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USPATOLD (U.S. Patents Pre-1976)

Subject Coverage

U.S. patents in all areas of technology 1790-1975

File Type

Bibliographic, Full text

Features

Thesaurus	National Patent Classification, Cooperative Patent Classification, International Patent Classification				
Alerts (SDIs)	None				
CAS Registry Number® Identifiers	☑	Page Images	☐	STN® AnaVist™	☐
Keep & Share	☑	SLART	☑	STN Easy®	☐
Learning Database	☐	Structures	☐		

Record Content

- Full text and classifications for the publications of U.S. patents issued by the United States Patent and Trademark Office (USPTO)
- Complete Chemical Abstracts indexing for one equivalent U.S. chemical patent may also be included in a record
- Patent classifications: NCL, CPC, IPC

File Size

More than 3.6 million records (12/2015)

Coverage

U.S. patents in all areas of technology 1790-1975

Updates

- U.S. Patent Classifications – bimonthly
- No new records are added to this database

Language

English

Database Producer

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2231 NZ Rijnsburg
The Netherlands
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Fax: (+31) 71 403 53 20
Email: info@univentio.com

Sources

U.S. patents issued by the USPTO from 1790-1975

User Aids

- Online Helps (HELP DIRECTORY lists all help messages available)
- STNGUIDE

December 2015

Clusters

- AUTHORS
- CASRNS
- CORPSOURCE
- ENGINEERING
- FULLTEXT
- HPATENTS
- MATERIALS
- MEDICINE
- METALS
- PATENTS
- PNTTEXT
- POLYMERS
- USPATALL

STN Database Clusters information (PDF).

Related Databases

- USPAT2
- USPATFULL

Pricing

Enter HELP COST at an arrow prompt (=>).

Search and Display Field Codes

The fields that allow left truncation are marked with an asterisk (*).

Search Field Name	Search Code	Search Examples	Display Codes
Basic Index * (contains single words from the title (TI), CAS title, abstract (AB), claims (CLM), and detailed description (DETD) fields) **(1)**	None (or /BI)	S GROWTH REGUL? S NAPHTHALENE? S ?ASSAY?	AB, CLM, DETD, TI, TI.CA
Abstract *	/AB	S (COBALT(S)CATALYST?)/AB S ?MODE?/AB	AB
Accession Number	/AN	S 1972:58620/AN	AN
Application Country	/AC	S US/AC AND L1	AI
Application Date **(2)**	/AD	S OCT 4 1938/AD S 19381004/AD	AI
Application Number **(3)**	/AP	S US 1901-143434/AP	AI
Application Year **(2)**	/AY	S 1942/AY	AI
CAS Registry Number (CAS data)	/RN	S 400-39-5/RN	IT, RN
Claim Text *	/CLM	S COBALT (S) SALT#/CLM	CLM
Classification Code (CAS data) (code and text) **(4)**	/CC	S 27/CC S HETEROCYCLIC/CC	CC
Controlled Term (CAS data)	/CT	S ANTISTATIC AGENTS/CT	CT, IT
Cooperative Patent Classification **(5,7)**	/CPC	S C12N0009/CPC	CPC
Cooperative Patent Classification, Action Date	/CPC.ACD	S 20121113/CPC.ACD	CPC.TAB
Cooperative Patent Classification, Combination Sets	/CPC.CS	S (B29C0066-71 (L) B29K2021-00)/CPC.CS S (B29C0066-71 AND B29K2021-00)/CPC.CS S C04B0028-04/CPC (T) COMBINATION SET/CPC.KW	CPC.TAB
Cooperative Patent Classification, Keywords **(7)**	/CPC.KW	S C12N0009/CPC (S) I/CPC.KW	CPC.TAB
Cooperative Patent Classification, Version	/CPC.VER	S 20130101/CPC.VER	CPC.TAB
Cooperative Patent Initial Classification	/CPCI	S A61K0006-0014/CPCI	CPCI
Document Type (code and text)	/DT (or /TC)	S UTILITY/DT	DT
Examiner Name	/EXNAM	S ADEE J?/EXNAM	EXNAM
Field Availability (code and text)	/FA	S CA INDEXING/FA S OS/FA	Not displayed
File Segment	/FS	S GRANTED/FS	FS
Index Term (CAS data)	/IT	S REACTION OF/IT S 61849-32-9P/IT	IT
International Patent Classification **(5,6)**	/IPC	S G03C001/IPC S G03C001-89/IPC S ENZYMES/IPC	IPC
International Patent Classification, Action Date	/IPC.ACD	S 20060101/IPC.ACD	IPC.TAB
International Patent Classification, Keyword Terms	/IPC.KW	S ADVANCED/IPC.KW	IPC.TAB
International Patent Classification, Version	/IPC.VER	S 20070101/IPC.VER	IPC.TAB
Inventor **(1)**	/IN (or /AU)	S KRESS RALPH H?IN	IN
Inventor Address, City	/IN.CTY	S ROCHESTER/IN.CTY	IN, INA
Inventor Address, Country	/IN.CNY	S JAPAN/IN.CNY	IN, INA
Inventor Address, State	/IN.ST	S NJ/IN.ST	IN, INA

Search and Display Field Codes (cont'd)

