

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



(43) International publication date

28 August 2003 (28.08.2003)

(10) International publication number

WO 03/070674 A1

PCT

(51) International patent classification⁷:
22/04

C07C 17/08,

(74) Attorneys: KINZEBACH, Werner etc.; Ludwigsplatz
4, 67059 Ludwigshafen (DE).

(21) International application number:

PCT/EP03/01877

(81) Designated states (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International filing date: 24 February 2003 (24.02.2003)

(25) Language of filing: German

(26) Language of publication: German

(30) Data relating to the priority:

102 07 963.3 25 February 2002 (25.02.2002) DE

(71) Applicant (*for all designated States except US*): BASF AKTIENGESELLSCHAFT [DE/DE]; 67056 Ludwigshafen (DE).

(72) Inventors; and

(75) Inventors/Applicants (*US only*): LANG, Gabriele [DE/DE]; Eichendorffstr. 41, 68167 Mannheim (DE). HÜFFER, Stefan [DE/DE]; Bauernwiesenstrasse 21, 67063 Ludwigshafen (DE). LANGE, Arno [DE/DE]; Oberes Gaistal 3b, 67098 Bad Dürkheim (DE). RATH, Hans, Peter [DE/DE]; Friedhofstr. 7, 67269 Grünstadt (DE).

(84) Designated states (*regional*): ARIPO Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European Patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- With the International Search Report.

For an explanation of the two-letter codes and the other abbreviations, reference is made to the explanations ("Guidance Notes on Codes and Abbreviations") at the beginning of each regular edition of the PCT Gazette.

As printed

(54) Title: PRODUCTION OF α -CHLOROISOPROPYL SUBSTITUTED AROMATICS

(54) Bezeichnung: HERSTELLUNG VON α -CHLORISOPROPYL-SUBSTITUIERTEN AROMATEN

(57) Abstract: α -Chloroisopropyl substituted aromatics are obtained in high yield by treatment of isopropenyl substituted aromatics with hydrogen chloride gas in the absence of a solvent. The α -chloroisopropyl substituted aromatics serve as initiators for the cationic polymerisation of isobutene.

(57) Zusammenfassung: α -Chlorisopropyl-substituierte Aromaten werden in hoher Ausbeute durch Behandeln von Isopropenyl-substituierten Aromaten mit Chlorwasserstoffgas in Abwesenheit eines Lösungsmittels erhalten. Die α -Chlorisopropyl-substituierten Aromaten dienen als Initiatoren für die kationische Polymerisation von Isobuten.

WO 03/070674 A1

Preparation of α -chloroisopropyl-substituted aromatics

The present invention relates to a process for preparing
 5 α -chloroisopropyl-substituted aromatics.

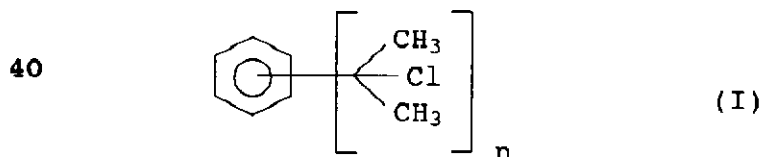
- α -Chloroisopropyl-substituted aromatics, such as m- or p-dicumyl chloride or 1,3,5-tricumyl chloride, served as inifer molecules for preparing linear or star-shaped telechelic polyisobutenes.
- 10 The reaction of the inifer with a Lewis acid results in a complex having 2 or 3 carbocationic or cationogenic centers which can add onto isobutene molecules. The carbocationic tert-butyl termini of the linear or star-shaped polyisobutenes obtained may be converted to olefinic or other functional groups, cf., for
 15 example, EP-A 0 713 883.

- J.P. Kennedy, L.R. Ross, J.E. Lackey, O. Nuyken, Polym. Bull. 1981, 4, 67-74 describe the synthesis of 1,3,5-tris(α -chloroisopropylbenzene) by reacting
 20 1,3,5-triisopropenylbenzene with hydrogen chloride in dichloromethane at 0°C. For the workup, the dichloromethane has to be distilled off.

- On the other hand, O. Nuyken, G. Maier, D. Young, M.B. Leitner, 25 Macromol. Chem., Macromol. Symp. 60, (1992) 57-63 disclose that 1,4-diisopropenylbenzene forms a polymer having 1,1,3-trimethylindane or α -methylstyrene repeating units under the influence of Lewis or Brönsted acids.

