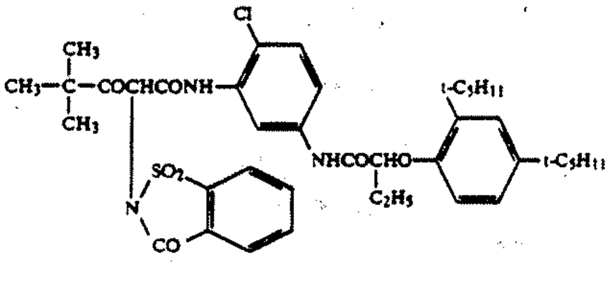

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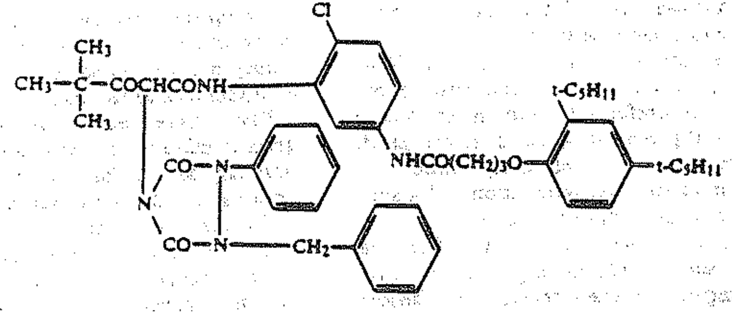

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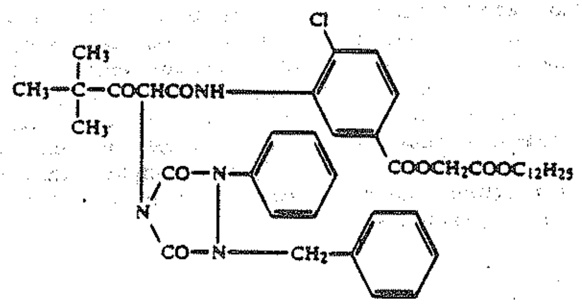

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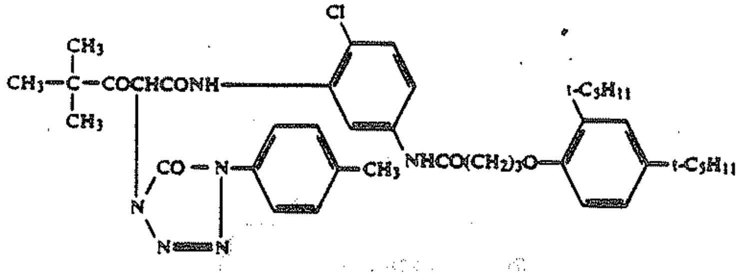

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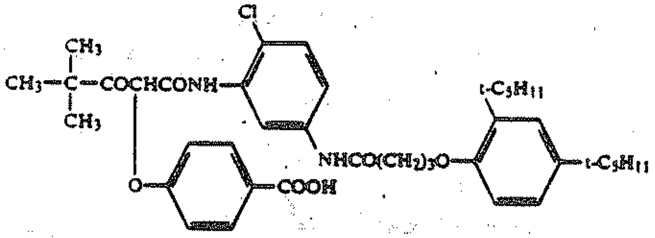

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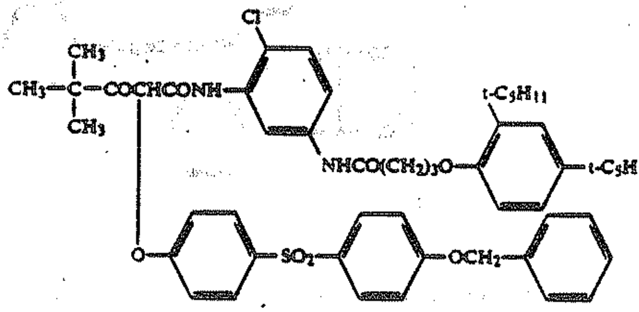

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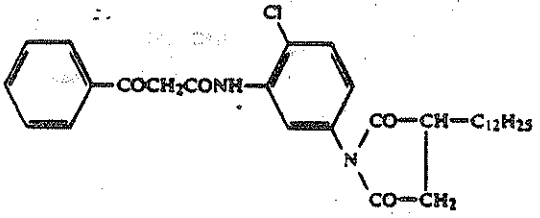

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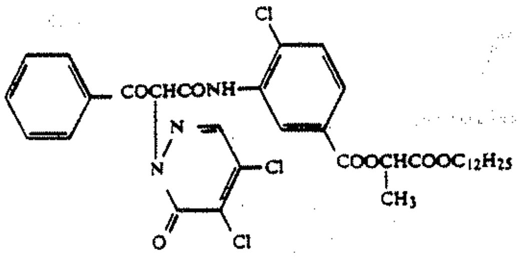

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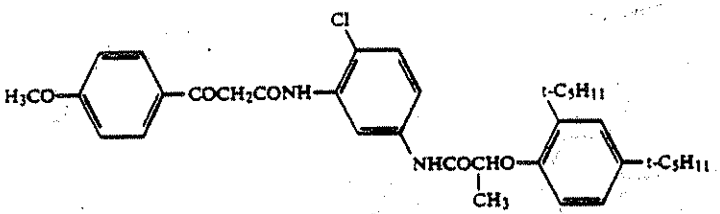

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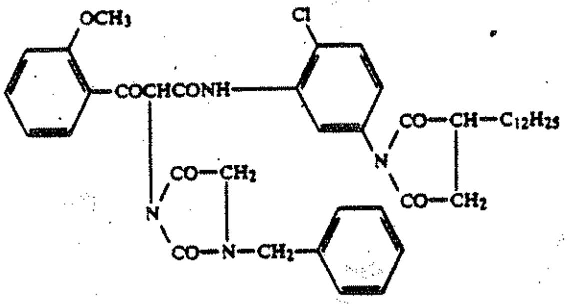

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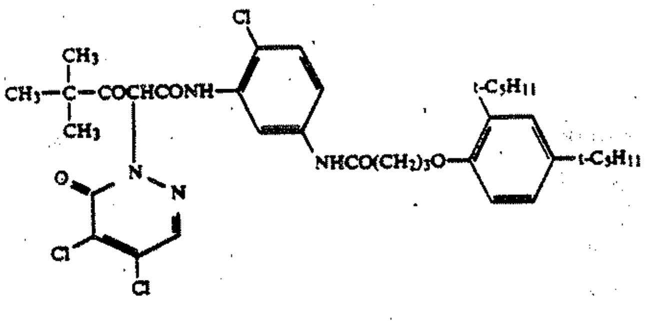

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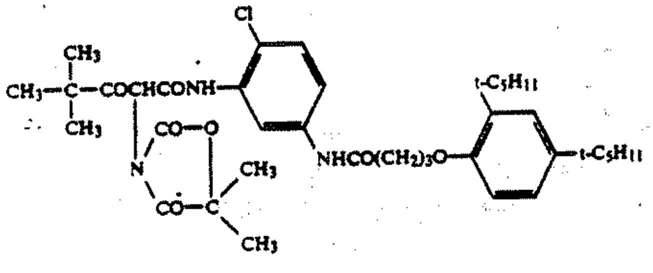

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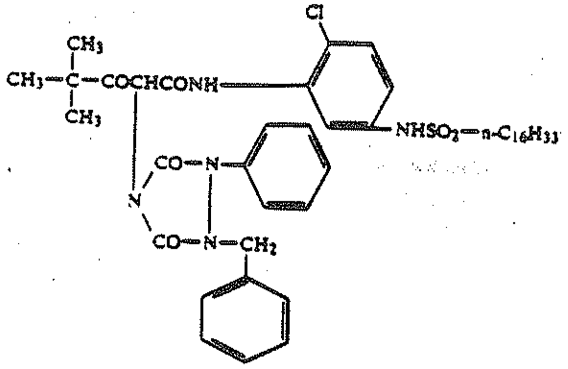

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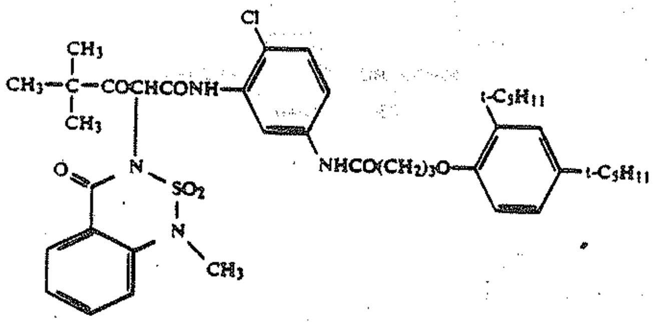

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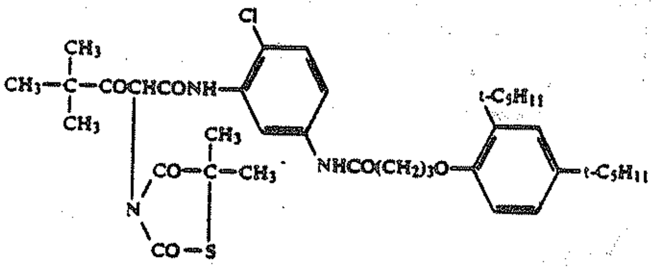

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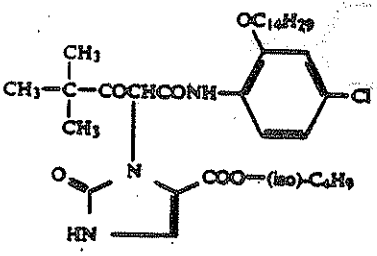

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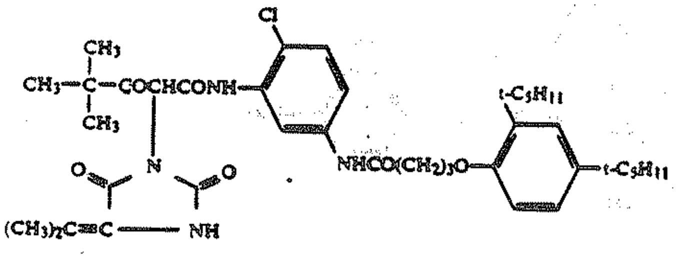

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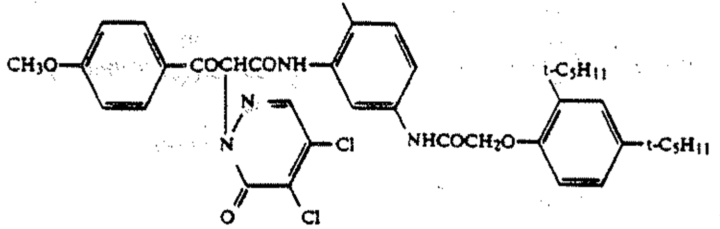
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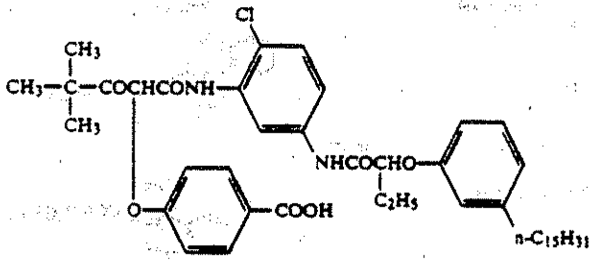
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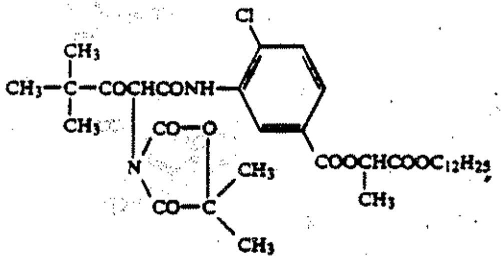
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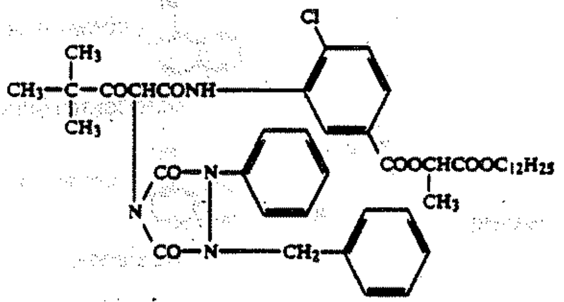
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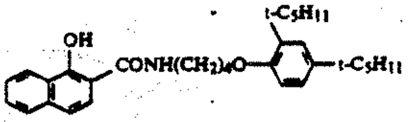
The above-described α-acylacetamide yellow couplers used in the present invention can be prepared by the methods described for example in West German Offenlegungsschrift Nos. 2,057,941 and 2,163,812, Japanese Provisional Patent Publication Nos. 26133/1972 and 29432/1973, U.S. Pat. Nos. 3,227,550, 2,875,057 and 3,265,506, Japanese Provisional Patent Publication Nos. 66834/1973, 66835/1973, 94432/1973, 1229/1973, 10736/1974, 34232/1975, 65231/1975, 117423/1975, 3631/1976 and 50734/1976.

The α-acylacetamide yellow couplers may be contained in the silver halide emulsion layer individually or as a mixture of two or more couplers. They may be incorporated by the above-mentioned procedures in an amount 1–30 mole % of blue-sensitive silver halide.

Typical examples of the cyan couplers used in the present invention are: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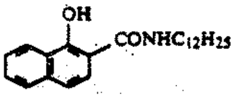
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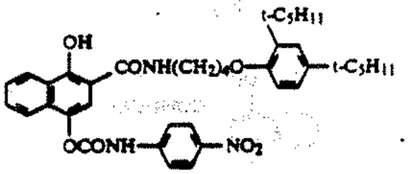
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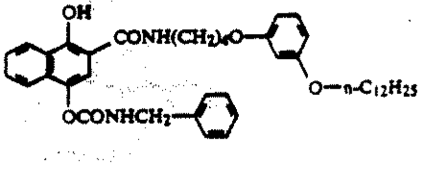
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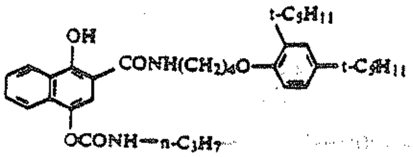
[C-5]



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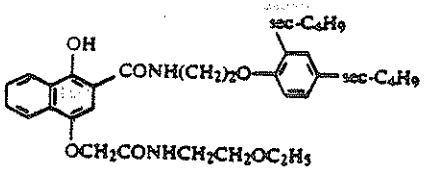

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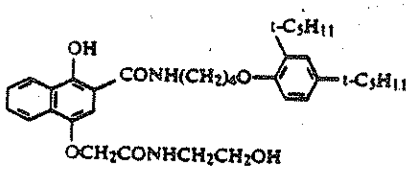

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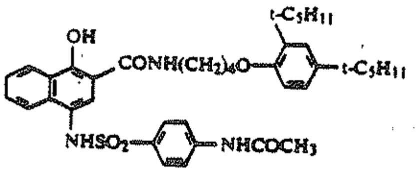

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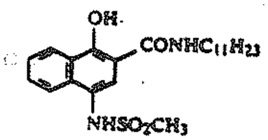

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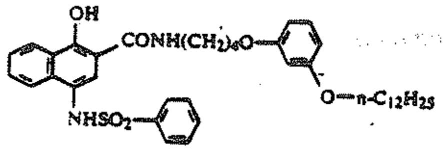

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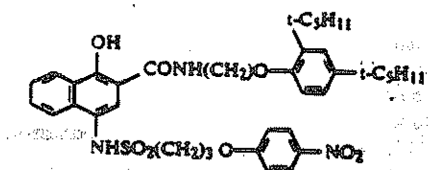

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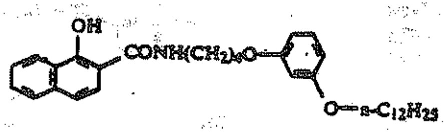

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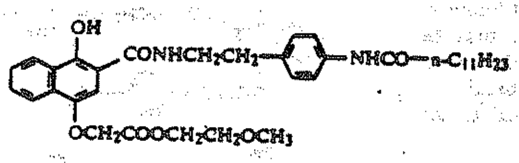

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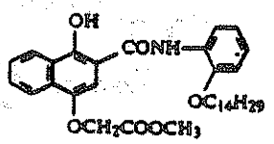

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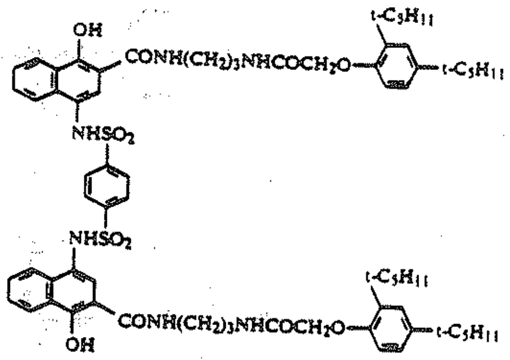

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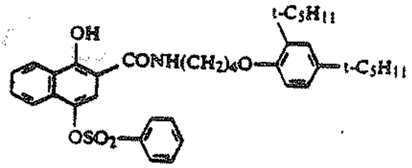

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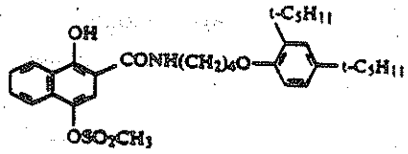

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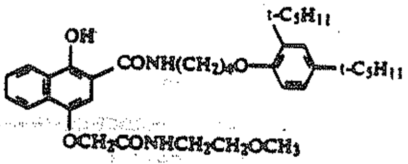

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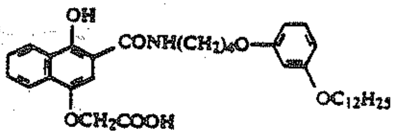

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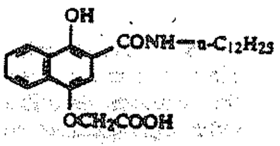

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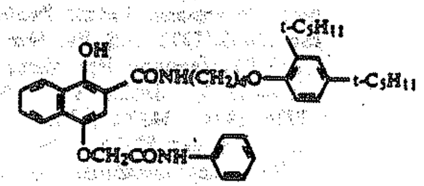

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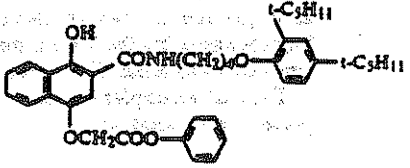

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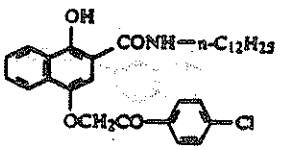

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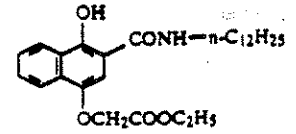
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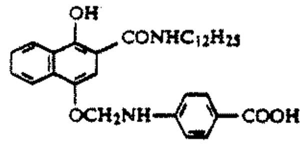
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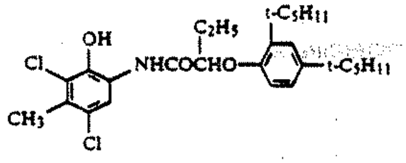
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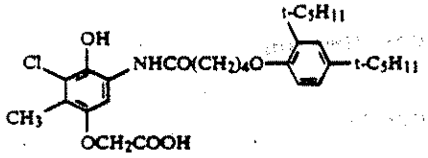
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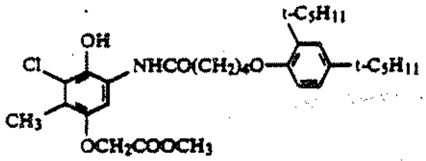
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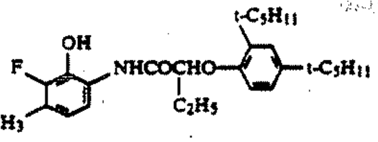
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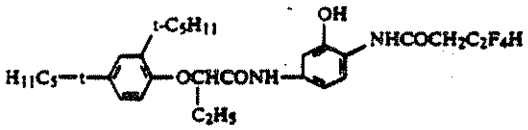
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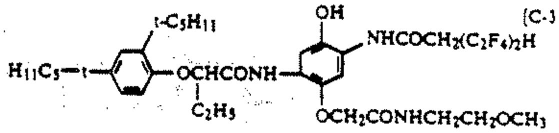
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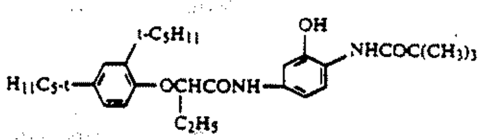
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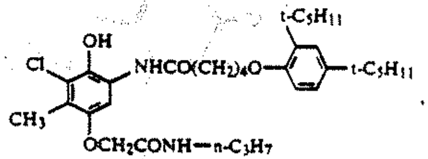
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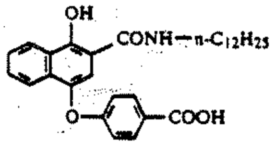
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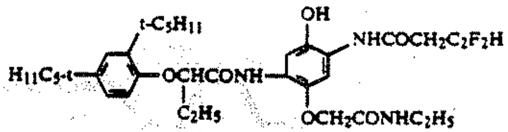
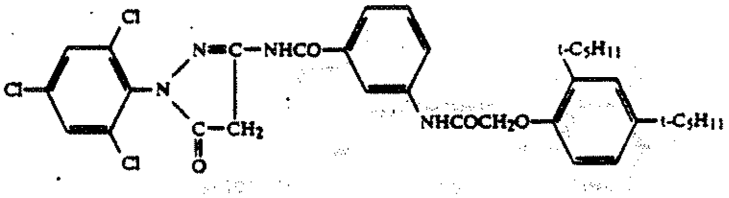

[C-35]

The cyan couplers used in the present invention can be prepared by the methods described for example in British Pat. No. 1,084,480, Japanese Provisional Patent Publication Nos. 117422/1975, 10135/1975, 37647/1976, 25228/1975 and 130441/1975. They are contained alone or in combination in the silver halide emulsion layer or contained in admixture with a so-called active-point arylazo-substituted colored coupler as described in U.S. Pat. No. 3,034,892, etc. They are incorporated by conventional procedure in an amount between 1 and 30 mole % of silver halide.

Examples of the preferable magenta couplers used in the present invention are: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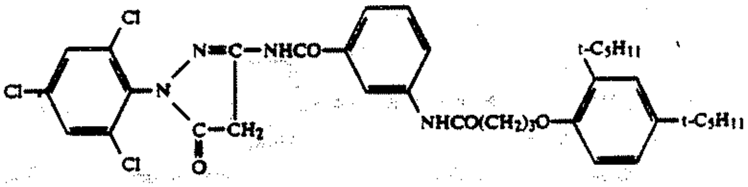
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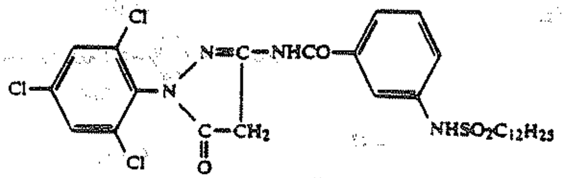

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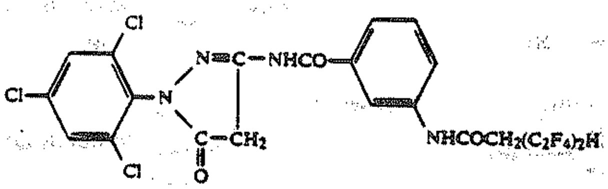

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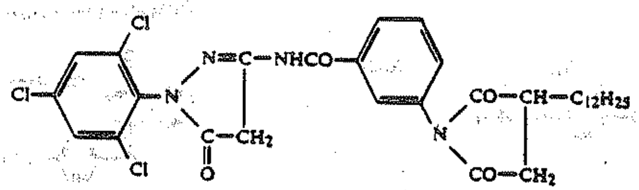

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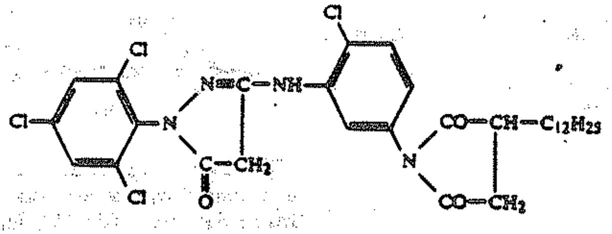

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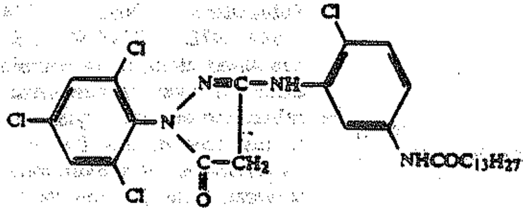

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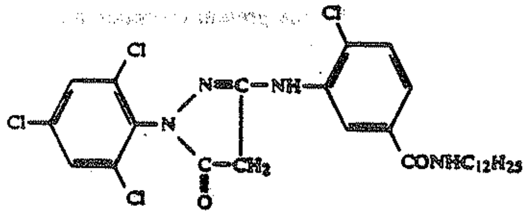

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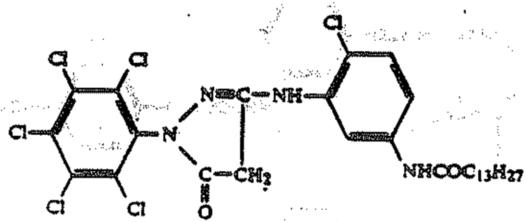

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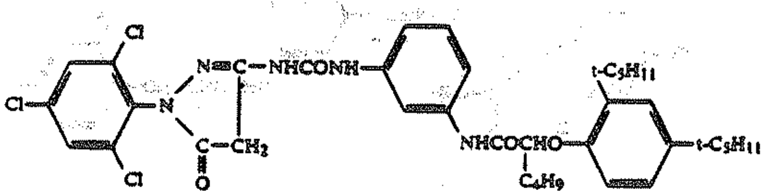

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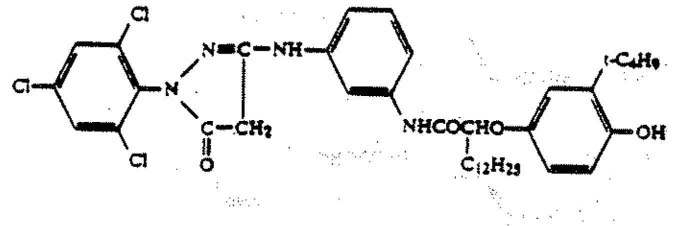

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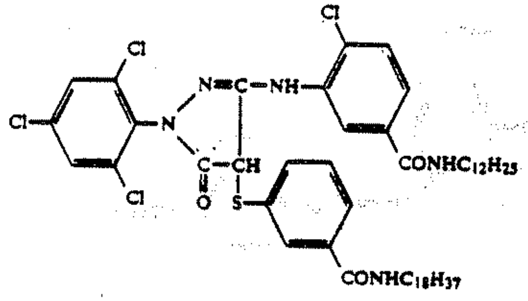

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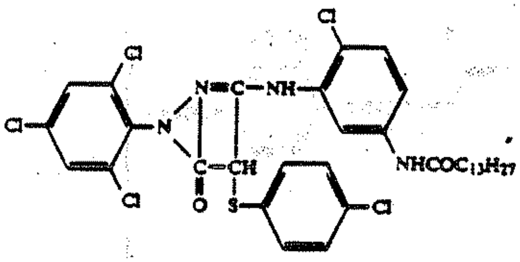

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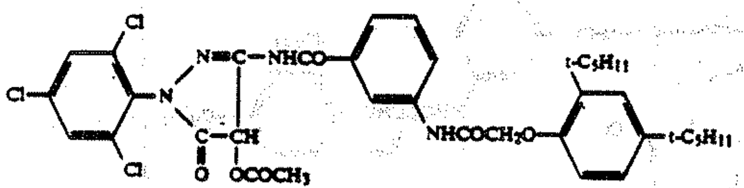

