

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 July 2004 (22.07.2004)

PCT

(10) International Publication Number
WO 2004/060857 A1

(51) International Patent Classification⁷: C07C 303/22,
309/82, C25B 3/08

(21) International Application Number:
PCT/US2003/034920

(22) International Filing Date:
4 November 2003 (04.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/322,226 17 December 2002 (17.12.2002) US

(71) Applicant: 3M INNOVATIVE PROPERTIES COM-
PANY [US/US]; 3M Center, Post Office Box 33427, Saint
Paul, MN 55133-3427 (US).

(72) Inventor: GUERRA, Miguel A.,; Post Office Box 33427,
Saint Paul, MN 55133-3427 (US).

(74) Agents: DAHL, Phillip Y., et al.; Office of Intellectual
Property Counsel, Post Office Box 33427, Saint Paul, MN
55133-3427 (US).

(81) Designated States (national): AE, AG, AL, AM, AT (util-
ity model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA,

CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (util-
ity model), DE, DK (utility model), DK, DM, DZ, EC, EE
(utility model), EE, EG, ES, FI (utility model), 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, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU,
SC, SD, SE, SG, SK (utility model), SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (BW, 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, RO, SE,
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PREPARATION OF PERFLUORINATED VINYL ETHERS HAVING A SULFONYL FLUORIDE END-GROUP

(57) Abstract: A method is provided for making a perfluorinated vinyl ether having a sulfonyl fluoride end-group according to the formula FSO₂(CF₂)_nO-CF=CF₂, where n is 2-5, comprising the steps of: a) fluorination of: (PLEASE INSERT THE CHEMICAL FORMULA HERE AS IT APPEARS IN THE PAPER COPY) to produce FSO₂(CF₂)_{n-1}COF; b) reaction of FSO₂(CF₂)_{n-1}COF with hexafluoropropylene oxide (HFPO) to produce FSO₂(CF₂)_nO-CF(CF₃)-COF; c) reaction of FSO₂(CF₂)_nO-CF(CF₃)-COF with a salt of a metal cation M_p, where p is the valence of M, to produce (FSO₂(CF₂)_nO-CF(CF₃)-COO)_pM_p; and d) thermal cracking of FSO₂(CF₂)_nO-CF(CF₃)-COO)_pM_p to produce FSO₂(CF₂)_nO-CF=CF₂.



WO 2004/060857 A1

**Preparation Of Perfluorinated Vinyl Ethers
having a Sulfonyl Fluoride End-Group**

5

Field of the Invention

This invention relates to a four-step method for preparation of perfluorinated vinyl ethers having sulfonyl fluoride end-groups according to the formula FSO₂-
10 (CF₂)_n-O-CF=CF₂, where n is 2-5, which are an important class of monomers in the synthesis of ion exchange resins.

Background of the Invention

US 4,749,526 discloses preparations for fluoroaliphatic ether-containing
15 carbonyl fluoride compounds by reacting a fluorinated carbonyl compound with hexafluoropropylene oxide in the presence of at least one catalyst selected from potassium iodide, potassium bromide, cesium iodide, cesium bromide, rubidium iodide and rubidium bromide.

US 5,902,908 discloses a method for preparing a fluorinated vinyl ether by
20 reacting a fluorinated carboxylic acid halogenide with a metal compound below the decomposition temperature for the corresponding metal salt in the absence of solvent and then raising the temperature of the produced corresponding metal salt above the decomposition temperature.

US 6,255,536, discloses a process for the preparation of a perfluorinated vinyl
25 ether of the formula CF₂=CF-O-R_f wherein R_f is a linear, branched or cyclic perfluorinated aliphatic group that may contain oxygen atoms thereby forming additional ether linkages.