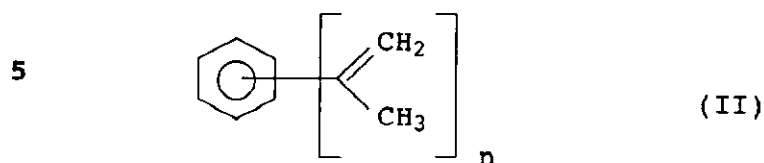
- 30 It is an object of the present invention to provide a process by which α -chloroisopropyl-substituted aromatics is obtained in high yield and with simple workups.

- We have found that this object is achieved by a process for
 35 preparing α -chloroisopropyl-substituted aromatics of the formula
 I



where n is an integer from 2 to 4

by treating isopropenyl-substituted aromatics of the formula II



10 with hydrogen chloride in the absence of a solvent.

The process according to the invention allows α -chloroisopropyl-substituted aromatics to be obtained in virtually quantitative yields. This is surprising to a high
15 degree, since those skilled in the art would have expected a reaction in the absence of a solvent to result in the occurrence of numerous undesired secondary reactions or the cationic polymerization of the isopropenyl-substituted aromatics (cf. O. Nuyken et al., loc. cit.). The success of the process according
20 to the invention is believed to be based on the instability of carbocations, from which undesired secondary reactions or polymerizations can start, in the absence of a solvent, in particular of a polar solvent.

25 The process according to the invention can be carried out in a simple manner by passing hydrogen chloride gas through the isopropenyl-substituted aromatics or by reacting it therewith in a pressure vessel. This utilizes the fact that both the reactant and the product of the process according to the invention are
30 liquid at reaction temperature and that the use of a solvent is unnecessary. The workup is generally limited to the removal of excess hydrogen chloride gas from the product, for example by stripping with inert gas such as nitrogen. Yield losses resulting from workup steps are avoided.

35 The process according to the invention is preferably effected at a temperature of from -10 to $+50^{\circ}\text{C}$, in particular from 0 to 15°C , and a pressure from 1 to 10 bar. It may be carried out batchwise or continuously.

40 The reaction may optionally be accelerated by using Lewis or Brönsted acid catalysts. Useful catalysts include Lewis acids such as aluminum trichloride, aluminum tribromide, boron trifluoride, boron trifluoride alkoxide, boron trifluoride
45 etherate, titanium tetrachloride, tin tetrachloride, ethylaluminum dichloride, iron trichloride, antimony pentachloride or antimony pentafluoride; Brönsted acids such as

3

sulfuric acid, phosphoric acid, trifluoromethanesulfonic acid and the like. Organic protic acids may also be present in polymerically bound form, for example as ion exchanger resins.

- 5 In the formulae I and II, n is preferably 2 or 3. Preferred isopropenyl-substituted aromatics are 1,3,5-triisopropenylbenzene, 1,4-diisopropenylbenzene and 1,3-diisopropenylbenzene, and particular preference is given to the latter. Apart from the isopropenyl substituents, the benzene
10 ring may bear further substituents which do not impair the reaction according to the invention, in particular C₁-C₄-alkyl radicals such as methyl, ethyl or t-butyl. Useful reactants for the process according to the invention also include mixtures of different isopropenyl-substituted aromatic.
15 The isopropenyl-substituted aromatics used as reactants are known and obtainable, for example, by dehydrating α -hydroxyl-substituted aromatics (cf. DE-A 1 618 449), Wittig reaction of acetylbenzenes (cf. J.P. Kennedy et al., Polym. Bull. 20 1981, 4, 67-74) or by dehydrogenating isopropylbenzenes (cf. JP-2001026558 and JP-2000327596).

- The α -chloroisopropyl-substituted aromatics obtained by the process according to the invention can be used in a manner known
25 per se for preparing homopolymers of isobutene or copolymers of isobutene with vinylaromatics by living cationic polymerization. On this subject, reference is made, for example, to EP-A 0 713 883, DE-A 199 37 562 or DE-A 100 61 715.

- 30 The invention is illustrated by the examples which follow.

Example 1:

- A 1 l four-necked flask was initially charged with 500 g
35 (3.16 mol) of 1,3-diisopropenylbenzene. 290 g (7.95 mol) of hydrogen chloride were passed in within 7.5 h with cooling to an internal temperature of 5°C and at atmospheric pressure. Unconverted HCl was then removed by stripping with nitrogen. 715 g (98%) of 1,3-bis(α -chloroisopropyl)benzene remained as a
40 colorless liquid; chlorine content 29.3%; ¹H-NMR (CD₂Cl₂, 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

Example 2:

- 45 A 500 ml four-necked flask was initially charged with 200 g (1.26 mol) of 1,3-diisopropenylbenzene. 135 g (3.70 mol) of

hydrogen chloride were passed in within 8 h with cooling to an internal temperature of 5°C and at atmospheric pressure.