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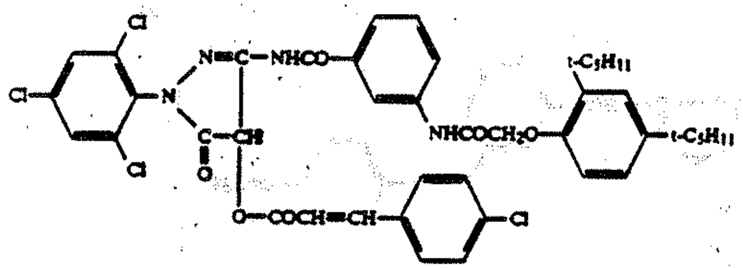

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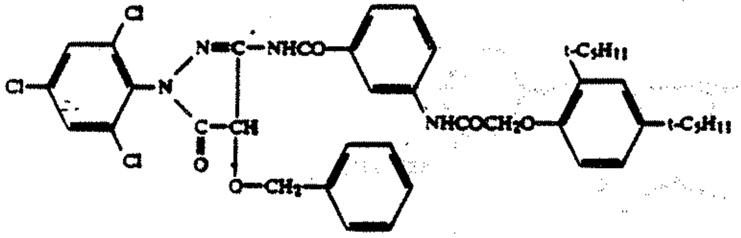

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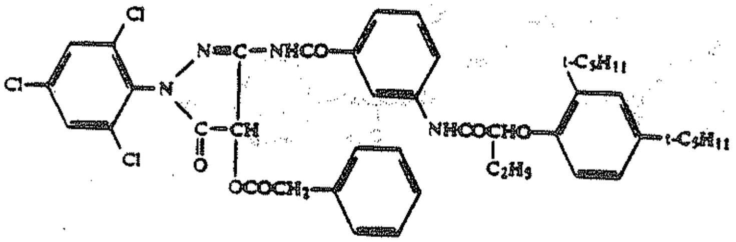

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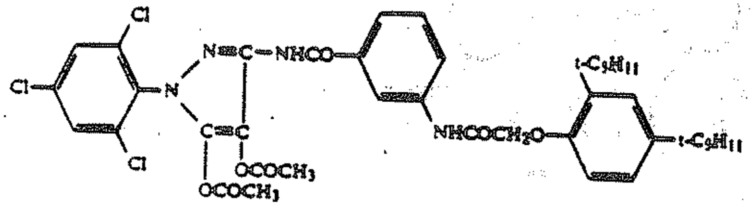

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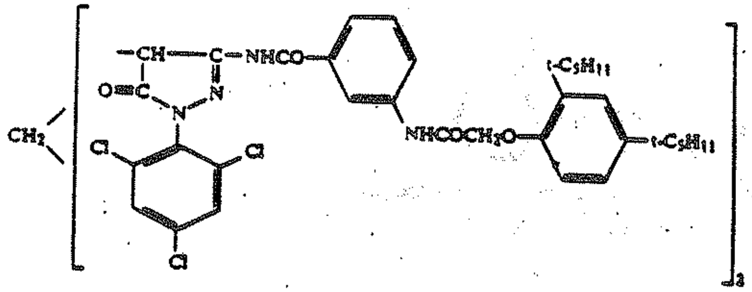

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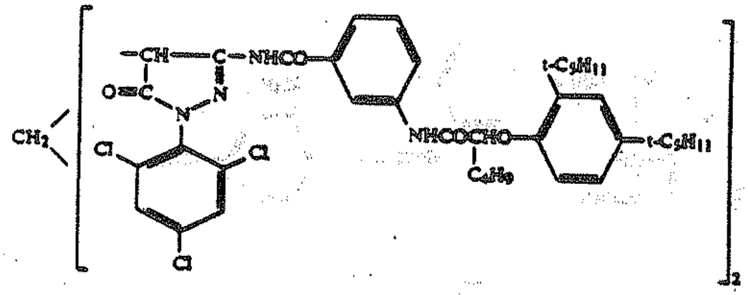

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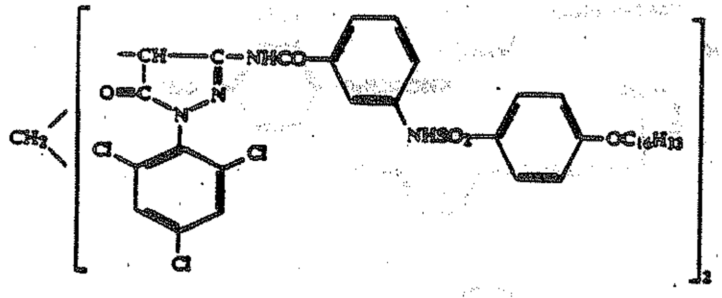

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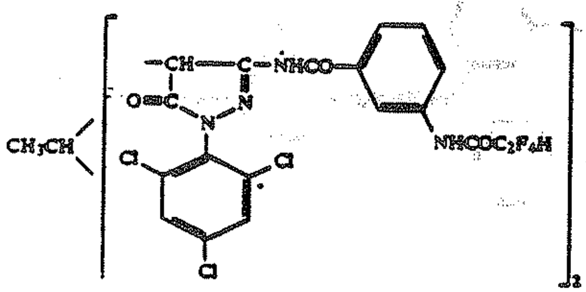

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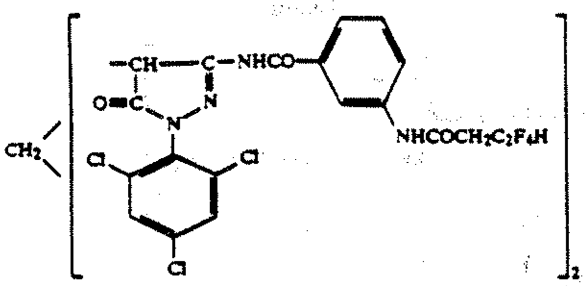
[M - 23]



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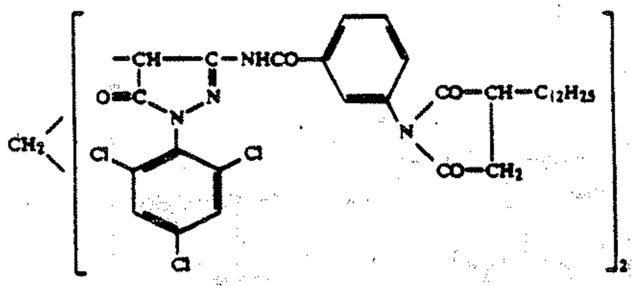

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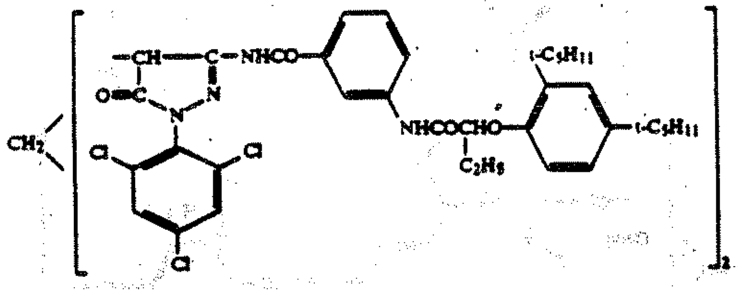

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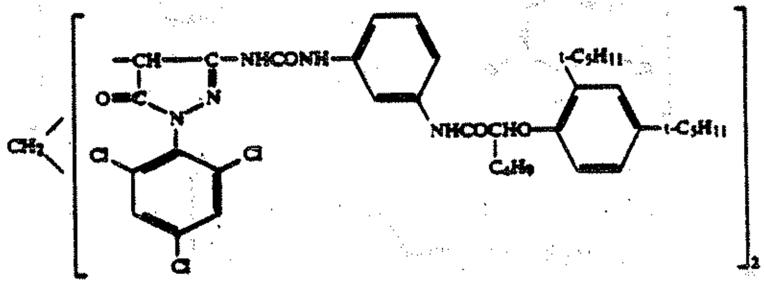

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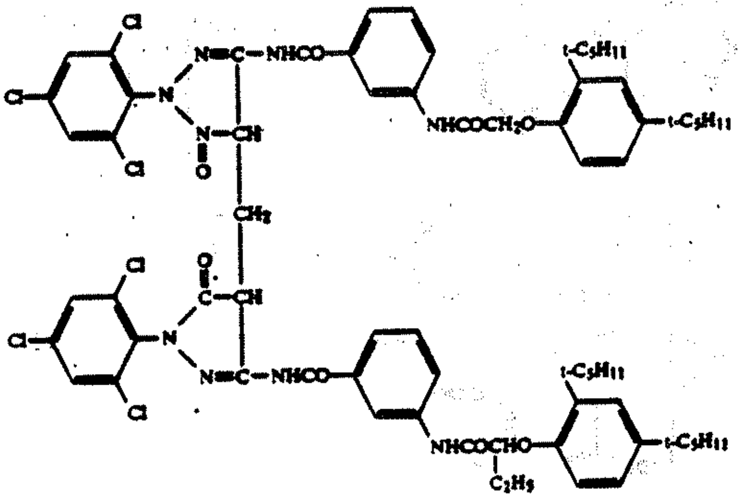

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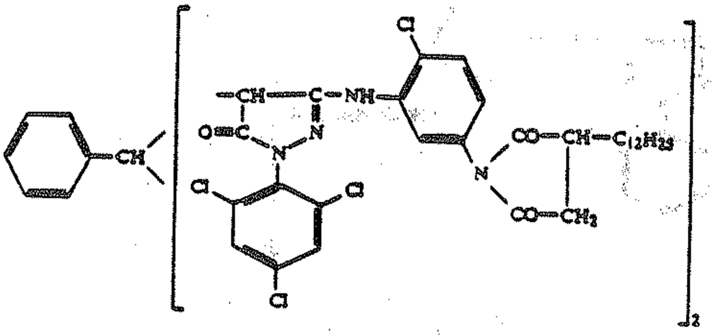

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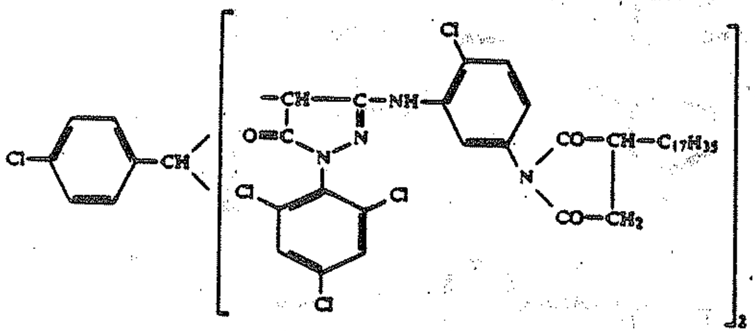

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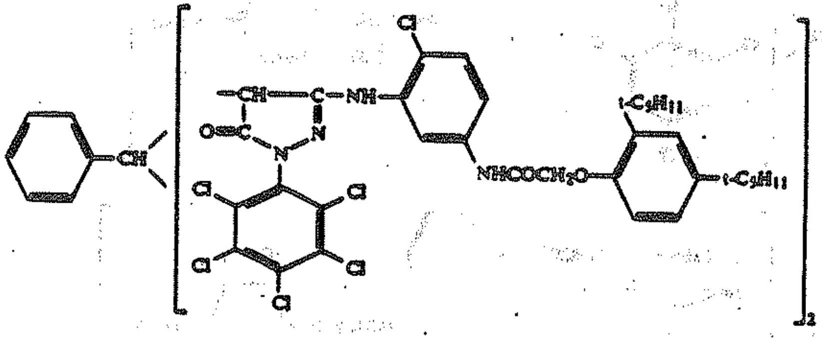

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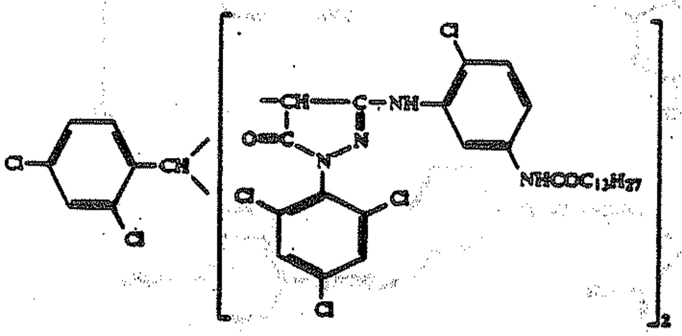

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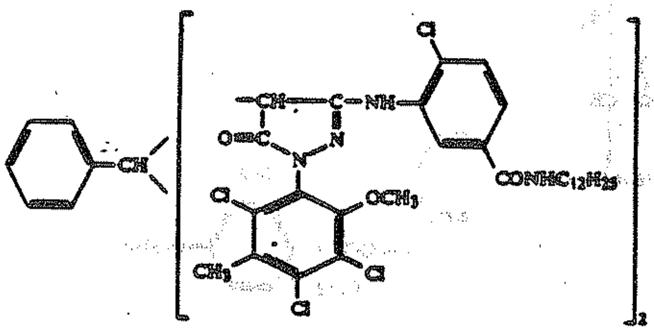

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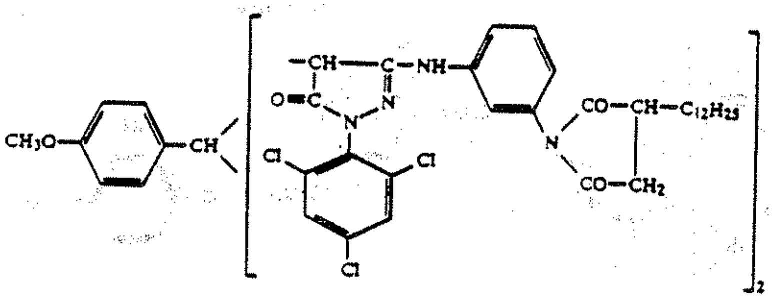

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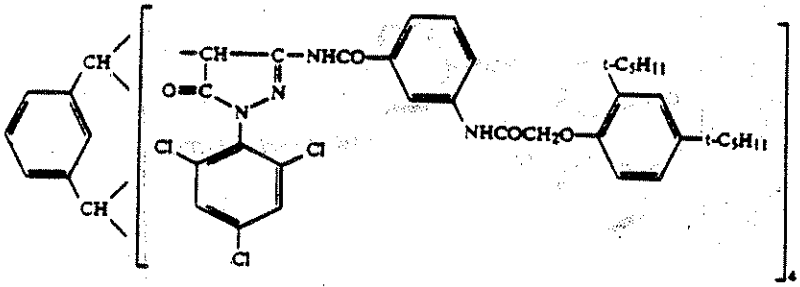

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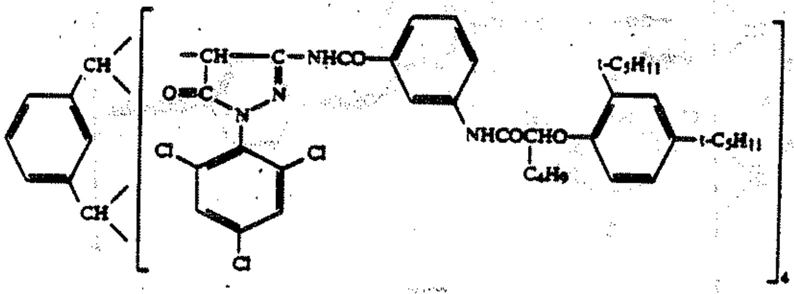

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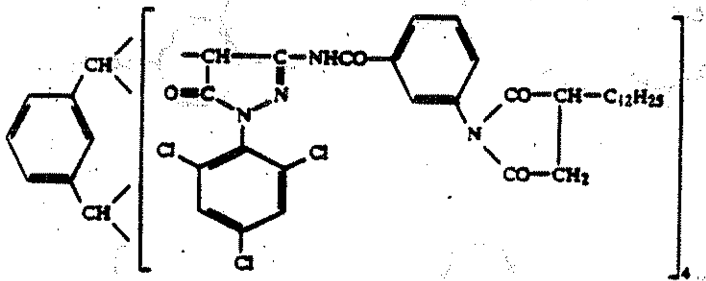

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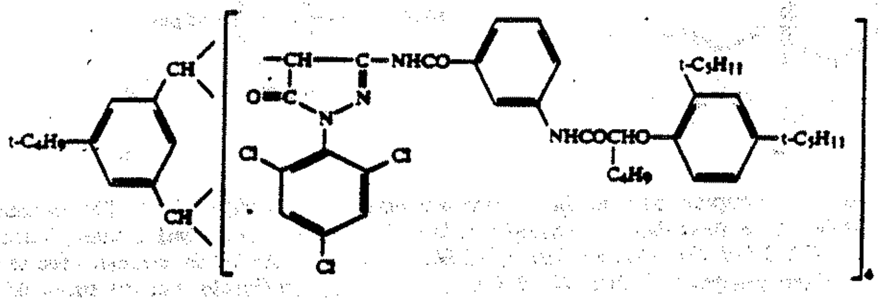

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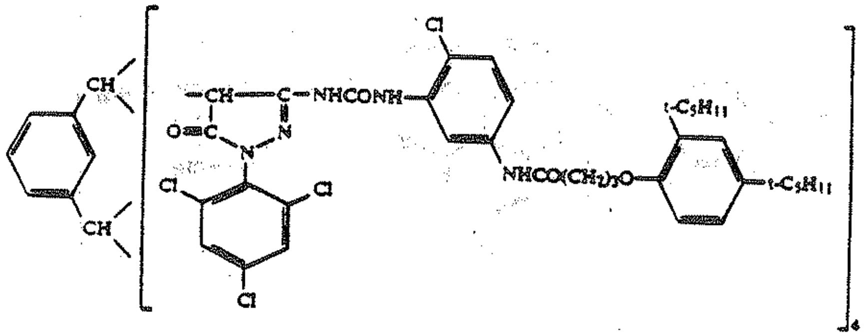

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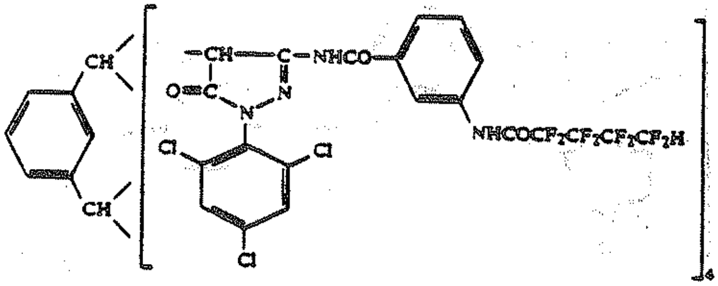

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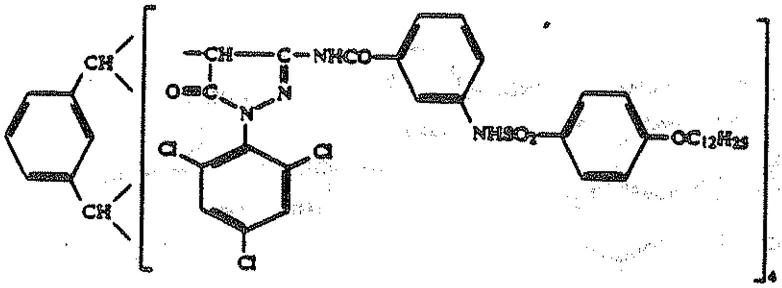

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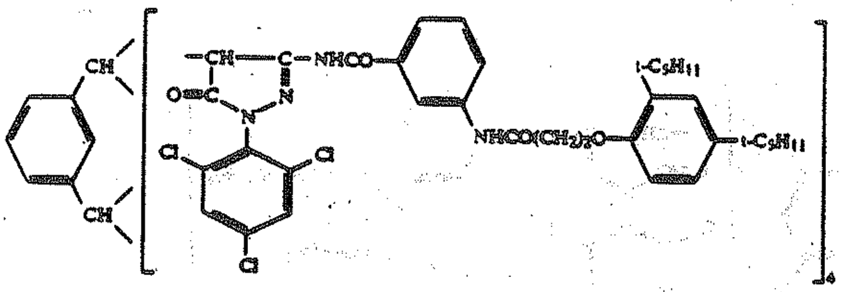

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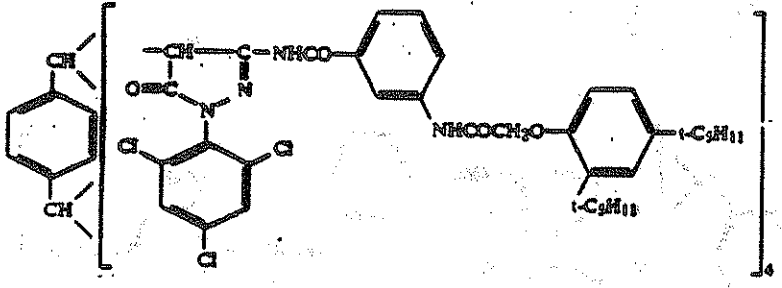


[M - 42]

The magenta couplers used in the present invention also includes those described for example in U.S. Pat. Nos. 3,311,476, 3,419,391, 3,888,680 and 2,618,641, West German Offenlegungsschrift Nos. 20 15 814, 23 57 105 and 23 57 122, Japanese Provisional Patent Publication Nos. 129538/1974, 105820/1976, 12555/1979, 48540/1979, 112342/1976, 112343/1976, 108842/1976 and 58533/1977. The methods of preparing them are also described in these litaratures.

As for the coupler used in the present invention, it is preferable that the speed of the reaction between the coupler and the oxidized product of the developing agent is high because in this case the number of dye molecules formed per unit amount of developed silver increases. Particularly, couplers exhibiting a specific rate, as measured by the method described below, which is higher than that of the compound M-1 are preferable.

(Measurement of specific rate)

In 30 ml of ethyl acetate and 15 ml of dibutyl phthalate, 0.02 mole of a coupler is dissolved. The solution thus obtained is mixed with 20 ml of a 10% aqueous solution of Alkanol B (alkylnaphthalenesulfonate available from du Pont) and 200 ml of a 5% aqueous gelatin solution. The mixture is then emulsified and dispersed in a colloid mill. The dispersion thus obtained is then added to a silver iodobromide emulsion containing 3.5 mole % of silver iodide so that the mole percentage of the coupler with respect to silver in the emulsion is 10%. The composition thus obtained is then applied to a triacetate film so that the silver amount is 15 mg/dm^2, and dried to yield a specimen. The obtained specimen is exposed through an optical wedge and processed according to the processes described below by using the processing solutions described below.

The percentage of the maximum density obtained with a color developing solution containing citrazinic acid with respect to the maximum density obtained with a color developing solution containing no cirtazinic acid is taken as the specific rate.

Processing (processing temperature: 38° C.)	Processing time
Color development	3 minutes 15 seconds
Bleaching	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Fixing	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Stabilization	1 minute 30 seconds
Drying	

Compositions of the processing solutions were used in the processing steps:

(Developing solution containing no citrazinic acid)	
4-Amino-3-methyl-N—ethyl-N—(β-hydroxyethyl)-aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine half-sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g

Made up to 1 liter with water, and adjusted to pH 10.3 with a IN aqueous potassium hydroxide or acetic acid.

(Developing solution containing citrazinic acid)

Citrazinic acid is added to the developing solution containing no citrazinic acid in an amount of 5 g per liter, and the resulting solution is adjusted to pH 10.3.

(Bleaching solution)	
Ferric ammonium salt of ethylenediaminetetraacetic acid	100.0 g
Diammonium salt of ethylenediaminetetraacetic acid	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml
Made up to 1 liter with water and adjusted to pH 6.0 with aqueous ammonia.	
(Fixing solution)	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.6 g
Sodium metasulfite	2.3 g
Made up to 1 liter with water and adjusted to pH 6.0 with acetic acid.	
(Stabilizing solution)	
Formalin (37% aqueous solution)	1.5 ml
Konidax (available from Konishiroku Photo Industry Co., Ltd.)	7.5 ml
Made up to 1 liter with water.	

In the light-sensitive color photographic material in accordance with the present invention, it is preferable that at least one of the light-sensitive layers contain a compound releasing a development inhibitor by the reaction with an oxidized product of the color developing agent. By using such a compound, the sharpness, graininess, color purity and wide latitude of exposure are remarkably improved over the conventional light-sensitive color photographic material.

Examples of known compounds releasing a development inhibitor by the the reaction with an oxidized product of the developing agent are compounds which couple with an oxidized product of a color developing agent to form a dye and release a development inhibitor (hereinafter referred to as the DIR couplers) as disclosed in U.S. Pat. Nos. 3,148,062 and 3,227,554, and compounds which release a development inhibitor without forming a dye by the coupling with an oxidized product of a color developing agent (hereinafter referred to as the DIR substances) as disclosed in U.S. Pat. No. 3,632,345. (Both DIR couplers and DIR substances are referred to as the DIR compounds.)

For example, when the present invention is applied to an ordinary multi-layer light-sensitive color photographic material containing a blue-, green- and red-sensitive emulsion layers, the DIR compounds should be contained in one or more of these layers. Particularly, it is preferable that they are contained at least in the green-sensitive emulsion layer. Further, when an emulsion layer exhibiting a color sensitivity comprises a plurality of layers exhibiting different sensitivities as in the present invention, the DIR compounds should be contained in at least one of the layers, preferably in the emulsion having a lower sensitivity.

The DIR compounds preferably used in the present invention are represented by the following general formula (I) or (II):

$$\text{A-TIME-Z} \qquad \text{(I)}$$

In the general formula (I), A designates a coupling component capable of reacting with an oxidized product of a color developing agent. The coupling component may be any component which can release the group TIME-Z by the reaction with an oxidized product of a color developing agent.

In the general formula (I), TIME designates a timing group, and Z designates a development inhibitor. Examples of the timing groups includes those based on the intramolecular nucleophilic substitution as described in Japanese Provisional Patent Publication No. 145135/1979, and those based on the electron movement along the conjugated chain as described in Japanese Provisional Patent Publication No. 17644/1980. In short, any compound may be used if it first releases the group TIME-Z through the breakage of the A-TIME bond and then releases Z through the breakage of the TIME-Z bond. Z includes the development inhibitors as described in "Research Disclosure", Vol. 176, No. 17643, Dec. 1978 (hereinafter referred to as the literature 1). Preferably, it is mercaptotetrazole, selenotetrazole, mercaptobenzothiazole, selenobenzothiazole, mercaptobenzoxazole, selenobenzoxazole, mercaptobenzimidazole, selenobenzimidazole, benzotriazole, benzodiazole or a derivative thereof.

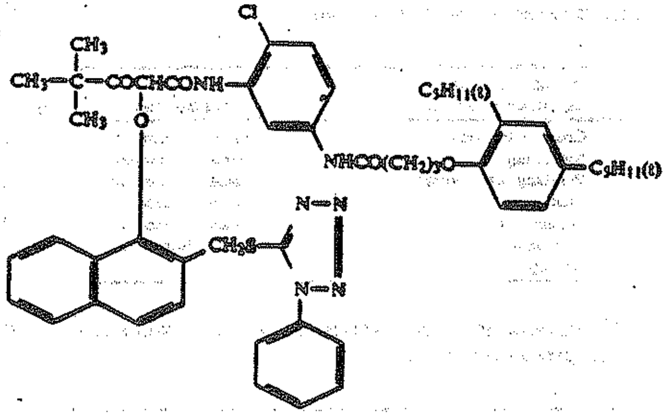
A-Z (II)

In the general formula (II), A and Z have the same meanings as described above with respect to the general formula (I).

Syntheses of the compounds represented by the general formula (I) are described for example in Japanese Provisional Patent Publication Nos. 14513/1979 and 17644/1980.

The DIR compounds represented by the general formula (II) involve the DIR couplers and the DIR substances. Examples of the DIR couplers represented by the general formula (II) are described e.g. in U.S. Pat. Nos. 3,227,554 and 3,773,201, and British Pat. No. 2,010,818. Syntheses thereof are also described in these patents.

Examples of the DIR substances represented by the general formula (II) are described e.g. in U.S. Pat. Nos. 3,958,993, 3,961,959 and 3,938,996, Japanese Provisional Patent Publication Nos. 147716/1975, 152731/1975, 105819/1976, 6724/1976 and 123025/1975, U.S. Pat. Nos. 3,928,041 and 3,632,345, and Japanese Provisional Patent Publication No. 125202/1975. Syntheses thereof are also described in these specifications.



