

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

(19) World Intellectual Property  
Organization  
International Bureau



(10) International Publication Number  
**WO 2014/004419 A1**

(43) International Publication Date  
3 January 2014 (03.01.2014)

(51) International Patent Classification:

*C08L 27/12* (2006.01)    *C08K 5/24* (2006.01)  
*C08K 5/3465* (2006.01)    *C08F 214/26* (2006.01)

(21) International Application Number:

PCT/US2013/047457

(22) International Filing Date:

25 June 2013 (25.06.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/531,697    25 June 2012 (25.06.2012)    US

(71) Applicant: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventors: **BISH, Christopher, J.**; 112 Quail Lane, Kennett Square, Pennsylvania 19348 (US). **MORKEN, Peter, A.**; 6 Weilers Bend, Wilmington, Delaware 19810 (US).

(74) Agent: **KIRVAN, George, E.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))



WO 2014/004419 A1

(54) Title: CURABLE FLUROELASTOMER COMPOSITION

(57) Abstract: Fluoroelastomer compositions comprising fluoroelastomers having copolymerized units of a nitrile-containing cure site monomer are cured with a phthalhydrazide hydrazine or hydroxylamine salt curative.

**TITLE OF INVENTION****CURABLE FLUROELASTOMER COMPOSITION**

5

**FIELD OF THE INVENTION**

This invention relates to curable fluoroelastomer compositions and more particularly to fluoroelastomer compositions containing certain phthalhydrazide salts as curing agents.

**BACKGROUND OF THE INVENTION**

10

Fluoroelastomers have achieved outstanding commercial success and are used in a wide variety of applications in which severe environments are encountered, in particular those end uses where exposure to high temperatures and aggressive chemicals occurs. For example, these polymers are often used in seals for aircraft engines, in oil-  
15 well drilling devices, and in sealing elements for industrial equipment that operates at high temperatures.

20

The outstanding properties of fluoroelastomers are largely attributable to the stability and inertness of the copolymerized fluorinated monomer units that make up the major portion of the polymer backbones  
20 in these compositions. Such monomers include vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene and perfluoro(alkyl vinyl) ethers. In order to develop elastomeric properties fully, fluoroelastomers are typically crosslinked, i.e. vulcanized. To this end, a small percentage of cure site monomer is copolymerized with the fluorinated monomer units.  
25 Cure site monomers containing at least one nitrile group, for example perfluoro-8-cyano-5-methyl-3,6-dioxa-1-octene, are especially preferred. Such compositions are described in U.S. Patents 4,281,092; 4,394,489; 5,789,489; 5,789,509 and in WO 2011084404.

30

Bisamidoximes (U.S. Patent 5,668,221) and bisamidrazones (U.S. Patents 5,605,973; 5,637,648) have been used as vulcanizing agents for fluoroelastomers having nitrile group cure sites. These cures may be

scorchy, i.e. crosslinking may begin before the final shaping of the composition. Also, the curatives require complex, multistep syntheses from expensive starting materials.

5 Other nitrogen containing nucleophilic compounds have been employed to crosslink fluoroelastomers having nitrile group cure sites (U.S. Patent 6,638,999 B2). Some of these curatives are scorchy while others are volatile at rubber milling temperatures.

10 Fluoropolymers having pendant amidrazone or amidoxime groups are also known (U.S. Patent 7,300,985 B2). These polymers require an additional polymer modification step in order to form crosslinks.

### **SUMMARY OF THE INVENTION**

15 The present invention is directed to curable fluoroelastomer compositions which comprise a fluoroelastomer having nitrile group cure sites and certain phthalhydrazide salts as curatives. More specifically, the present invention is directed to a curable composition comprising:

- A) a fluoroelastomer comprising copolymerized units of a nitrile group-containing cure site monomer; and
- 20 B) a phthalhydrazide salt of hydrazine or hydroxylamine.

Another aspect of the present invention is a cured article made from the above composition.

### **DETAILED DESCRIPTION OF THE INVENTION**

25 The fluoroelastomer that may be employed in the composition of the invention may be partially fluorinated or perfluorinated. Fluoroelastomers preferably contain between 25 and 70 weight percent, based on the total weight of the fluoroelastomer, of copolymerized units of a first monomer which may be vinylidene fluoride (VF<sub>2</sub>) or

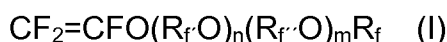
30 tetrafluoroethylene (TFE). The remaining units in the fluoroelastomers are comprised of one or more additional copolymerized monomers, different from said first monomer, selected from the group consisting of

fluoromonomers, hydrocarbon olefins and mixtures thereof.