Summary of the Invention

Briefly, the present invention provides a method of making a perfluorinated vinyl ether having a sulfonyl fluoride end-group according to the formula $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF=CF}_2$, where n is 2-5, comprising the steps of: a) fluorination of:



5

to produce $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)}\text{-COF}$; b) reaction of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)}\text{-COF}$ with hexafluoropropylene oxide (HFPO) to produce $\text{FSO}_2\text{-(CF}_2\text{)}_{(n)}\text{-O-CF(CF}_3\text{)-COF}$; c) reaction of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n)}\text{-O-CF(CF}_3\text{)-COF}$ with a salt of a metal cation M^{+p} , where p is the valence of M, to produce $(\text{FSO}_2\text{-(CF}_2\text{)}_{(n)}\text{-O-CF(CF}_3\text{)-COO}^-)_p\text{M}^{+p}$; and
10 d) thermal cracking of $(\text{FSO}_2\text{-(CF}_2\text{)}_{(n)}\text{-O-CF(CF}_3\text{)-COO}^-)_p\text{M}^{+p}$ to produce $\text{FSO}_2\text{-(CF}_2\text{)}_{(n)}\text{-O-CF=CF}_2$.

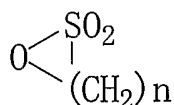
15

It is an advantage of the present invention to provide a convenient and efficient method for preparation of perfluorinated vinyl ethers having sulfonyl fluoride end-groups according to the formula $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF=CF}_2$, which uniquely adapted to the case where n is 2-5, and especially the case where n is 4, these species being important monomers in the synthesis of ion exchange resins. It is a further advantage of the present invention to provide a method for preparation of perfluorinated vinyl ethers having sulfonyl fluoride end-groups according to the formula $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF=CF}_2$, where n is 2-5, which does not require the use of tetrafluoroethylene (TFE),
20 with its associated hazards and difficulty.

Detailed Description of Preferred Embodiments

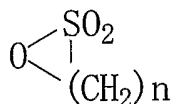
Briefly, the present invention provides a method of making a perfluorinated vinyl ether having a sulfonyl fluoride end-group according to the formula $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF=CF}_2$, where n is 2-5, comprising the steps of: a) fluorination of:

25



to produce $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)\text{-COF}}$; b) reaction of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)\text{-COF}}$ with hexafluoropropylene oxide (HFPO) to produce $\text{FSO}_2\text{-(CF}_2\text{)}_{(n)\text{-O-CF(CF}_3\text{)-COF}$; c) reaction of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n)\text{-O-CF(CF}_3\text{)-COF}$ with a salt of a metal cation M^{+p} , where p is the valence of M, to produce $(\text{FSO}_2\text{-(CF}_2\text{)}_{(n)\text{-O-CF(CF}_3\text{)-COO}^-)_p\text{M}^{+p}$; and d) thermal cracking of $(\text{FSO}_2\text{-(CF}_2\text{)}_{(n)\text{-O-CF(CF}_3\text{)-COO}^-)_p\text{M}^{+p}$ to produce $\text{FSO}_2\text{-(CF}_2\text{)}_{(n)\text{-O-CF=CF}_2$. The value of n is 2-5, typically 3-4, and most typically 4. The value of p is typically 1 or 2, and most typically 1. The salt of a metal cation M^{+p} is most typically Na_2CO_3 .

Step a) involves fluorination of a sultone, which is a 4-7 member ring according to the formula:



where n is 2-5, to produce $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)\text{-COF}}$. Fluorination may be accomplished by any suitable means, but is most typically accomplished by electrochemical fluorination as described in U.S. Pat. No. 2,732,398.

Step b) involves reaction of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)\text{-COF}}$ with hexafluoropropylene oxide (HFPO) to produce $\text{FSO}_2\text{-(CF}_2\text{)}_{(n)\text{-O-CF(CF}_3\text{)-COF}$. Step b) may be accomplished by any suitable means, but is typically accomplished by addition of HFPO to a solution of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)\text{-COF}}$ in a suitable polar solvent such diglyme. Typically, a catalyst is present. The catalyst is typically a fluoride catalyst, most typically KF. The reaction may be performed in the absence of any catalyst other than a fluoride catalyst. Typically, HFPO is added in a molar amount that does not exceed the molar amount of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)\text{-COF}}$ present. More typically, the molar amount of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)\text{-COF}}$ present remains in excess of the molar amount of HFPO present by at least 10%, more typically 20%, and more typically 30%. Step b) may be accomplished by methods disclosed in copending U.S. patent application 10/322,254 (Attorney Docket No. 57659US002), filed on even date herewith.