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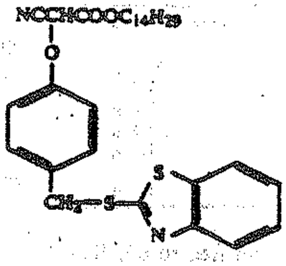

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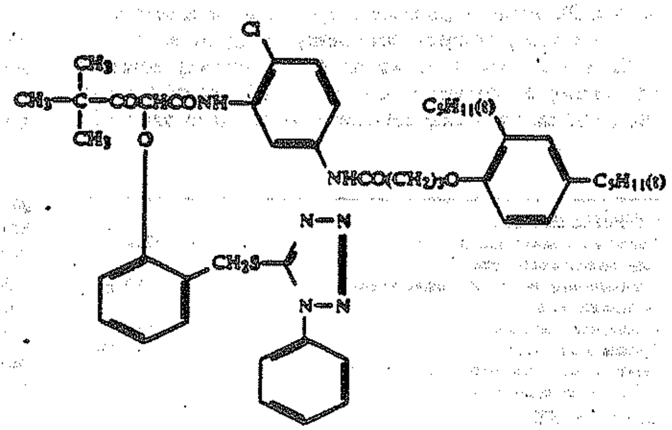

[D-3]

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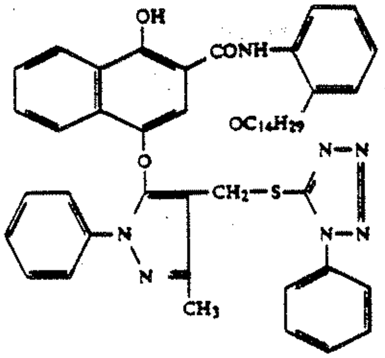
[D-4]



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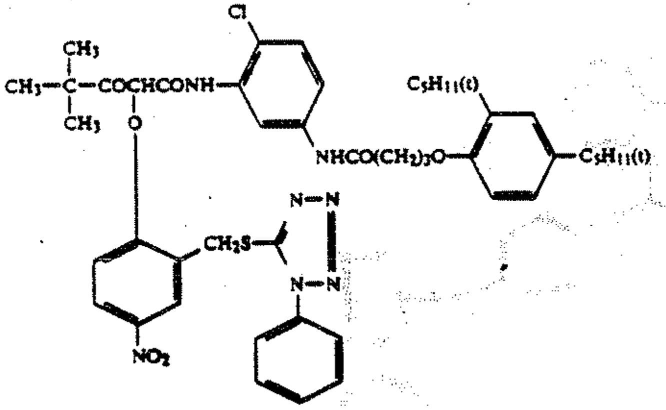

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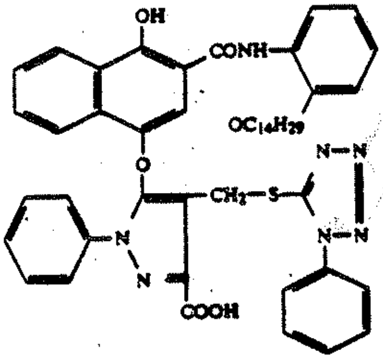

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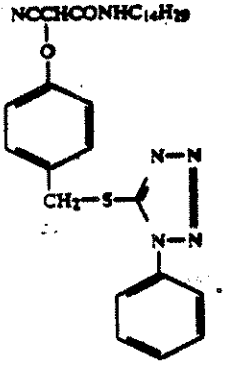

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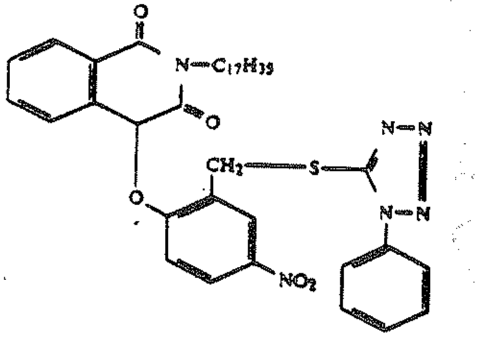

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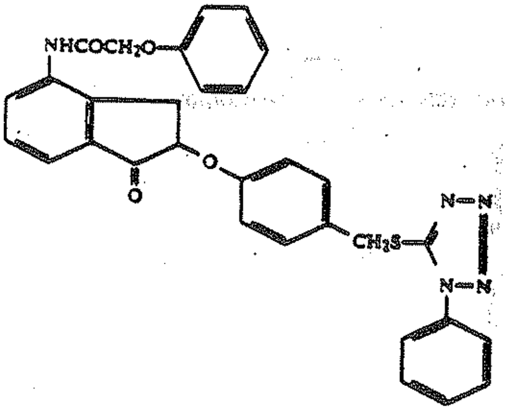
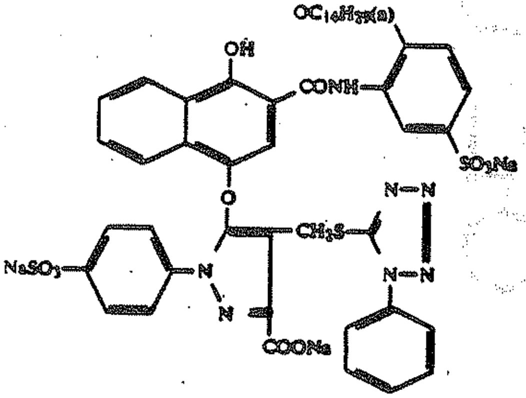


[D-9]



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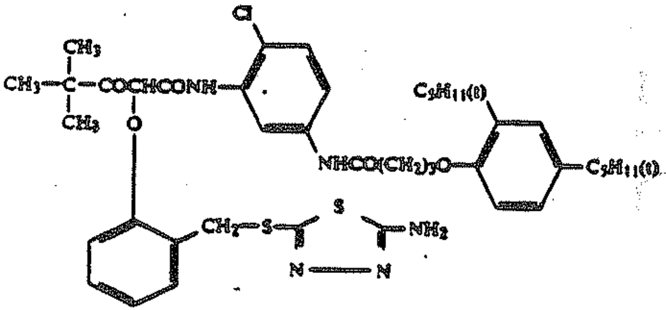

[D-11]

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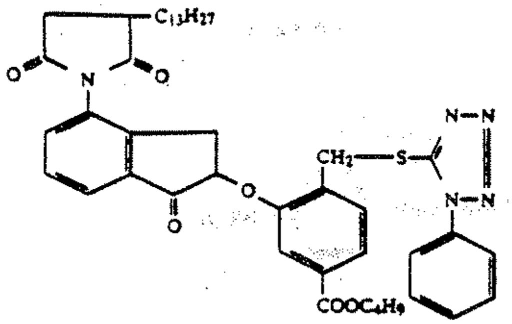
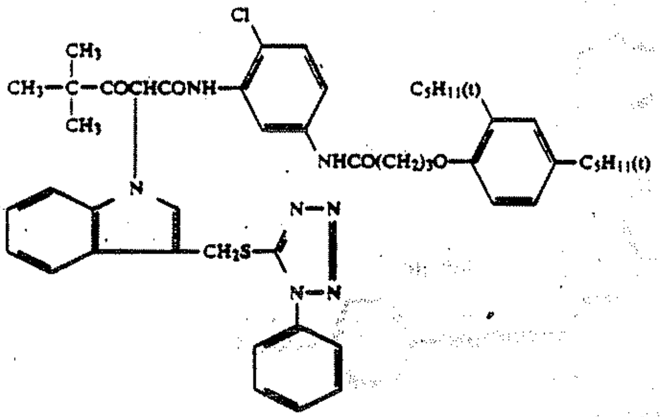
[D-12]



[D-13]



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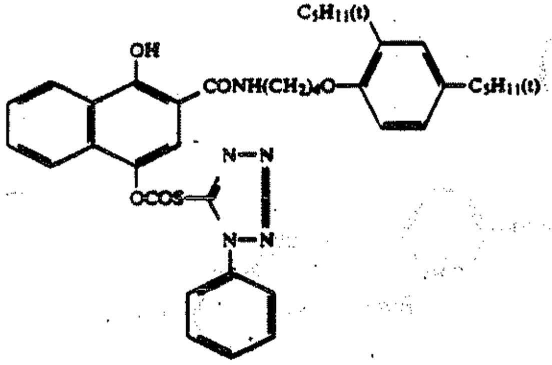
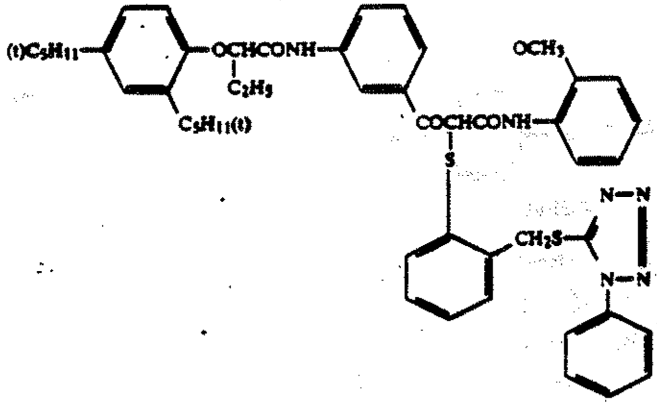


[D-15]



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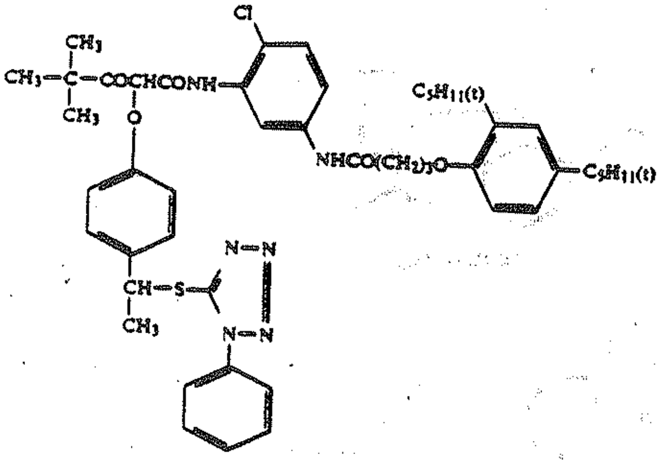
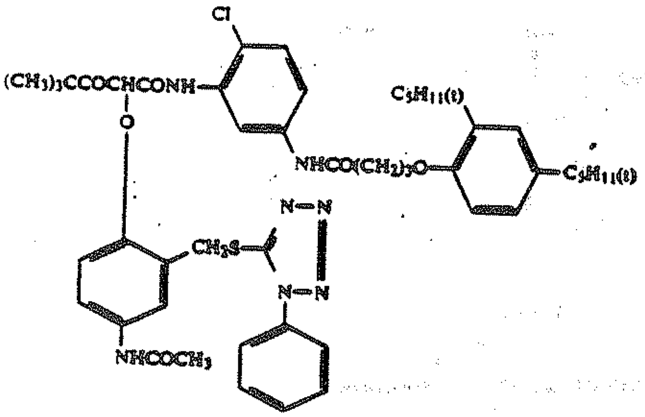
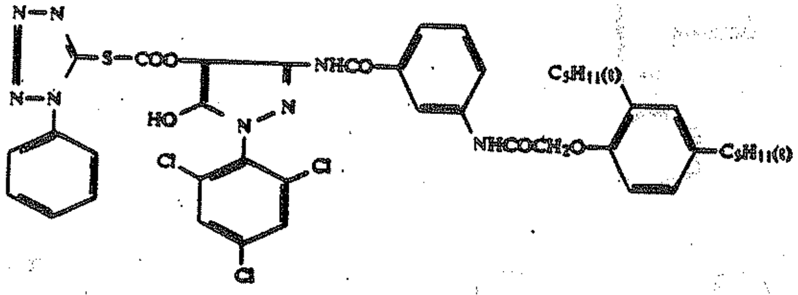


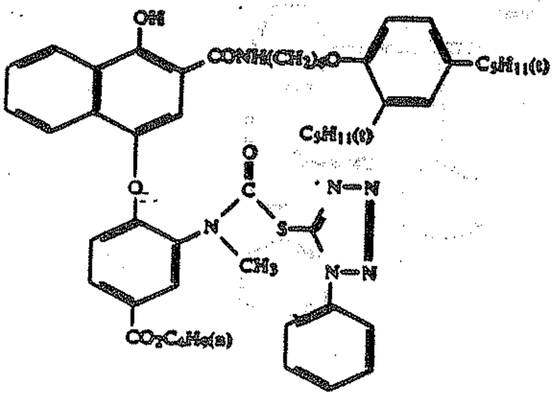
[D-16]



[D-17]



[D-18]



[D-19]

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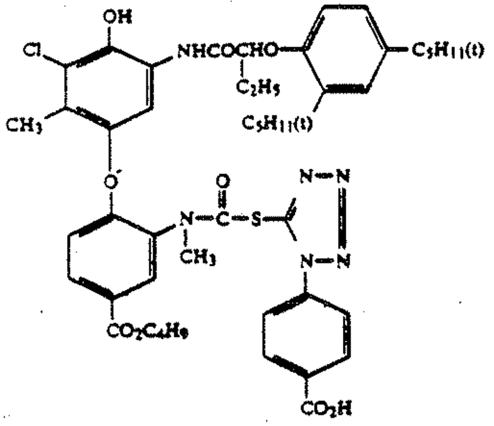
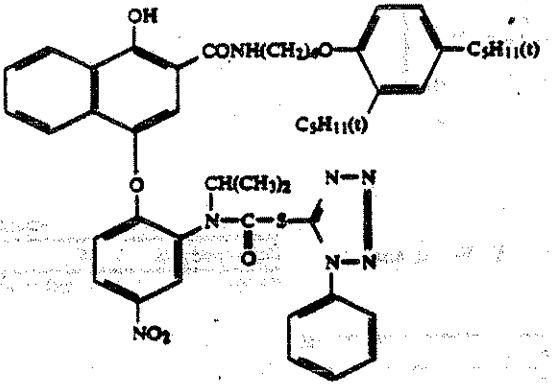
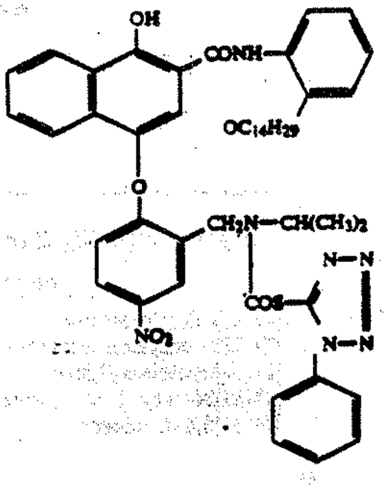


[D-20]



[D-21]



[D-22]

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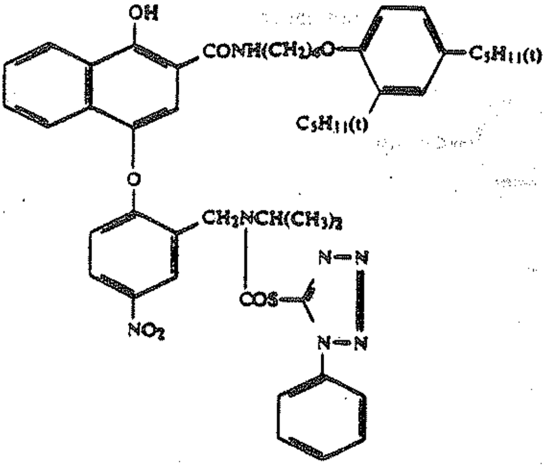
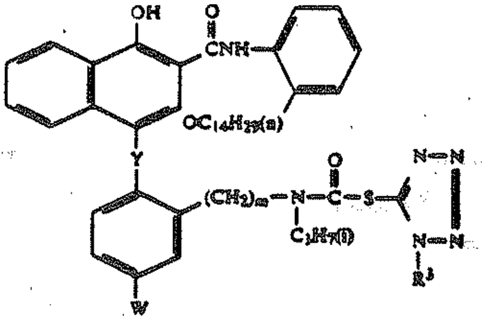
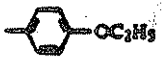
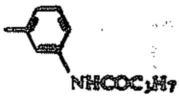


[D-23]

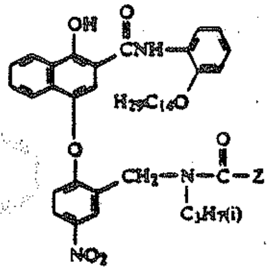


[D-24] ~ [D-31]

In the formula for [D-24]~[D-31], Y, W, m and R^3 each represent the following:

Compound No.	Y	W	m	R_3
[D-24]	O	NO_2	O	
[D-25]	S	NO_2	1	
[D-26]	O	NO_2	1	
[D-27]	O	NO_2	1	
[D-28]	O	NO_2	1	
[D-29]	O	$-NHSO_2C_4H_9$	O	

-continued

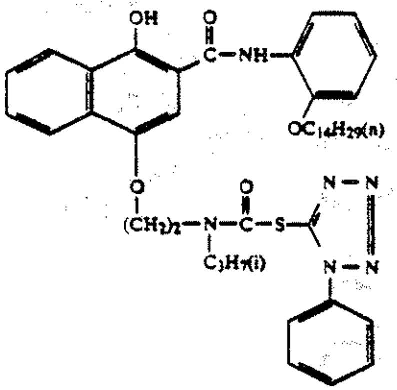
Compound No.	Y	W	m	R_3
[D-30]	O	$-NHSO_2C_8H_{17}$	1	
[D-31]	S	H	O	
[D-32] ~ [D-36]				

In [D-32]~[D-36], Z represents the following:

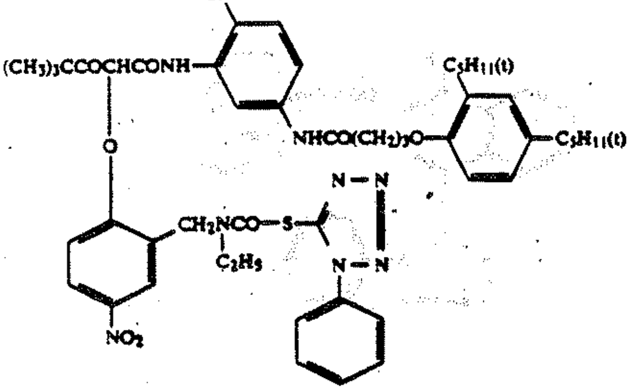
Compound No.

[D-32]ethylthiotetrazole
[D-33]n-butylthiotetrazole
[D-34]cyclohexylthiotetrazole
[D-35]N-butylthiotetrazole
[D-36]5,6-dichlorobenzotriazole

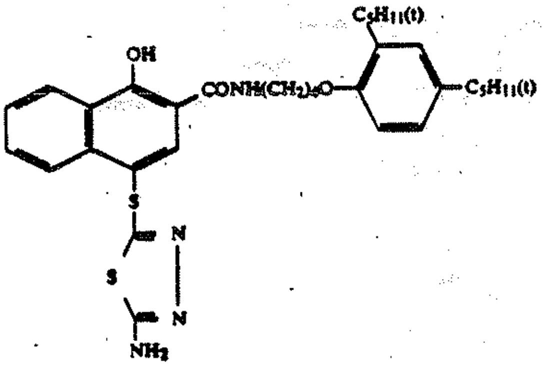
[D-37]



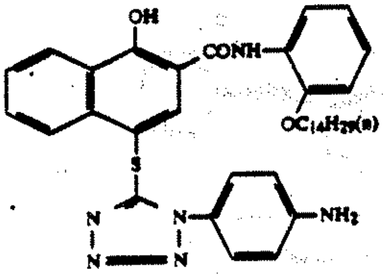
[D-38]



[D-39]



[D-40]



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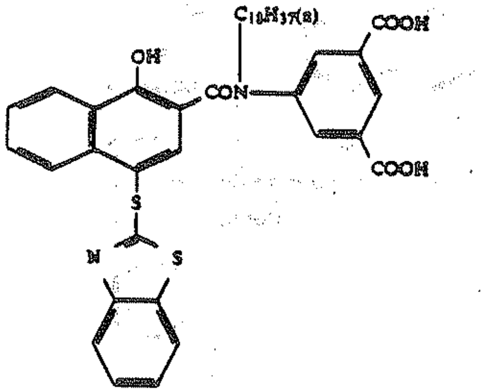
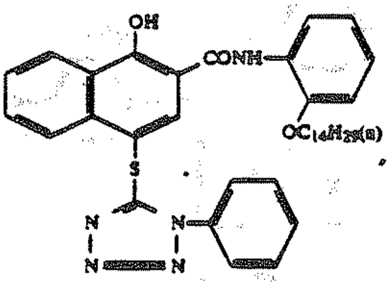
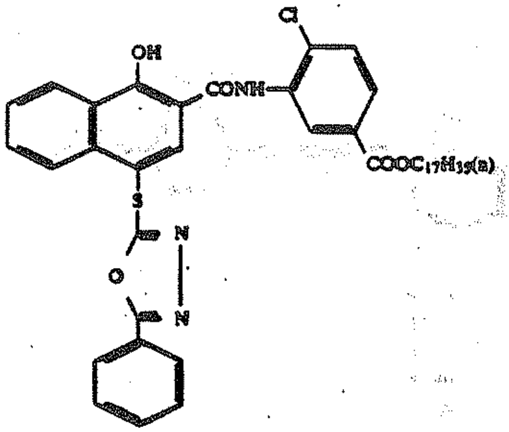


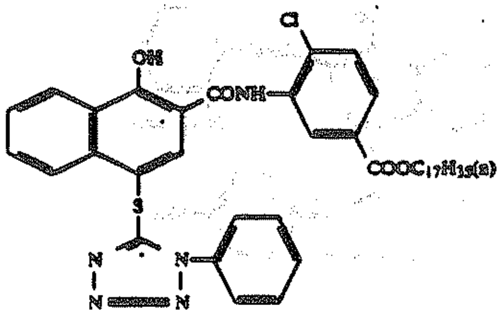
[D-41]



[D-42]



[D-43]



[D-44]

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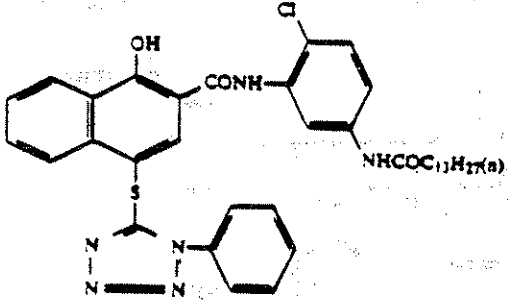
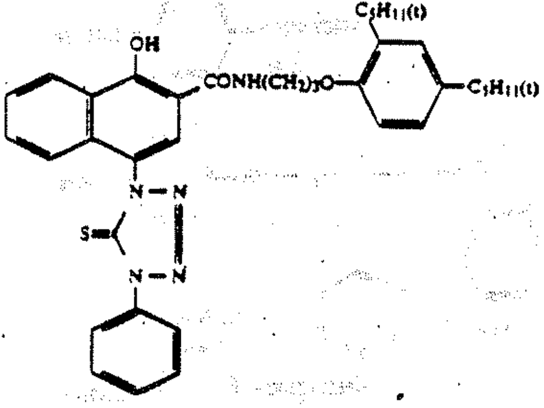
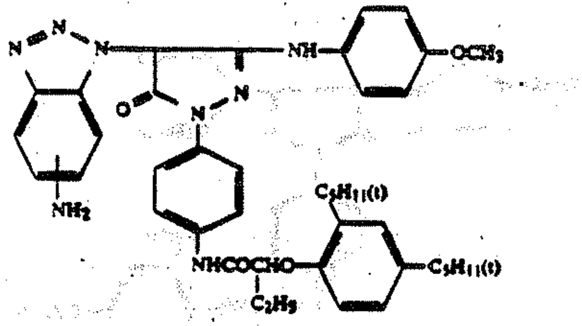
[D-45]



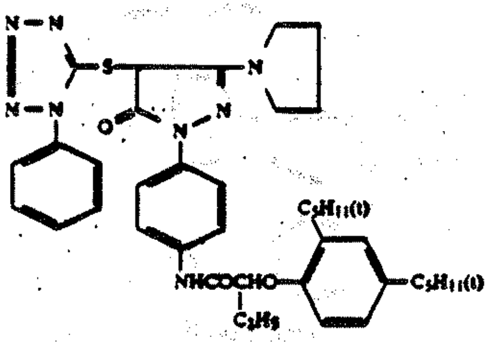
[D-46]



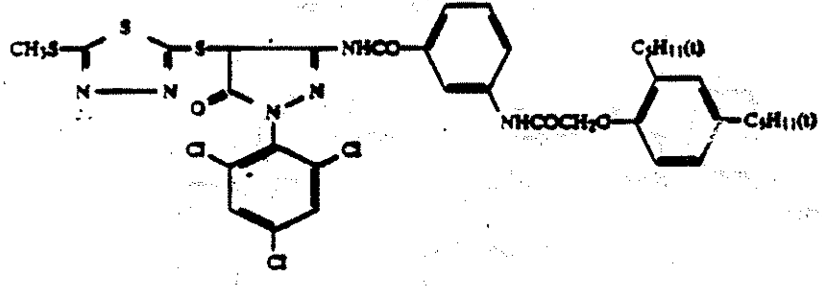
[D-47]



[D-48]



[D-49]



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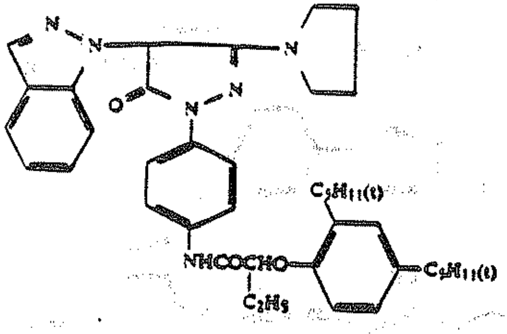
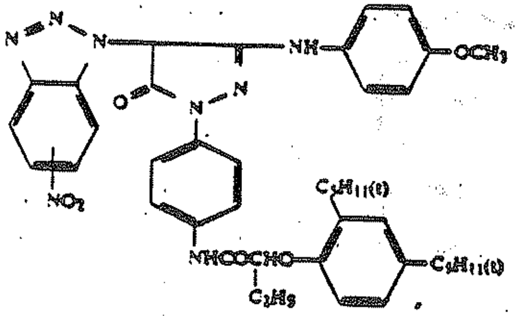
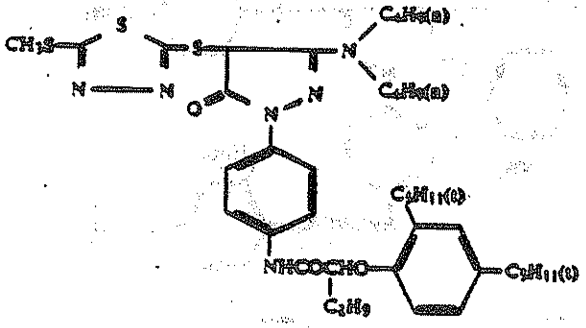
[D-50]



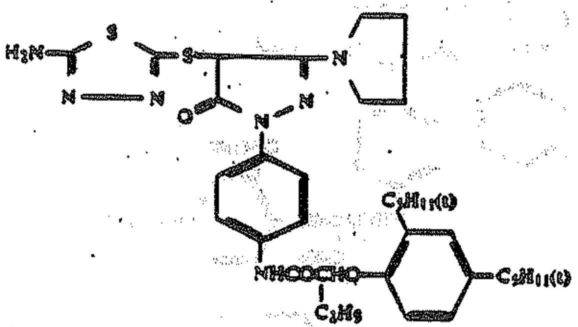
[D-51]



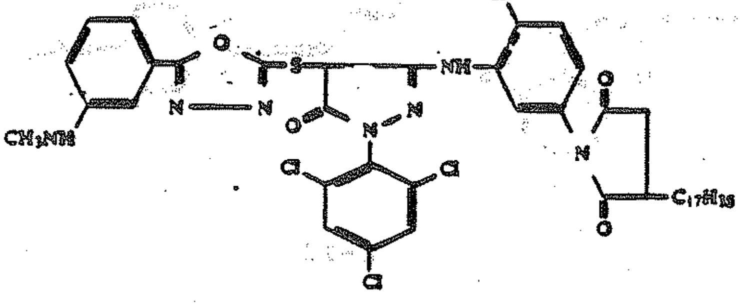
[D-52]



[D-53]



[D-54]



