



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2512005 C 2012/02/07

(11)(21) **2 512 005**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2003/11/26
(87) Date publication PCT/PCT Publication Date: 2004/07/22
(45) Date de délivrance/Issue Date: 2012/02/07
(85) Entrée phase nationale/National Entry: 2005/06/28
(86) N° demande PCT/PCT Application No.: US 2003/038196
(87) N° publication PCT/PCT Publication No.: 2004/060964
(30) Priorité/Priority: 2002/12/30 (US10/331,816)

(51) Cl.Int./Int.Cl. *C08G 65/00* (2006.01),
C08G 65/329 (2006.01)
(72) Inventeurs/Inventors:
FLYNN, RICHARD M., US;
VITCAK, DANIEL R., US;
BUCKANIN, RICHARD S., US;
ELSBERND, CHERYL L. S., US
(73) Propriétaire/Owner:
3M INNOVATIVE PROPERTIES COMPANY, US
(74) Agent: SMART & BIGGAR

(54) Titre : COMPOSITIONS A BASE DE POLYETHER FLUORE
(54) Title: FLUORINATED POLYETHER COMPOSITIONS

(57) **Abrégé/Abstract:**

Described are fluorinated polyether compounds having a molecular weight range between 750 g/mol and 4000 g/mol where such polyether compounds are intermediates used in fluorinated compositions for treating various substrates.



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

(19) World Intellectual Property
Organization
International Bureau



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

PCT

(10) International Publication Number
WO 2004/060964 A1

(51) International Patent Classification⁷: **C08G 65/00**

(21) International Application Number:
PCT/US2003/038196

(22) International Filing Date:
26 November 2003 (26.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/331,816 30 December 2002 (30.12.2002) US

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

(72) Inventors: **FLYNN, Richard, M.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **VITCAK, Daniel, R.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **BUCKANIN, Richard, S.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **ELSBERND, Cheryl, L., S.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: **JORDAN, Robert, H.** 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, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, 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, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, 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: FLUORINATED POLYETHER COMPOSITIONS

(57) Abstract: Described are fluorinated polyether compounds having a molecular weight range between 750 g/mol and 4000 g/mol where such polyether compounds are intermediates used in fluorinated compositions for treating various substrates.

WO 2004/060964 A1

60557-7366

FLUORINATED POLYETHER COMPOSITIONS1. Field of Invention

The present invention relates to a select molecular weight range of fluorinated polyethers as intermediates for preparing useful fluorochemical polymeric compositions.

2. Background

Fluorinated polyethers have been known for many years. For example, such polyethers have been described in U.S. Patent Nos. 3,214,478, 3,242,218, 3,322,826, and by Millauer et al. in *Angewandte Chemie Int. Ed.*, Vol. 24(3), 1995, pp. 161-179. These polyfluorinated ethers have been used as intermediates in the preparation of useful compositions to be applied to substrates such as hard surface substrates and fibrous substrates to impart oil and/or water repellant properties. For example, perfluorinated polyether compounds as intermediates in such compositions are described in EP 1,038,919, EP 273,449, JP-A-04-146917, JP-A-10-081873, U.S. Patent Nos. 3,536,710, 3,814,741, 3,553,179, and 3,446,761.

In seeking these useful and efficient compositions, selection of specific fluorinated polyethers for use is important. For example, there is also a requirement that the fluorochemical compositions be environmentally friendly. By this is meant that fluorochemical polymeric compositions are obtained substantially free of fluorochemical components that eliminate slowly from the body of living organisms.

In addition to environmental friendliness, processing efficiency is also desired to reduce costs and ease in the manufacturing of such fluorochemical compositions.

3. Summary of the Invention

We have found that fluorochemical compositions derived from a perfluorinated polyether or fluorinated polyether compound having a molecular weight between about 750 g/mol and about 4000 g/mol surprisingly provide environmentally friendly resulting compositions, but also compositions that may be prepared without processing difficulties.