Unconverted HCl was then removed under reduced pressure. 288 g (99%) of 1,3-bis(α -chloroisopropyl)benzene remained as a

- 5 colorless liquid; chlorine content 28.6%; $^1\text{H-NMR}$ (CD_2Cl_2 , 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

Comparative Example 3:

10

A 2 l four-necked flask was initially charged with 200 g (1.26 mol) of 1,3-diisopropenylbenzene in 750 ml of CH_2Cl_2 and this was then admixed with about 1 ml of ethanol. 12.5 g (3.42 mol) of hydrogen chloride were passed in within 7 h with cooling

- 15 to an internal temperature of 5°C and at atmospheric pressure. The solvent and also unconverted HCl was then removed under reduced pressure. 264 g (90%) of 1,3-bis(α -chloroisopropyl)benzene remained as a colorless liquid; chlorine content 29.2%; $^1\text{H-NMR}$ (CD_2Cl_2 , 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

Example 4:

An autoclave was initially charged with 490 g (3.10 mol) of

- 25 1,3-diisopropenylbenzene. 200 g (5.6 mol) of HCl were metered in within 3 h in such a manner that the internal pressure was 5 bar and the internal temperature did not exceed 30°C. The remaining HCl was removed by stripping with nitrogen. 705 g (99%) of 1,3-bis(α -chloroisopropyl)benzene were obtained as a colorless
- 30 liquid; chlorine content 30.6%; $^1\text{H-NMR}$ (CD_2Cl_2 , 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

Example 5:

35

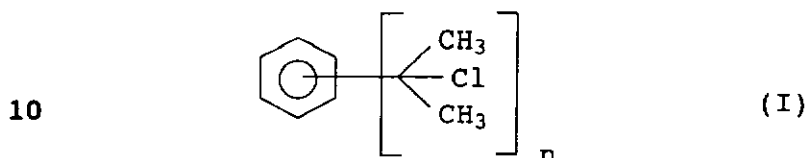
A 40 l V4A steel stirred reactor was initially charged with 18.0 kg (114 mol) of 1,3-diisopropenylbenzene. 10.1 kg (277 mol) of hydrogen chloride were passed in within 8 h at an internal temperature of 5-10°C (brine cooling) and an internal pressure of

- 40 1.1 bar. The remaining HCl was removed by stripping with nitrogen. 26 kg (99%) of 1,3-bis(α -chloroisopropyl)benzene were obtained as a colorless liquid; chlorine content 30.1%; $^1\text{H-NMR}$ (CD_2Cl_2 , 360 MHz): 2.00 (s, 12 H, methyl), 7.29-7.52 (m, 3 H, aromat. H), 7.82-7.83 (m, 1 H, aromat. H).

45

We claim:

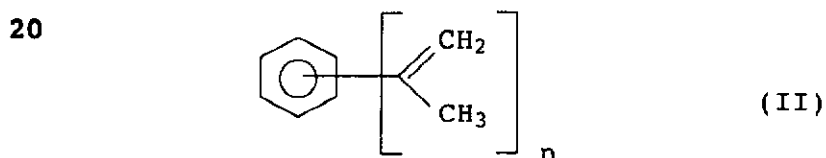
1. A process for preparing α -chloroisopropyl-substituted aromatics of the formula I



where n is an integer from 2 to 4

15

by treating isopropenyl-substituted aromatics of the formula II



25

with hydrogen chloride in the absence of a solvent.

30

2. A process as claimed in claim 1, wherein the treatment is effected at a temperature of from -10 to 50°C.
3. A process as claimed in claim 1 or 2, wherein the treatment is effected at a pressure of from 1 to 10 bar.
4. A process as claimed in any of the preceding claims, wherein 1,3-diisopropenylbenzene is used as isopropenyl-substituted aromatic of the formula II.

35

40

45

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/01877

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C17/08 C07C22/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, BEILSTEIN Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KENNEDY, JOSEPH P. ET AL: "New telechelic polymers and sequential copolymers by polyfunctional initiator-transfer agents (inifers). 10. Three-arm star telechelic polyisobutylenes carrying chlorine, olefin, or primary alcohol endgroups" POLYMER BULLETIN (BERLIN, GERMANY) (1981), 4(1-2), 67-74 , XP001149000 cited in the application page 72 -/-	1-4

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

13 May 2003

Date of mailing of the international search report

27/05/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5816 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bonnevalle, E