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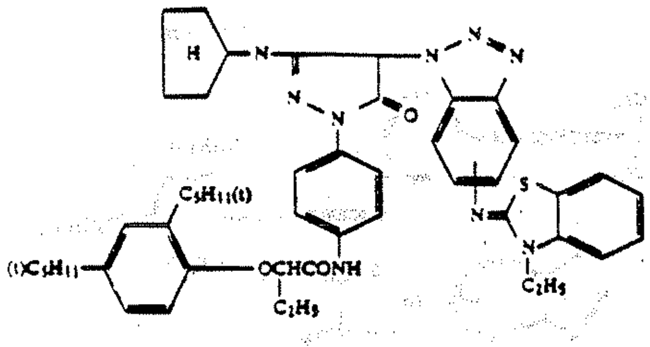
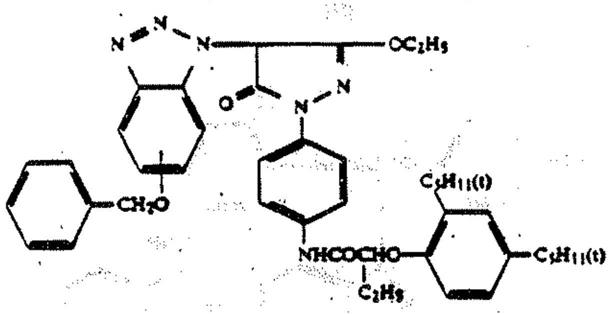
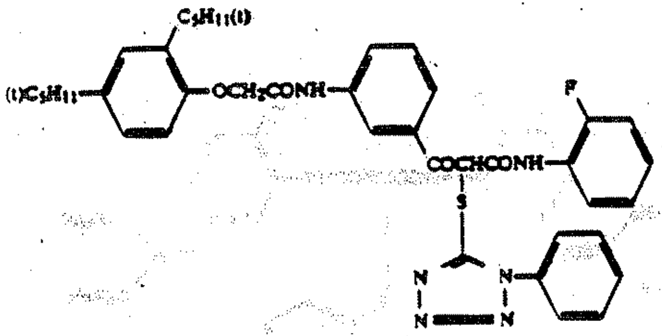
[D-55]



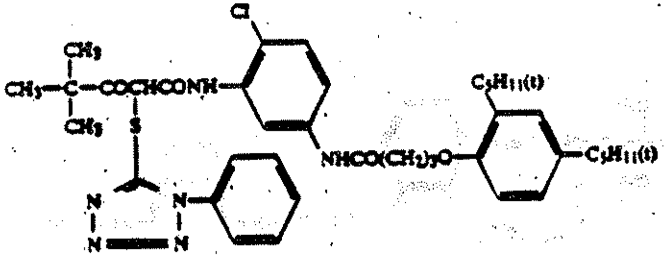
[D-56]



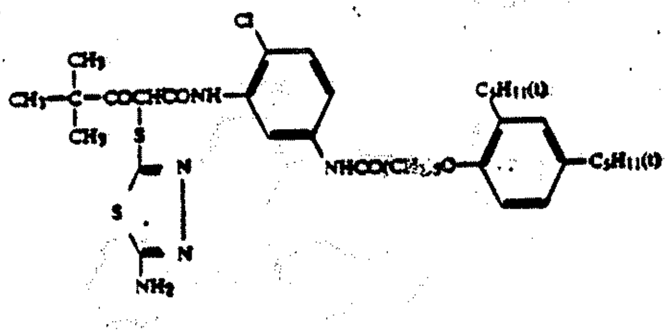
[D-57]



[D-58]



[D-59]



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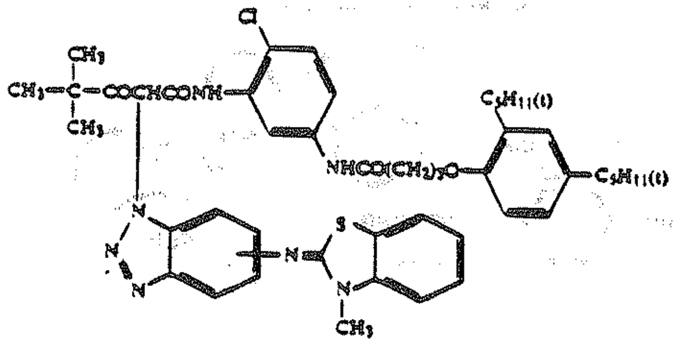
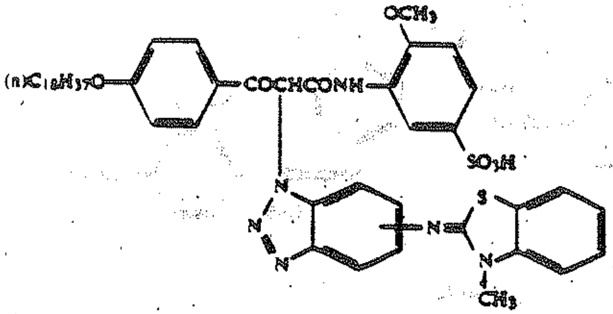
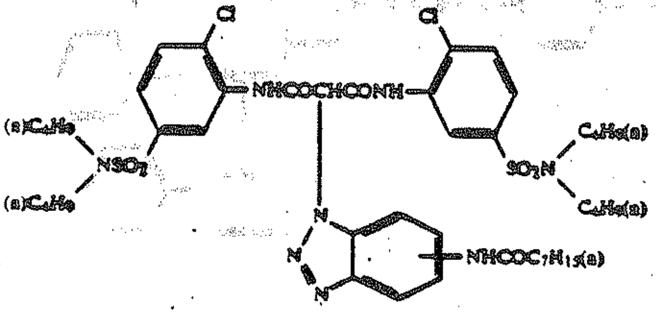
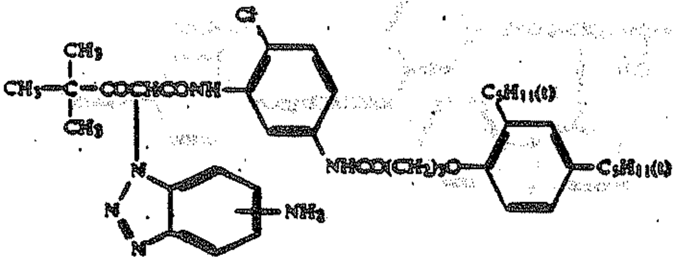

[D-60]


[D-61]


[D-62]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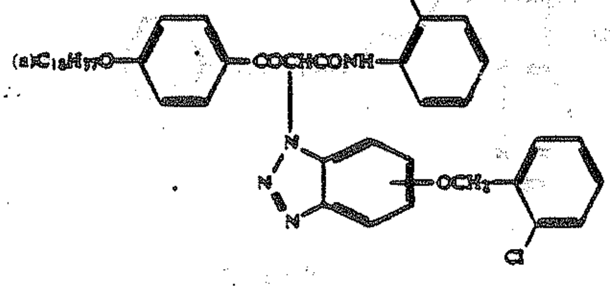
[D-64]

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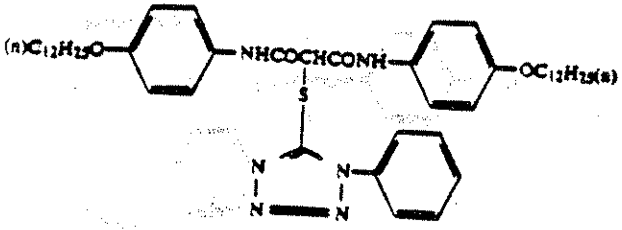

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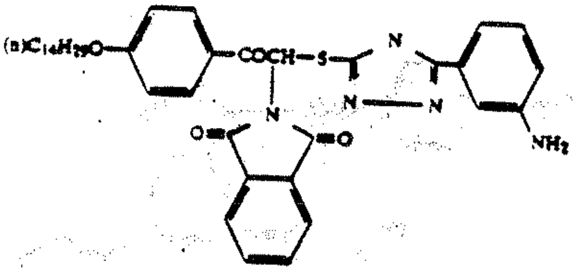
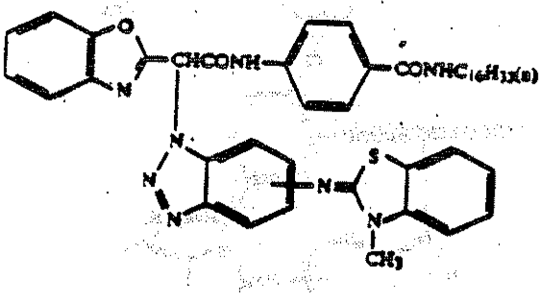
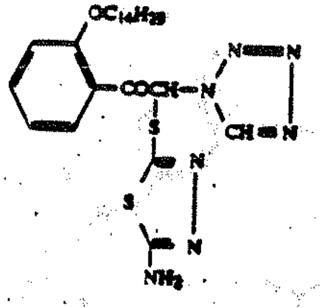


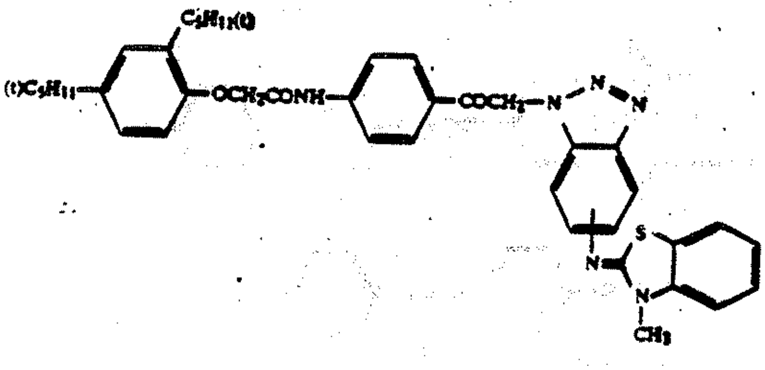
[D-66]



[D-67]



[D-68]



[D-69]

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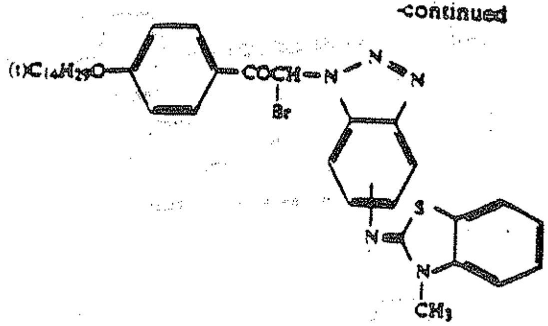
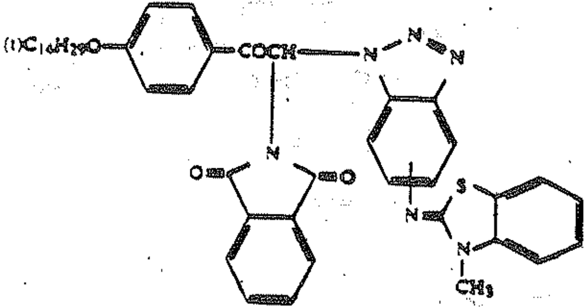
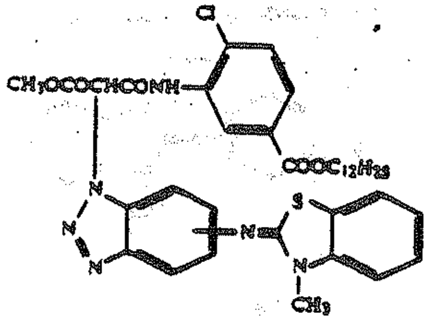
[D-70]



[D-71]



[D-72]



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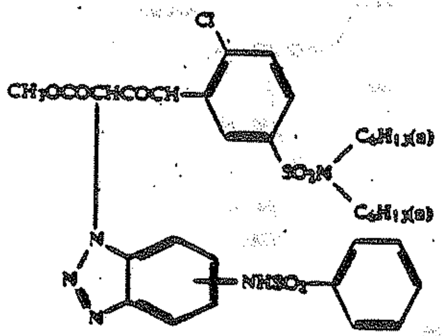
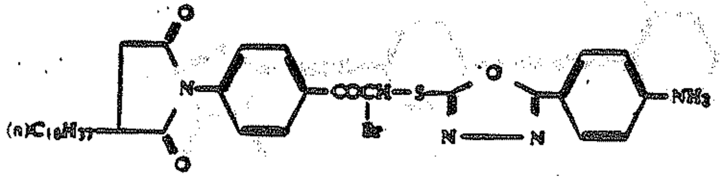
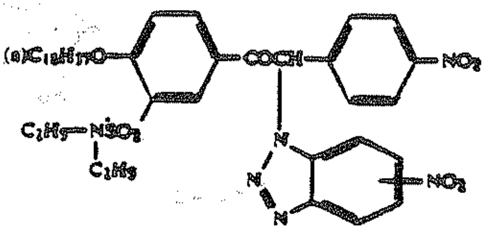


[D-74]



[D-75]



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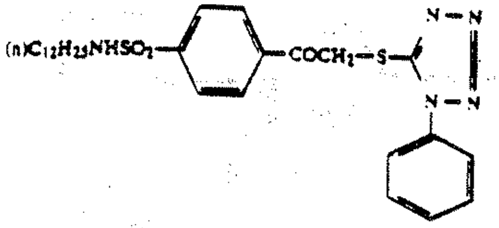
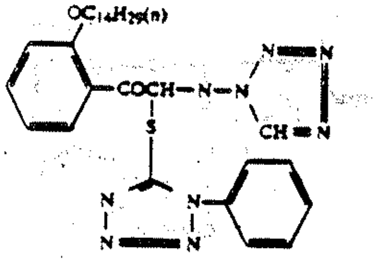
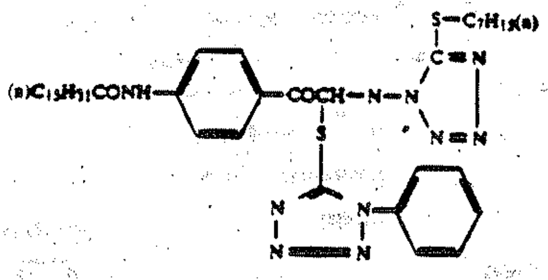


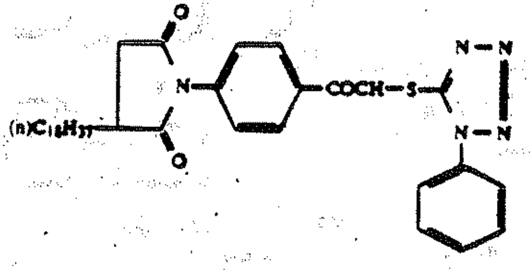
[D-76]



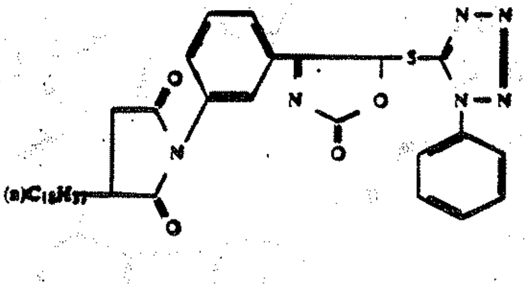
[D-77]



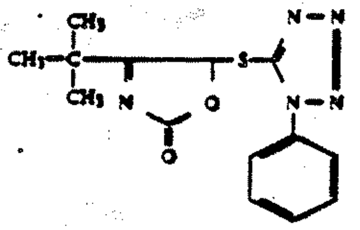
[D-78]



[D-79]



[D-80]



[D-81]

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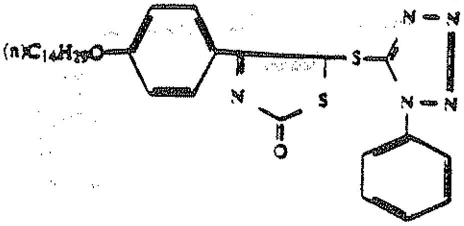
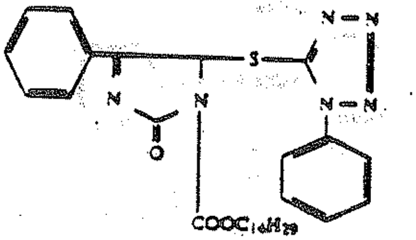
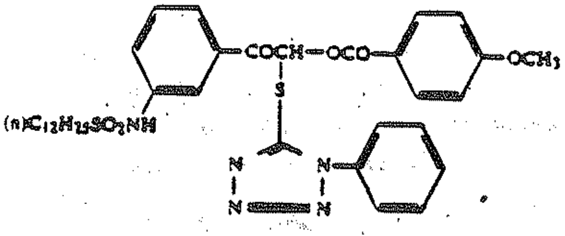


[D-82]

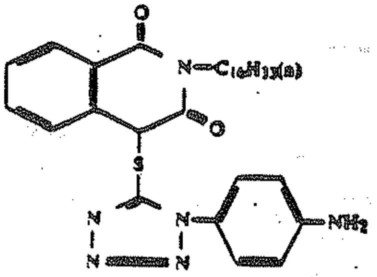


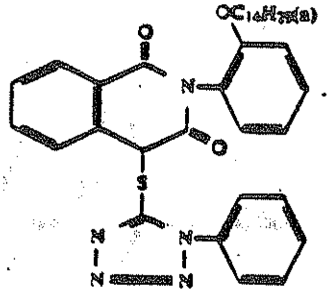
[D-83]

[D-84]

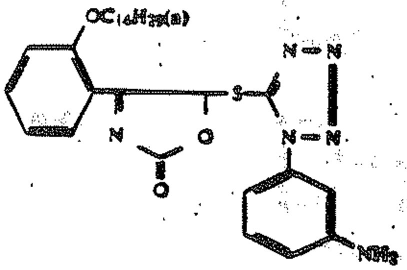


[D-85]





[D-86]



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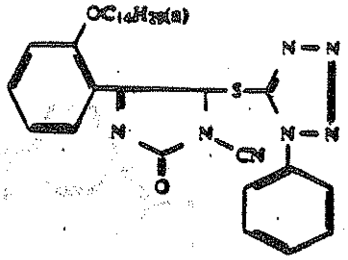
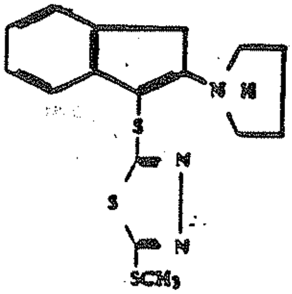
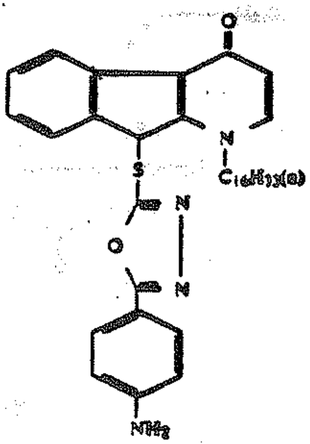


[D-88]

[D-89]





[D-90]

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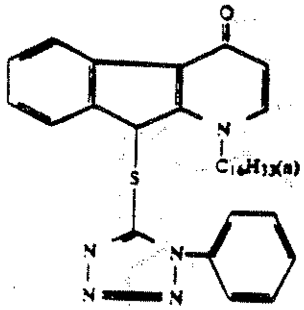

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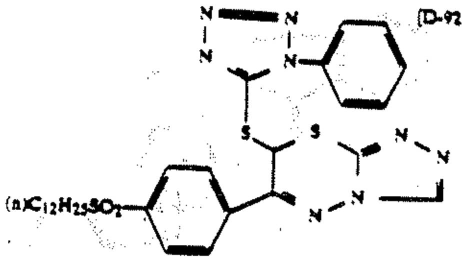

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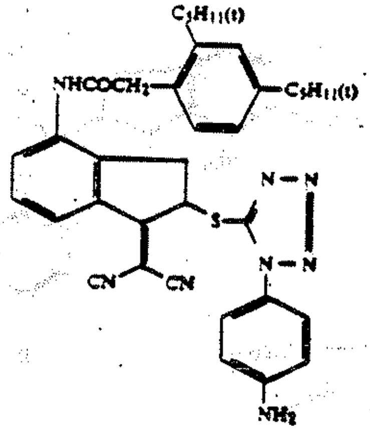

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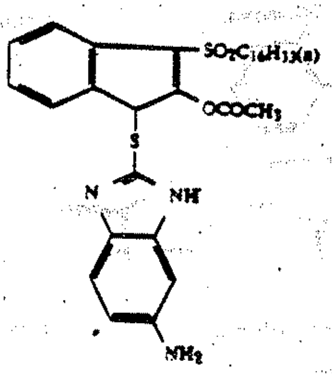

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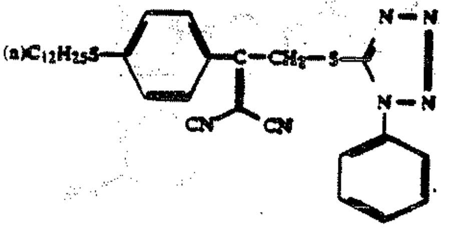

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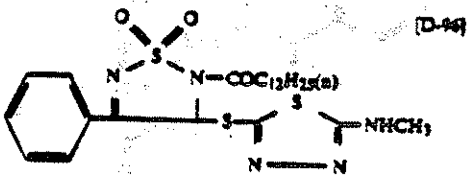

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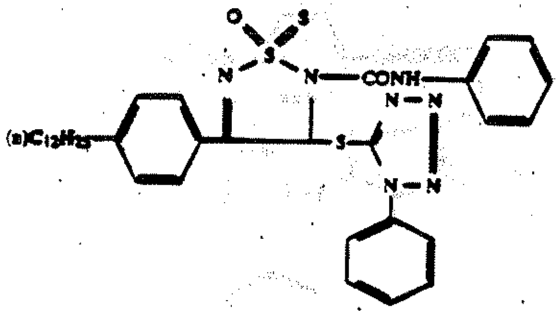

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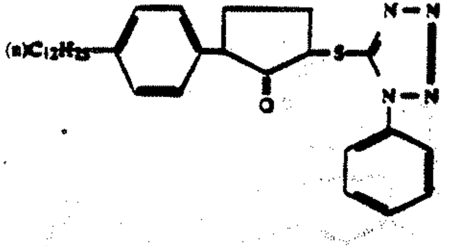

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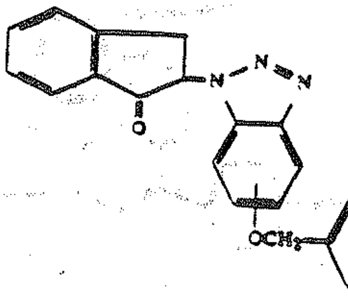

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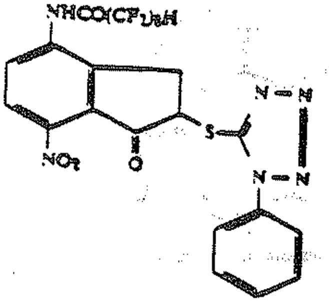

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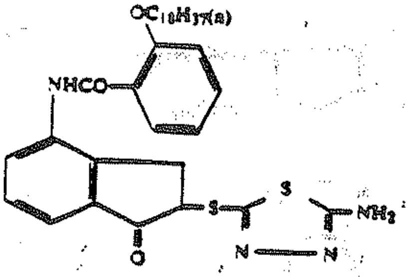

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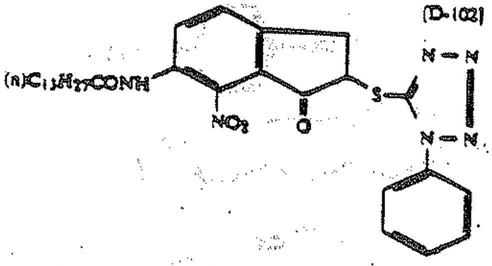

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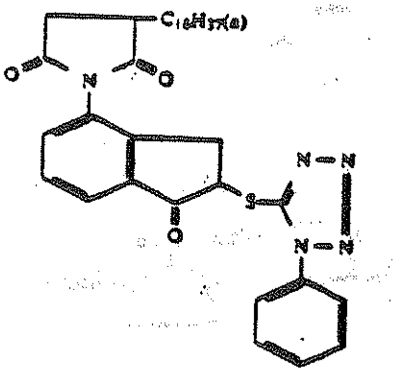

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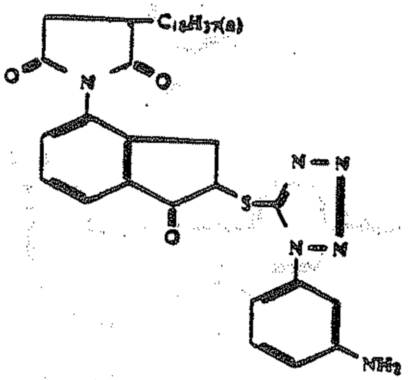

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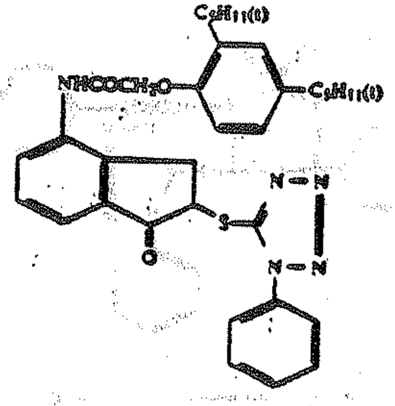

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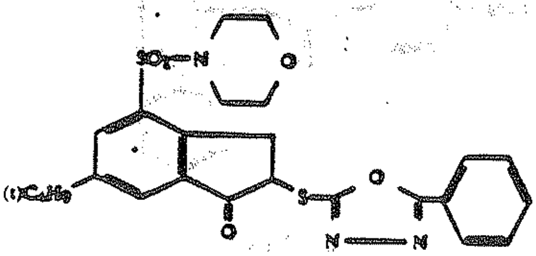

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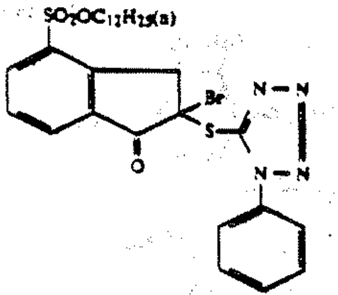

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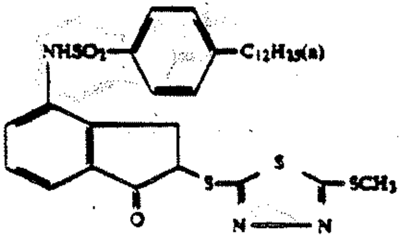

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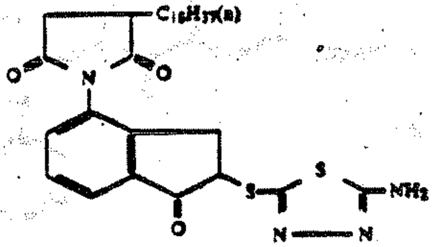

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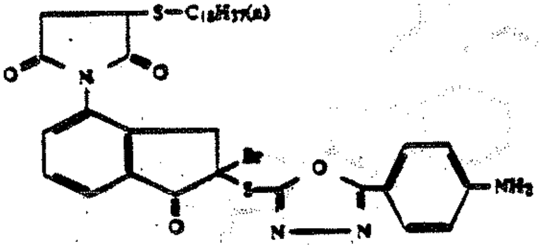

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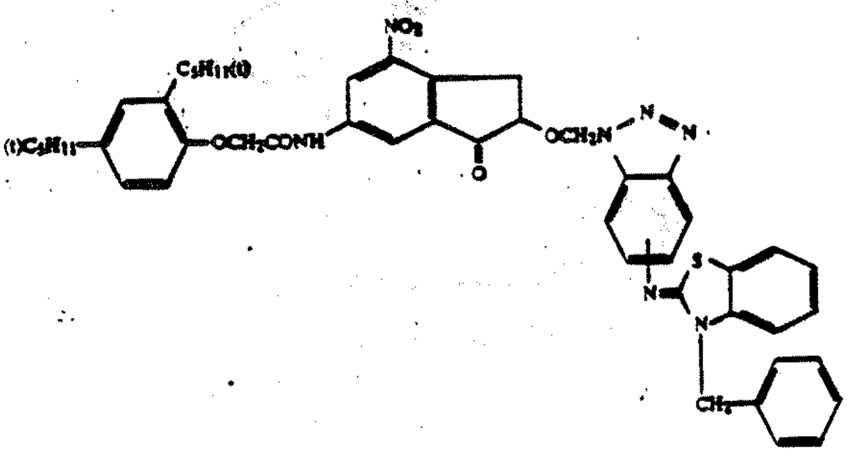