Step c) involves reaction of $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF(CF}_3\text{)-COF}$ with a salt of a metal cation M^{+p} , where p is the valence of M , to produce $\text{(FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF(CF}_3\text{)-COO}^-)_p\text{M}^{+p}$. The valence p may be any valence but is typically 1 or 2 and most typically 1. M may be any suitable metal, but is typically selected from Na , K , Rb and Cs and is most typically Na . The anion of the salt is any suitable anion, but typically one that is not so basic as to remove the fluorine from the sulfonyl fluoride function. The salt of a metal cation M^{+p} is most typically Na_2CO_3 . Step c) is typically carried out in a polar solvent, such as glyme, diglyme, and the like. Step c) is typically carried out at elevated temperature, typically between 40 and 100 °C.

Step d) involves thermal cracking of $\text{(FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF(CF}_3\text{)-COO}^-)_p\text{M}^{+p}$ to produce $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF=CF}_2$, after removal of solvent. Any heat source sufficient to raise the temperature of produce $\text{(FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF(CF}_3\text{)-COO}^-)_p\text{M}^{+p}$ to its decomposition temperature may be used. Decomposition temperatures vary with reactants, but will typically fall between 160 °C and 210 °C. Typically, any remaining solvent is removed prior to thermal cracking, typically by application of vacuum or reduced pressure. The product may then be collected, isolated and purified by any suitable means.

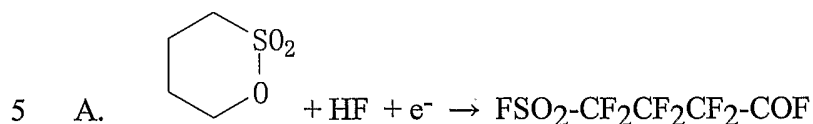
It will be appreciated that isolation and purification of reaction products may be desirable following one or more of the steps of the present method.

This invention is useful in the synthesis of perfluorinated vinyl ethers having sulfonyl fluoride end-groups, which are an important class of monomers in the synthesis of ion exchange resins.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

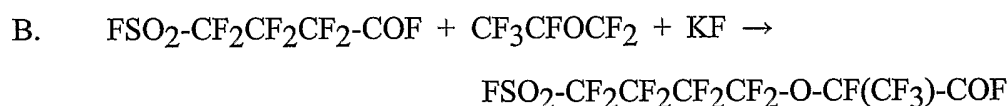
Example

Unless otherwise noted, all reagents were obtained or are available from Aldrich Chemical Co., Milwaukee, WI, or may be synthesized by known methods.

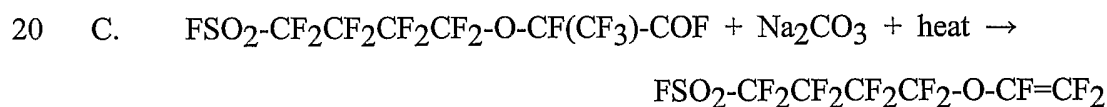


1,4-Butane sultone (6900g, 50.7m) was electrochemically fluorinated in HF as described in U.S. Pat. No. 2,732,398 to give 4-(fluorosulfonyl)hexafluorobutyryl fluoride, FSO₂(CF₂)₃COF (4000g, 14.3m for a 28% yield).

10



2162g (7.7m) of 4-(fluorosulfonyl) hexafluorobutyryl fluoride, FSO₂(CF₂)₃COF, was reacted with an equimolar amount of hexafluoropropylene oxide (HFPO) (1281g, 7.7m) in 2L diglyme with 114g potassium fluoride to give perfluoro-4-(fluorosulfonyl)butoxypropionyl fluoride (2250g, 5.1m for a 65% yield) and 675g of a higher boiling byproduct that had an additional hexafluoropropylene oxide unit.