Fluoromonomers include fluorine-containing olefins and fluorine-containing vinyl ethers.

5 Fluorine-containing olefins which may be employed to make fluoroelastomers include, but are not limited to vinylidene fluoride (VF<sub>2</sub>), hexafluoropropylene (HFP), tetrafluoroethylene (TFE), 1,2,3,3,3-pentafluoropropene (1-HPFP), 1,1,3,3,3-pentafluoropropene (2-HPFP), chlorotrifluoroethylene (CTFE) and vinyl fluoride.

10 Fluorine-containing vinyl ethers that may be employed to make fluoroelastomers include, but are not limited to perfluoro(alkyl vinyl) ethers. Perfluoro(alkyl vinyl) ethers (PAVE) suitable for use as monomers include those of the formula



15 where R<sub>f</sub> and R<sub>f'</sub> are different linear or branched perfluoroalkylene groups of 2-6 carbon atoms, m and n are independently 0-10, and R<sub>f</sub> is a perfluoroalkyl group of 1-6 carbon atoms.

A preferred class of perfluoro(alkyl vinyl) ethers includes compositions of the formula



where X is F or CF<sub>3</sub>, n is 0-5, and R<sub>f</sub> is a perfluoroalkyl group of 1-6 carbon atoms.

A most preferred class of perfluoro(alkyl vinyl) ethers includes those ethers wherein n is 0 or 1 and R<sub>f</sub> contains 1-3 carbon atoms. Examples of  
25 such perfluorinated ethers include perfluoro(methyl vinyl ether) (PMVE), perfluoro(ethyl vinyl ether) (PEVE) and perfluoro(propyl vinyl ether) (PPVE). Other useful monomers include those of the formula



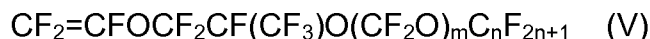
where R<sub>f</sub> is a perfluoroalkyl group having 1-6 carbon atoms,  
30 m = 0 or 1, n = 0-5, and Z = F or CF<sub>3</sub>. Preferred members of this class are those in which R<sub>f</sub> is C<sub>3</sub>F<sub>7</sub>, m = 0, and n = 1.

Additional perfluoro(alkyl vinyl) ether monomers include compounds of the formula



5 where  $m$  and  $n$  independently = 0-10,  $p$  = 0-3, and  $x$  = 1-5. Preferred members of this class include compounds where  $n$  = 0-1,  $m$  = 0-1, and  $x$  = 1.

Other examples of useful perfluoro(alkyl vinyl ethers) include

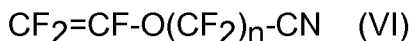


10 where  $n$  = 1-5,  $m$  = 1-3, and where, preferably,  $n$  = 1.

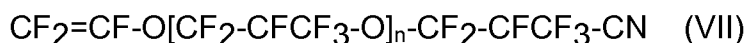
If copolymerized units of PAVE are present in fluoroelastomers employed in the invention, the PAVE content generally ranges from 25 to 75 weight percent, based on the total weight of the fluoroelastomer. If perfluoro(methyl vinyl ether) is used, then the fluoroelastomer preferably  
 15 contains between 30 and 65 wt.% copolymerized PMVE units.

Hydrocarbon olefins useful in the fluoroelastomers employed in the invention include, but are not limited to ethylene and propylene. If copolymerized units of a hydrocarbon olefin are present in the fluoroelastomers, hydrocarbon olefin content is generally 4 to 30 weight  
 20 percent.

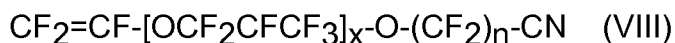
The fluoroelastomer further contains copolymerized units of at least one cure site monomer, generally in amounts of from 0.1-5 mole percent. The range is preferably between 0.3-1.5 mole percent. Although more than one type of cure site monomer may be present, most commonly one  
 25 cure site monomer is used and it contains at least one nitrile substituent group. Suitable cure site monomers include nitrile-containing fluorinated olefins and nitrile-containing fluorinated vinyl ethers. Useful nitrile-containing cure site monomers include those of the formulas shown below.



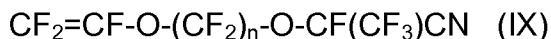
30 where  $n$  = 2-12, preferably 2-6;



where  $n$  = 0-4, preferably 0-2;

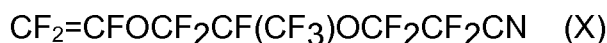


where  $x = 1-2$ , and  $n = 1-4$ ; and



5 where  $n = 2-4$ .