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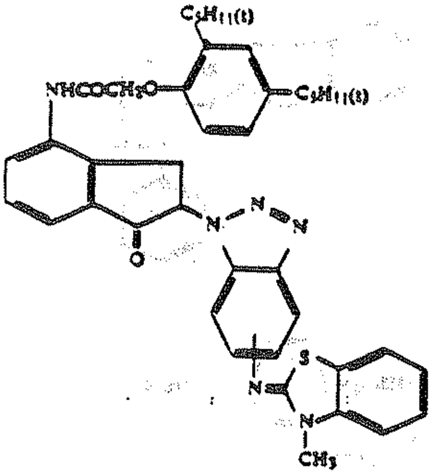

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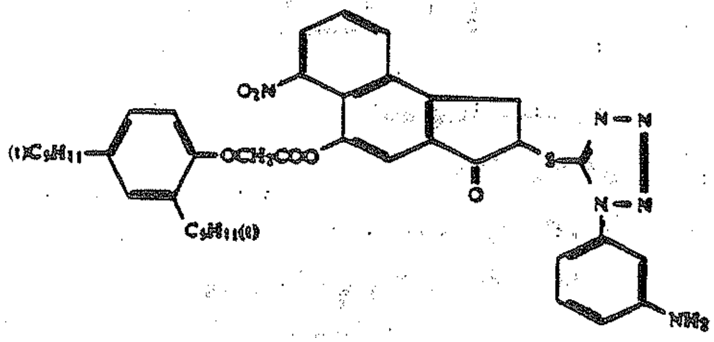

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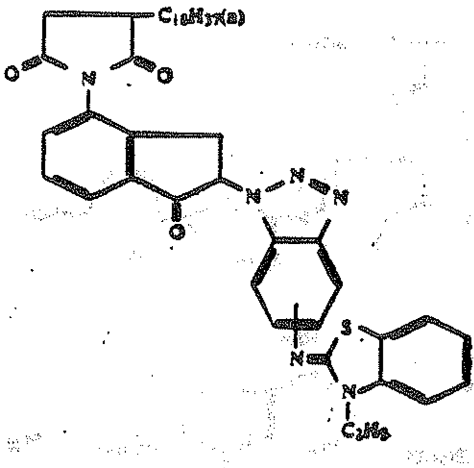

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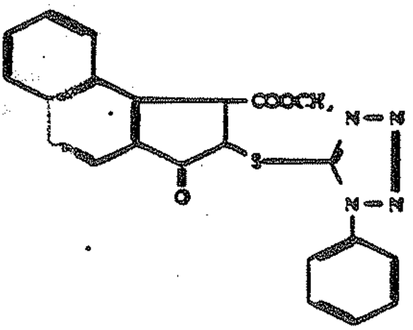

[D-115]

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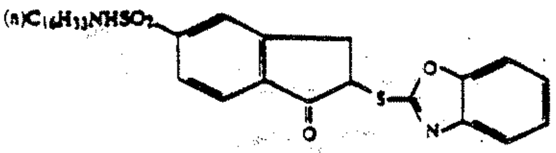
[D-116]



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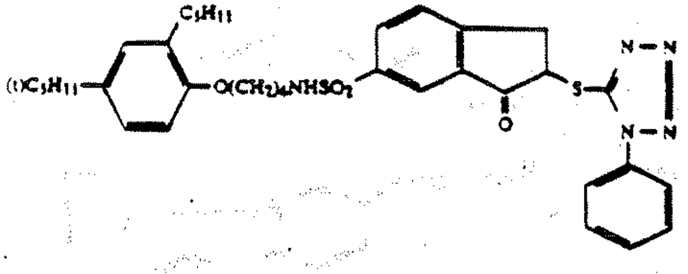

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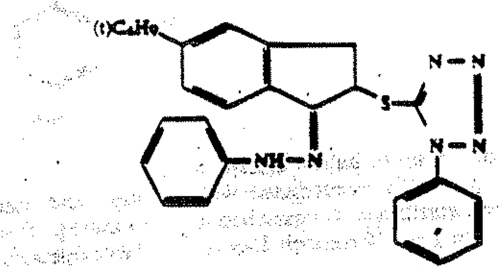

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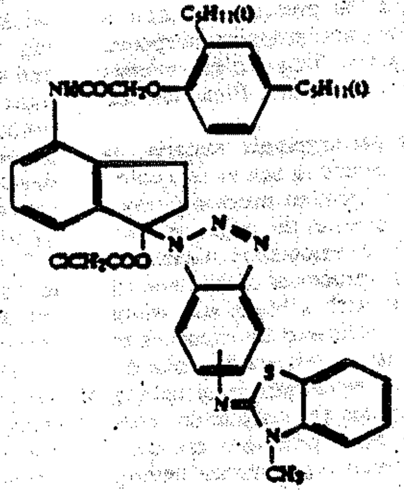

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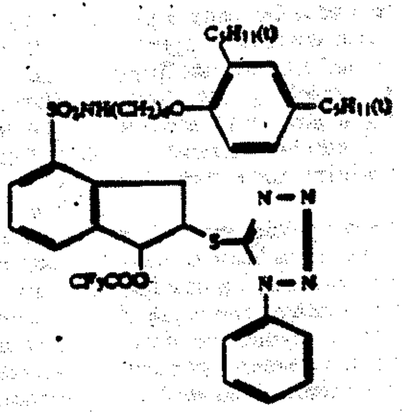

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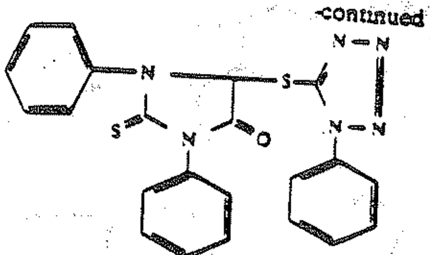

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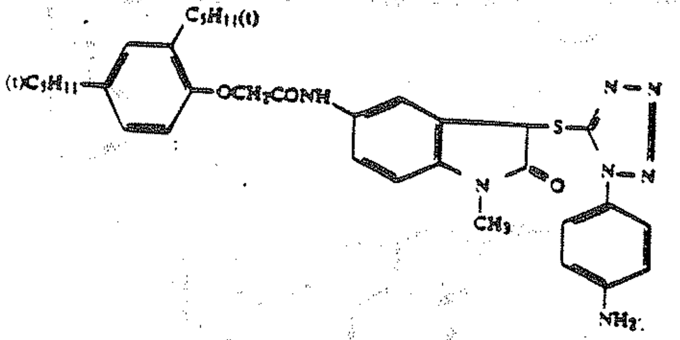


[D-122]

The other compositions of the silver halide light-sensitive color photographic material in accordance with the present invention may be determined as described in the above-mentioned literature 1 or "Research Disclosure" No. 18431.

The silver halide light-sensitive color photographic material in accordance with the present invention is highly sensitive and used for photographing purposes, for example, for color negative films, color reversal films, 8 mm color films, motion picture films and the like.

The light-sensitive color photographic material in accordance with the present invention can yield a color image by ordinary color development process following exposure. The basic processes in the negative-positive method include the color development, bleaching, and fixing processes. The basic processes of the reversal method include development with a black and white negative developing solution, followed by exposure to white light or treatment with a processing solution containing fogging agent, color development, bleaching and fixing. These basic processes are conducted independently or, two or more basic processes are conducted in one step using a processing solution having the respective functions. For example, a combined color processing method is conduced by using a processing solution containing a color developing agent, a ferric salt bleaching constituent and a thiosulfate fixing constituent, and a combined bleaching and fixing method is conducted by using a processing solution containing iron (III) complex of ethylenediaminetetraacetic acid as the bleaching constituent and a thiosulfate fixing constituent.

The light-sensitive color photographic material in accordance with the present invention may be processed by any processing method consisting for example of color development, combined bleaching and fixing, if necessary followed by washing and stabilization; color development, bleaching, fixing, if necessary followed by washing and stabilization; pre-hardening, neutralization, color development, combined stopping and fixing, washing, bleaching, fixing, washing, post-hardening, and washing; color development, washing, subsidiary color development, stopping, bleaching, fixing, washing, and stabilization; pre-hardening, neutralization, washing, first development, stopping, washing, color development, stopping, washing, bleaching, fixing, and washing; pre-hardening, neutralization, first development, stopping, washing, color development, stopping, washing, bleaching, organic acid bath, fixing, and washing; first development, non-fixing silver dye bleachi and washing, color development, acid rinsing, washin bleaching, washing, fixing, washing, stabilization, and washing; halogenation belaching of developed silver generated by color development, followed by color development to increase the amount of dye formed; or processing of a low-silver light-sensitive material with an amplifier such as peroxide or cobalt complex.

Typical examples of the color developing agents use in the developing solution are aromatic primary amir compounds such as p-phenylenediamines and p-amin phenols. The typical examples of these compounds ar:

N,N-Dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine, 3-methyl-N,N-diethyl-p-phenylenediamine, N-carbamidemethyl-N-methyl-p-phenylenediamine, N-carbamidemethyl-N-tetrahydrofurfuryl-2-methyl-p-phenylenediamine, N-ethyl-N-carboxymethyl-2-methyl-p-phenylenediamine, N-carbamidemethyl-N-ethyl-2-methyl-p-phenylenediamine, 3-β-methanesulfonamidoethyl-4-amino-N,N-diethylaniline, N-ethyl-N-tetrahydrofurfuryl-2-methyl-p-aminophenol, 3-acetylamino-4-aminodimethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, N-ethyl-N-β-methanesulfonamidoethyl-4-aminoaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, N-methyl-N-β-sulfoethyl-p-phenylenediamine, N-ethyl-N-β-(β-methoxyethoxy)ethyl-3-methyl-4-aminoaniline, N-ethyl-N-β-[β-(β-methoxyethoxy)ethoxy]-ethyl-3-methyl-4-aminoaniline, o-aminophenol, p-aminophenol, 5-amino-2-oxy-toluen inorganic acid salt such as hydrochloric acid or sulfur acid, or organic acid salt such as p-toluenesulfonate and the like.

Typical examples thereof are also described in Japanese Provisional Patent Publication Nos. 64932/1973.

131526/1975 and 95849/1976, and by Bent et al. in "Journal of the American Chemical Society", Vol. 73, pages 3100–3125, 1951.

The amount of the aromatic primary amino compound used is determined by the desired activity of the developing solution. To increase the activity, the amount used should be raised. It is generally used in an amount between 0.0002 mol/liter and 0.7 mol/liter. According to the purposes, it is possible to use a combination of two or more compounds, for example, 3-methyl-4-amino-N,N-diethylaniline and 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline; 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline and 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline; 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline and N-ethyl-N-β-[β-(β-methoxyethoxy)ethoxy]ethyl-3-methyl-4-aminoaniline; 3-methyl-4-amino-N,N-diethylaniline and 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethyl- and 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline and N-ethyl-N-β-[β-(β-methoxyethoxy)ethoxy]ethyl-3-methyl-4-aminoaniline; 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline and 3-methyl-4-amino-N-β-methoxyethylaniline.

The color developing solution may further contain various constituents ordinarily used in such solutions, for example, alkali agents such as sodium hydroxide, sodium carbonate and potassium carbonate, alkali metal sulfite, alkali metal bisulfite, alkali metal thiocyanate, alkali metal halide, benzyl alcohol, water softening agent, thickening agent and development accelerator. The pH value of the color developing solution is normally 7 or more, most generally between about 9 and about 13.

Additives used as required in the color developing solution include for example hydroxides, carbonates, and phosphates of alkali metals and ammonium for keeping the pH value constant; pH adjusting or buffering agents (e.g. weak acids such as acetic acid and boric acid, weak bases, and their salts); development accelerators such as pyridinium compounds, cationic compounds, potassium nitrate and sodium nitrate, polyethylene glycol condensates, phenyl cellosolve, phenylcarbitol, alkyl cellosolve, phenylcarbitol, dialkylformamide, alkyl phosphate and derivatives thereof, nonionic compounds such as polythioethers, polymers having sulfite esters, organic amines such as pyridine and ethanolamine, benzyl alcohol and hydrazine.

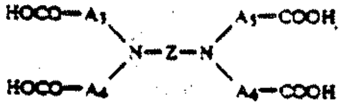
Examples of fog restrainers include bromides such as potassium bromide, sodium bromide and ammonium bromide, compounds used for quick processing solutions such as alkali iodide, nitrobenzoimidazole, mercaptobenzoimidazole, 5-methylbenzotriazole, and 1-phenyl-5-mercaptotetrazole, nitro benzoate, benzothiazolium derivatives and phenazine N-oxide.

It is also possible to use stain preventing agents, sludge preventing agents, interlayer effect accelerators, preservatives (e.g. sulfite, acid sulfite, hydroxylamine hydrochloride, formsulfite, alkanolamine sulfite adduct), and chelating agents.

Examples of the chelating agents are phosphates such as polyphosphates, aminopolycarboxylic acids such as nitrilotriacetic acid and 1-3-diamino-2-propanoltetraacetic acid, oxycarboxylic acids such as citric acid and gluconic acid, and 1-hydroxy-1,1'-diphosphonic acid. These chelating agents may be used in combination with each other or with lithium sulfate.

Metal complexes of organic acids used as the bleaching agent in the bleaching solution or in the combined bleaching and fixing solution oxidize the metallic silver formed by the development and convert it into silver halides, and at the same time cause the noncolor-forming portion of the color forming agent to develop color. The metal complexes of organic acids have a structure in which metal ions such as iron, cobalt and copper are coordinated with organic acids such as aminopolycarboxylic acid, oxalic acid or citric acid. The most preferable organic acids used for forming such metal complexes are aminopolycarboxylic acids represented by the general formulas (III) and (IV):

$$HOCO\text{-}A_1\text{-}Z\text{-}A_2\text{-}COOH \qquad (III)$$



(IV)

in which A_1, A_2, A_3, A_4, A_5 and A_6 each designate a substituted or unsubstituted hydrocarbon group, and Z designates a hydrocarbon group, oxygen atom, sulfur atom or $>N\text{-}A_7$ wherein A_7 denotes a hydrocarbon group or a lower aliphatic carboxilic acid.

These aminopolycarboxylic acids may be used in the form of an alkali metal salt, an ammonium salt or a water-soluble amine salt. The typical examples of the aminopolycarboxylic acids represented by the general formulas (III) and (IV) and the other aminopolycarboxylic acids are:

Ethylenediaminetetraacetic acid,
diethylenetriaminepentaacetic acid,
ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetic acid
propylenediaminetetraacetic acid,
nitrilotriacetic acid,
cyclohexanediaminetetraacetic acid,
iminodiacetic acid,
dihydroxyethylglycine,
ethyletherdiaminetetraacetic acid,
glycoletherdiaminetetraacetic acid,
ethylenediaminetetrapropionic acid,
phenylenediaminetetraacetic acid,
disodium ethylenediaminetetraacetate,
tetra(trimethylammonium)ethylenediaminetetraacetate
tetrasodium ethylenediaminetetraacetate,
pentasodium diethylenetriaminepentaacetate,
sodium ethylenediamine-N-(β-oxyethyl)-N,N',N' triacetate,
sodium propylenediaminetetraacetate,
sodium nitrilotriacetate, and
sodium cyclohexanediaminetetraacetate.

In addition to the above-mentioned metal complexe of organic acids as the bleaching agents, various add tives may be contained in the bleaching solution. Th additives may preferably be re-halogenating agen such as alkali halides and ammonium halides e.g. potassium bromide, sodium bromide, sodium chloride an ammonium bromide. It is also possible to add pH buffering agents such as borate, oxalate, acetate, carbonat and phosphate, and other additives which is usuall used in bleaching solutions such as polyaminocarbo ylic acids and their salts, alkylamines and polyethylen oxides.

When a combined bleaching and fixing solutio (bleach-fixing solution) is used in the bleaching pro ss a bleach-fixing solution containing the above-mentioned metal complexes of organic acids as the belaching agents and silver halide fixing agents such as thiosulfates, thiocyanates and thioureas is used. The solution may also contain a small or large amount of halogen compounds such as potassium bromide. It is also possible to use a special bleaching and fixing solution consisting of a combination of a bleaching agent and a large amount of halogen compounds such as potassium bromide. The above-mentioned halogen compounds may be potassium bromide, hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, ammonium bromide, potassium iodide and ammonium iodide.

Typical examples of the silver halide fixing agents contained in the bleach-fixing solution are the compounds forming water-soluble complexes by the reaction with silver halides, which are used in usual fixing, e.g. thiosulfates such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate, thiocyanates such as potassium thiocyanate, sodium thiocyanate, and ammonium thiocyanates, or thioureas and thioethers.

Like a bleaching solution, the bleach-fixing solution may further contain pH buffering agents such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide alone or in combination. The solution may also contain various brightening agents, anti-foaming agents and surface active agents. It is also possible to add preservatives such as bisulfite addition compounds of hydroxylamine, hydrazine, and aldehyde compounds, organic chelating agents such as aminopolycarboxylic acids, stabilizers such as nitroalcohol nitrate, organic solvents such as methanol, dimethylsulfoamide, and dimethylsulfoxide.

The silver halide fixing agents are the compounds forming water-soluble complexes by the reaction with silver halides, which are used in usual fixing. The typical examples thereof are thiosulfates such as potassium thiosulfate, sodium thiosulfate, and ammonium thiosulfate, thiocyanates such as potassium thiocyanate, sodium thiocyanate, and ammonium thiocyanate, or thioureas and thioethers. These agents may be used alone or in combination. In the latter case, they may be combined in any proportion. The halides of alkali metals or ammonium sometimes exhibit the fixing action.

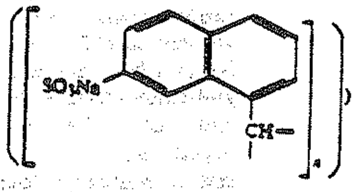
The fixing solution may be incorporated with various additives as required, e.g. pH buffering agents such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide alone or in combination. The solution may also contain various brightening agents, anti-foaming agents and surface active agents. It is also possible to add preservatives such as sulfurous acid, bisulfite addition compounds of hydroxylamine, hydrazine, and aldehyde compounds, organic chelating agents such as aminopolycarboxylic acids, stabilizers such as nitroalcohol nitrate, organic solvents such as methanol, dimethylsulfoamide, and dimethylsulfoxide. Conventional fixing accelerators may be added optionally.

The present invention is hereinafter illustrated by the following nonlimitative examples.

First, the preparations of the emulsions used in the examples are described below.

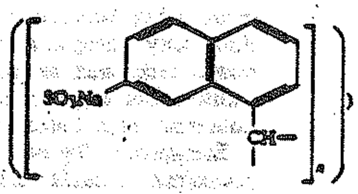
(Preparation of polydispersed emulsion)

An ammoniacal silver nitrate solution and an aqueous alkali halide solution were naturally dropped into a reactor containing an aqueous gelatin solution and an excess of halide and maintained at 60° C. Then after an aqueous Demool-N (made by KAO Atlas Co. Ltd. solution and aqueous magnesium sulfate solution were added to cause precipitation, desalting was done, and gelatin was added to obtain an emulsion having a pAg value of 7.8 and a pH value of 6.0. Further, sodium thiosulfate, chloroauric acid and ammonium thiocyanate were added, and the resulting mixture was subjected to chemical ripening at 52° C. for 70 minutes. Thereafter, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 6-nitrobenzoimidazole were added, and gelatin was added to obtain a polydispersed silver iodobromide emulsion. The molar percentage of the silver iodide was changed by changing the composition of the alkali halide, and the average crystal size and crystal size distribution were changed by changing the time for adding the ammoniacal silver nitrate solution and the aqueous alkali halide solution.



(Preparation of monodispersed emulsion)

An aqueous ammoniacal silver nitrate solution and an aqueous potassium bromide solution were added to a reactor containing potassium iodide and an aqueous gelatin solution while the pAg value in the reactor was maintained constant. This addition was done in proportion to the increase in the surface area of crystals during the growth thereof. Then, after an aqueous Demool-N (made by KAO Atlas Co., Ltd. solution and aqueous magnesium sulfate solution were added to cause precipitation, desalting was done, and gelatin was added to obtain an emulsion having a pAg value of 7.8 and a pH value of 6.0. Further, sodium thiosulfate, chloroauric acid and ammonium thiocyanate were added, and the resulting mixture was subjected to chemical ripening. Thereafter, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 6-nitrobenzoimidazole were added, and gelatin was further added to obtain a monodispersed silver iodobromide emulsion. The molar percentage of the silver iodide was changed by changing the ratio of potassium iodide to potassium bromide. The crystal size was changed by changing the amounts of the ammoniacal silver nitrate and the potassium halide added. Furthermore crystal shape was changed by varying the pAg value during a precipitation procedure, which however should be kept constant during the reaction.



EXAMPLE 1

Specimen No. 1 was prepared by sequentially applying the layers described below on a transparent support made of an under-coated cellulose triacetate film. (In all examples below, addition amount to the silver halide light-sensitive color photographic material is the amount per 1 m^2, and the amounts of the silver halide emulsion and the colloidal silver are expressed in terms of silver.)

(Specimen No. 1)

Layer 1: Antihalation layer containing 0.4 g of black colloidal silver and 3 g of gelatin.

Layer 2: Low-sensitivity red-sensitive emulsion layer containing 1.5 g of silver iodobromide low-sensitivity red-sensitive emulsion (obtained by red-sensitization of emulsion 2 in Table 2), 1.6 g of gelatin and 0.4 g of tricresyl phosphate (hereinafter referred to as TCP) in which 0.80 g of 1-hydroxy-4-[β-methoxyethylaminocarbonylmethoxy)-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthoamide (hereinafter referred to as cyan coupler C-18), and 0.028 g of 1-hydroxy-4-[4-(1-hydroxy-8-acetamido-3,6-disulfo-2-naphthylazo)phenoxy]-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthoamide disodium salt (hereinafter referred to as colored cyan coupler CC-1) were dissolved.

Layer 3: High-sensitivity red-sensitive emulsion layer containing 1.1 g of a silver iodobromide high-sensitivity red-sensitive emulsion (obtained by red-sensitive of emulsion 1 in Table 2), 1.2 g of gelatin and 0.15 g of TCP in which 0.23 g of the cyan coupler C-18, and 0.020 g of the colored cyan coupler CC-1 were dissolved.

Layer 4: Intermediate layer containing 1.2 g of gelatin and 0.04 g of di-n-butyl phthalate (hereinafter referred to as DBP) in which 0.07 g of 2,5-di-tert-octylhydroquinone (hereinafter referred to as stain preventing agent HQ-1) was dissolved.

Layer 5: Low-sensitivity green-sensitive emulsion layer containing 1.6 g of a silver iodobromide low-sensitivity green-sensitive emulsion (obtained by green-sensitization of emulsion 2 in Table 2), 1.7 g of gelatin and 0.3 g of TCP in which 0.30 g of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido]-5-pyrazolone (hereinafter referred to as magenta coupler M-1), 0.20 g of 4,4-methylenebis-[1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido]benzeneamido]-5-pyrazolone (hereinafter referred to as magenta coupler M-19) and 0.066 g of 1-(2,4,6-trichlorophenyl)-4-(1-naphthylazo)-3-(2-chloro-5-octadecenylsuccinimidoanilino)-5-pyrazolone (hereinafter referred to as colored magenta coupler CM-1) were dissolved.

Layer 6: High-sensitivity green-sensitive emulsion layer containing 1.5 g of a silver iodobromide high-sensitivity green-sensitive emulsion (obtained by green-sensitization of emulsion 1 in Table 2), 1.9 g of gelatin and 0.12 g of TCP in which 0.093 g of the magenta coupler M-1, 0.094 g of the magenta coupler M-19, and 0.049 g of the colored magenta coupler CM-1 were dissolved.

Layer 7: Yellow filter layer containing 0.2 g of yellow colloidal silver, 0.11 g of DBP in which 0.2 g of stain preventing agent HQ-1 was dissolved. and 2.1 g of gelatin.

Layer 8: Low-sensitivity blue-sensitive emulsion layer containing 0.95 g of a silver iodobromide low-sensitivity blue-sensitive emulsion (emulsion 2 in Table 2), 1.9 g of gelatin and 0.93 g of DBP in which 1.84 g of α-[4-(1-benzyl-2-phenyl-3,5-dioxo-1,2,4-triazolidinyl)]-α-pivaloyl-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)butylamido]acetanilide (here inafter referred to as yellow coupler Y-4) was dis solved.

Layer 9: High-sensitivity blue-sensitive emulsio layer containing 1.2 g of a silver iodobromide higl sensitivity blue-sensitive emulsion (emulsion 1 Table 2), 2.0 g of gelatin and 0.23 g of DBP which 0.46 g of the yellow coupler Y-4 was d solved.

Layer 10: Protective layer containing 2.3 g of gelat

Other specimens were prepared in the same way specimen No. 1, except that emulsions obtained by color-sensitization of the silver iodobromide emulsi listed in Table 1 were used in respective light-sensit layers. The physical values of respective silver iodob mide emulsions were as shown in Table 2.

TABLE 1

	Specimen No. 1 (Comparative)	Specimen No. 2 (Comparative)	Specimen No. 3 (Comparative)	Specimen No. 4 (Comparative)	Specimen No. 5 (According to the present invention)	Specimen No (According to present invent
Layer 2	EM-2	EM-4	EM-6	EM-8	EM-6	EM-8
Layer 3	EM-1	EM-3	EM-1	EM-3	EM-5	EM-7
Layer 5	EM-2	EM-4	EM-2	EM-4	EM-6	EM-8
Layer 6	EM-1	EM-3	EM-5	EM-7	EM-5	EM-7
Layer 8	EM-2	EM-4	EM-2	EM-4	EM-6	EM-8
Layer 9	EM-1	EM-3	EM-1	EM-3	EM-5	EM-7

TABLE 2

	EM-1	EM-2	EM-3	EM-4	EM-5	EM-6	EM-7	E
Mole % of silver iodide	7%	7%	7%	7%	2%	2%	2%	
Average crystal size ($\bar{r}$)	1.05μ	0.65μ	1.04μ	0.65μ	1.06μ	0.66μ	1.05μ	0
Standard deviation (S)	0.25μ	0.16μ	0.093μ	0.05μ	0.27μ	0.16μ	0.084μ	0
$S/\bar{r}$	0.24	0.25	0.09	0.08	0.25	0.24	0.08	0
Form of grains	Twinned and cubic	Twinned and cubic	Cubic	Cubic	Twinned and cubic	Twinned and cubic	Cubic	(

The obtained six specimens were respective jected to exposure giving the maximum density sure giving the maximum density after the expo white light through an optical wedge and proce the processes described below). They were ther tively processed gy the processes described below to yield the specimens having dye images.

Processing (processing temperature: 38° C.)	Processing time
Color development	3 minutes 15 seconds
Bleaching	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Fixing	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Stabilization	3 minutes 15 seconds
Drying	1 minute 30 seconds

The following processing solutions were used in the above-mentioned processing steps:

(Color developing solution)		
4-Amino-3-methyl-N—ethyl-N—(β-hydroxyethyl)-aniline sulfate	4.75	g
Anhydrous sodium sulfite	4.25	g
Hydroxylamine half-sulfate	2.0	g
Anhydrous potassium carbonate	37.5	g
Sodium bromide	1.3	g
Trisodium nitrilotriacetate (monohydrate)	2.5	g
Potassium hydroxide	1.0	g
Made up to 1 liter with water		
(Bleaching solution)		
Ferric ammonium salt of ethylenediaminetetraacetic acid	100.0	g
Diammonium salt of ethylenediaminetetraacetic acid	10.0	g
Ammonium bromide	150.0	g
Glacial acetic acid	10.0	ml
Made up to 1 liter with water and adjusted to pH 6.0 with aqueous ammonia.		
(Fixing solution)		
Ammonium thiosulfate	175.0	g
Anhydrous sodium sulfite	8.6	g
Sodium metasulfite	2.3	g
Made up to 1 liter with water and adjusted to pH 6.0 with acetic acid.		
(Stabilizing solution)		
Formalin (37% aqueous solution)	1.5	ml
Konidax (available from Konishiroku Photo Industry Co., Ltd.)	7.5	ml
Made up to 1 liter with water.		