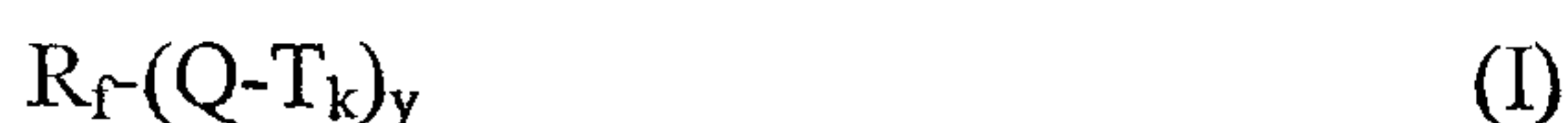
Moreover, it is believed that fluorochemical degradation products that may form from these materials likewise eliminate well from the body of living organisms. In particular, indications show that the fluorinated polyether compounds that have a

60557-7366

perfluorinated polyether moiety having a molecular weight of at least 750g/mol and perfluorinated polyether degradation products that may form therefrom would eliminate more effectively from the body of living organisms. In particular, there are indications that fluorinated polyether compounds having a fluorinated polyether moiety derivable
 5 from a polycondensation of hexafluoropropylene oxide and having a molecular weight of at least 750g/mol would more effectively eliminate from the body of living organisms as compared to long chain perfluoroaliphatic compounds.

Accordingly, the present invention provides for a fluorochemical composition comprising:

10 a perfluorinated polyether of the formula



wherein

R_f represents a monovalent or divalent perfluorinated polyether group having a molecular weight between about 750g/mol and 4000 g/mol;

15 Q is a chemical bond or a divalent or trivalent organic linking group;

T is a functional group selected from -C(O)F, -CO₂R₃, where R₃ is hydrogen, lower alkyl, cycloalkyl or alkanol, -C(O)N(R₁)(R₂), -OH, -SH, and -NH₂ where R₁ and R₂ are independently lower alkyl, cycloalkyl or alkanol;

20 k is 1 or 2, and

y is 1 or 2,

or a mixture thereof.

60557-7366

According to another aspect of the present invention, there is provided a fluorochemical composition comprising two or more fluorinated polyethers, at least one fluorinated polyether having the formula: $R_f(Q-T_k)_y$ (I) and having a molecular weight between about 750g/mol and about 4000gmol, wherein R_f represents a monovalent or divalent perfluorinated polyether group; Q represents a chemical bond or a divalent or trivalent organic linking group; T is selected from the group consisting of $-C(O)F$, $-CO_2R_3$, where R_3 is hydrogen, C_{1-6} alkyl, cycloalkyl or alkanol, $-C(O)N(R_1)(R_2)$, where R_1 and R_2 are independently C_{1-6} alkyl, cycloalkyl or alkanol, $-OH$, $-SH$ -, and NH_2 ; k is 1 or 2; and y is 1 or 2, wherein no more than 10% by weight of perfluorinated polyethers having a molecular weight of less than 750 gmol or greater than 4000 g/mol are present in the composition.

4. Detailed Description of Illustrative Embodiments of the Invention

The fluorinated compound used in the fluorochemical composition is of the formula (I):



wherein R_f represents a monovalent or divalent perfluorinated polyether group, Q represents a chemical bond or a divalent or trivalent non-fluorinated organic linking group, T represents a functional group selected from $-C(O)F$, $-CO_2R_3$, where R_3 is hydrogen, lower alkyl, cycloalkyl or alkanol, $-C(O)N(R_1)(R_2)$, $-OH$, $-SH$, and $-NH_2$ where R_1 and R_2 are independently lower alkyl, cycloalkyl or alkanol, k is 1 or 2 and n is 1 or 2.

The term "lower alkyl" includes a straight or branched alkyl group containing 1 to 6 carbon atoms such as, for example, methyl, ethyl, propyl, 1-methyl-2-ethyl, butyl, and the like.

5 The term "cycloalkyl" includes a cyclic hydrocarbon group of from 3 to 6 carbon atoms such as, for example, cyclopropyl or cyclohexyl, and the like.

The term "alkanol" is a straight or branched chain of methylene groups attached together and being substituted by one or more hydroxyl groups such as, for example, -CH₂OH, -CH₂CH(OH)CH₃, -CH₂CH(OH)CH₂OH, and the like.