Search Field Name	Search Code	Search Examples	Display Codes
Inventor Address, ZIP code **(2)**	/IN.ZIP	S 44313/IN.ZIP	IN, INA
IPC, Reclassified	/IPCR	S B01B001-00/IPCR	IPCR
Language (code and text)	/LA	S L1 AND EN/LA	LA
Line Count (2)	/LN.CNT	S 1000-1500/LN.CNT	LN.CNT
National Patent Classification, Current, Main and Secondary **(5,6)**	/NCL	S 430529000/NCL S 430/529.000/NCL S 430/NCL S ZEOLITES+NT/NCL	NCL
National Patent Classification, Current, Main	/NCLM	S 423121000/NCLM S 423/NCLM S ZEOLITES+NT/NCLM	NCLM
National Patent Classification Current, Secondary **(5,6)**	/NCLS	S 423206200/NCLS S 423/NCLS S ZEOLITES+NT/NCLS	NCLS
National Patent Classification, Issue **(5,6)**	/INCL	S 264016000/INCL S 264/INCL S ZEOLITES+NT/INCL	INCL
National Patent Classification, Issue, Main **(5,6)**	/INCLM	S 433173000/INCLM S 433/INCLM S ZEOLITES+NT/INCLM	INCLM
National Patent Classification, Issue, Secondary **(5,6)**	/INCLS	S 502064000/INCLS S 502/INCLS S ZEOLITES+NT/INCLS	INCLS
Other Source (CAS data)	/OS	S 13:10008/OS	OS
Patent Assignee **(1,4)**	/PA (or /CS)	S AMERICAN CYANAMID/PA	PA
Patent Country	/PC	S US/PC AND L2	PI
Patent Kind	/PK	S USA/PK	PI
Patent Number **(3)**	/PN	S US630001/PN	PI
Patent Number/Kind Code	PNK	S US3847871/PNK	PNK
Priority Country	/PRC	S JP/PRC	PRAI
Priority Date **(2)**	/PRD	S PRD>=MAR 24 1900 S PRD>=19000324	PRAI
Priority Number **(3)**	/PRN	S GB1916-354203/PRN	PRAI
Priority Year **(2)**	/PRY	S PRY>=1955	PRAI
Publication Date **(2)**	/PD	S MAR 11 1942/PD	PI
Publication Year **(2)**	/PY	S PY<=1900	PI
Reference Patent Country	/RPC	S AR/RPC	REP
Reference Patent Number	/RPN	S US211975/RPN	REP
Section Cross Reference (CAS data) **(4)**	/SX	S 1/CC,SX S PHARMACOLOGY/CC,SX	CC
Supplementary Term (CAS data)	/ST	S POLYURETHANE?/ST	ST
Title * **(1)**	/TI	S FILM?/TI S ?MYCIN?/TI	TI

(1) Also searches CAS data for this field when available.
(2) Numeric search field that may be searched with numeric operators or ranges.
(3) Either STN or Derwent format may be used.
(4) Search with implied (S) proximity is available in this field.
(5) An online thesaurus is available for this field.
(6) This field is range-searchable in Manual of Classification order. However, it is not a numeric field and may not be searched by using numeric operators.
(7) When searching combinations of CPC and CPC.KW data, use (S) proximity operator.

Super Search Fields (1)

Search Field Name	Search Code	Fields Searched	Search Examples	Display Codes
Application Number Group **(2)**	/APPS	/AP, /PRN	S US1964-50545/APPS	AI, PRAI
Cooperative Patent Classification **(2)**	/CPC	/CPCI, /CPCR	S C12N0009/CPC	CPC, CPCI, CPCR
Patent Country Group	/PCS	/PC, /RPC	S US/PCS	PI
Patent Number Group **(2)**	/PATS	/PN, /RPN	S US630010/PATS	PI

(1) Super search fields facilitate crossfile and multifile searching. Enter a super search code to search in one or more fields that may contain the desired information. EXPAND may not be used with super search fields. Use EXPAND with the individual field codes instead.
(2) Either STN or Derwent format may be used.

Thesaurus Fields

A thesaurus is present for the National Patent Classification fields (/INCL, /INCLM, /INCLS, /NCL, /NCLM, /NCLS) and the International Patent Classification fields. The classifications and catchwords for the main headings and subheadings from the 8th edition of the WIPO International Patent Classification (IPC) manual are available in the /IPC and IPCR fields. The classifications from the previous editions (1-7) are also available as separate thesauri. To EXPAND and SEARCH in the thesauri for editions 1-8, use the field code followed by the edition number, e.g., /IC2, /ICM2, /ICS2 for the 2nd edition. Catchwords are included only in the thesauri for the 8th, 7th, 6th, and 5th editions.

Code	Content	Example
ALL	All associated terms	E 264016000+ALL/INCL E A01N025-04+ALL/IPC
AUTO **(1)**	Automatic Relationship (BT, SELF))	E A01N025-04/IPC REL=ON
HIE	Hierarchy (Broader and Narrower Terms (all Broader and Narrower Terms) (BT, SELF, NT)	E 523523000+HIE/NCL E A01B001-06+HIE/IPC
TI	Complete Title of the SELF Term	E 135+TI/NCLM E A01B001-04+TI/IPC
BT	Broader Terms (BT, SELF)	E 423206200+BT/NCLS E 423206200+BT/NCLS
KT	Keyword Terms (SELF, KT) **(2)**	E ZEOLITES+KT/NCL
NT	Narrower Terms (SELF, NT)	E 264016000+NT/INCL E A01N025-00+NT/IPC
NEXT	Next Classification	E 135086000+NEXT15/INCL E A01B001-16+NEXT5/IPC
PREV	Previous Classification	E 523523000+PREV3/NCLS E A01B001-18+PREV5/IPC
BRO	Complete Class	E 135019000+BRO5/INCL E A01B003-14+BRO3/IPC
RT	Related Terms	E A01B001-16+RT/IPC

(1) AUTOMATIC relationship is SET OFF. If you SET RELATION ON, the result of EXPAND without any relationship code is the same as described for AUTO.
(2) Keyword terms are the catchwords corresponding to the USPTO Manual of Classifications subject index headings and subheadings.