Gelatin of the obtained image was decomposed with pronase for respective layers. Silver iodobromide crystals were separated by centrifuging, and observed by using a scanning type electronic microscope (JSM-T200 available from Nippon Denshi K.K.) to measure the percentage of the undeveloped grains with respect to the total crystals in each layer (dead grain percentage). The results were as shown in Table 3.

TABLE 3

	Specimen No. 1 (Comparative)	Specimen No. 2 (Comparative)	Specimen No. 3 (Comparative)	Specimen No. 4 (Comparative)	Specimen No. 5 (According to the present invention)	Specimen No. 6 (According to the present invention)
Layer 2	67%	65%	65%	43%	27%	20%
Layer 3	55%	52%	46%	44%	34%	27%
Layer 5	53%	48%	44%	40%	29%	23%
Layer 6	[illegible]	57%	59%	55%	36%	30%
Layer 8	50%	65%	48%	46%	25%	22%
Layer 9	59%	55%	57%	52%	34%	28%

As shown in Table 3, specimen Nos. 5 and 6 in accordance with the present invention exhibited reduced dead grains.

EXAMPLE 2

Specimen No. 1 used in Example 1 was exposed to blue, green and red light through an optical wedge, and developed in the same way as in Example 1. In this way, the minimum exposure log Eo in the exposure to blue, green and red light, which gave the maximum density, was determined. On the other hand, specimen Nos. 1 to 6 used in Example 1 were respectively divided into two sections, and all of these specimens were subjected to the minimum exposure. One section of each specimen was developed in the same way as in Example 1 to obtain a dye image. The other section of each specimen was subjected to the color development conducted in Example 1, a stop processing with a 2% aqueous acetic acid solution, and the fixing and subsequent processes in Example 1 so as to obtain a dye image in which the silver image was not removed. As for the dye image in which the silver image was not removed, the amount of developed silver (Ag) per m² of the specimen was determined by X-ray fluorimetry. The utilization efficiency of silver for the formation of dye image was determined as the quotient of the image density divided by the amount of developed silver (D/Ag). The results were as shown in Table 4. The amount of developed silver was the value compensated for the colloidal silver amount added during coating.

TABLE 4

Specimen		Amount of developed silver (g/m²)	D/Ag
1	Exposure to blue light	0.82	0.96
	Exposure to green light	0.96	1.39
	Exposure to red light	0.50	1.56
2	Exposure to blue light	0.90	0.98
	Exposure to green light	1.06	1.92
	Exposure to red light	0.52*	1.57
3	Exposure to blue light	0.85	0.97
	Exposure to green light	0.99	1.90
	Exposure to red light	0.55	1.59
4	Exposure to blue light	0.92	0.99
	Exposure to green light	1.17	1.94
	Exposure to red light	0.57	1.60
5	Exposure to blue light	1.24	1.38
	Exposure to green light	1.51	2.03
	Exposure to red light	0.7	1.66
6	Exposure to blue light	1.35	1.10
	Exposure to green light	1.65	2.16
	Exposure to red light	0.75	1.69

As shown in Table 4, specimen Nos. 5 and 6 according to the present invention in which a silver iodobromide emulsion containing a low molar percentage of iodine exhibited lesser dead grains and increased developed silver amount compared with specimen Nos. 1 and 2 in which a silver iodobromide emulsion containing a high molar percentage of silver iodide and specimen No. 3 partially containing a layer of a silver iodobromide emulsion containing a low molar percentage of silver iodide. Further, the specimens in accordance with the present invention exhibited remarkably increased density of dye image obtained from silver iodobromide per unit, and increased utilization efficiency of silver for the formation of dye image.

EXAMPLE 3

Specimen No. 7 was prepared by sequentially applying the layers described below on a transparent support made of an under-coated cellulose triacetate film.

(Specimen No. 7)

Layer 1: Antihalation layer containing 0.4 g of black colloidal silver and 3 g of gelatin.

Layer 2: Low-sensitivity red-sensitive emulsion layer containing 1.5 g of silver iodobromide low-sensitivity red-sensitive emulsion (obtained by red-sensitization of emulsion 9 in Table 6), 1.6 g of gelatin and 0.4 g of TCP in which 0.80 g of the cyan coupler C-18 and 0.018 g of the DIR compound D-100 were dissolved.

Layer 3: High-sensitivity red-sensitive emulsion layer containing 1.1 g of a silver iodobromide high-sensitivity red-sensitive emulsion (obtained by red-sensitization of emulsion 1 in Table 2), 1.2 g of gelatin and 0.15 g of TCP in which 0.23 g of the cyan coupler C-18 and 0.013 g of the DIR compound D-100 were dissolved.

Layer 4: Intermediate layer containing 1.2 g of gelatin and 0.04 g of DBP in which 0.07 g of stain preventing agent HQ-1 was dissolved.

Layer 5: Low-sensitivity green-sensitive emulsion layer containing 1.6 g of a silver iodobromide low-sensitivity green-sensitive emulsion (obtained by green-sensitization of emulsion 9 in Table 6), 1.7 g of gelatin and 0.3 g of TCP in which 0.30 g of magenta coupler M-1, 0.20 g of magenta coupler M-19 and 0.025 g of the DIR compound D-100 were dissolved.

Layer 6: High-sensitivity green-sensitive emulsion layer containing 1.5 g of a silver iodobromide high-sensitivity green-sensitive emulsion (obtained by green-sensitization of emulsion 1 in Table 2), 1.9 g of gelatin and 0.12 g of TCP in which 0.093 g of the magenta coupler M-1, 0.094 g of the magenta coupler M-19 and 0.008 g of the DIR compound D-100 were dissolved.

Layer 7: Yellow filter layer containing 0.2 g of yellow colloidal silver, 0.11 g of DBP in which 0.2 g of stain preventing agent HQ-1 was dissolved, and 2.1 g of gelatin.

Layer 8: Low-sensitivity blue-sensitive emulsion layer containing 0.95 g of a silver iodobromide low-sensitivity blue-sensitive emulsion (emulsion 9 in Table 6), 1.9 g of gelatin and 0.93 g of DBP in which 1.84 g of yellow coupler Y-4 and 0.025 g of the DIR compound D-100 were dissolved.

Layer 9: High-sensitivity blue-sensitive emulsion layer containing 1.2 g of a silver iodobromide high-sensitivity blue-sensitive emulsion (emulsion 1 in Table 2), 2.0 g of gelatin and 0.23 g of DBP in which 0.46 g of the yellow coupler Y-4 and 0.008 g of the DIR compound D-100 were dissolved.

Layer 10: Protective layer containing 2.3 g of gelatin.

Specimen Nos. 8 to 12 were prepared in the same way as specimen No. 7, except that emulsions obtained by the color-sensitization of the silver iodobromide emulsions listed in Table 5 were used in respective light-sensitive layers. The physical values of respective emulsions were as shown in Table 6. The amount of the DIR compound was altered to obtain the equal gamma value. The addition amount for respective specimens were as shown in Table 5.

TABLE 5

		Layer 2	Layer 3	Layer 5	Layer 6	Layer 8	Layer 9
Specimen No. 7	Emulsion used	EM-9	EM-1	EM-9	EM-1	EM-9	EM-1
(Comparative)	Amount of D-100 used (g)	0.018	0.013	0.025	0.008	0.025	0.008
Specimen No. 8	Emulsion used	EM-10	EM-3	EM-10	EM-3	EM-10	EM-3
(Comparative)	Amount of D-100 used (g)	0.027	0.019	0.036	0.012	0.035	0.012
Specimen No. 9	Emulsion used	EM-9	EM-1	EM-6	EM-11	EM-9	EM-1
(Comparative)	Amount of D-100 used (g)	0.018	0.013	0.032	0.010	0.025	0.008
Specimen No. 10	Emulsion used	EM-10	EM-3	EM-8	EM-12	EM-10	EM-3
(Comparative)	Amount of D-100 used (g)	0.027	0.019	0.038	0.014	0.035	0.012
Specimen No. 11	Emulsion used	EM-6	EM-11	EM-6	EM-11	EM-6	EM-11
(According to the present invention)	Amount of D-100 used (g)	0.026	0.018	0.032	0.010	0.031	0.011
Specimen No. 12	Emulsion used	EM-8	EM-12	EM-8	EM-12	EM-8	EM-12
(According to the present invention)	Amount of D-100 used (g)	0.030	0.020	0.038	0.014	0.038	0.014

In Table 5, EM-1, EM-3, EM-6 and EM-8 were the emulsions listed in Table 2 and used in Example 1. EM-9, EM-10, EM-11 and EM-12 were the emulsions listed in Table 6.

TABLE 6

	EM-9	EM-10	EM-11	EM-12
Mole % of silver iodide	6%	6%	3%	3%
Average crystal size (r)	0.64μ	0.66μ	1.05μ	1.04μ
Standard deviation (S)	0.17μ	0.06μ	0.27μ	0.09μ
S/r	0.27	0.09	0.26	0.09
Form of grains	Twinned and cubic	Cubic	Twinned and cubic	Cubic

The obtained specimens were individually brought into close contact with a transparent square wave chart or wedge, and exposed to blue, green and red monochromatic light, followed by the color development according to the procedure described in Example 1. The results of the photographic characteristics, sharpness and graininess were as shown in Table 7.

The effect of improvement in the image sharpness was evaluated by determining the modulation transfer function (MTF) and comparing the MTF values at spatial frequencies of 10 lines/mm and 30 lines/mm.

The graininess (RMS) was evaluated by obtaining the standard deviation of the fluctuation in the density values occurring when a color image having a color image density of 1.0 is scanned with a microdensitometer ing a circular scanning aperture of diameter of 25μ, and comparing the value obtained by magnifying the standard deviation by a factor of 1000.

The gamma value is expressed by tan α in which α designates the angle between the extension of the straight section of the photographic characteristic curve and the horizontal axis. The sensitivity is expressed by the relative value of the logarithm of the reciprocal of the exposure that is able to give the density of fog density plus 0.1. The blue, green and red sensitivities of each specimen were expressed by the relative values, with those of specimen No. 7 taken as 100.

TABLE 7

Specimen No.		Relative sensitivity.	γ (gamma)	MTF value (%) 10 lines/mm	MTF value (%) 30 lines/mm	RMS
7 (Comparative)	Exposure to blue light	100	0.87	89	57	55
	Exposure to green light	100	0.85	86	49	34
	Exposure to red light	100	0.88	78	33	39
8 (Comparative)	Exposure to blue light	105	0.86	111	82	47
	Exposure to green light	106	0.86	112	75	27
	Exposure to red light	104	0.88	98	53	32
9 (Comparative)	Exposure to blue light	99	0.87	90	56	54
	Exposure to green light	100	0.85	90	52	35
	Exposure to red light	98	0.88	77	35	40
10 (Comparative)	Exposure to blue light	107	0.87	110	79	46
	Exposure to green light	105	0.85	118	78	28
	Exposure to red light	105	0.83	103	59	31
11 (According to the present invention)	Exposure to blue light	103	0.86	128	85	53
	Exposure to green light	102	0.88	127	80	36
	Exposure to red light	103	0.85	109	65	39
12 (According to the present invention)	Exposure to blue light	106	0.88	132	101	45
	Exposure to green light	107	0.85	130	97	27
	Exposure to red light	105	0.86	119	78	30

The above six specimens were respectively subjected to exposure giving the maximum density. They were then developed and subjected to the separation processing for respective layers in the same way as in Example 1. The dead grain percentage was measured to obtain the results shown in Table 8.

TABLE 8

	Specimen No. 7 (Comparative)	Specimen No. 8 (Comparative)	Specimen No. 9 (Comparative)	Specimen No. 10 (Comparative)	Specimen No. 11 (According to the present invention)	Specimen No. 12 (According to the present invention)
Layer 2	45%	44%	45%	41%	27%	21%
Layer 3	54%	52%	52%	50%	36%	29%
Layer 5	52%	46%	42%	39%	30%	23%
Layer 6	61%	59%	49%	47%	37%	31%
Layer 8	48%	43%	47%	43%	29%	24%
Layer 9	57%	53%	57%	52%	35%	29%

As shown in Table 8, the present invention can reduce dead grains even when the gamma characteristics are controlled with the DIR compound. Table 8 also shows that the sharpness is greatly improved if the light-sensitive material in accordance with the present invention is combined with the DIR compound. Thus, the present invention is advantageous also for improving the image quality.

EXAMPLE 4

Specimen No. 13 was prepared by sequentially applying the layers described below on a transparent support made of an under-coated cellulose triacetate film.

(Specimen No. 13)

Layer 1: Antihalation layer containing 0.4 g of black colloidal silver and 3 g of gelatin.

Layer 2: Low-sensitivity red-sensitive emulsion layer containing 1.5 g of silver iodobromide low-sensitivity red-sensitive emulsion (obtained by red-sensitization of EM-8 used in Example 1), 1.6 g of gelatin and 0.80 g of the cyan coupler C-18.

Layer 3: High-sensitivity red-sensitive emulsion layer containing 1.1 g of a silver iodobromide high-sensitivity red-sensitive emulsion (emulsion obtained by red-sensitization of EM-7 used in Example 1), 1.2 g of gelatin and 0.15 g of TCP in which 0.23 g of the cyan coupler C-18 was dissolved.

Layer 4: Intermediate layer containing 1.2 g of gelatin and 0.04 g of DBP in which 0.07 g of the stain preventing agent HQ-1 was dissolved.

Layer 5: Low-sensitivity green-sensitive emulsion layer containing 1.6 g of a silver iodobromide low-sensitivity green-sensitive emulsion (emulsion obtained by green-sensitization of EM-8 used in Example 1), 1.7 g of gelatin and 0.3 g of TCP in which 0.40 g of 1-(2,4,6-trichlorophenyl)-3-[3-(octadecenylsuccinimide)-2-chloro]anilino-5-pyrazolone (magenta coupler M-6) was dissolved.

Layer 6: High-sensitivity green-sensitive emulsion layer containing 1.5 g of a silver iodobromide high-sensitivity green-sensitive emulsion (obtained by green-sensitization of EM-7 used in Example 1), 1.9 g of gelatin and 0.12 g of TCP in which 0.14 g of the magenta coupler M-6 was dissolved.

Layer 7: Yellow filter layer containing 0.2 g of yellow colloidal silver, 0.11 g of DBP in which 0.2 g of stain preventing agent HQ-1 was dissolved, and 2.1 g of gelatin.

Layer 8: Low-sensitivity blue-sensitive emulsion layer containing 0.95 g of a silver iodobromide low-sensitivity blue-sensitive emulsion (EM-8 used in Example 1), 1.9 g of gelatin and 0.93 g of DBP in which 1.84 g of α-[4-(1-benzyl-2-phenyl-3,5-dioxo-1,2,4-triazolidin-4-yl)]-α-pivaloyl-2-chloro-5-[γ-(2,4-di-tert-amylphenoxyl)butaneamido]acetanilide (yellow coupler Y-5) was dissolved.

Layer 9: High-sensitivity blue-sensitive emulsion layer containing 1.2 g of a silver iodobromide high-sensitivity blue-sensitive emulsion (EM-7 in Example 1), 2.0 g of gelatin and 0.23 g of DBP in which 0.46 g of the yellow coupler Y-5 was dissolved.

Layer 10: Protective layer containing 2.3 g of gelatin.

Specimen No. 14 was prepared in the same way as specimen No. 13 except that 1-hydroxy-2-[8-(2,4-di-tertamylphenoxybutyl]naphthoamide (cyan coupler C-1) was used instead of C-18, the magenta coupler M-1 was used instead of M-6, and α-(1-benzyl-2,4-dioxo-imidazolidin-3-yl)-α-pivaloyl-2-chloro-5-[γ-(2,4-di-tertamylphenoxy)butaneamido]acetanilide (yellow coupler Y-2) was used instead of the yellow coupler Y-4.

The obtained two specimens were respectively subjected to exposure giving the maximum density. They were then developed and subjected to the separation processing for respective layers in the same way as in Example 1. The dead grain percentage was measured to obtain the results shown in Table 9.

TABLE 9

	Specimen No. 13	Specimen No. 14
Layer 2	20%	26%
Layer 3	28%	35%
Layer 5	19%	27%
Layer 6	27%	34%
Layer 8	17%	25%
Layer 9	23%	31%

The couplers used in respective specimens and the specific rates with respect to M-1 were as shown in Table 10.

TABLE 10

	Specimen No. 13		Specimen No. 14	
	Coupler	Specific rate	Coupler	Specific rate
Layer 2, 3	C-18	1.22	C-1	0.98
Layer 5, 6	M-6	1.28	M-1	1.00
Layer 8, 9	Y-5	1.39	Y-2	0.70

Both specimen Nos. 13 and 14 fall within the scope of the present invention. Table 10 shows that dead grains reduce to a larger degree when a coupler exhibiting a specific rate larger than that of M-1 is used.

EXAMPLE 5

Specimen Nos. 15 to 17 were prepared by sequentially applying the layers described below on a transparent support made of an under-coated cellulose triacetate film.

Layer 1: Antihalation layer containing 0.4 g of black colloidal silver and 3 g of gelatin.

Layer 2: Low-sensitivity red-sensitive emulsion layer containing 1.5 g of silver iodobromide low-sensitivity red-sensitive emulsion (obtained by red-sensitization of an emulsion in Table 11), 1.6 g of gelatin and 0.4 g of TCP in which 0.80 g of the cyan coupler C-18 was dissolved.

Layer 3: High-sensitivity red-sensitive emulsion layer containing 1.1 g of a silver iodobromide high-sensitivity red-sensitive emulsion (obtained by red-sensitization of an emulsion in Table 11), 1.2 g of gelatin and 0.15 g of TCP in which 0.23 g of the cyan coupler C-18 was dissolved.

Layer 4: Intermediate layer containing 1.2 g of gelatin and 0.04 g of DBP in which 0.07 g of the stain preventing agent HQ-1 was dissolved.

Layer 5: Low-sensitivity green-sensitive emulsion layer containing 1.6 g of a silver iodobromide low sensitivity green-sensitive emulsion (obtained by green-sensitization of an emulsion in Table 11), 1.7 g of gelatin and 0.3 g of TCP in which 0.40 g of the magenta coupler M-1 was dissolved.

Layer 6: High-sensitivity green-sensitive emulsion layer containing 1.5 g of a silver iodobromide high sensitivity green-sensitive emulsion (obtained by green-sensitization of an emulsion in Table 11), 1.9 g of gelatin and 0.12 g of TCP in which 0.14 g of the magenta coupler M-1 was dissolved.

Layer 7: Yellow filter layer containing 0.2 g of yellow colloidal silver, 0.11 g of DBP in which 0.2 g of stain preventing agent HQ-1 was dissolved, and 2.1 g of gelatin.

Layer 8: Low-sensitivity blue-sensitive emulsion layer containing 0.95 g of a silver iodobromide low-sensitivity blue-sensitive emulsion (an emulsion in Table 11), 1.9 g of gelatin and 0.93 g of DBP in which 1.84 g of the yellow coupler Y-1 was dissolved.

Layer 9: High-sensitivity blue-sensitive emulsion layer containing 1.2 g of a silver iodobromide high sensitivity blue-sensitive emulsion (an emulsion Table 11), 2.0 g of gelatin and 0.23 g of DBP in which 0.46 g of the yellow coupler Y-1 was dissolved.

Layer 10: Protective layer containing 2.3 g of gelatin

TABLE 11

	Specimen No. 15	Specimen No. 16	Specimen No. 17
Layer 2	EM-8	EM-13	EM-15
Layer 3	EM-7	EM-14	EM-16
Layer 5	EM-8	EM-13	EM-15
Layer 6	EM-7	EM-14	EM-16
Layer 8	EM-8	EM-13	EM-15
Layer 9	EM-7	EM-14	EM-16

EM-7, EM-8: Emulsions listed in Table 2 and used in Example 1.

TABLE 12

	EM-13	EM-14	EM-15	EM-16
Mole % of silver iodide	2%	2%	2%	2%
Average crystal size ($\bar{r}$)	0.64μ	1.03μ	0.63μ	1.05μ
Standard deviation (S)	0.05μ	0.10μ	0.06μ	0.09μ
S/$\bar{r}$	0.08	0.10	0.10	0.9
Form of grains	Octahedral	Octahedral	Tetradecahedral	Tetradecahedral

The obtained three specimens were respectively subjected to exposure giving the maximum density. They were then developed and subjected to the separation processing for respective layers in the same way as

Example 1. The dead grain percentage was measured to obtain the results shown in Table 13.

TABLE 13

	Specimen No. 15	Specimen No. 16	Specimen No. 17
Layer 2	20%	17%	18%
Layer 3	28%	24%	24%
Layer 5	23%	19%	19%
Layer 6	31%	28%	27%
Layer 8	23%	17%	18%
Layer 9	23%	23%	24%

Specimen Nos. 15, 16 and 17 fall within the scope of the present invention. As shown in Table 11, the effect of the present invention is larger when octahedral or tetradecahedral silver iodobromide crystals are used than when cubic crystals are used.

EXAMPLE 6

The light-sensitive photographic materials in accordance with the present invention, which were used in Example 3 (specimen Nos. 7, 8, 11 and 12) were separation-exposed to blue, green and red light through a wedge, and processed by the processes described below to yield the specimens having the dye images.

Processes (processing temperature: 25° C.)	Processing time
Color development	3 minutes 30 seconds
Bleaching	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Fixing	6 minutes 30 seconds
Washing with water	3 minutes 15 seconds
Stabilization	1 minute 30 seconds
Drying	

The compositions of the processing solutions used in the above-mentioned processes were the same as those in Example 1.

The photographic characteristics of the obtained color images were compared with those obtained by processing the specimen Nos. 7, 8, 11 and 12 in Example 3 at a processing temperature of 38° C. The results were as shown in Table 14.

TABLE 14

Specimen No.		Processing at 38° C.		Processing at 25° C.	
		Relative sensitivity	Gamma	Relative sensitivity	Gamma
7	Exposure to blue light	100	0.87	65	0.57
	Exposure to green light	100	0.83	57	0.48
	Exposure to red light	100	0.88	51	0.45
8	Exposure to blue light	105	0.84	70	0.60
	Exposure to green light	106	0.86	63	0.50
	Exposure to red light	106	0.88	57	0.50
11	Exposure to blue light	103	0.86	98	0.86
	Exposure to green light	102	0.89	97	0.89
	Exposure to red light	103	0.85	96	0.81
12	Exposure to blue light	106	0.88	101	0.88
	Exposure to green light	107	0.85	99	0.86
	Exposure to red light	105	0.86	98	0.84

As shown in Table 14, even when the specimens in accordance with the present invention are processed at a low temperature, they exhibit characteristics equivalent to those obtained with a high-temperature development conducted for the same development time. This indicates that the light-sensitive material in accordance with the present invention allows quick processing even at low temperatures.

We claim:

1. A light-sensitive color photographic material having a support and, coated thereon, at least two light-sensitive silver halide emulsion layers respectively sensitive to light of a different spectral region, each of said emulsion layers comprising at least two light-sensitive emulsion sublayers having different sensitivity to light and containing negative type light-sensitive silver halide crystals consisting essentially of silver iodobromide containing silver iodide in an amount of from 1 to 3 mole %.

2. The light-sensitive color photographic material according to claim 1 wherein the negative type silver halide crystals contained in at least one of said at least two light-sensitive emulsion sublayers have a monodispersed size distribution satisfying the following relationship:

$$S/\bar{r} \leqq 0.15$$

wherein

$$S = \sqrt{\Sigma(\bar{r} - r_i)^2 n_i / \Sigma n_i}$$

$$\bar{r} = \Sigma n_i r_i / \Sigma n_i$$

in which S designates the standard deviation, $\bar{r}$ designates the average crystal size, r_i designates the crystal sizes of the individual crystals, and n_i designates the number of crystals.

3. The light-sensitive color photographic material according to claim 2 wherein the negative type silver halide crystals contained in all of said light-sensitive emulsion sublayers have a monodispersed size distribution satisfying the following relationship:

$$S/\bar{r} \leqq 0.15$$

wherein

$$S = \sqrt{\Sigma(\bar{r} - r_i)^2 n_i / \Sigma n_i}$$

$$\bar{r} = n_i r_i / n_i$$

in which S designates the standard deviation, $\bar{r}$ designates the average crystal size, r_i designates the crystal sizes of the individual crystals, and n_i designates the number of crystals.

4. The light-sensitive color photographic material according to claim 2 wherein the negative type silver halide crystals contained in at least one of said at least two light-sensitive emulsion sublayers consists essen-

tially of octahedrons, tetradecahedrons, or a combination of octahedrons and tetradecahedrons.

5. The light-sensitive color photographic material according to claim 4 wherein the negative type silver halide crystals contained in all of said light-sensitive emulsion sublayers consist essentially of octahedrons, tetradecahedrons or a combination of octahedrons and tetradecahedrons.

6. The light-sensitive color photographic material according to claim 1 wherein at least one of said emulsion layers comprises at least two light-sensitive emulsion sublayers containing silver halide crystals having different average crystal sizes.

7. The light-sensitive color photographic material according to claim 2 wherein at least one of said emulsion layers comprises at least two light-sensitive emulsion sublayers containing silver halide crystals having different average crystal sizes.

8. The light-sensitive color photographic material according to claim 3 wherein at least one of said emulsion layers comprises at least two light-sensitive emulsion sublayers containing silver halide crystals having different average crystal sizes.

9. The light-sensitive color photographic material according to claim 5 wherein at least one of said emulsion layers comprises at least two light-sensitive emulsion sublayers containing silver halide crystals having different average crystal sizes.

* * * * *

United States Patent [19]

Ikematsu et al.

[11] 4,446,290

[45] May 1,

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[54] PROCESS FOR PRODUCING CONJUGATED DIENE POLYMER

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[52] U.S. Cl. 526/174

[58] Field of Search 526/174

[56] References Cited

U.S. PATENT DOCUMENTS

3,629,213	12/1971	Onishi et al.	526/181
3,846,385	11/1974	Hargis et al.	526/174
4,080,492	3/1978	de Zarauz	526/177
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FOREIGN PATENT DOCUMENTS

37616	10/1981	European Pat. Off.	526/174

Primary Examiner—Joseph L. Schofer

Assistant Examiner—Peter F. Kulkosky

Attorney, Agent, or Firm—Birch, Stewart, Kolasch & Birch

[57] ABSTRACT

Conjugated diene polymers and copolymers having a high ratio of a trans-1,4 structure content to a cis-1,4 structure content in the diene moiety can be advantageously solution polymerized by using a novel catalyst complex consisting essentially of the following components (a) and (b) or (a), (b), and (c): (a) an organosodium compound, metallic sodium or a sodium amide compound, or a mixture of at least one thereof with an organic compound of sodium other than the sodium amide compound; (b) an organic or organometallic compound of barium, strontium, or calcium; (c) an organometallic compound of an electron deficient metal selected from lithium, beryllium, magnesium, zinc, cadmium, boron, aluminum, gallium, or indium.

12 Claims, No Drawings

PROCESS FOR PRODUCING CONJUGATED DIENE POLYMER

The present invention relates to a process for producing conjugated diene polymers and copolymers having a high ratio of a trans-1,4 structure content to a cis-1,4 structure content in the diene moiety by means of a solution polymerization method by using a novel catalyst complex.

Various processes for polymerizing conjugated dienes by using as a polymerization catalyst alkali metals or organometallic compounds of alkali metals have been proposed. On the other hand, only a few processes for polymerizing conjugated dienes by using as a polymerization catalyst alkaline earth metals (i.e. II A metals of the periodic table of elements) or organometallic compounds of alkaline earth metals have been proposed. Of the II A metals, the organometallic compounds of beryllium and magnesium can be relatively readily synthesized. However, the reactivity thereof is inferior to that of the organometallic compounds of alkali metals and, therefore, the polymerization activity thereof in the case of conjugated dienes can only be effective under limited conditions although the polymerization activity is remarkably low. For this reason, the organometallic compounds of beryllium and magnesium can not be practically used in the polymerization of conjugated dienes. Furthermore, the organometallic compounds of barium, strontium, and calcium are extremely difficult to synthesize. Polymerization processes of conjugated dienes in the presence of special organometallic compounds of alkaline earth metals have recently been proposed. However, the polymerization activity is extremely low and, therefore, these polymerization processes cannot now be utilized commercially.