10 The perfluorinated polyether moiety R_f of the fluorinated polyether of formula (I) preferably corresponds to the formula:



wherein R_f¹ represents a perfluorinated alkyl or alkylene group, R_f² represents a perfluorinated polyalkyleneoxy group consisting of perfluorinated alkyleneoxy groups having 1, 2, 3 or 4 carbon atoms or a mixture of such perfluorinated alkyleneoxy groups, 15 R_f³ represents a perfluorinated alkylene group, q is 0 or 1 and y is 1 or 2. The perfluorinated alkyl or alkylene group R_f¹ in formula (II) may be linear, branched or cyclic and may contain catenary heteroatoms, such as N, O or S, and may contain 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms. A typical perfluorinated alkyl group is CF₃-CF₂-CF₂-. R_f³ is a linear or branched perfluorinated alkylene group that will typically have 1 to 20 6 carbon atoms. For example, R_f³ is -CF₂- or -CF(CF₃)-. Examples of perfluoroalkyleneoxy groups of perfluorinated polyalkyleneoxy group R_f² include:

25 -CF₂-CF₂-O-,
 -CF(CF₃)-CF₂-O-,
 -CF₂-CF(CF₃)-O-,
 -CF₂-CF₂-CF₂-O-,
 -CF₂-O-,
 -CF(CF₃)-O-, and
 -CF₂-CF₂-CF₂-CF₂-O.

30 The perfluoroalkyleneoxy group may be comprised of the same perfluoroalkyleneoxy units or of a mixture of different perfluoroalkyleneoxy units. When the perfluoroalkyleneoxy group is composed of different perfluoroalkyleneoxy units, they can

60557-7366

be present in a random configuration, alternating configuration or they can be present as blocks. Typical examples of perfluorinated polyalkylene oxy groups include:

- $-\text{[CF}_2\text{-CF}_2\text{-O]}_r-$; $-\text{[CF(CF}_3\text{)-CF}_2\text{-O]}_n-$; $-\text{[CF}_2\text{CF}_2\text{-O]}_l-$; $-\text{[CF}_2\text{O]}_j-$;
- 5 $-\text{[CF}_2\text{-CF}_2\text{-O]}_l-$; and $-\text{[CF}_2\text{CF(CF}_3\text{)-O]}_m-$. A preferred perfluorinated polyether moiety that corresponds to formula (II) is $\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-O-[CF(CF}_3\text{)-CF}_2\text{O]}_n\text{-CF(CF}_3\text{)-}$ wherein n is an integer of 3 to 23. This perfluorinated polyether group has a molecular weight of 783 when n equals 3 and can be derived from an oligomerization of hexafluoropropylene oxide. Such perfluorinated polyether
- 10 groups are preferred in particular because of their benign environmental properties.

Examples of linking groups Q include organic groups that comprise aromatic or aliphatic groups that may be interrupted by O , N or S and that may be substituted, alkylene groups, oxy groups, thio groups, and/or carbonyl groups. In

15 one embodiment, Q is selected from the group consisting of alkylene, oxyalkylene, aminoalkylene, amidoalkylene, carboxyalkylene.

In a particular embodiment, the fluorinated polyether corresponds to the following formula (III):



- 20 wherein R_f^1 represents a perfluorinated alkyl or alkylene group, e.g., a linear or branched perfluorinated alkyl group having 1 to 6 carbon atoms, n is an integer of 3 to 23, Q is a chemical bond or an organic divalent or trivalent linking group for example as mentioned for the linking group above, k is 1 or 2, T is as mentioned above and each T may be the same or different, and y is 1 or 2.
- 25 Particularly preferred compounds are those in which R_f^1 represents $\text{CF}_3\text{CF}_2\text{CF}_2-$. In accordance with a particular embodiment, the moiety $Q\text{-T}_k$ is a moiety of the formula $-\text{CO-X-R}^a(\text{OH})_k$ wherein k is 1 or 2, X is O or NR^b with R^b representing hydrogen or an alkyl group of 1 to 4 carbon atoms, and R^a is an alkylene of 1 to 15 carbon atoms.

60557-7366

Representative examples of the moiety Q-T_k in above formula (III) include:

1. -CONR^c-CH₂CHOHCH₂OH wherein R^c is hydrogen or an alkyl group of for example 1 to 4 carbon atoms;
- 5 2. -CH₂OH;
3. -CH₂OCH₂CH(OH)CH₂OH;
4. -COOCH₂CH(OH)CH₂OH; and
5. -CONR^d-(CH₂)_mOH;
6. -N(CH₂CH₂OH)CH₂CH₂OH

7. $-\text{C}(\text{O})\text{F}$
8. $-\text{C}(\text{O})\text{OR}^{\text{d}}$
9. $-\text{CO}_2\text{H}$

where R^{d} is hydrogen or an alkyl group such as methyl, ethyl, propyl, butyl, or
5 hexyl and m is 2 -12.