CPC (/CPC) Thesaurus

The Cooperative Patent Classification (CPC) is jointly developed and maintained by the European Patent Office and the US Patent and Trademark Office. This thesaurus is available in the /CPC search field. All relationship codes can be used with both the EXPAND and SEARCH commands.

Relationship Code	Content	Search Examples
ALL	All usually required terms (BT, SELF, CODE, DEF)	E C12M0001-00+ALL/CPC
AUTO **(1)**	Automatic relationship (BT, SELF, CODE, DEF)	E G01J003-443+AUTO/CPC
BT	Broader terms (BT, SELF)	E G01J0003-443+BT/CPC
CODE	Classification Code (SELF, CODE)	E CARTRIDGES+CODE/CPC
DEF	Definition (SELF, DEF)	E B65G0045-16+DEF/CPC
HIE	Hierarchy terms (all broader and narrower terms) (BT, SELF, DEF, NT)	E A01B0001-00+HIE/CPC
KT	Keyword terms (SELF, KT)	E LASER+KT/CPC
MAX	All associated terms	E G01J0003-44+MAX/CPC
NEXT	Next classification within the same class (SELF, NEXT)	E A01B0001-24+NEXT/CPC
NEXT(n)	Next n classification within the same class	E A01B0001-24+NEXT3/CPC
NT	Narrower terms	E G05B0001-04+NT/CPC
PREV	Previous Code within the same class (SELF, PREV)	E G05B0019-00+PREV/CPC
PREV(n)	Previous n classifications within the same class	E G05B0019-00+PREV2/CPC
TI	Complete Title of SELF Term and Broader Terms (BT, SELF)	E G05B0001-03+TI/CPC

(1) Automatic Relationship is SET OFF. In case of SET REL ON the result of EXPAND or SEARCH without any relationship code is the same as described for AUTO.

Full-Text Browsing

User Request	Example	System Response
DISPLAY BROWSE	=> DISPLAY BROWSE ENTER (L1) OR L#:. ENTER (DIS), ANSWER NUMBERS, OR END:	NOVICE version
D BRO	=> D BRO L1 :	EXPERT version
Answer number(s)	:1-3	display answers 1, 2, and 3 in default format
	:.	display next answer in default format
Answer number(s) and format	:4 HIT	display answer 4 in HIT format
Format only	:TI CLM	display title and claim text of last answer displayed
*Format	:*KWIC	change default to KWIC; no answer displayed
Forward n fields	:F3	move forward three fields
Backward n fields	:B1	move backward one field
Search forward for a character string	:S GROWTH REGUL	search forward within record for "growth regul"
	:S	repeat search forward for the current string
Search backward for a character string	:S- ALKANOIC ACID	search backward within record for "alkanoic acid"
	:S-	repeat search backward for the current string
End DISPLAY BROWSE	:END =>	exit DISPLAY BROWSE and return to arrow prompt

DISPLAY and PRINT Formats

Any combination of formats may be used to display or print answers. Multiple codes must be separated by spaces or commas, e.g., D L3 1-10 TI,AB or D L3 1-10 TI AB. The fields are displayed or printed in the order requested.

Hit-term highlighting is available in all fields except RPN. Highlighting must be on when a SEARCH is performed to use the FHITSTR, HIT, HITRN, HITSTR, KWIC, and OCC formats.

Format	**Content**	**Examples**
AB	Abstract	D 1-3 AB
AI (AP) **(1)**	Application Information	D 4 9 AI
AN **(2)**	Accession Number	D AN
CC (SX)	Classification Code and Section cross-reference (CAS data)	D L3 CC 1-5
CLM	Patent Claim Text	D CLM L8
CPC	Cooperative Patent Classification	D CPC
CPCI	CPC Initial Classification	D CPCI
CPCR	CPC Reclassification	D CPCR
CT **(2)**	Controlled Term (CAS data)	D 4 CT
DETD	Detailed Description	D 1-4 DETD
DT (TC)	Document Type	D DT 2,6-10
EXNAM	Examiner Name	D EXNAM 4-8,11
FS **(2)**	File Segment	D FS
IN (AU)	Inventor (includes INA)	D IN
IN.CA	Inventor (CAS data)	D IN.CA
INA **(3)**	Inventor Address	D L5 1-4 INA
INCLM **(2)**	Issue Main National Patent Classification Code	D 2,5 INCLM
INCLS **(2)**	Issue Secondary National Patent Classification Code	D L2 1-3 INCLS
IPCR **(2)**	IPC, Reclassification	D L6 7 IPCR
IT	Index Term (CAS data)	D 1,5,10 IT
LA **(3)**	Language	D LA
LN.CNT	Line Count	D LN.CNT
NCLM **(2)**	Current Main National Patent Classification Code	D 1-2 NCLM
NCLS **(2)**	Current Secondary National Patent Classification Code	D 1-5 NCLS
OS	Other Source Chemical Abstracts	D OS
PA (CS)	Patent Assignee (includes PAA and PAT)	D 1-3 PA
PA.CA	Patent Assignee (CAS data)	D 1-3 PA.CA
PI (PN) **(1)**	Patent Information	D PI L8
PNK	Patent Number/Kind Code	D PNK
PRAI (PRN) **(1)**	Priority Information	D PRAI
REP (RPN)	Reference Patent Information	D 1-4 REP
RN **(3)**	CAS Registry Number (CAS data)	D RN 2,6-10
ST	Supplementary Terms (CAS data)	D ST
TI **(2)**	Title	D 2,5 TI
TI.CA	Title (CAS data)	D 2,5 TI.CA
ABS	AB	D L3 1-5 ABS
ALL **(1)**	AN, TI, IN, INA, PA, PI, AI, PRAI, DT, FS, REP, EXNAM, AB, DETD, CLM, INCL (INCLM, INCLS), NCL (NCLM, NCLS), CPC (CPCI, CPCR), IPC (IPCR)	D 3 ALL
APPS **(1)**	AI, PRAI	D APPS
BIB **(1)**	AN, TI, IN, INA, PA, PI, AI, PRAI, DT, FS, EXNAM, LN.CNT	D BIB
CAS	OS, CC, SX, ST, IT	D CAS 3 L2
CBIB	Compressed bibliographic information	D CBIB
CPC	CPCI, CPCR, for the basic patent and patent family members	D CPC
CPC.TAB	CPC, CPC.KW, CPC.ACD, CPC.VER in tabular format	D CPC.TAB
CPC.UNIQ	Deduplicated list of CPC codes for the patent family	D CPC.UNIQ
DALL **(1)**	ALL, delimited for postprocessing	D 1-15 DALL