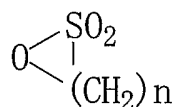
1108g (2.5m) of perfluoro-4-(fluorosulfonyl)butoxypropionyl fluoride was then reacted with sodium carbonate (603g, 5.7m) in glyme at 70 °C to make the sodium salt of the acid. Solvent was then removed under vacuum and the dried salt was heated to 165 °C to break vacuum with the carbon dioxide byproduct and continuing to heat up to 182 °C to isolate perfluoro-4-(fluorosulfonyl)butoxyvinyl ether (703g, 1.9m for a 74% yield).

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and principles of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth hereinabove.

We claim:

1. A method of making a perfluorinated vinyl ether having a sulfonyl fluoride end-group according to the formula $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF=CF}_2$, where n is 2-5, comprising the steps of:

5 a) fluorination of:



to produce $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)}\text{-COF}$;

b) reaction of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)}\text{-COF}$ with hexafluoropropylene oxide (HFPO) to produce $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF(CF}_3\text{)-COF}$;

10 c) reaction of $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF(CF}_3\text{)-COF}$ with a salt of a metal cation M^{+p} , where p is the valence of M, to produce $(\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF(CF}_3\text{)-COO}^-)_p\text{M}^{+p}$; and

d) thermal cracking of $(\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF(CF}_3\text{)-COO}^-)_p\text{M}^{+p}$ to produce $\text{FSO}_2\text{-(CF}_2\text{)}_n\text{-O-CF=CF}_2$.

15

2. The method according to claim 1 wherein n=4.

3. The method according to claim 1 wherein step c) is performed in a polar solvent.

20

4. The method according to claim 1 wherein said salt of a metal cation is Na_2CO_3 .

5. The method according to claim 3 wherein said salt of a metal cation is Na_2CO_3 .

25

6. The method according to claim 1 wherein said step b) is performed in the presence of a fluoride catalyst.

7. The method according to claim 6 wherein said step b) is performed in the absence of any catalyst other than a fluoride catalyst.
8. The method according to claim 6 wherein said fluoride catalyst is KF.
- 5 9. The method according to claim 7 wherein said fluoride catalyst is KF.
10. The method according to claim 1 wherein, throughout said step b), the molar amount of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)\text{-COF}}$ present remains in excess of the molar amount of HFPO present by at least 10%.
- 10 11. The method according to claim 6 wherein, throughout said step b), the molar amount of $\text{FSO}_2\text{-(CF}_2\text{)}_{(n-1)\text{-COF}}$ present remains in excess of the molar amount of HFPO present by at least 10%.
- 15 12. The method according to claim 1 wherein said step a) comprises electrochemical fluorination.
13. The method according to claim 2 wherein said step a) comprises electrochemical fluorination.
- 20 14. The method according to claim 5 wherein said step a) comprises electrochemical fluorination.
- 25 15. The method according to claim 6 wherein said step a) comprises electrochemical fluorination.
16. The method according to claim 10 wherein said step a) comprises electrochemical fluorination.
- 30

17. The method according to claim 11 wherein said step a) comprises electrochemical fluorination.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/34920

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C303/22 C07C309/82 C25B3/08

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 C25B

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)

EPO-Internal, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 062 430 A (ASAHI KASEI KOGYO KK) 13 October 1982 (1982-10-13) examples 1-2	1-9, 12-15
Y	GB 2 051 831 A (ASAHI KASEI KOGYO KK) 21 January 1981 (1981-01-21) page 28, line 120 - page 30, line 107; pages 38-39, examples 2-3	1-9, 12-15
A	page 29, lines 64-76	10,11
Y	V.S. YUMINOV: RUSSIAN JOURNAL OF ORGANIC CHEMISTRY, vol. 31, no. 8, 1995, pages 1037-1039, XP001166914 the whole document	1-9, 12-15
	-/--	

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.