Compounds according to formula (III) can for example be obtained by
oligomerization of hexafluoropropylene oxide (HFPO) which results in a
perfluoropolyether carbonyl fluoride. This carbonyl fluoride may be converted into an
acid, acid salt, ester, amide or alcohol by reactions well known to those skilled in the art.

10 The carbonyl fluoride or acid, ester or alcohol derived therefrom may then be reacted
further to introduce the desired reactive groups according to known procedures. For
example, the alcohol functional group can be converted easily to the (meth)acrylate
function by esterification of the alcohol with (meth)acryloyl chloride. Also, EP 870 778
describes suitable methods to produce compounds according to formula (III) having
15 desired moieties $-\text{Q}-\text{T}_k$. Compounds having moiety 1 listed above can be obtained by
reacting the methyl ester derivative of a fluorinated polyether with 3-amino-2-hydroxy-
propanol. Compounds having the moiety 5 listed above can be obtained in a similar way
by reacting with an amino-alcohol that has only one hydroxy function. For example 2-
aminoethanol would yield a compound having the moiety 5 listed above with R^{d} being
20 hydrogen and m being 2.

Still further examples of compounds according to above formula (I) are disclosed
in EP 870 778 or US 3,536,710.

It will be evident to one skilled in the art that a mixture of fluorinated polyethers
according to formula (I) may be used to prepare the fluorinated polyether compound of the
25 fluorochemical composition. Generally, the method of making the fluorinated polyether
according to formula (I) for the present invention will result in a mixture of fluorinated
polyethers that have different molecular weights and are free of (1) fluorinated polyether
compounds having a perfluorinated polyether moiety having a molecular weight of less
than 750g/mol and (2) fluorinated polyether compounds having a polyfluorinated
30 polyether moiety having a molecular weight greater than 4000 g/mol.

The use of fluorinated polyethers corresponding to molecular weights greater than
about 4000 g/mol can induce processing problems. These problems are typically due to the

fact that the higher molecular weight materials lead to emulsion, instability and insolubility concerns. Additionally, the presence of higher molecular weight fluorinated polyether derivatives has considerable impact on the efficiency of the separation process of materials via fractionation.

5 The fluorochemical composition will be free of or substantially free of perfluorinated polyether moieties having a molecular weight of less than 750g/mol and those moieties having a molecular weight greater than 4000 g/mol. By the term “substantially free of” is meant that the particular perfluorinated polyether moieties outside the molecular weight range are present in amounts of not more than 10% by
10 weight, preferably not more than 5% by weight and most preferably not more than 0.05% by weight based on the total weight of perfluorinated polyether moieties in the composition. Compositions that are free of or substantially free of these moieties are preferred because of their beneficial environmental properties and their processability in the further reaction steps.

15 The present fluorinated polyether compounds may be used as intermediates for preparing fluorinated compositions for treating substrates such as hard surfaces or fibrous substrates such as textiles.

 The present perfluorinated polyether compounds prepared by known methods but having molecular weight greater than 750 g/mol and less than 4000 g/mol are made free of
20 those moieties outside the molecular weight range by careful fractional distillation or azeotropic distillation using aprotic organic solvents, such as diglyme, or by careful control of the oligomerization parameters such as catalyst choice, catalyst amount, temperature, solvent, and purity of starting materials and starting materials ratios.

25

60557-7366

EXAMPLES

The average molecular weight (MW_{avg}) of the HFPO oligomers was determined by summation of the product of the glc area % for each individual oligomer and its corresponding molecular weight.

HFPO Oligomer General Formula: $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)COF$