DISPLAY and PRINT Formats (cont'd)

Format	Content	Examples
FP	PI, TI, IN, INA, PA, AI, PRAI, IPC (IPCR), INCL (INCLM, INCLS), NCL (NCLM, NCLS), CPC (CPCI, CPCR), REP, EXNAM, AB	D FP
FPALL	PI, TI, IN, INA, PA, AI, PRAI, IPC (IPCR), INCL (INCLM, INCLS), NCL (NCLM, NCLS), CPC (CPCI, CPCR), REP, EXNAM, AB, DETD, CLM	D FPALL 6
FPBIB	PI, TI, IN, INA, PA, AI, PRAI, REP, EXNAM	D FPBIB
FHITSTR	First HIT RN, its text modification, its CA index name, and its structure diagram	D FHITSTR 2
CPC.HIT (HITCPC)	HIT display of CPC code searched	D CPC.HIT or D HITCPC
HIT	Fields containing hit terms	D HIT
HITRN	Hit CAS Registry Number and its text modification	D HITRN
HITSTR	HITRN, its text modification, CA index name, and structure diagram	D HITSTR 4
IABS	ABS, with a text label	D 1-4 IABS
IALL **(1)**	ALL, indented with text labels	D IALL 2
IBIB **(1)**	BIB, indented with text labels	D IBIB 4-10
IMAX **(1)**	MAX, indented with text labels	D IMAX 1
INCL **(2)**	Issue National Patent Classification Code (INCLM, INCLS)	D 1,5 L4 INCL
IND	INCL (INCLM, INCLS), NCL (NCLM, NCLS), CPC (CPCI, CPCR), IPC (IPCR), OS, CC, SX, ST, IT	D L2 IND 1-4
IPC **(2)**	International Patent Classifications (IPCR)	D 1-4 L2 IPC
IPC.TAB **(2)**	IPC in tabular format	D IPC.TAB
ISTD **(1)**	STD, indented with text labels	D ISTD 1,5
MAX **(1)**	AN, TI, IN, INA, PA, PI, AI, PRAI, DT, FS, REP, EXNAM, AB, DETD, CLM, INCL (INCLM, INCLS), NCL (NCLM, NCLS), CPC (CPCI, CPCR), IPC (IPCR), OS, CC, SX, ST, IT	D MAX L1 1
NCL **(2)**	Current National Patent Classification Code (NCLM, NCLS)	D 6,12 L1 NCL
PATS **(1)**	PI, REP	D PATS 1-3
SBIB **(1)**	AN, TI, IN, INA, PA, PI, AI, RLI, PRAI, DT, FS, LN.CNT	D SBIB
SCAN **(2,4)**	AN, TI, NCL (NCLM, NCLS), CPC (CPCI, CPCR), IPC (IPCR) (random answer display, no answer number)	D SCAN
STD **(1)**	AN, TI, IN, INA, PA, PI, AI, PRAI, DT, FS, LN.CNT, INCL (INCLM, INCLS), NCL (NCLM, NCLS), CPC (CPCI, CPCR), IPC (IPCR) (STD is the default)	D STD 1, 8
TRIAL (FREE) **(2)**	AN, TI, INCL (INCLM, INCLS), NCL (NCLM, NCLS), CPC (CPCI, CPCR), IPC (IPCR)	D TRIAL
KWIC	Up to 20 words before and after hit terms (KeyWord-In-Context)	D KWIC
OCC **(2)**	Number of occurrences of hit terms and fields in which they occur	D OCC

(1) By default, patent, application, and priority numbers are displayed in STN format. To display them in Derwent format, enter SET PATENT DERWENT at an arrow prompt (=>). To reset display to STN format, enter SET PATENT STN.
(2) No online display fee for the format.
(3) Custom display only.
(4) SCAN must be specified on the command line, i.e., D SCAN or DISPLAY SCAN.

SELECT, ANALYZE, and SORT Fields

The SELECT command is used to create E-numbers containing terms taken from the specified field in an answer set.

The ANALYZE command is used to create an L-number containing terms taken from the specified field in an answer set.

The SORT command is used to rearrange the search results in either alphabetic or numeric order of the specified field(s).