On the other hand, several polymerization processes of conjugated dienes using a combination catalyst of the organic compounds of alkaline earth metals such as barium, strontium, and calcium and other organometallic compounds have been proposed. For instance, U.S. Pat. No. 3,629,213 discloses a method for preparing butadiene polymers using a catalyst consisting of, for example, an organolithium compound and an organic compound of barium. U.S. Pat. No. 3,846,385 discloses a method for preparing butadiene polymers using a catalyst complex of barium di-tert-butoxide and dibutyl magnesium. Furthermore, U.S. Pat. No. 4,080,492 discloses a process for preparing conjugated diene polymers using a catalyst composition of an organo-lithium, -barium or -strontium compound and an organometallic compound of the II B or II A metals. These polymerization processes using catalyst complexes or compositions containing organometallic compounds of alkaline earth metals can provide rubberlike polymers having a high ratio of a trans-1,4 structure content to a cis-1,4 structure content in the diene moiety thereof and having a relatively high molecular weight. These polymers are believed to be useful in the manufacture of various rubber products including automotive tires since they have excellent characteristics including green strength, tensile strength, and abrasion resistance of the vulcanizates thereof.

However, these polymerization processes using the above-mentioned catalyst complexes or compositions involve various disadvantages or problems. For example, in the case where polymers having a molecular weight sufficient to provide the desired properties are to be obtained, the amounts of the catalysts to be used should be decreased, which decrease would result in a remarkable decrease in the polymerization activity. In the case where the desired polymers are to be obtained at a high yield, the molecular weight distribution of the resultant polymers is remarkably broad, resulting in a remarkable decrease in the strength and abrasion resistance of the vulcanizates. In the case where copolymers of conjugated dienes and aromatic vinyl hydrocarbons are to be obtained, the copolymerization characteristics are not sufficient to produce the desired copolymers having the desired strength and heat buildup properties of the vulcanizates. Furthermore, although the polymers having a high trans-1,4 structure content and being obtained by the use of the above-mentioned catalyst complexes or compositions have the excellent physical properties mentioned above, these polymers have disadvantages such as poor processability and undesirable heat build-up of the vulcanizates, which disadvantages are due to the crystallization of the polymers at non-extension conditions, which crystallization is believed to be caused by the presence of long trans-1,4 structure chains.

Accordingly, an object of the present invention is to eliminate the above-mentioned disadvantages or problems of the prior art and to provide a process for preparing conjugated diene polymers or copolymers having a high ratio of trans-1,4 structure content to a cis-1,4 structure content in the diene moiety, a relatively narrow molecular weight distribution, and no crystallization property as determined by a differential thermal analyzer.

Another object of the present invention is to provide a catalyst complex suitable for use in the polymerization and copolymerization of conjugated dienes which has a remarkably excellent polymerization activity compared with that of conventional catalysts and can produce copolymers of conjugated dienes with aromatic vinyl hydrocarbons having an excellent random property.

Other objects and advantages of the present invention will be apparent from the following description.

In accordance with the present invention, there is provided a process for producing a conjugated diene polymer, a copolymer of a conjugated diene with at least one other conjugated diene, or a copolymer of a conjugated diene with an aromatic vinyl hydrocarbon comprising the step of polymerizing said monomer or monomers in the presence of a catalyst complex consisting essentially of the following components (a) and (b or (a), (b), and (c):

(a) an organosodium compound, metallic sodium or a sodium amide compound, or a mixture of at least one thereof with an organic compound of sodium other than the sodium amide compound;

(b) an organic or organometallic compound of barium, strontium, or calcium;

(c) an organometallic compound of an electron deficient metal selected from lithium, beryllium, magnesium, zinc, cadmium, boron, aluminum, gallium, or indium.

The term "an organometallic compound (e.g. an organosodium compound)" used herein means an organic compound containing a metallic atom (e.g. sodium directly bonded to a carbon atom, whereas the term "an organic compound of a metal (e.g. sodium)" used herein means an organic compound containing only a metallic atom (e.g. sodium) bonded to a carbon atom via an atom such as oxygen, sulfur, nitrogen, or the like.

The catalyst complexes used in the present invention have a remarkably excellent polymerization activity as compared to that of conventional catalysts and can produce copolymers having an excellent random structure of conjugated dienes such as butadiene and isoprene and aromatic vinyl hydrocarbons such as styrene. Furthermore, the polymers or copolymers of conjugated dienes obtained by the use of the above-mentioned catalyst complexes have the following advantages:

(i) The conjugated diene polymers or copolymers have a high trans/cis ratio in the micro-1,4-structure, for example, a trans/cis ratio of 2.0 or more in the case of butadiene.

(ii) The conjugated diene polymers or copolymers have no crystallization property as determined by a differential thermal analyzer.

(iii) The conjugated diene polymers or copolymers have a relatively narrow molecular weight distribution, for instance, a ratio of weight-average molecular weight/number-average molecular weight of 1.2 through 3.0.

According to the present invention, the conjugated diene polymers or copolymers having excellent rubber characteristics and being suitable for use as raw materials in the manufacture of automotive tires can be produced in good yield in a relatively short period of time.

The monomers usable in the process of the present invention are selected from the group of (1) conjugated dienes, (2) mixtures of a certain conjugated diene and one or more conjugated dienes, and (3) mixtures of conjugated diene(s) and aromatic vinyl hydrocarbon(s). The conjugated dienes desirably used in the present invention are those having 4 through 12 carbon atoms in a molecule thereof. Examples of such conjugated dienes are 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene, and 2-phenyl-1,3-butadiene. The aromatic vinyl hydrocarbons usable in the process of the present invention are those containing at least one vinyl group bonded to the carbon atom of the aromatic ring. The aromatic vinyl compounds desirably used in the present invention are those having 8 through 20 carbon atoms in a molecule thereof. Examples of such aromatic vinyl hydrocarbons are styrene, divinylbenzene, vinyltoluene, 1-vinylnaphthalene, α-methylstyrene, and methoxystyrene.

The most desirable commercial polymerization processes of the present invention are butadiene homopolymerization, butadiene-isoprene copolymerization, and styrene-butadiene copolymerization.

The sodium compounds usable as the first component (a) of the novel catalyst complexes of the present invention are selected from the group of organosodium compounds, metallic sodium or sodium amide compounds, or mixtures of at least one of said sodium compounds (including metallic sodium) and organic compound(s) of sodium other than the sodium amide compounds.

The organosodium compounds are represented by the following general formula:

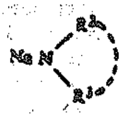
$$R'(Na)_m$$

wherein R' is an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms or an unsaturated hydrocarbon group having at least one allyl hydrogen and desirably having 3 to 30 carbon atoms, and m integer of 1 through 4.

Examples of the desirable R' group are the methyl, ethyl, iso-propyl, n-butyl, sec-butyl, n-amyl, tert-octyl, n-decyl, phenyl, naphthyl, 4-butylphenyl, cyclohexyl, 4-butylcyclohexyl, benzyl, allyl, triphenylmethyl, and fluorenyl groups.

The metallic sodium can be desirably used in the form of a dispersion in, for example, mineral oil, paraffin or wax. However, the metallic sodium can also be used in the form of an alloy such as an amalgam.

The sodium amide compounds are represented by the following general formula:



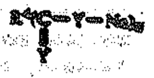
wherein

represents either a cyclized structure or a non-cyclized structure and R^2 and R^3 represent, in combination, a methylene chain having 2 to 10 carbon atoms in the case of a cyclized structure and R^2 and R^3 independently represent an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably h ing 6 to 30 carbon atoms in the case of a non-cycl structure.

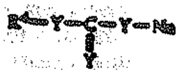
Examples of the desirable amide groups are the dimethylamide, diethylamide, di-iso-propylamide, di-n-butylamide, di-iso-butylamide, dioctylamide, diallylamide, dicyclohexylamide, diphenylamide, dibenzylamide, and N-ethylanilide groups. Examples of cyclized structures are the ethyleneimide, trimethyleneimide, pyrrolidido, piperidido, and hexamethyleneimide groups.

The organic compounds of sodium are selected from the group of compounds having the following general formulae:

$$R^4(Y-Na)_n \qquad (1)$$


(2)

$$R^4(\underset{\substack{\| \\ Y}}{C}-Y-Na)_n \qquad (2)$$


(3)

$$R^4-Y-\underset{\substack{\| \\ Y}}{C}-Y-Na \qquad (3)$$

$$R^4SO_3Na \qquad (4)$$

$$R^4OSO_3Na \qquad (5)$$

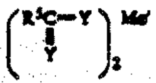
wherein R^4 is an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms, Y is an oxygen or sulfur atom, and n is an integer of 1 through 4.

Examples of such desirable compounds are sodiu salts of the following compounds: ethyl alcohol, n-pr pyl alcohol, iso-propyl alcohol, tert-butyl alcohol, n-hexyl alcohol, cyclohexyl alcohol, allyl alcohol, cyclopentenyl alcohol, benzyl alcohol, ethanethiol, n-butanethiol, phenol, catechol, 1-naphthol, 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, nonylphenol, 4-phenylphenol, thiophenol, 2-naphthalenethiol, capric acid, lauryl acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, naphthoic acid, benzoic acid, hexane thio acid, decane thio acid, tridecane thio acid, thiobenzoic acid, acid tert-butyl carbonate, acid hexyl carbonate, acid phenyl carbonate, thio acid tert-butyl carbonate butane sulfonic acid, hexane sulfonic acid, decane sulfonic acid, tridecane sulfonic acid, dodecylbenzene sulfonic acid, tetradecylbenzene sulfonic acid, octadecylbenzene sulfonic acid, dibutylnaphthalene sulfonic acid, di-iso-propylnaphthalene sulfonic acid, n-hexylnaphthalene sulfonic acid, dibutylphenyl sulfonic acid, sulfate ester of lauryl alcohol, sulfate ester of oleyl alcohol, and sulfate ester of stearyl alcohol.

The organic compounds or organometallic compounds of barium, strontium, or calcium usable as the second component (b) of the novel catalyst complexes of the present invention are selected from the group of compounds having the following general formulae:

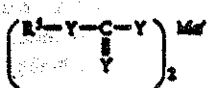
$$(R^5Y)_2Me' \qquad (1)$$

(2)



$$\left(R^5\underset{\underset{Y}{\|}}{C}-Y\right)_2 Me'$$

(3)

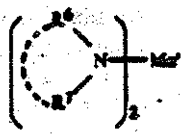


$$\left(R^5-Y-\underset{\underset{Y}{\|}}{C}-Y\right)_2 Me'$$

$$(R^5SO_3)_2Me' \qquad (4)$$

$$(R^5OSO_3)_2Me' \qquad (5)$$

(6)



$$(R^5C{\equiv}C)_2Me' \qquad (7)$$

$$(R^5)_2Me' \qquad (8)$$

$$R^5Me'X \qquad (9)$$

wherein R^5 is an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms,

represents either a cyclized structure or a non-cyclized structure, and R^6 and R^7 represent, in combination, a methylene chain having 2 to 10 carbon atoms in the case of a cyclized structure and R^6 and R^7 independently represent an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms in the case of a non-cyclized structure provided that one of R^6 and R^7 can be hydrogen, Y is an oxygen or sulfur atom, Me' is a barium, strontium, or calcium atom, and X is a halogen atom such as fluorine, chlorine, bromine, or iodine.

Examples of the desirable organic compounds of the II A metals are barium, strontium, or calcium salts of the following compounds: ethyl alcohol, n-propyl alcohol, iso-propyl alcohol, tert-butyl alcohol, n-hexyl alcohol, cyclohexyl alcohol, allyl alcohol, cyclopentenyl alcohol, benzyl alcohol, ethanethiol, n-butanethiol, phenol, catechol, 1-naphthol, 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, nonylphenol, 4-phenylphenol, thiophenol, 2-naphthalenethiol, capric acid, lauryl acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, naphthoic acid, benzoic acid, hexane thio acid, decane thio acid, tridecane thio acid, thiobenzoic acid, acid tert-butyl carbonate, acid hexyl carbonate, acid phenyl carbonate, thio acid tert-butyl carbonate butane sulfonic acid, hexane sulfonic acid, decane sulfonic acid, tridecane sulfonic acid, dodecylbenzene sulfonic acid, tetradecylbenzene sulfonic acid, octadecylbenzene sulfonic acid, dibutylnaphthalene sulfonic acid, di-iso-propylnaphthalene sulfonic acid, n-hexylnaphthalene sulfonic acid, dibutylphenyl sulfonic acid, sulfate ester of lauryl alcohol, sulfate ester of oleyl alcohol, sulfate ester of stearyl alcohol, dimethylamine, diethylamine, di-iso-propylamine, di-n-butylamine, mono-n-butylamine, di-iso-butylamine, mono-iso-butylamine, dioctylamine, diallylamine, dicyclohexylamine, phenylamine, diphenylamine, benzylamine, dibenzylamine, and N-ethylaniline.

Examples of the desirable organometallic compounds of the II A metals are dimethyl calcium, n-butyl calcium iodide, ethyl strontium idodide, dimethyl strontium, ethyl barium iodide, dimethyl barium, phenyl barium iodide, dicyclopentadienyl barium, bistriphenylmethyl barium, dipropargyl barium, and barium di-2-ethylacetylide.

The organometallic compounds of electron deficient metals usable as the third component (c) of the novel catalyst complexes of the present invention are lithium (Li) in the Group I A metals of the Mendeleev Periodic Table of Elements, beryllium (Be) and magnesium (Mg) in the Group II A metals, zinc (Zn) and cadmium (Cd) in the Group II B metals, and boron (B), aluminum (Al), gallium (Ga), and indium (In) in the Group III A metals and mixtures thereof.

These compounds are represented by the following general formula:

$$R^9{}_{p-q}Me^2X_q$$

wherein R^9 is an aliphatic group, desirably having 1 t 30 carbon atoms, an alicyclic group, desirably having to 30 carbon atoms, or an aromatic group, desirabl having 6 to 30 carbon atoms, X is a halogen atom suc as fluorine, chlorine, bromine, or iodine, a hydroge atom, or an alkoxy group, Me^2 is Li, Be, Mg, Zn, Cd, B Al, Ga, or In, p is the valence of Me^2, and q $0 \leq q \leq p-1$.

Examples of such desirable compounds are ethy lithium, n-propyl lithium, iso-propyl lithium, n-buty lithium, tert-butyl lithium, n-amyl lithium, n-hexyl lithium, allyl lithium, n-propenyl lithium, benzyl lithium phenyl lithium, polybutadienyl lithium, polyisopreny lithium, polystyryl lithium, diethyl beryllium, di-n-pro pyl beryllium, di-n-butyl beryllium, ethyl berylliun chloride, diethyl magnesium, di-n-propyl magnesium, di-iso-propyl magnesium, di-tert-butyl magnesium, ethyl-n-butyl magnesium, di-n-hexyl magnesium, diphenyl magnesium, ethyl magnesium chloride, ethyl magnesium hydride, ethyl magnesium-iso-propoxide, iso-propyl magnesium chloride, n-butyl magnesium chloride, n-butyl magnesium bromide, phenyl magnesium chloride, diethyl zinc, ethyl zinc chloride, di-n-propyl zinc, di-iso-propyl zinc, diethyl cadmium, di-iso-propyl cadmium, ethyl cadmium chloride, trimethyl boron, triethyl boron, triethyl aluminum, tri-iso-butyl aluminum, diethyl aluminum chloride, diethyl aluminum hydride, diethyl aluminum propoxide, di-iso-butyl aluminum chloride, di-iso-butyl aluminum hydride, trihexyl aluminum, triphenyl aluminum, triethyl gallium, and triethyl indium.

The amounts of the components (a) and (b) or the components (a), (b), and (c) can vary greatly depending upon, for example, the purposes of polymerization and upon the polymerization methods and conditions. However, generally speaking, the use of the components in the following range is recommended:

Component (a): 0.01 through 50 m mol per 100 g of the total monomer(s)

Component (b): 0.01 through 10 times based on the mol of the component (a)

Component (c): 0 through 5 times based on the mol of the component (a)

In the case where the amount of the component (a) is too small, the polymerization activity tends to decrease. Contrary to this, in the case where the amount of the component (a) is too large, the molecular weight of the resultant polymer tends to decrease so that the resultant polymer is not suitable for use in general rubber industrial fields (e.g. the manufacture of automotive tires). In the case where the amount of the component (b) is too small, the molecular weight of the resultant polymer tends to decrease and the ratio of a trans-1,4/cis-1,4 structure content in the diene moiety also tends to decrease. Contrary to this, in the case where the amount of the component (b) is too large, the polymerization activity tends to decrease. Furthermore, in the case where the amount of the component (c) is too large, not only the polymerization activity tends to decrease but also the copolymerizability of conjugated dienes and aromatic vinyl hydrocarbons tends to decrease.

Especially in the case of polymers (or copolymers) having a relatively high molecular weight and being suitable for use as a starting material in the manufacture of automotive tires, the components can be desirably used in the following range:

Component (a): 0.1 through 1 m mol per 100 g of the total monomer(s)

Component (b): 0.1 through 1 times based on the mol of the component (a)

Component (c): 0 through 2 times based on the mol of the component (a)

The polymerization processes of the present invention can be desirably carried out in a solution polymerization manner using a hydrocarbon solvent, although a bulk polymerization method can be used. Examples of such hydrocarbon solvents are butane, pentane, hexane, heptane, octane, cyclohexane, cyclooctane, benzene, toluene, xylene, ethylbenzene, and mixtures thereof. Minor amounts of polar compounds can be added to the hydrocarbon solvent to improve the solubility and the catalytic activity of the catalyst complex. Examples of such polar compounds are ether compounds such as tetrahydrofuran, diethyl ether, and ethyleneglycol diethyl ether and amine compounds such as triethyl amin and tetramethyl ethylenediamine. The amount of hydrocarbon solvents used in the polymerization processes of the present invention can vary greatly depending upon the types and molecular weights of the polymers (or copolymers) to be produced. Generally speaking, the desirable amount of solvents to be used in 300 through 1000 parts by weight based on 100 parts by weight of the total monomer(s).

The polymerization process of the present invention can be generally carried out at a temperature of −40° C. through 160° C. The desirable polymerization temperature is 30° C. through 120° C., especially when conjugated diene polymers or copolymers having a relatively high molecular weight and being suitable for use as starting materials in the manufacture of automotive tires are to be produced. The polymerization processes of the present invention should be carried out under an inert gas atmosphere such as nitrogen and argon. The contamination of the polymerization system with compounds capable of reacting with the organometallic compounds, such as water, carbon dioxide, oxygen, and halogen compounds, should be avoided. The pressure of the polymerization system may be sufficient to maintain the polymerization mixture in a liquid state. Usually, about 1 through 5 atmosphere are used.

The conjugated diene polymers or copolymers obtained from the process of the present invention have extremely excellent characteristics, for example, processabilities such as green strength and tackiness and vulcanizate properties such as tensile strength, abrasion resistance and heat build-up. The conjugated diene polymers or copolymers can be compounded and vulcanized in any conventional manner. These conjugated diene polymers or copolymers can, therefore, be used alone or after blending with natural rubber or other synthetic rubbers in the application fields of automotive tires including tire treads, carcasses and side walls, as well as extruded articles, automotive window frames and various industrial articles. Furthermore, the conjugated diene polymers or copolymers can be grafted onto or blended with various plastics to improve the physical properties such as the impact strength.

The present invention will now be further illustrated by, but is by no means limited to, the Examples set forth hereinbelow.

EXAMPLE 1

One hundred grams of 1,3-butadiene and 400 g of a cyclohexane solvent were charged into an approximately one liter pressure-resistant glass bottle filled with dry nitrogen. A catalyst complex of 0.5 m mol of n-amyl sodium and 0.25 m mol of barium di-t-butoxide was then added to the bottle and the mixture was polymerized at a temperature of 50° C. for 7 hours.

The yield, molecular weight, molecular weight distribution and micro structure of the resultant polymer are shown in Table 1 below.

TABLE 1

	Molecular weight determined by GPC*1		Microstructure*2			
Yield (%)	$\overline{M}w$ (× 10⁴)	$\overline{M}w/\overline{M}n$	1,2-structure (%)	trans-1,4 structure (%)	cis-1,4 structure (%)	trans/cis ratio
100	22.6	1.29	53	36	11	3.3

*1GPC = Gel Permeation Chromatography

*2Microstructure was determined according to a D. Morero method by using an infrared absorption spectrum.

As is clear from the results shown in Table 1, the butadiene polymer having a high trans-1,4 structure content and a relatively narrow molecular weight distribution could be obtained by using a catalyst complex of the organosodium compound and the barium compound.

EXAMPLE 2

Example 1 was repeated, except that isoprene was used as a monomer in lieu of butadiene. The results are shown in Table 2 below.

TABLE 2

	Molecular weight by GPC		Microstructure*1	
Yield (%)	$\overline{M}w$ (× 10⁴)	$\overline{M}w/\overline{M}n$	3,4-structure (%)	1,4-structure (%)
100	22.5	1.32	48	52

*1Microstructure was determined by using an infrared absorption spectrum.

EXAMPLES 3 TO 7 AND COMPARATIVE EXAMPLES 1 TO 6

Twenty five grams of styrene, 75 g of 1,3-butadiene and 400 g of a cyclohexane solvent were added to an approximately one liter pressure-resistant glass bottle filled with dry nitrogen. A catalyst complex each listed in Table 3 below was then added to the bottle and the mixture was polymerized at a temperature of 50° C. for 7 hours. A portion of the polymer solution was withdrawn from the bottle at the conversion of less than 20% during the course of the polymerization and the bound styrene of the initial polymer was determined.

As comparative examples, the above-mentioned polymerization experiments were repeated, except that conventional catalysts listed in Table 3 below were used in lieu of the catalyst complexes.

As is clear from Table 3 below, the polymers of Examples 3 to 7 obtained by using the catalyst complexes consisting essentially of the organosodium compounds and the organic compounds of the II A metals have a high trans/cis ratio in the 1,4-structure of the butadiene moiety, as compared with those of Comparative Examples 1 to 4. The polymers having a high trans/cis ratio, for example, a trans/cis ratio of 1.8 or more can also be obtained by using conventional catalysts as shown in Comparative Examples 5 and 6. These catalysts, however, result in a low polymerization conversion and a poor styrene-butadiene copolymerization reactivity ratio as shown in the initial bound styrene contents in Table 3. Furthermore, these polymers have a disadvantage in that the molecular weight distribution thereof is broad.

As is clear from a comparison of the Examples with the Comparative Examples in Table 3 below, the polymerization processes of conjugated dienes using the novel catalyst complexes according to the present invention have the following advantages:

(a) The polymerization activity of the catalysts is high;

(b) Copolymers having an excellent random distribution of conjugated dienes (e.g. butadiene) and aromatic vinyl hydrocarbons (e.g. styrene) can be obtained;

(c) Copolymers having a high trans/cis ratio in the 1,4-structure of the butadiene moiety can be obtained; and

(d) Copolymers having a relatively narrow molecular weight distribution can be obtained.

It is also clear from the results shown in Table 3 below that the 1,2-structure content and the ratio of the trans-1,4 structure/cis-1,4 structure of the copolymers can be controlled by changing the combination and composition of the catalyst complexes.

TABLE 3

	Catalyst						Molecular weight by GPC		Microstructure in butadiene moiety			
	Catalyst component*4 (1)	Catalyst component*5 (2)	Initial bound styrene*1 (%)	Yield (%)	Bound styrene (%)	Block styrene*3 (%)	$\overline{M}w$ (× 10⁴)	$\overline{M}w/\overline{M}n$	1,2-structure (%)	Trans-1,4 structure (%)	Cis-1,4 structure (%)	Trans/cis ratio
Example												
3	$nC_5H_{11}Na$ 0.5	$Ba-[OC(CH_3)_3]_2$ 0.5	26	96	25	0	24.9	1.31	44	45	11	4.1
4	$nC_5H_{11}Na$ 0.5	$Ba-[OC(CH_3)_3]_2$ 0.25	26	100	25	0	22.8	1.33	53	37	10	3.7
5	$nC_5H_{11}Na$ 0.5	$Ba-[OC(CH_3)_3]_2$ 0.125	27	100	25	0	19.6	1.34	58	33	9	3.7
6	$nC_5H_{11}Na$ 0.5	$Sr-[OC(CH_3)_3]_2$ 0.25	29	100	25	0	18.2	1.40	59	30	11	2.7
7	$nC_5H_{11}Na$ 0.5	$Ca-[OCH(CH_3)_2]_2$ 0.25	29	98	25	0	11.8	1.76	64	25	11	2.3
Comparative Example												
1	$nC_5H_{11}Na$ 0.5	None	32	48	30	0	1.2	1.96	68	20	12	1.7
2	$nC_5H_{11}Na$ 0.5	$LiOC(CH_3)_3$ 0.5	30	100	25	0	34.3	1.22	60	25	15	1.7
3	nC_4H_9Li	None	3	86	8	17.0	17.5	1.05	10	52	38	1.4

TABLE 3-continued

	Catalyst									Microstructure in butadiene moiety			
	Catalyst component*4 (1)	Catalyst component*4 (2)	Initial bound styrene*1 (%)	Yield (%)	Bound styrene (%)	Block styrene*2 (%)	Molecular weight by GPC $\overline{Mw}$ (× 10^4)	$\overline{Mw}/\overline{Mn}$	1,2-structure (%)	Trans-1,4 structure (%)	Cis-1,4 structure (%)	Trans/cis ratio
4	0.5 nC$_4$H$_9$Li	Tetrahydrofuran 5.0	13	100	25	0	22.1	1.03	34	40	26	1.5
5	0.5 nC$_4$H$_9$Li	Ba—(OC(CH$_3$)$_3$)$_2$ 0.25	13	89	22	0	11.6	2.21	12	63	25	2.5
6	0.5 (C$_4$H$_9$)$_2$Mg	Ba—(OC(CH$_3$)$_3$)$_2$ 0.25	13	62	21	0	6.7	1.91	9	79	22	3.6

*1 Determined by ultraviolet absorption spectrum
*2 Determined according to Kolthoff method (I. M. Kolthoff, J. Polymer Sci., 1, 429–433 (1946))
*3 Determined by infrared absorption spectrum according to a Hampton method
*4 M mol per 100 g of the total monomers

EXAMPLES 8 TO 22

The copolymerization runs were repeated in the same manner as described in Examples 3 to 7, except that the components of the catalyst complexes of the present invention were changed. The amounts of the catalyst components used in these runs, based on 100 g of the total monomers, were as follows.

Component (a): 0.5 m mol
Component (b): 0.25 m mol
Component (c): 0.25 m mol

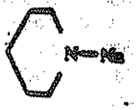
The results are shown in Table 4 below.

Examples 8 to 10 used sodium amide, metallic sodium and a mixture of the organosodium compound and the organic compound of sodium as the catalyst component (a). As is clear from the results shown in Table 4 below, these catalyst components (a) result in the advantages similar to those obtained by using the organosodium compounds.

Examples 11 to 13 used the barium salts of various organic compounds as the catalyst component (b). As is clear from the results shown in Table 4, these various barium salts are effective as the catalyst component (b) of the catalyst complexes of the present invention.

Examples 14 to 22 use the organometallic compounds of various electron deficient metals as the component (c). As is clear from the results in Table 4, the ratio of trans-1,4/cis-1,4 structures can be further increased.