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/01877

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SCHAPPACHER, M. ET AL: "Activated.alpha.-chloro ether and.alpha.-bromo ether end groups as propagating species for the living cationic polymerization of vinyl ethers" MACROMOLECULES (1991), 24(8), 2140-2 , XP001151839 page 2140	1-4
Y	CHEMICAL ABSTRACTS, vol. 107, no. 15, 12 October 1987 (1987-10-12) Columbus, Ohio, US; abstract no. 134023, SERGEEV, G. B. ET AL: "Mixture of o- and p-isomers of bis(.alpha.-chloroethyl)benzene" XP002240897 abstract & SU 1 286 586 A (MOSCOW STATE UNIVERSITY, USSR) 30 January 1987 (1987-01-30)	1-4
Y	US 3 024 291 A (OLAH GEORGE A ET AL) 6 March 1962 (1962-03-06) claims	1-4
Y	US 4 241 222 A (MACLEAY RONALD E) 23 December 1980 (1980-12-23) example 1	1-4
Y	US 5 300 717 A (ROEHRSCHIED FREIMUND) 5 April 1994 (1994-04-05) column 6	1-4

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/01877

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
SU 1286586	A	30-01-1987	SU 1286586 A1	30-01-1987
US 3024291	A	06-03-1962	NONE	
US 4241222	A	23-12-1980	BR 8005828 A	24-03-1981
			DE 3034234 A1	02-04-1981
			JP 1516617 C	07-09-1989
			JP 56046864 A	28-04-1981
			JP 63064423 B	12-12-1988
US 5300717	A	05-04-1994	DE 59303534 D1	02-10-1996
			EP 0564979 A2	13-10-1993
			JP 6048966 A	22-02-1994

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
IPK 7 C07C17/08 C07C22/04

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)

IPK 7 C07C

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

CHEM ABS Data, EPO-Internal, BEILSTEIN Data, WPI Data, PAJ

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
Y	KENNEDY, JOSEPH P. ET AL: "New telechelic polymers and sequential copolymers by polyfunctional initiator-transfer agents (inifers). 10. Three-arm star telechelic polyisobutylenes carrying chlorine, olefin, or primary alcohol endgroups" POLYMER BULLETIN (BERLIN, GERMANY) (1981), 4(1-2), 67-74 , XP001149000 in der Anmeldung erwähnt Seite 72 --- -/-	1-4

☒ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

☒ Siehe Anhang Patentfamilie

* Besondere Kategorien von angegebenen Veröffentlichungen :

A Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist

E älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist

L Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt)

O Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht

P Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist

T Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angegeben ist

X Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann allein aufgrund dieser Veröffentlichung nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden

Y Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist

Z Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche

13. Mai 2003

Absenddatum des internationalen Recherchenberichts

27/05/2003

Name und Postanschrift der internationalen Recherchenbehörde

Europäisches Patentamt, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Bevollmächtigter Bediensteter

Bonnevalle, E

G.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
Y	SCHAPPACHER, M. ET AL: "Activated.alpha.-chloro ether and.alpha.-bromo ether end groups as propagating species for the living cationic polymerization of vinyl ethers" MACROMOLECULES (1991), 24(8), 2140-2 , XP001151839 Seite 2140	1-4
Y	--- CHEMICAL ABSTRACTS, vol. 107, no. 15, 12. Oktober 1987 (1987-10-12) Columbus, Ohio, US; abstract no. 134023, SERGEEV, G. B. ET AL: "Mixture of o- and p-isomers of bis(.alpha.-chloroethyl)benzene" XP002240897 Zusammenfassung & SU 1 286 586 A (MOSCOW STATE UNIVERSITY, USSR) 30. Januar 1987 (1987-01-30)	1-4
Y	--- US 3 024 291 A (OLAH GEORGE A ET AL) 6. März 1962 (1962-03-06) Ansprüche	1-4
Y	--- US 4 241 222 A (MACLEAY RONALD E) 23. Dezember 1980 (1980-12-23) Beispiel 1	1-4
Y	--- US 5 300 717 A (ROEHRSCHEID FREIMUND) 5. April 1994 (1994-04-05) Spalte 6	1-4

INTERNATIONALER RECHERCHENBERICHT

internationales Aktenzeichen

PCT/EP 03/01877

Im Recherchenbericht angeführtes Patentdokument		Datum der Veröffentlichung	Mitglied(er) der Patentfamilie		Datum der Veröffentlichung
SU 1286586	A	30-01-1987	SU	1286586 A1	30-01-1987
US 3024291	A	06-03-1962	KEINE		
US 4241222	A	23-12-1980	BR	8005828 A	24-03-1981
			DE	3034234 A1	02-04-1981
			JP	1516617 C	07-09-1989
			JP	56046864 A	28-04-1981
			JP	63064423 B	12-12-1988
US 5300717	A	05-04-1994	DE	59303534 D1	02-10-1996
			EP	0564979 A2	13-10-1993
			JP	6048966 A	22-02-1994