Example 1. HFPO Oligomer with $n \geq 5$

A mixture of HFPO oligomers (460 grams, $MW_{avg} \sim 1336$ with 13.5% hexamer and below, as determined by glc; can be prepared as described in US Pat. No. 3,242,218), was vacuum fractionated using a silver coated vacuum jacketed column (61 cm length and 25.4 mm I.D.; available from Ace Glass Incorporated, Vineland, NJ); and packed with Pro-PakTM distillation packing (0.24 in (6.0 mm) available from Ace Glass Incorporated) . A 1L distilling flask (available from Ace Glass Catalog # 6935-78) equipped with a distilling head (available from Ace Glass Incorporated; Catalog # 6598-10), magnetic stirrer, and a dry ice-acetone slush bath (to collect distillate) was used. The distillation was carried out at a vacuum of 0.1 mmHg. Vacuum was broken if necessary during the distillation using dry nitrogen. The column was equilibrated for 1-hour at total reflux before distillate was removed at a 60 to 1 reflux ratio; that is to say, 60 parts returned to the column and 1 part was removed as distillate. Distillate was removed up to a column head temperature of 140 °C/ 0.1 mmHg and 130 grams of distillate was recovered which contained 42 grams of diglyme as a top phase. After cooling, the overhead and column were removed and replaced with an addition funnel, all under a nitrogen blanket. Anhydrous methanol (28 g.) was slowly added dropwise while maintaining the reaction temperature under 30 °C. After thirty minutes, deionized water (34 g) was added and the resulting methyl ester solution washed and the phases separated. The desired methyl ester formed the lower phase (284 g) of material and contained only 0.19% HFPO hexamer as determined by glc and which had MW_{avg} of 1434 g/mole.

Example 2. HFPO Oligomer with $n = 4$ and 5 (hexamer and heptamer)

A mixture of HFPO oligomers was fractionated as described in Example 1 to obtain a 182 gram fractionation cut containing 65% hexamer and 33 % heptamer as determined by glc.

5 This cut was redistilled under vacuum using a concentric tube column (available from Ace Glass Incorporated, Catalog # 9331-12). The following table summarizes this fractionation performed using a 7 to 1 reflux ratio and a vacuum of 0.5 mmHg (66.7 Pa).

Table 1. Summary of Fractionations.

Cut #	Distillation Head Temperature (°C)	Distillate Amount (g)	Hexamer (%)	Heptamer (%)
1	N/R*	10.0	94.05	0.18
2	N/R	17.0	95.54	2.71
3	N/R	9.0	95.70	2.74
4	N/R	14.0	95.20	3.64
5	120	23.0	95.20	3.45
6	N/R	24.0	65.50	31.90
7	160	20.0	2.20	95.70

10 * not recorded

Cuts 2-5 were combined and the methyl ester prepared as previously described. The resulting product was 95.0% hexamer methyl ester as analyzed by glc.

15 Cut 7 was used to prepare the 95.0% pure heptamer methyl ester by the same procedure as used for the hexamer.

Example 3 : HFPO Oligomer with $n = 2$ (tetramer)

20

One hundred milliliters of crude HFPO oligomers containing 27% tetramer as determined by glc and prepared as described in Example 1, was fractionated at atmospheric pressure using the same concentric tube column described in Example 2. A 20-gram tetramer

distillation cut was obtained using a 30 to 1 reflux ratio at 160 °C head temperature. Following esterification with anhydrous methanol and water washing, 20 grams of tetramer at 94.5% glc purity was obtained.

5 Example 4 : HFPO Oligomer with $n = 3$ (pentamer)

A sample of HFPO oligomer methyl esters was distilled (3 mmHg) in the packed column distillation apparatus essentially identical to that described in Example 1. A fraction was obtained as the pot temperature was raised from 144 to 185 °C which contained 31.4% of
10 the pentamer by glc. This fraction was redistilled and the fraction boiling at 118 °C/8 mmHg obtained which comprised the pentamer methyl ester in a purity of 95.1% by glc.

Example 5 : HFPO Oligomer with $n \geq 4$

15 A sample of HFPO oligomer methyl esters was prepared as described in Example 1 and which was found to contain about 0.3% by weight HFPO trimer ($n=1$) and about one tenth that amount HFPO dimer ($n = 0$). To this sample was added 50 ml anhydrous diglyme and the mixture distilled at atmospheric pressure. After a few milliliters of distillate was obtained, the material remaining in the distillation vessel was analyzed by glc and found to
20 contain no more than about 84ppm of the trimer. This material was washed several times with anhydrous methanol to remove the residual diglyme. The MW_{avg} was 1742.

Example 6 : HFPO Oligomer with $n \geq 5$.

25 This sample was prepared essentially as described in Example 1 to obtain a sample of HFPO oligomers of $MW_{avg} = 1648$ containing only 22 ppm of the tetramer and no lower homologs.