Field Name	Field Code	ANALYZE/ SELECT (1)	SORT
Abstract	AB	Y	N
Accession Number	AN	Y	N
Application Country	AC	Y **(2)**	Y
Application Date	AD	Y **(2)**	Y
Application Information	AI	Y **(2,3,4)**	Y
Application Number	AP	Y **(2,3)**	Y
Application Number Group	APPS	Y **(2,3,5)**	N
Application Year	AY	Y **(2)**	Y
Author (Inventor)	AU	Y **(6)**	Y
CAS Registry Number (CAS data)	RN	Y **(2)**	N
Citation	CIT	Y **(2,7)**	N
Claim Text	CLM	Y	N
Classification Code (CAS data)	CC	Y	Y
Controlled Term	CT	Y **(2)**	N
CPC Classification	CPC	Y **(17)**	N
CPC, Initial	CPCI	Y **(18)**	N
CPC, Reclassified	CPCR	Y **(18)**	N
CPC Hit Display	CPC.HIT (HITCPC)	Y	Y
CPC Codes Deduplicated for patent family	CPC.UNIQ	Y	Y
Corporate Source (Patent Assignee)	CS	Y **(8)**	Y
Current Main National Patent Classification Code	NCLM	Y	Y
Current National Patent Classification Code, Main and Secondary	NCL	Y	Y
Current Secondary National Patent Classification Code	NCLS	Y	N
Detailed Description	DETD	Y **(9)**	N
Document Type	DT	Y	Y
Examiner Name	EXNAM	Y	Y
Index Term (CAS data)	IT	Y **(2)**	N
International Patent Classifications, (All Codes)	IPC	Y	N
Inventor	IN	Y	Y
Inventor (CAS data)	IN.CA	Y	Y
Inventor Address	INA	N	Y
Inventor Address, City	IN.CTY	Y	Y
Inventor Address, Country	IN.CNY	Y	Y
Inventor Address, State	IN.ST	Y	Y
Inventor Address, ZIP Code	IN.ZIP	Y	Y
IPC, First Invention	IPC.F	Y **(10)**	N
IPC Reclassification	IPCR	Y **(10)**	N
Issue Main National Patent Classification Code	INCLM	Y	Y
Issue National Patent Classification Code, Main and Secondary	INCL	Y	Y
Issue Secondary National Patent Classification	INCLS	Y	N
Language	LA	Y	Y
Line Count	LN.CNT	N	Y

SELECT, ANALYZE, and SORT Fields (cont'd)

Field Name	Field Code	ANALYZE/ SELECT (1)	SORT
Occurrence Count of Hit Terms	OCC	N	Y
Other Source Chemical Abstracts	OS	Y **(2)**	N
Other Source Patent Number	OSPN	Y **(2,11)**	N
Patent Assignee	PA	Y	Y
Patent Assignee (CAS data)	PA.CA	Y	Y
Patent Country	PC	Y **(2)**	Y
Patent Country Group	PCS	Y **(2,12)**	N
Patent Date	PD	Y **(2)**	Y
Patent Information	PI	Y **(2,3,13)**	Y
Patent Kind	PK	Y	Y
Patent Number	PN	Y **(2,3)**	Y
Patent Number Group	PATS	Y **(2,3,14)**	N
Patent Number/Kind Code	PNK	Y	N
Patent Year	PY	Y **(2)**	Y
Priority Country	PRC	Y **(2)**	Y
Priority Date	PRD	Y **(2)**	Y
Priority Information	PRAI	Y **(2,3,15)**	Y
Priority Number	PRN	Y **(2,3)**	Y
Priority Year	PRY	Y **(2)**	Y
Reference Patent Country	RPC	Y	N
Reference Patent Information	REP	Y	N
Reference Patent Number	RPN	Y	N
Section Cross-reference (CAS data)	SX	Y	Y
Supplementary Term (CAS data)	ST	Y	N
Title	TI	Y (default)	Y
Title (CAS data)	TI.CA	Y	Y
Treatment Code	TC	Y **(16)**	Y

(1) HIT may be used to restrict terms extracted to terms that match the search expression used to create the answer set, e.g., SEL HIT TI.
(2) SELECT HIT and ANALYZE HIT are not valid with this field.
(3) Enter SET PATENT DERWENT at an arrow prompt to SELECT or ANALYZE patent and application numbers in Derwent format.
(4) Selects or analyzes the application number with /AP appended to the terms created by SELECT.
(5) Selects or analyzes AP, PRN, and RLN and appends /APPS to the terms created by SELECT.
(6) Appends /IN to the terms created by SELECT.
(7) Extracts patent number, appends the publication year with a truncation symbol, and appends /RE to the terms created by SELECT.
(8) Appends /PA to the terms created by SELECT.
(9) Appends /BI to the terms created by SELECT.
(10) Appends /IPC to the terms create by SELECT.
(11) Appends /PN to the terms created by SELECT.
(12) Selects or analyzes the PC and RPC and appends /PCS to the terms created by SELECT.
(13) Selects or analyzes the PN and appends /PN to the terms created by SELECT.
(14) Selects or analyzes PN, RPN, and RLPN and appends /PATS to the terms created by SELECT.
(15) Selects or analyzes the PRAI and appends /PRN to the terms created by SELECT.
(16) Selects or analyzes the TC and appends /DT to the terms created by SELECT.
(17) Select CPC selects all CPCI and CPCR classifications and appends /CPC as a field code.
(18) SELECT appends /CPC.