TABLE 4

	Catalyst complex									Microstructure in butadiene moiety	
Example	Catalyst component (a)	Catalyst component (b)	Catalyst component (c)	Initial bound styrene (%)	Yield (%)	Bound styrene (%)	Block styrene (%)	Molecular weight by GPC $\overline{Mw}$ (× 10^4)	$\overline{Mw}/\overline{Mn}$	1,2-structure (%)	Tra… cis ratio
8		Ba—(OC(CH$_3$)$_3$)$_2$	None	26	89	25	0	16.3	1.46	54	4.1
9	Sodium dispersion	″	″	26	86	26	0	41.6	1.44	48	4.5
10	*1	″	″	26	99	25	0	35.7	1.32	51	3.9
11	nC$_5$H$_{11}$Na		″	26	100	25	0	22.9	1.31	52	3.8
12	″		″	26	98	25	0	25.3	1.49	51	3.9
13	″	(C$_{17}$H$_{35}$COO)$_2$ Ba	″	26	97	25	0	25.6	1.41	51	3.9
14	″	Ba—(OC(CH$_3$)$_3$)$_2$	LinC$_4$H$_9$	26	100	25	0	12.7	1.29	32	4.3
15	″	″	Ba(C$_2$H$_5$)$_2$	26	99	25	0	23.1	1.35	25	4.8
16	″	″	Mg(nC$_4$H$_9$)$_2$	25	100	25	0	11.9	1.31	26	4.7
17	″	″	Zn(C$_2$H$_5$)$_2$	25	100	25	0	23.8	1.39	46	4.7
18	″	″	Cd(C$_2$H$_5$)$_2$	26	100	25	0	22.4	1.30	47	4.6
19	″	″	B(C$_2$H$_5$)$_3$	25	95	24	0	26.7	1.29	49	5.1
20	″	″	Al(C$_2$H$_5$)$_3$	24	99	25	0	25.5	1.24	41	5.6
21	″	″	Ga(C$_2$H$_5$)$_3$	25	100	25	0	22.3	1.39	45	4.6
22	″	″	In(C$_2$H$_5$)$_3$	25	100	25	0	22.6	1.31	45	4.6

*1 A mixture of 0.25 m mol of n-C$_5$H$_{11}$Na and 0.25 m mol of (CH$_3$)$_3$CONa

EXAMPLE 23

The copolymerization run of Example 1 was repeated, except that 25 g of styrene and 75 g of isopre… were used as monomers. The results are shown in Tab… 5 below.

TABLE 5

Yield (%)	Styrene content (%)	Molecular weight $\bar{M}w$ (× 10^4)	Molecular weight $\bar{M}w/\bar{M}n$	Microstructure 1,4-structure (%)	Microstructure 1,4-structure (%)
99	25	19.8	1.41	46	54

EXAMPLE 24

The copolymerization run of Example 1 was repeated, except that a mixed solvent of 400 g of cyclohexane and 1.0 m mol of tetramethyl ethylenediamine was used. The results are shown in Table 6 below.

TABLE 6

Yield (%)	Molecular weight by GPC $\bar{M}w$ (× 10^4)	Molecular weight by GPC $\bar{M}w/\bar{M}n$	Microstructure in butadiene moiety 1,2 structure (%)	Microstructure in butadiene moiety Trans-1,4 structure (%)	Microstructure in butadiene moiety Cis-1,4 structure (%)	Microstructure in butadiene moiety Trans cis ratio
100	21.1	1.21	80	15	5	3.0

EXAMPLE 25 AND COMPARATIVE EXAMPLE 7

The monomers and the catalyst complexes having the compositions listed in Table 7 below were charged, together with 4 kg of a cyclohexane solvent, into an approximately 10 liter autoclave filled with dry nitrogen gas and polymerized at a temperature of 65° C. for 3 hours. After completing the polymerization, a small amount of methanol was added to the polymerization mixture to deactivate the living polymer. Thereafter, 0.3 parts by weight of BHT (i.e. 3,5-di-tert-butyl-3-hydroxytoluene) based on 100 parts by weight of the copolymer was added as a stabilizer and the cyclohexane was vaporized and removed from the polymer solution. Thus, polymers A to E of Example 25 and polymers F to K of Comparative Example 7 were obtained. The Mooney viscosity, molecular weight distribution, styrene content, microstructure in the butadiene moiety and melting point of the resultant polymers are also shown in Table 7 below. Polymers F and G of Comparative Example 7 had a high 1,2-structure content and a low trans/cis ratio in the 1,4-structure. Polymers H through K were those having a high trans/cis ratio in the 1,4-structure of the butadiene moiety, prepared from conventional processes.

TABLE 7

	Example 25					Comparative Example 7					
	A	B	C	D	E	F	G	H	I	J	K
Butadiene (kg)	1	0.82	0.75	0.75	0.75	1	0.75	1	0.75	1	0.75
Styrene (kg)	0	0.18	0.25	0.25	0.25	0	0.25	0	0.25	0	0.25
Catalyst and additive (m mol)	$nC_5H_{11}Na$ ←4 m mol→ $Ba\text{-}(OC(CH_3)_3)_2$ 2 m mol			*1	*2	nC_4H_9Li 4 m mol EDME		nC_4H_9Li 3 m mol $Ba\text{-}(OC(CH_3)_3)_2$ 1.5 m mol		$(C_4H_9)_2Mg$ 3 m mol $Ba\text{-}(OC(CH_3)_3)_2$ 1.5 m mol	
Conversion (%)	100	99	98	96	92	100	100	92	77	79	59
Mooney viscosity (ML_{1+4} 100° C.)	47	52	51	46	48	55	46	42	43	47	41
Molecular weight distribution (Mw/Mn)	1.32	1.36	1.38	1.41	1.46	1.08	1.10	2.36	2.41	1.88	1.97
Bound styrene (%)	0	18	25	25	25	0	25	0	22	0	20
Block styrene (%)	0	0	0	0	0	0	0	0	0	0	0
1,2-structure (%)	39	41	42	35	29	38	40	12	13	9	9
Trans/cis ratio	3.1	3.4	3.5	3.7	3.9	1.5	1.5	2.5	2.4	3.6	3.5
Melting point (°C.)*3	None	None	None	None	None	None	None	None	None	23	None

*1 $nC_5H_{11}Na$ 3 m mol + $Ba\text{-}(OC(CH_3)_3)_2$ 2 m mol + $Mg(nC_4H_9)_2$ 0.5 m mol
*2 $nC_5H_{11}Na$ 2 m mol + $Ba\text{-}(OC(CH_3)_3)_2$ 2 m mol + $Mg(nC_4H_9)_2$ 1 m mol
*3 Determined by a differential thermal analyzer

Polymers A to E of Example 25 and polymers F to K of comparative Example 7 as well as a commercially available solution polymerization type butadiene polymer (i.e. Diene NF 50R available from Asahi Kasei Kogyo Kabushiki Kaisha in Japan), a solution polymerization type styrene-butadiene copolymer (i.e. Tufdene 2000R available from Asahi Kasei Kogyo Kabushiki Kaisha in Japan) and an emulsion polymerization type styrene-butadiene copolymer (i.e. SBR-1502 available from Nihon Gosei Gomu Kabushiki Kaisha) were independently mixed in the compositions listed in Table 8 below by using a B-type Banbury mixer to produce compounds.

TABLE 8

Compounding Formulation	
Component	Parts by Weight
Polymer	100
Aromatic process oil*1	20
HAF carbon	60
Zinc oxide	4
Stearic acid	3
Antioxidant B*2	1.3
Sulfur	2
Vulcanizing accelerator CZ*3	1.5

*1 Specific density = 0.951, VGC = 0.961
*2 Reaction product of diphenylamine and acetone
*3 N-cyclohexyl benzothiazole sulfenamide

The processability of the compounds thus obtained and the properties of the vulcanizates thereof were evaluated. Vulcanization was carried out by heating the compounds at a temperature of 141° C. for 40 minutes. The results are shown in Table 9 below.

The roll operation ability of the compounds of polymers A to E of Example 25 was clearly superior to that of the compounds of polymers F to K of Comparative Example 7, and was substantially comparable to that of the commercially available products.

The compound of polymer J of Comparative Example 7 having a high trans/cis ratio in the 1,4-structure of the butadiene moiety exhibited an extremely high green strength. However, unvulcanized polymer J showed a crystallization property in the DSC analysis and the tackiness of the compound was extremely low due to the crystallization property of polymer J. Contrary to this, polymers A to E of Example 25 according to the present invention have no crystallization property in the DSC analysis, in spite of their high trans/cis ratios in the 1,4-structure of the butadiene moiety. Furthermore, the balance of the processability represented by the roll operation ability, green strength, elongation and tackiness of polymers A to E of Example 25 was superior to that of polymers F to K of Comparative Example 7 and was comparable to that of commercially available emulsion polymerization type SBR (i.e. SBR 1502).

The physical properties of the vulcanizates of, for example, the styrene-butadiene copolymers of Example 25 according to the present invention (i.e. polymers B to E) are advantageous in respect to the following points, as compared with the styrene-butadiene copolymers of Comparative Example 7 (i.e. polymers G, I, K), the commercially available solution polymerization type styrene-butadiene rubber (i.e. Tufdene 2000R) and the commercially available emulsion polymerization type styrene-butadiene rubber (i.e. SBR-1502).

(a) The tensile strengths of copolymers B to E according to the present invention are comparable to the commercially available emulsion type SBR and are superior to the commercially available solution type SBR and copolymers G, I and K of Comparative Example 7.

(b) Generally speaking, an anti-wet skid property is contrary to an abrasion resistance property. That is, a polymer having a good anti-wet skid property generally has a poor abrasion resistance. However, copolymers B to E according to the present invention have an anti-wet skid property comparable to or greater than that of the commercially available emulsion polymerization type SBR (i.e. SBR 1502) and superior to that of the commercially available solution polymerization type SBR (i.e. Tufdene 2000R). On the other hand, copolymers B to E according to the present invention have an abrasion resistance property superior to that of SBR 1502 and near that of Tufdene 2000R. Contrary to this, copolymers G, I and K do not have a good balance of both properties, although the copolymers having either a good abrasion resistance property or a good anti-wet skid property are present.

(c) Copolymers B to E according to the present invention have a low heat build-up property superior to those of all the comparative copolymers, that is, comparative copolymers G, I and J, Tufdene 2000R and SBR 1502.

Furthermore, as is clear from the comparison of butadiene polymers, the polymer according to the present invention (i.e. polymer A) also has the above-mentioned good properties as compared with the comparative butadiene polymers (i.e. polymers F, H and J and the commercially available Diene NF50R).

As is clear from the above discussion, the polymers (or copolymers) obtained from the polymerization processes using the catalyst complexes have a good balance of properties with respect to the processability of the polymers and the strength, heat build-up property, anti-wet skid property and abrasion resistance property of the vulcanizates thereof.

TABLE 9

	Example 25				
	A	B	C	D	E
Compound mooney viscosity*6 (ML1+4 100° C.)	65	68	67	64	65
Rolling ability	Good	Good	Good	Good	Good
<u>Green characteristics</u>					
Green strength (kg/cm²)	2.7	2.3	2.5	2.9	3.1
Elongation*4 (%)	450	450	500	500	550
Tackiness*3 (kg/cm²)	0.33	0.36	0.49	0.41	0.41
<u>Vulcanizate properties</u>					
Hardness*4 (JIS)	63	63	64	63	63
100% modulus*4 (kg/cm²)	74	87	94	91	91
Tensile strength*4 (kg/cm²)	208	228	243	244	252
Elongation*4 (%)	640	670	690	660	680
Anti-wet skid*5 (index)	88	100	106	102	100
Impact resilience*4 (%)	54	49	39	41	43
Abrasion resistance*6 (index)	163	112	101	109	116
Heat build-up*7 ΔT(°C.)	32	32	33	31	31

	Comparative Example 7						Diene	Tufdene	SBR
	F	G	H	I	J	K	NF50R*8	2000R*8	1502
Compound mooney viscosity*6 (ML1+4 100° C.)	71	68	56	58	60	55	64	61	64
Rolling ability	Poor	Poor	Fair	Fair	Poor	Fair	Good	Good	Good
<u>Green characteristics</u>									
Green strength (kg/cm²)	2.6	2.3	1.8	1.5	20.3	2.8	2.5	2.2	1.7
Elongation*3 (%)	120	170	400	500	250	550	250	120	450
Tackiness*3 (kg/cm²)	0.13	0.16	0.33	0.37	0.03	0.31	0.18	0.26	0.37
<u>Vulcanizate properties</u>									
Hardness*4 (JIS)	63	63	62	62	60	60	62	64	64
100% modulus*4 (kg/cm²)	78	96	71	84	60	65	74	82	95
Tensile strength*4 (kg/cm²)	170	198	174	193	162	184	166	226	239
Elongation*4 (%)	560	560	620	610	620	640	580	670	650
Anti-wet skid*5 (index)	87	108	73	91	74	88	76	94	100
Impact resilience*4 (%)	56	39	53	46	53	47	54	46	44
Abrasion resistance*6 (index)	132	76	165	117	166	117	183	120	100

TABLE 9-continued

Heat build-up*7 ΔT(°C.)	33	35	41	40	44	43	40	38	39

*1 JIS-K6300
*2 JIS #1 dumbbell, stress rate 500 mm/min
*3 Monsanto tackmeter
*4 JIS-K6301
*5 Gravitational friction coefficient between the vulcanizates and wetted concrete road surface was determined using a slide rheometer developed by British Road Institute.
*6 Pico abrasion tester, ASTM D-2228
*7 Goodrich flexometer, ASTM D-623-58(A)
*8 Available from Asahi Kasei Kogyo Kabushiki Kaisha

EXAMPLES 26 TO 57

The copolymerization runs were repeated in the same manner as described in Examples 3 to 7, except that the components of the catalyst complexes were changed. The structures and amounts of the catalyst components used and the results are shown in Table 10 below.

Examples 26 to 36 use the mixtures of an organosodium compound, metallic sodium or a sodium amide compound and organic compounds of sodium as the component (a) of the present catalyst complex. As is clear from the results of Examples 26 to 36, various sodium salts of organic compounds are effective as the organic compound of sodium of the catalyst component (a).

Examples 37 to 48 use the organic compounds or the organometallic compounds of barium as the catalyst component (b). Barium is selected as a typical examp of the metals of the component (a) (i.e. barium, strc tium and calcium). It is clear from the results of Exa ples 37 to 48 that these compounds are effective as t component (b) of the present catalyst complexes.

Examples 49 to 57 use the organometallic compoun of magnesium or aluminum, which is selected as a ty cal example of the electron deficient metals of the co ponent (a). It is also clear from the results of Exampl 49 to 57 that various organometallic compounds havu the general formula

$$R^9_{p-q}Me^2X_q$$

wherein R^9, Me^2, p and q are the same as defined abo are effective as the component (c) of the present ca lyst complexes.

TABLE 10

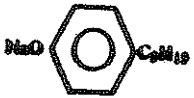
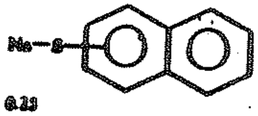
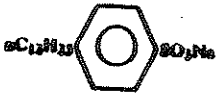
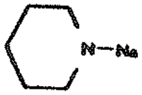
Example	Catalyst system Component*4 (1)	Component*4 (1')	Component*4 (2)	Initial bound styrene*1 (%)	Yield (%)	Bound styrene (%)	Block styrene*2 (%)	Molecular weight by GPC $\overline{Mn}$ (× 10⁴)	$\overline{Mw}/\overline{Mn}$	Microstructure in butadiene moiety*3 1,2-structure (%)	Trans-1,4 structure (%)	Cis-1,4 structure (%)	Trans/cis ratio
26	$nC_5H_{11}Na$ 0.5	$NaS—n\text{-}C_4H_9$ 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	27	100	23	0	19.3	1.48	54	37	9	4.1
27	$nC_5H_{11}Na$ 0.5	 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	27	100	23	0	18.7	1.33	49	40	11	3.6
28	$nC_5H_{11}Na$ 0.5	 0.25	$Ba \dagger (OC(CH_3)_3)_2$ 0.25	27	99	23	0	18.8	1.36	53	37	10	3.7
29	$nC_5H_{11}Na$ 0.5	$NaOCO—n\text{-}C_{17}H_{35}$ 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	27	97	23	0	19.5	1.42	53	37	10	3.7
30	$nC_5H_{11}Na$ 0.5	$NaSCS—n\text{-}C_{12}H_{25}$ 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	27	96	23	0	20.2	1.41	55	36	9	4.0
31	$nC_5H_{11}Na$ 0.5	$NaOCOCOO—n\text{-}C_8H_{17}$ 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	28	96	23	0	20.4	1.44	56	35	9	3.9
32	$nC_5H_{11}Na$ 0.5	$NaSCSCS—n\text{-}C_4H_9$ 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	28	95	24	0	20.9	1.46	55	36	9	4.0
33	$nC_5H_{11}Na$ 0.5	$nC_{18}H_{37}OSO_3Na$ 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	28	98	23	0	19.0	1.39	53	38	9	4.2
34	$nC_5H_{11}Na$ 0.5	 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	27	98	23	0	19.3	1.37	53	38	9	4.2
35	Sodium dispersion 0.5	$NaOC(CH_3)_3$ 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	27	89	24	0	27.1	1.46	52	38	10	3.8
36	 0.5	$NaOC(CH_3)_3$ 0.25	$Ba \dagger OC(CH_3)_3)_2$ 0.25	27	83	24	0	18.6	1.48	54	37	9	4.1

TABLE 10-continued

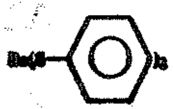
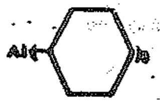
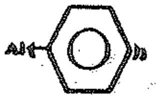
Example	Catalyst system			Initial bound styrene*1 (%)	Yield (%)	Bound styrene (%)	Block styrene*2 (%)	Molecular weight by GPC: Mn (× 10^4)	Molecular weight by GPC: $\overline{Mw}/\overline{Mn}$	Microstructure in butadiene moiety*3: 1,2-structure (%)	Microstructure in butadiene moiety*3: Trans-1,4 structure (%)	Microstructure in butadiene moiety*3: Cis-1,4 structure (%)	Microstructure in butadiene moiety*3: Trans/cis ratio
	Component*4 (1)		Component*4 (2)										
37	nC$_4$H$_9$Na 0.5		Ba(O—n-C$_3$H$_7$)$_2$ 0.25	27	100	25	0	22.2	1.32	53	37	10	3.7
38	nC$_4$H$_9$Na 0.5		Ba(S—n-C$_4$H$_9$)$_2$ 0.25	27	100	25	0	22.1	1.34	50	40	10	4.0
39	nC$_4$H$_9$Na 0.5		 Ba(S—)$_2$ 0.25	27	100	25	0	21.3	1.35	55	35	10	3.5
40	nC$_4$H$_9$Na 0.5		Ba+SCS—n-C$_6$H$_{13}$)$_2$ 0.25	27	99	25	0	23.7	1.34	52	38	10	3.8
41	nC$_4$H$_9$Na 0.5		Ba+OCOCOO—n-C$_6$H$_{13}$)$_2$ 0.25	26	97	25	0	24.1	1.44	51	39	10	3.9
42	nC$_4$H$_9$Na 0.5		Ba+SCSCH$_2$—tert-C$_4$H$_9$)$_2$ 0.25	26	95	26	0	24.3	1.48	50	39	11	3.5
43	nC$_4$H$_9$Na 0.5		 (nC$_{12}$H$_{25}$— —SO$_3$)$_2$Ba 0.25	27	100	25	0	22.3	1.33	54	36	10	3.6
44	nC$_4$H$_9$Na 0.5		(n-C$_{18}$H$_{37}$OSO$_3$)$_2$Ba 0.25	27	99	25	0	22.5	1.30	52	37	11	3.4
45	nC$_4$H$_9$Na 0.5		Ba+N(C$_2$H$_5$)$_2$]$_2$ 0.25	26	100	25	0	19.6	1.34	57	34	9	3.7
46	nC$_4$H$_9$Na 0.5		Ba+C≡C—C$_2$H$_5$)$_2$ 0.25	27	100	25	0	20.1	1.43	55	35	10	3.5
47	nC$_4$H$_9$Na 0.5		Ba(CH$_3$)$_2$ 0.25	28	100	25	0	21.8	1.49	56	35	9	3.9
48	nC$_4$H$_9$Na 0.5		C$_2$H$_5$BaI 0.25	28	100	25	0	19.9	1.41	50	39	11	3.5
	Component*4 (1)	Component*4 (2)	Component*4 (3)										
49	n-C$_5$H$_{11}$Na 0.5	Ba+OC(CH$_3$)$_3$]$_2$ 0.25	C$_2$H$_5$MgCl 0.25	24	93	25	0	22.2	1.32	23	64	13	4.9
50	n-C$_5$H$_{11}$Na 0.5	Ba+OC(CH$_3$)$_3$]$_2$ 0.25	C$_2$H$_5$MgH 0.25	25	98	25	0	18.5	1.38	25	62	13	4.8
51	n-C$_5$H$_{11}$Na 0.5	Ba+OC(CH$_3$)$_3$]$_2$ 0.25	C$_2$H$_5$MgOCH(CH$_3$)$_2$ 0.25	25	99	25	0	19.9	1.33	26	61	13	4.7
52	n-C$_5$H$_{11}$Na 0.5	Ba+OC(CH$_3$)$_3$]$_2$ 0.25	(C$_2$H$_5$)$_2$AlCl 0.25	24	95	25	0	28.6	1.21	39	51	10	5.1

TABLE 10-continued

Example	Catalyst system			Initial bound styrene*1 (%)	Yield (%)	Bound styrene (%)	Block styrene*2 (%)	Molecular weight by GPC		Microstructure in butadiene moiety*3			
								$\bar{M}n$ (× 10^4)	$\bar{M}w/\bar{M}n$	1,2-structure (%)	Trans-1,4 structure (%)	Cis-1,4 structure (%)	Trans/cis ratio
33	n-$C_5H_{11}Na$ 0.5	$Ba[OC(CH_3)_3]_2$ 0.25	$(C_2H_5)_2AlH$ 0.25	25	99	25	0	25.3	1.28	41	50	9	5.6
34	n-$C_5H_{11}Na$ 0.5	$Ba[OC(CH_3)_3]_2$ 0.25	$(C_2H_5)_2AlOCH(CH_3)_2$ 0.25	25	98	25	0	25.5	1.25	42	49	9	5.4
35	n-$C_5H_{11}Na$ 0.5	$Ba[OC(CH_3)_3]_2$ 0.25	$C_2H_5Al[OCH(CH_3)_2]_2$ 0.25	25	96	25	0	26.7	1.32	43	48	9	5.3
36	n-$C_5H_{11}Na$ 0.5	$Ba[OC(CH_3)_3]_2$ 0.25	 0.25	25	100	25	0	25.3	1.27	40	51	9	5.7
37	n-$C_5H_{11}Na$ 0.5	$Ba[OC(CH_3)_3]_2$ 0.25	 0.25	26	100	25	0	23.2	1.31	45	46	9	5.1

*1, *2, *3 and *4: Please refer to Remarks of Table 1.

We claim:

1. A process for producing a conjugated diene polymer, a copolymer of a conjugated diene with at least one other conjugated diene, or a copolymer of a conjugated diene with an aromatic vinyl hydrocarbon comprising the step of polymerizing said monomer or monomers in the presence of an effective catalytic amount of a catalyst complex consisting essentially of the following components (a) and (b) or (a), (b) and (c):

(a)(1) an organosodium compound, having the general formula

$R'(Na)_m$

wherein R' is an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms or an unsaturated hydrocarbon group having at least one allyl hydrogen and desirably having 3 to 30 carbon atoms, and m is an integer of 1 through 4, (2) metallic sodium or (3) a sodium amide compound having the general formula

wherein

represents either a cyclized structure or a non-cyclized structure and R^2 and R^3 represent, in combination, a methylene chain having 2 to 10 carbon atoms in the case of a cyclized structure and R^2 and R^3 independently represent an aliphatic group, desirably having 1 to 30 carbon atoms, an alicyclic group, desirably having 5 to 30 carbon atoms, or an aromatic group, desirably having 6 to 30 carbon atoms in the case of a non-cyclized structure of (4) a mixture of at least one of the above components (1), (2), and (3) with an organic compound of sodium other than said sodium amide compound;

(b) an organic or organometallic compound of barium, strontium, or calcium; and

(c) an organometallic compound of an electron deficient metal selected from lithium, beryllium, magnesium, zinc, cadmium, boron, aluminum, gallium or indium, the amount of component (a) being 0.01 to 50 m mol per 100 g of the total monomers, the amount of component (b) being from 0.01 to 10 times the molar amount of component (a) and the amount of component (c) being from 0 to 5 times the molar amount of component (a).

2. A process as claimed in claim 1, wherein said catalyst component (b) is an organic compound of barium.

3. A process as claimed in claim 1, wherein said catalyst component (c) is an organolithium compound, an organomagnesium compound, or an organoaluminum compound.

4. A process as claimed in claim 1, wherein said conjugated diene is butadiene or isoprene and said aromatic vinyl hydrocarbon is styrene.

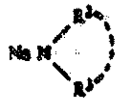
5. A process as claimed in claim 1, wherein polyme
zation is carried out in 300 to 1000 parts by weight
100 parts by weight of the total monomer of a hydroc
bon solvent at a temperature of 30° to 120° C. in t
presence of a catalyst complex comprising 0.1 to 1
mol of the component (a) based on 100 g of the to
monomers, an amount of component (b) of 0.1 to 1 ti
the molar amount of component (a) and an amount
component (c) of 0 to 2 times the molar amount
component (a).

6. A catalyst complex suitable for use in the produ
tion of a conjugated diene polymer, a copolymer o
conjugated diene with at least one other conjuga
diene, or a copolymer of a conjugated diene with
aromatic vinyl hydrocarbon consisting essentially of
following components (a) and (b) or (a), (b) and (c):

(a)(1) an organosodium compound, having the g
eral formula

$R'(Na)_m$

wherein R' is an aliphatic group, desirably havin
to 30 carbon atoms, an alicyclic group, desira
having 5 to 30 carbon atoms, or an aromatic gro
desirably having 6 to 30 carbon atoms or an unsa
rated hydrocarbon group having at least one a
hydrogen and desirably having 3 to 30 cart
atoms, and m is an integer of 1 through 4, (2) me
lic sodium or (3) a sodium amide compound hav
the general formula



wherein

represents either a cyclized structure or a
cyclized structure and R^2 and R^3 represent, in c
bination, a methylene chain having 2 to 10 ca
atoms in the case of a cyclized structure and R^2
R^3 independently represent an aliphatic gr
desirably having 1 to 30 carbon atoms, an alic
group, desirably having 5 to 30 carbon atoms,
aromatic group, desirably having 6 to 30 ca
atoms in the case of a non-cyclized structure o
a mixture of at least one of the above compo
(1), (2), and (3) with an organic compound o
dium other than said sodium amide compoun

(b) an organic or organometallic compound of
ium, strontium, or calcium; and

(c) an organometallic compound of an electron
cient metal selected from lithium, beryllium,
nesium zinc, cadmium, boron, aluminum, ga
or indium, the amount of component (a) being
to 50 m mol per 100 g of the total monomer
amount of component (b) being from 0.01
times the molar amount of component (a) an
amount of component (c) being from 0 to 5
the molar amount of component (a).

7. A catalyst complex as claimed in claim 6, wherein said catalyst component (b) is an organic compound of barium.

8. A catalyst complex as claimed in claim 6, wherein said catalyst component (c) is an organolithium compound, an organomagnesium compound, or an organoaluminum compound.

9. A catalyst complex as claimed in claim 9, wherein said conjugated diene is butadiene or isoprene and said aromatic vinyl hydrocarbon is styrene.

10. A catalyst complex as claimed in wherein the catalyst complex comprises 0.1 to 1 m mol of the component (a) based on 100 g of the total monomers, an amount of component (b) of 0.1 to 1 times the molar amount of component (a) and an amount of component (c) of 0 to 2 times the molar amount of component (a).

11. A catalyst complex as claimed in claim 9, wh[illegible] the catalyst complex comprises 0.1 to 1 m mol [illegible] component (a) based on 100 g of the total monom[illegible] amount of component (b) of 0.1 to 1 times the molar amount of component (a) and an amount of component (c) of 0 to 2 times the molar amount of component (a).

12. The process of claim 4, wherein polymerization is carried out in 300 to 1000 parts by weight per 100 parts by weight of the total monomer of a hydrocarbon solvent at a temperature of 30° to 120° C. in the presence of a catalyst complex comprising 0.1 to 1 m mol of the component (a) based on 100 g of the total monomers, an amount of component (b) of 0.1 to 1 times the molar amount of component (a) and an amount of component (c) of 0 to 2 times the molar amount of component (a).

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