Z document member of the same patent family

Date of the actual completion of the international search

7 May 2004

Date of mailing of the international search report

14/05/2004

Name and mailing address of the ISA

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

Authorized officer

Van Amsterdam, L

INTERNATIONAL SEARCH REPORT

tional Application No PCT/US 03/34920
--

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 749 526 A (R.M. FLYNN) 7 June 1988 (1988-06-07) cited in the application example 11 -----	1
A	US 5 902 908 A (S. MORITA ET AL) 11 May 1999 (1999-05-11) cited in the application column 4, lines 17-22; claims -----	1,4

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No

PCT/US 03/34920

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0062430	A	13-10-1982	JP 1371127 C	25-03-1987
			JP 57164991 A	09-10-1982
			JP 61040040 B	06-09-1986
			AT 23578 T	15-11-1986
			DE 3274264 D1	02-01-1987
			EP 0062430 A1	13-10-1982
			SU 1152517 A3	23-04-1985
			US 4425199 A	10-01-1984
			US 4466881 A	21-08-1984
<hr/>				
GB 2051831	A	21-01-1981	JP 1317358 C	15-05-1986
			JP 55160029 A	12-12-1980
			JP 60045653 B	11-10-1985
			JP 1367344 C	26-02-1987
			JP 55160007 A	12-12-1980
			JP 61034725 B	09-08-1986
			JP 1235860 C	17-10-1984
			JP 56012362 A	06-02-1981
			JP 59010658 B	10-03-1984
			JP 1235861 C	17-10-1984
			JP 56015260 A	14-02-1981
			JP 59012116 B	21-03-1984
			JP 56016460 A	17-02-1981
			JP 1235865 C	17-10-1984
			JP 56090054 A	21-07-1981
			JP 59011581 B	16-03-1984
			JP 1235866 C	17-10-1984
			JP 56092263 A	25-07-1981
			JP 59011582 B	16-03-1984
			JP 1367351 C	26-02-1987
			JP 55160008 A	12-12-1980
			JP 61034726 B	09-08-1986
			BR 8003432 A	05-01-1981
			CA 1185398 A1	09-04-1985
			CA 1168263 A2	29-05-1984
			DE 3020057 A1	27-05-1981
			DE 3046501 A1	17-02-1983
			DE 3050439 A1	22-07-1982
			DE 3050782 C2	26-05-1988
			DE 3050931 C2	09-06-1994
			FI 801733 A ,B,	01-12-1980
			FR 2457880 A1	26-12-1980
FR 2473533 A1	17-07-1981			
FR 2483431 A1	04-12-1981			
FR 2508039 A1	24-12-1982			
GB 2053902 A ,B	11-02-1981			
GB 2123812 A ,B	08-02-1984			
GB 2118541 A ,B	02-11-1983			
IN 153451 A1	14-07-1984			
IN 154418 A1	27-10-1984			
IT 1193942 B	31-08-1988			
NL 8003174 A ,C	02-12-1980			
NO 801637 A ,B,	01-12-1980			
PT 72130 A ,B	01-12-1980			
PT 72131 A ,B	01-12-1980			
SE 449999 B	01-06-1987			
SE 8003901 A	01-12-1980			
SU 1494869 A3	15-07-1989			

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No PCT/US 03/34920
--

Patent document cited in search report	A	Publication date	Patent family member(s)	Publication date
GB 2051831	A		US 4329434 A US 4510328 A	11-05-1982 09-04-1985
<hr style="border-top: 1px dashed black;"/>				
US 4749526	A	07-06-1988	AU 601481 B2 AU 7814487 A CA 1296355 C DE 3761762 D1 EP 0265052 A1 JP 2525426 B2 JP 63077835 A KR 9508283 B1	13-09-1990 17-03-1988 25-02-1992 05-04-1990 27-04-1988 21-08-1996 08-04-1988 27-07-1995
<hr style="border-top: 1px dashed black;"/>				
US 5902908	A	11-05-1999	JP 3360689 B2 JP 6009474 A DE 69316012 D1 DE 69316012 T2 EP 0647609 A1 WO 9400412 A1	24-12-2002 18-01-1994 05-02-1998 23-07-1998 12-04-1995 06-01-1994
<hr style="border-top: 1px dashed black;"/>				