Sample Records

DISPLAY IMAX

```
ACCESSION NUMBER:       1974:75537  USPATOLD  Full-text
TITLE:                  POLYMERS AND COPOLYMERS OF 1 FERROCENYL 1,3 BUTADIENE
INVENTOR(S):            COMBS C
                        STEPHENS W
                        WILLIS T
PATENT ASSIGNEE(S):     COMBS C,, STEPHENS W,, WILLIS T

                             NUMBER       KIND    DATE
                        ---------------- ------ --------
PATENT INFORMATION:     US 3847871         A    19741112
APPLICATION INFO.:      US 1972-252390          19720501

                               NUMBER           DATE
                        ------------------      --------
PRIORITY INFORMATION:   US 1972-252390          19720511
DOCUMENT TYPE:          Utility
FILE SEGMENT:           GRANTED

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BACKGROUND OF THE INVENTION

Field of the Invention This invention relates to a method of using ferrocene so
as to take advantage of its unusual properties. Ferrocene is dicyclopentadienyl
iron, the nucleus of which has been noted for its abilities to absorb
ultraviolet radiation. This unusual property of ferrocene has caused widespread
interest in utilizing the material as an additive in rubbery polymeric
materials in order to stabilize these materials against degradation of physical
properties caused by sunlight. In addition, the ferrocene nucleus is highly
stable towards gamma radiation. As a result of these stabilizing properties,
there has been much interest in the use of ferrocene and ferrocene compounds in
coatings for space vehicles to protect exposed surfaces.

The use of ferrocene or ferrocene derivatives to achieve the objectives
outlined above has been hampered by the high volatility of ferrocene and
ferrocene derivatives. The result of this volatility is that when ferrocene is
incorporated as an additive to polymeric materials, the high vapor pressure of
the ferrocene causes the material to sublime out of the polymeric matrix
thereby rendering the ferrocene or ferrocene derivative unavailable for
stabilizing physical properties.

Description of the Prior Art In general, the solution to the problem of
retaining ferrocene in a polymeric matrix has been to not add ferrocene or
ferrocene derivatives as additives, but rather to include the ferrocene nucleus
in the polymeric material so that it is chemically bonded to the polymer chain
and therefore cannot escape from the rubber or plastic product. In the past,
numerous efforts have been made to find a monomer which can be polymerized, or
copolymerized with a comonomer, without destroying the special properties which
the comonomer would give to the final product. For instance, polymers of
butadiene have certain highly desirable properties such as elongation and
tensile strength. If the ferrocene unit is attached to a monomer which is used
in a copolymerization of butadiene, it is possible that the physical properties
of polybutadiene would be significantly impaired, unless the proper monomer is
used. Thus, the use of the proper ferrocene-containing monomer is very
important in achieving the desired properties.

Several polymers and copolymers of ferrocene derivatives have been prepared in
the past. However, most of these polymers were either brittle solids, or were
relatively insoluble and difficult to handle.
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It is an object of the present invention to provide polymeric materials which have ferrocene incorporated in the polymer chemically bonded to the polymeric claim so that the disadvantages inherent in the use of ferrocene as an additive may be overcome.

It is a further object of this invention to provide liquid polymeric materials which contain the ferrocene nucleus chemically bonded to the polymer chain.

Another object of this invention is to provide polymeric materials which contain the ferrocene nucleus chemically bonded to the polymer chain, which polymers are soluble in various solvents and therefore easier to handle.

These, and other objectives of the present invention, are achieved through the use of l-ferrocenyl-l,3Jbutadiene as a monomer and comonomer with other polymerizable materials.

These and other objectives will become more apparent to one skilled in the art from the following detailed description and examples.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

One of the essential components of this invention is the l-ferrocenyl-l,3-butadiene. This monomer is prepared by a two-step reaction sequence, the first step of which involves a Grignard reaction of allylmagnesium halide with ferrocene aldehyde. The reaction product after hydrolysis is l-ferrocenyl-3-butene-l-ol. This alcohol is then dehydrated by stirring a benzene solution of the alcohol in the presence of aluminum oxide.

More particularly, a solution consisting of grams of ferrocene aldehyde dissolved in ml. of benzene is added dropwise to a stirred solution of 213 grams of allylmagnesium bromide in 1200 ml. of ether under reflux. Refluxing and stirring are continued for two hours after the addition is completed. The reaction mixture is then allowed to cool to room temperature and is poured into ml. of a cold 10% solution of ammonium chloride in water containing grams of sodium disulfate in order to eliminate the impurities in the Grignard reagent. The mixture is then filtered and the organic layer from the filtrate is evaporated yielding 219 grams of l-ferrocenyl3-butene-l-ol.

This reaction product is stirred with 2.2 kg. of acidic aluminum oxide (Ventron Acidic Alumina of Ventron Corporation) in 3.2 liters of benzene for one hour to . dehydrate the alcohol. The aluminum oxide is then removed by filtration and l-ferrocenyl-l,3-butadiene, a red solid, is recovered by evaporation of the solvent.

Polymers of l-ferrocenyl-l,3-butadiene may be made by treating the monomer with an appropriate catalyst with solvent. Copolymers of l-ferrocenyl-l.S-lmtadiene with dienes may be made by treating a mixture of the two monomers with an appropriate catalyst. Also, copolymers of l-ferrocenyl-l,3-butadiene with esters of acrylic acid may likewise be prepared by treatment of a mixture of . the monomers with or without solvent with a suitable polymerization catalyst. Furthermore, copolymers of 1ferrocenyl-l,3-butadiene with vinyl ketones, vinyl ethers, and vinyl ferrocene may be made by treatment of a mixture of the two monomers with or without solvent with a suitable polymerization catalyst.