Those of formula (VIII) are preferred. Especially preferred cure site monomers are perfluorinated polyethers having a nitrile group and a trifluorovinyl ether group. A most preferred cure site monomer is



10 i.e. perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene) or 8-CNVE.

A first aspect of this invention is a curable composition comprising A) a fluoroelastomer comprising copolymerized units of a nitrile group containing cure site monomer; and B) a phthalhydrazide salt of hydrazine or hydroxylamine.

15 The phthalhydrazide may optionally contain one or more functional groups on the aromatic ring, e.g. hydrocarbon groups, halogens, nitriles, ethers, aromatic groups, amines, esters, nitro groups or sulfones. Also one of the phthalhydrazide N-H groups may be optionally substituted by N-R where R is an alkyl or aryl group. The phthalhydrazide may be a mono-,  
20 di-, or poly-hydrazide.

Phthalhydrazide salts of hydrazine or hydroxylamine may be made by treatment of phthalhydrazide with hydrazine or hydroxylamine in a solvent followed by isolation of the salt.

25 It is theorized that these phthalhydrazide salts act as curing agents by causing the dimerization of polymer chain bound nitrile groups to form 1,2,4-triazole or oxadiazole rings, thus crosslinking the fluoroelastomer. The phthalhydrazide salts are less volatile than curatives such as hydrazine or t-butyl carbazate, making the phthalhydrazide salt curatives less likely to be fugitive during mixing and shaping processes.

30 In order to be useful as either the major, or as the only curative for these fluoroelastomers, the level of phthalhydrazide salt should be about 0.05 to 7 parts phthalhydrazide salt per 100 parts fluoroelastomer,

preferably about 0.1 to 3 parts phthalhydrazide salt per 100 parts  
fluoroelastomer, most preferably about 0.5 to 2 parts phthalhydrazide salt  
per 100 parts fluoroelastomer. As used herein, "parts" refers to parts by  
5 weight, unless otherwise indicated.

An appropriate level of phthalhydrazide salt can be selected by  
considering cure properties, for example the time to develop maximum  
moving die rheometer (MDR) torque and minimum Mooney scorch of the  
curable compositions. The optimum level will depend on the particular  
10 combination of fluoroelastomer and phthalhydrazide salt.

Optionally, a curative accelerator, e.g. a compound that releases  
ammonia at curing temperatures, may be used in combination with a  
phthalhydrazide salt curative. Examples of compounds that decompose to  
release ammonia at curing temperatures include those disclosed in U.S.  
15 6,281,296 B1 and U.S. 2011/0009569.

Optionally, another curative commonly employed to crosslink  
fluoroelastomers having nitrile-group cure sites may be used in addition to  
the phthalhydrazide salt. Examples of such other curatives include, but  
are not limited to diaminobisphenol AF, 2,2-bis(3-amino-4-  
20 anilinophenyl)hexafluoropropane, mono- or bis-amidines, mono- or bis-  
amidrazones, mono- or bis-amidoximes, or an organic peroxide plus  
coagent.

Additives, such as carbon black, fluoropolymer micropowders,  
stabilizers, plasticizers, lubricants, fillers, and processing aids typically  
25 utilized in fluoroelastomer compounding can be incorporated into the  
compositions of the present invention, provided they have adequate  
stability for the intended service conditions.

The curable compositions of the invention may be prepared by  
mixing the fluoroelastomer, phthalhydrazide salt and other components  
30 using standard rubber compounding procedures. For example, the  
components may be mixed on a two roll rubber mill, in an internal mixer  
(e.g. a Banbury® internal mixer), or in an extruder. The curable

compositions may then be crosslinked (i.e. cured) by application of heat and/or pressure. When compression molding is utilized, a press cure cycle is generally followed by a post cure cycle during which the press  
5 cured composition is heated at elevated temperatures in excess of 300°C for several hours.

The curable compositions of the present invention are useful in production of gaskets, tubing, and seals. Such cured articles are generally produced by molding a compounded formulation of the curable  
10 composition with various additives under pressure, curing the part, and then subjecting it to a post cure cycle. The cured compositions have excellent thermal stability, steam and chemical resistance. Volume swell (ASTM D1414) after exposure to 225°C water for at least 70 hours, preferably 168 hours, most preferably at least 336 hours, is less than 5%.  
15 Also compression set, 300°C, 70 hours, 25% compression (ASTM D395) is less than 70%. The cured compositions are particularly useful in applications such as seals and gaskets for manufacturing semiconductor devices, and in seals for high temperature automotive uses.