Example 7 : Preparation of the alcohol : $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)CONHC_2H_4OH$

30

The HFPO methyl esters described in Examples 1-6 were converted to the amide alcohols in very similar manners. The ester was mixed at ambient temperature with excess

ethanolamine (about 1.25 moles ethanolamine per mole ester). After stirring for 16 hours, the solution was completely homogeneous. The co-product methanol was then removed by placing the sample under vacuum, typically 10-15 mmHg at about 50 °C until the foaming caused by the removal of the methanol had essentially stopped. This procedure did not
5 remove the excess ethanolamine but this did not interfere with the biological testing. For the ester of Example 6 a slightly different procedure was employed. The product mixture after reaction of the ester with excess ethanolamine was dissolved in about 200 ml diethyl ether. The ether solution was then washed twice with about 5% aqueous sodium chloride and once with about 2N HCl and again twice with the sodium chloride solution. After
10 drying the ether solution over anhydrous magnesium sulfate, the ether was removed by rotary evaporation at about 15 mmHg and 50 °C until no more foaming was observed. GC-MS and IR confirmed the structure of the alcohol products.

Comparative Example C1 and Examples 1 – 5

15 Toxicokinetic Study with HFPO alcohols:



The objective of this study was to assess the oral absorption and serum elimination half-
20 life of six hexafluoropropylene oxide (HFPO)-alcohol oligomers $(\text{CF}_3\text{CF}_2\text{CF}_2\text{O}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_x\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{OH})$, or mixtures thereof, in rats. Male Sprague-Dawley rats (N = 4 to 6 rats per dose group) received a single 30 mg/kg dose of the various HFPO alcohol oligomers in propylene glycol by oral gavage at a volume of 5 ml/kg. Necropsies were performed on day one and day four post dose.

25 Serum samples obtained at necropsy were analyzed for total fluorine based on published methods (1) using an Antek 9000F Fluoride Analysis System. The method was based on oxy-pyrohydrolysis at 1050° C, whereby the C-F bond is broken and the resulting product, hydrogen fluoride (HF), is trapped in a buffer solution and measured with the fluoride ion
30 electrode. The total fluorine levels obtained by this method reflect the total organic fluorine in the serum samples and are reported in Table 2.

These data indicate that the apparent half-life serum fluorine levels for the HFPO alcohol example C1 is approximately four days. The HFPO alcohol oligomers with average molecular weights of 750 g/mole or greater (examples 1-5) were not apparent in the serum on day one or day four post-dose as measured by total organic fluorine suggesting that these higher molecular weight oligomers have a relatively lower to no bioavailability as compared to the C1 example.

Table 2. Total Fluorine found in male rat serum after a single oral dose of HFPO-alcohol oligomers $(\text{CF}_3\text{CF}_2\text{CF}_2\text{O}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_x\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{OH})$.

Example	x	MW_{avg}	Amount of Total F ppm (SD) in serum	
			Day 1 Post-Dose	Day 4 Post-Dose
C1	2	705	7.55 (1.34)	3.90 (0.00)
1	3	871	0.15 (0.00)	0.15 (0.00)
2	4	1037	0.15 (0.00)	0.15 (0.00)
3	5	1203	0.15 (0.00)	0.15 (0.00)
4	$2 \leq x \leq 11$	1354	0.15 (0.00)	0.15 (0.00)
5	$5 \leq x \leq 11$	1460	0.15 (0.00)	0.15 (0.00)

The limit of detection (LOD) was 0.3 ppm, therefore the standard FDA approach of using one-half the LOD was used to calculate averages.

Reference:

1. Van Gogh, H., *Pharm. Weeblad*, 1966, 101, 881-898

60557-7366

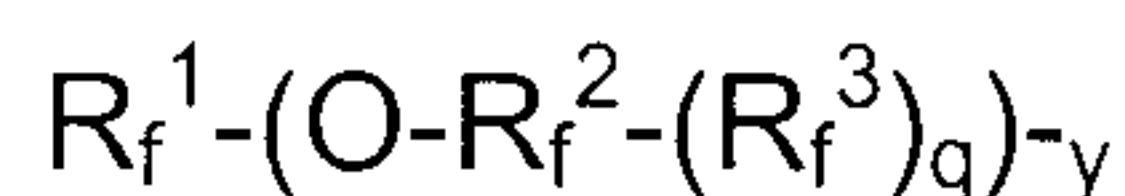
CLAIMS:

1. A fluorochemical composition comprising two or more fluorinated polyethers, at least one fluorinated polyether having the formula:



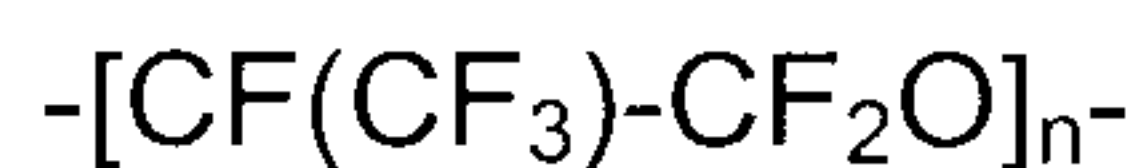
5 and having a molecular weight between about 750g/mol and about 4000gmol, wherein R_f represents a monovalent or divalent perfluorinated polyether group; Q represents a chemical bond or a divalent or trivalent organic linking group; T is selected from the group consisting of $-C(O)F$, $-CO_2R_3$, where R_3 is hydrogen, C_{1-6} alkyl, cycloalkyl or alkanol, $-C(O)N(R_1)(R_2)$, where R_1 and R_2 are independently C_{1-6} alkyl, cycloalkyl or alkanol, $-OH$, $-SH-$, and NH_2 ; k is 1 or 2; 10 and y is 1 or 2, wherein no more than 10% by weight of perfluorinated polyethers having a molecular weight of less than 750 g/mol or greater than 4000 g/mol are present in the composition.

2. A composition according to claim 1 wherein R_f in formula (I) is of the 15 formula:



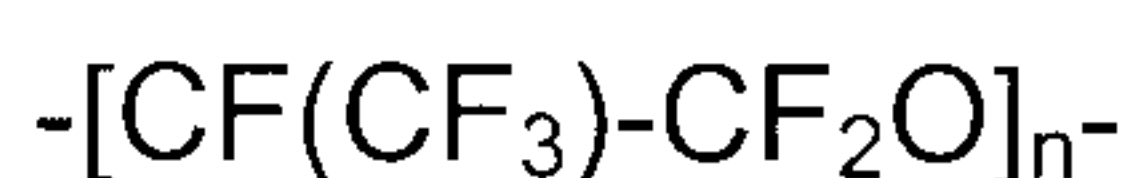
wherein R_f^1 is a perfluorinated alkyl or alkylene group, R_f^2 is a perfluorinated polyalkyleneoxy group consisting of perfluorinated alkyleneoxy groups having 1, 2, 3 or 4 carbon atoms or a mixture of such perfluorinated 20 alkyleneoxy groups; R_f^3 is a perfluorinated alkylene group; q is 0 or 1, and y is 1 or 2.

3. A composition according to claim 2 wherein R_f^2 is of the formula:



wherein n is an integer of 3 to 23.

25 4. A composition according to claim 2 or 3, wherein R_f^3 is $CF(CF_3)$, q is 1 and R_f^2 is of the formula:



60557-7366

wherein n is an integer of 3 to 23.

5. A composition according to any one of claims 1 to 4 wherein T is selected from the group consisting of hydroxy and amino groups.

6. A composition according to any one of claims 1 to 4, wherein T is
5 selected from the group consisting of $-\text{C}(\text{O})\text{F}$, $-\text{CO}_2\text{R}_3$, where R_3 is hydrogen, C_{1-6} alkyl, cycloalkyl or alkanol, $-\text{C}(\text{O})\text{N}(\text{R}_1)(\text{R}_2)$, where R_1 and R_2 are independently C_{1-6} alkyl, cycloalkyl or alkanol.

7. A composition according to claim 1 wherein said fluorinated polyether of formula (I) corresponds to the formula:

10 $\text{R}_f^1-[\text{O}-[\text{CF}(\text{CF}_3)-\text{CF}_2\text{O}]_n-\text{CF}(\text{CF}_3)-\text{Q}-\text{T}_k]_y$

wherein R_f^1 represents a perfluorinated alkyl or alkylene group, n is an integer of 3 to 23, Q is a chemical bond or an organic divalent or trivalent linking group and T is hydroxy or amino; k is 1 or 2, and y is 1 or 2.

8. A composition according to any one of claims 1 to 7, wherein said
15 organic linking group Q is selected from the group consisting of alkylene, oxyalkylene, aminoalkylene, amidoalkylene, carboxyalkylene.

9. A composition according to any one of claims 1 to 8, wherein y is 1.