The following examples illustrate the preparation of the polymers and copolymers of the present invention.

EXAMPLE IA polymer of 1-ferrocenyl-1,3-butadiene was prepared by dissolving the l-ferrocenyl-l,3-butadiene in ethyl ether and then adding a trace of sulfuric acid as the catalyst. Instantaneous polymerization occurred at room temperature. The solvent was then evaporated and the product purified by washing, leaving a brittle yellow solid polymer of l-ferrocenyl-l,3-butadiene which was soluble in methylene chloride. That the polymer actually resulted was proven by (1) thin layer chromatography and (2) evacuation under high vacuum.

Thin layer chromatography (TLC) is performed by dissolving a sample of the reaction product in a small amount of solvent in a test tube and placing a small spot of the solution on the bottom of a TLC plate. The plates used in this test were supplied by Brinkman Instruments Company and are MN Silica-gel S-HR/UV254 chromatographic plates, and the solvent was a mixture of hexane and acetone. Monomeric molecules, such as any unreacted (i.e. unpolymerized) l-ferrocenyl-l,3-butadiene, are carried up the chromatographic strip as a single spot moving slightly behind the solvent front as it climbs the strip. When polymers are present, these materials are moved much more slowly, and usually appear as a continuous smear with a dark brown streak all the way from the origin up to approximately half the distance to the solvent front. Since the polymer molecular weights are significantly higher than the molecular weights of the monomers involved, the migration rates of the polymers would be expected to be much lower, and therefore these materials "" would not be found as high on the chromatographic plate. In addition, since the polymeric products are generally mixtures of molecules of different molecular weights the polymer appears as a smear, or a streak, rather than as a single spot as in the case of the monomer or simple low molecular weight compounds. The TLC plates were developed by exposure to an iodine atmosphere. The brittle yellow solid polymer of this example produced a chromatographic plate with a smear which proved that the polymerization had occurred.

Evacuation under high vacuum is performed by subjecting samples recovered from the polymerization reaction mixtures to a vacuum of less than one millimeter at a temperature of C. Under these conditions, the lower molecular weight materials are sublimed and lost by evaporation into the cold trap in the vacuum system. Anything which is not lost by this process necessarily has a much higher molecular weight, and is therefore polymeric. The polymer of this example acted as expected g under the vacuum, thereby proving that polymerization occurred.

The molecular weight of the resultant polymer was found to be 2,737 by vapor pressure osmometry.

The iron content of the resultant polymer was found to g be 23.15% which corresponds closely to the theoretical value of 23.3%.

EXAMPLE II A polymer of l-ferrocenyl-l,3-butadiene was prepared by a different process. The monomer was dissolved in methylene chloride and cooled to -79 C. A trace amount of boron trifluoride etherate was added and the mixture was stirred for approximately minutes. The catalyst was destroyed by the addition of ammonium 6i chloride, whereupon the polymeric product was obtained by filtering the mixture, evaporating the solvents, dissolving the product in ethyl ether, and precipitating it with methanol. The product was a brittle yellow solid polymer of l-ferrocenyl-l,3-butadiene which is soluble in methylene chloride and ethyl ether. Evacuation under high vacuum and TLC as described in Example I proved that a polymer actually formed.

The polymer had an iron content of 22.48%, and a molecular weight of 2,780.

EXAMPLE III

In a third process for polymerizing l-ferrocenyl-1,3butadiene grams of the monomer, ml. water, 0.2 g. potassium persulfate, and 0.5 g. sodium lauryl sulfate were combined and these ingredients were heated at C. for four hours. The polymeric product was precipitated by the addition of a sodium chloride solution. The precipitate was dissolved in benzene and reprecipitated with . methanol yielding a soluble yellow-orange solid polymer of l-ferrocenyl-l,3-butadiene, the existence of which was proven by TLC and high vacuum evacuation as described in Example I.

The poly-l-ferrocenyl-1,3 - butadiene of this Example had a molecular weight of 2,814 and an iron content of 22.17%.

EXAMPLE IV A copolymer of l-ferrocenyl-l,3-butadiene and isoprene was prepared by adding grams of each of the monomers, 1.6 grams of potassium persulfate, and 4. grams of sodium lauryl sulfate to ml. of water. The mixture was stirred and heated at C. for four hours. The reaction mixture was allowed to cool and then was >r extracted with benzene. A viscous (tar-like consistency) orange-red liquid polymer was obtained by precipitation with methanol. Evacuation under high vacuum and TLC as described in Example I proved that a copolymer formed.

The resultant copolymer had a molecular weight of 1,695.

An analysis of the iron content of the copolymer showed 20.2% iron as opposed to a homopolymer iron content of 23.3%. Therefore, the resultant polymeric product was comprised of approximately 86% 1-ferrocenyl-l,3-butadiene monomer and approximately 14% isoprene.

EXAMPLE V A copolymer of l-ferrocenyl-l,3-butadiene and butadiene was formed in this example. Butadiene (120 grams), l-ferrocenyl-l,3-butadiene (40 grams), 4,4-azobis-(4cyanopentanoic acid) (13 grams), and dioxane (320 ml.) were stirred at C. in a sealed bomb for four days. The g solvent was removed in a vacuum and the product was precipitated from ethyl ether with methanol. The product was an orange-red liquid copolymer the existence of which was again proven by TLC and high vacuum evacuation, as described in Example I.

n The molecular weight of the resultant copolymer was 3,200.

The chemical analysis of the copolymer showed 12.3% iron, a fact which indicates that a copolymer composed of about weight percent l-ferrocenyl-l,3-butadiene and g about weight percent butadiene was formed.

EXAMPLE VI A copolymer of l-ferrocenyl-l,3-butadiene and methyl acrylate was prepared by stirring methyl acrylate (10 grams), l-ferrocenyl-l,3-butadiene (10 grams), 4,4-azobis-(4-cyanopentanoic acid) (1.3 grams), and dioxane (80 ml.) under nitrogen for four days at to C. The dark red liquid polymeric product was obtained by precipitation from ether with methanol. TLC and high vacuum evacuation showed the existence of the copolymer as was done in Example I.