Other fluoropolymers containing nitrile cure sites, such as  
20 fluoroplastics may be substituted for fluoroelastomers in the compositions of the invention.

The invention is now illustrated by certain embodiments wherein all parts are by weight unless otherwise specified.

25

## **EXAMPLES**

### **TEST METHODS**

#### Cure Characteristics

Cure characteristics were measured using a Monsanto MDR 2000 instrument under the following conditions:

30

Moving die frequency: 1.66 Hz

Oscillation amplitude:  $\pm 0.5$  degrees

Temperature: 190°C, unless otherwise noted

Sample size: Disks having diameter of 1.5 inches (38 mm)

Duration of test: 30 minutes

5 The following cure parameters were recorded:

$M_H$ : maximum torque level, in units of dN·m

$M_L$ : minimum torque level, in units of dN·m

Tc90: time to 90% of maximum torque, minutes

10 Test specimens were prepared from elastomer compounded with appropriate additives, as described in the formulations listed in the Examples below. Compounding was carried out on a rubber mill. The milled composition was formed into a sheet and a 10 g sample was die cut into a disk to form the test specimen.

15 Compression set of O-ring samples was determined in accordance with ASTM D395. Mean values are reported.

Volume swell in water was measured at 225°C for the time  
20 indicated in the Tables in accordance with ASTM D1414

Thermogravimetric analysis (TGA) of curatives was carried out in a N<sub>2</sub> atmosphere from 20 to 350°C at a heating rate of 10 °C/min.

The following fluoroelastomer polymers were used in the Examples:

25 FFKM1 - A terpolymer containing 61.8 mole percent units of TFE, 37.4 mole percent units of PMVE and 0.80 mole percent units of 8-CNVE was prepared according to the general process described in U.S. Patent No. 5,789,489.

FFKM2 – FFKM1 polymer which has been heat treated at 275°C for 3  
30 hours in an air oven in order to at least partially decarboxylate the polymer endgroups.

The following curatives were prepared for use in the Examples.

### Hydrazine Phthalhydrazide

The general procedure from H. J. Barber et. al. Journal of the  
5 Chemical Society, 1948, page 1458 was followed. A 250 mL round  
bottom flask equipped with a magnetic stir bar and a condenser further  
attached to a N<sub>2</sub> source was charged with 10.0 g (61.7 mmol, available  
from Aldrich,) phthalhydrazide, 9.57g (191 mmol, available from Aldrich)  
hydrazine hydrate, and 60 mL of water. The mixture was heated to 90°C  
10 at which point it became substantially homogeneous, then filtered while  
warm. The filtrate was added to about 1L of ethanol then the precipitate  
was collected by filtration and dried in vacuo at room temperature to afford  
9.0 g (46 mmol, 75% yield) of fluffy, white powder. TGA analysis showed  
15.7 wt% loss by 150°C (16.5% is theoretical loss of hydrazine).

15

### Hydroxylamine Phthalhydrazide

A 500 mL round bottom flask equipped with a magnetic stir bar,  
dropping funnel, and a condenser further attached to a N<sub>2</sub> source was  
charged with 2.5 g (15 mmol, available from Aldrich,) phthalhydrazide and  
20 100 mL anhydrous DMF (available from Aldrich). The mixture was heated  
to 100°C to dissolve the phthalhydrazide, cooled to room temperature,  
then 3.0 g (45 mmol, available from Aldrich, 50 wt% in H<sub>2</sub>O)  
hydroxylamine was quickly added via the dropping funnel. The resultant  
clear, pale yellow solution was stirred 2 hours at room temperature, then  
25 precipitated by dropwise addition to 1L of toluene. The fine white powder  
was removed by filtration, washed with toluene, then dried in vacuo at  
room temperature to afford 2.9 g (15 mmol, 100% yield) of product. TGA  
analysis showed 16.9 wt% loss by 110°C (16.9% is theoretical loss of  
hydroxylamine).

30

### Examples 1-2

Curable compositions were compounded on a two-roll rubber mill in the proportions shown in Table I. The compounded compositions are labeled Example 1 (hydrazine phthalhydrazide) and Example 2  
5 (hydroxylamine phthalhydrazide) in Table I. Cure characteristics of the compounded compositions are also shown in Table I. O-rings were made by press curing the curable compositions at a temperature of 190°C for Tc90 plus 5 minutes, followed by a post cure in a nitrogen atmosphere at a temperature of 305°C for 26 hours after a slow temperature ramp up from  
10 room temperature. Compression set and volume swell values are also shown in Table I.

In order to compare volume swells of the compositions of the invention with a prior art composition, o-rings were made from a similar compound, but containing 0.25 phr urea as curative, rather than a  
15 phthalhydrazide salt. After only 168 hours of exposure to 225°C water, the urea cured o-rings exhibited a 15.7 % volume swell.

**TABLE I**

<u>Formulation</u> (phr <sup>1</sup> )	<u>Example 1</u>	<u>Example 2</u>
FFKM1	100	0
FFKM2	0	100
Carbon Black MT N990	30	30
Hydrazine phthalhydrazide	1.47	0
Hydroxylamine phthalhydrazide	0	1.48
<u>Cure</u> <u>Characteristics</u>		
M <sub>L</sub> (dN·m)	5.02	1.96
M <sub>H</sub> (dN·m)	19.8	7.46
Tc90, minutes	5.06	24
<u>Compression set</u> , 300°C, 70 hours, 25% compression, %	22	36
<u>Volume swell, 70</u> <u>hours, %</u>	1.1	1.8

<sup>1</sup>Parts by weight per hundred parts by weight fluoroelastomer

**CLAIMS****What is Claimed is:**

- 5 1. A curable composition comprising:  
A) a fluoroelastomer comprising copolymerized units of  
a nitrile group-containing cure site monomer; and  
B) a phthalhydrazide salt of hydrazine or hydroxylamine.
2. A curable composition of claim 1 wherein said phthalhydrazide salt  
10 is hydrazine phthalhydrazide.
3. A curable composition of claim 1 wherein said phthalhydrazide salt  
is hydroxylamine phthalhydrazide.
4. A curable composition of claim 1 further comprising a curative  
accelerator.
- 15 5. A curable composition of claim 1 further comprising a curative in  
addition to said phthalhydrazide salt.
6. A cured article made from the composition of claim 1.
7. A cured article of claim 6 having a volume swell, measured  
according to ASTM D1414, after exposure to 225°C water for at least 70  
20 hours of less than 5% and a compression set, 300°C, 70 hours, 25%  
compression, measured according to ASTM D395, of less than 70%.

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/US2013/047457

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C08L27/12 C08K5/3465 C08K5/24 C08F214/26  
 ADD.  
 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)  
 C08L C08K

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 practicable, search terms used)  
 EPO-Internal, WPI Data, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 727 413 A1 (NIPPON MEKTRON KK [JP]) 21 August 1996 (1996-08-21) claims 6-8	1-7
A	EP 0 373 973 A2 (AUSIMONT SRL [IT]) AUSIMONT SPA [IT]) 20 June 1990 (1990-06-20) example 1; table 1 claim 1	1-7
X,P	US 8 338 542 B1 (BISH CHRISTOPHER J [US]) ET AL) 25 December 2012 (2012-12-25) examples 1,2 claims	1-7

Further documents are listed in the continuation of Box C.

See patent family 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 application or patent 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 <b>3 September 2013</b>	Date of mailing of the international search report <b>26/09/2013</b>
--	---

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <b>Russell, Graham</b>
--	--

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/047457

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP 0727413	A1	21-08-1996	CN 1140705 A	22-01-1997
			DE 69602047 D1	20-05-1999
			DE 69602047 T2	09-09-1999
			EP 0727413 A1	21-08-1996
			JP 2770769 B2	02-07-1998
			JP H08217742 A	27-08-1996
			US 5621145 A	15-04-1997
			-----	
EP 0373973	A2	20-06-1990	AT 113306 T	15-11-1994
			AU 633289 B2	28-01-1993
			AU 4676489 A	21-06-1990
			CA 2005356 A1	16-06-1990
			CN 1043511 A	04-07-1990
			DE 68919063 D1	01-12-1994
			DE 68919063 T2	09-03-1995
			EP 0373973 A2	20-06-1990
			ES 2063148 T3	01-01-1995
			IT 1228054 B	27-05-1991
			JP 2807005 B2	30-09-1998
			JP H02214758 A	27-08-1990
			RU 2087497 C1	20-08-1997
			US 5399633 A	21-03-1995
			US 5502115 A	26-03-1996
ZA 8909527 A	31-10-1990			
-----				
US 8338542	B1	25-12-2012	NONE	
-----				