EXAMPLE VII _ A copolymer of l-ferrocenyl-l,3-butadiene and methyl vinyl ketone was formed by dissolving equal quantities of the two monomers in a six-fold volume of hexane. A trace of sulfuric acid was added to the mixture at 0 C. The reaction mixture was allowed to stand .for five minutes and the solvent was evaporated yielding a red oily copolymer > of l-ferrocenyl-l,3-butadiene and methyl vinyl ketone.

3,847, TLC and high vacuum evacuation showed the existence of the copolymer, as described in Example I.

EXAMPLE VIII A copolymer of l-ferrocenyl-l,3-butadiene and vinyl g isobutyl ether was prepared. Equal amounts of 1-ferrocenyl-l,3-butadiene and vinyl isobutyl ether were dissolved in a six-fold volume of hexane. A trace amount of sulfuric acid was added to the mixture at 0 C. The mixture was then allowed to stand for approximately five minutes. The solvent was next evaporated yielding a viscous red copolymer of 1 - ferrocenyl-l,3-butadiene and vinyl isobutyl ether. TLC and high vacuum evacuation showed the existence of the copolymer, as described in Example I.

EXAMPLE IX A copolymer of l-ferrocenyl-l,3-butadiene and vinyl ferrocene was prepared by heating grams of each of the monomers with 0.5 grams of potassium persulfate, grams of sodium lauryl sulf ate, and ml. of water with 2 0.3 grams of acrylic acid at C. for three hours. The reaction mixture was precipitated, washed, dissolved in ether, and reprecipitated with methyl alcohol, yielding a clear red-orange plastic polymer. TLC and high vacuum evacuation showed the existence of the copolymer as was described in Example I.

The resultant copolymer had a molecular weight of 1,236.

It is to be understood that the foregoing examples and description are for the purposes of illustration only, and that various changes may be made therein without departing from the spirit and scope of the invention.

What is claimed is:
What is claimed is:

1. As a composition of matter, homopolymers of 1ferrocenyl-l,3-butadiene prepared by reacting 1-ferrocenyl-l,3-butadiene with a catalyst, in the presence of a solvent, at a temperature of from about -79 to C., for a period of from about 1 minute to 4 hours.

2. As a composition of matter, copolymers of 1-ferrocenyl-l,3-butadiene and a comonomer selected from the group consisting of dienes, acrylic acid, vinyl ketones, vinyl ethers, and vinyl ferrocene, prepared by reacting 1ferrocenyl-l,3-butadiene and a comonomer with a catalyst, in the presence of a solvent, at a temperature of from about 0 to C., for a period of from about 5 minutes to 4 days.

3. The copolymers of claim 2 wherein the diene is isoprene.

4. The copolymer of claim 2 wherein the diene is butadiene.

5. The copolymer of claim 2 wherein the ester of acrylic acid is methyl acrylate.

6. The copolymer of claim 2 wherein the vinyl ketone is methyl vinyl ketone.

7. The copolymer of claim 2 wherein the vinyl ether is vinyl isobutyl ether.

8. The product produced by dissolving 1-ferrocenyl1,3-butadiene in ethyl ether, adding sulfuric acid at room temperature, subsequently evaporating the ether, and purifying the product by washing.

9. The product produced by dissolving 1-ferrocenyll,3jbutadiene in methylene chloride, cooling the mixture to -79 C., adding boron trifluoride etherate, stirring the mixture for minutes, adding ammonium chloride, filtering the mixture, evaporating the methylene chloride, dissolving the product in ethyl ether, and precipitating it with methanol.

10. The product produced by combining 1-ferrocenyl1,3-butadiene, water, potassium persulfate, and sodium lauryl sulfate; heating these ingredients at C. for four hours; precipitating the product by the addition of sodium chloride; dissolving the precipitate in benzene; and reprecipitating the product with methanol.

11. The product produced by combining equal amounts of l-ferrocenyl-l,3-butadiene and isoprene with potassium persulfate, sodium lauryl sulfate, and water; stirring the mixture; heating at C. for four hours; cooling the reaction mixture; and extracting the product with benzene.

12. The product produced by combining butadiene, 1ferrocenyl-l,3-butadiene, 4,4-azobis-(4 - cyanopentanoic acid) and dioxane; stirring at C. in a sealed bomb for four days; removing the solvent in a vacuum; and precipitating the product from ethyl-ether with methanol.

13. The product produced by stirring methyl acrylate, l-ferrocenyl-l,3-butadiene, 4,4-azobis-(4-cyanopentanoic acid), and dioxane under nitrogen for four days at to 70 C.; and precipitating the polymeric product from, ether with methanol.

14. The product produced by dissolving 1-ferrocenyl1,3-butadiene and methyl vinyl ketone in hexane; adding sulfuric acid to the mixture at 0 C.; allowing the mixture to stand for 5 minutes; evaporating the solvent; and purifying the product by washing.

15. The product produced by dissolving 1-ferrocenyl1,3-butadiene and vinyl isobutyl ether in hexane; adding sulfuric acid to the mixture at 0 C.; allowing the mixture to stand for 5 minutes; evaporating the solvent to yield the product; and purifying the product by washing.

16. The product produced by heating l-ferrocenyl-1,3butadiene, vinyl ferrocene, potassium persulfate, sodium lauryl sulfate, water, and acrylic acid at C. for

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three hours; precipitating the mixture; washing the product; dissolving the
product in ether; and reprecipitating the product with methyl alcohol.

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                         PATENT      KIND   DATE
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CA CLASSIF.:       35-3 (Synthetic High Polymers)
SUPPL. TERM:       ferrocenylbutadiene polymn
INDEX TERM:        Polymerization
                       (of ferrocenylbutadiene)
INDEX TERM:        32613-29-9P   52953-54-5P   54633-59-9P   54633-60-2P
                   54633-61-3P   54633-62-4P   54787-80-3P
                       (manufacture of)
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TI     BITUMINOUS COMPOSITIONS CONTAINING PLASTIC OR ELASTOMER POLYSULPHIDE
       POLYMERS
TI.CA  Bitumen preparation containing organic polysulfides
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       NICOLAU A
       SIGNOURET J
IN.CA  Garrigues, Claude; Nicolau, Albert; Signouret, Jean Baptiste
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