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(54) **FLUORINATED LUBRICANTS**

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(57) **ABSTRACT**

Fluorinated lubricants comprising "pour point depressant" additives of structure:

$$X_1—O(CF_2O)_n(CF_2CF_2O)_m(CF_2CF_2CF_2O)_p(CF_2CF_2CF_2CF_2O)_q—X_2 \quad (I)$$

wherein

X_1, X_2, have formula $—(CF_2)_zCF_3$ wherein z is an integer from 0 to 3; n is an integer between 1 and 200; m is an integer between 0 and 200; p, q are integers between 0 and 10; $(p+q)/(p+q+m+n) \leqq 0.05$; $m/n \leqq 0.7$; the number average molecular weight of (I) is between 1,000 and 10,000.

FLUORINATED LUBRICANTS

[0001] The present invention relates to fluorinated derivatives capable to lower the pour point temperature of lubricating oils.

[0002] Specifically the invention relates to the use of perfluoropolyether-based compounds as additives to reduce the pour point temperature of fluorinated oils, in particular having a perfluoropolyether structure, and to the lubricating compositions comprising said additives.

[0003] It is known in the prior art to use perfluoropolyether oils as lubricants in a wide temperature range, in particular in applications where a good lubricating capability at very low temperatures is required, for example in the aerospace and in the refrigeration industry. Among these lubricants having a perfluoropolyether structure available on the market, it can be mentioned FOMBLIN® marketed by Solvay Solexis S.p.A., used as lubricating oil at temperatures even lower than −80° C.

[0004] It is also known that the lower limit at low temperatures of lubricating oils, fluorinated and non fluorinated, is connected to the temperature corresponding to their pour point, under which their use requires a strong energy due to the difficulty to move the lubricant itself. As a matter of fact in non fluorinated oils, in correspondence of the pour point, crystallization takes place, while in fluorinated oils, for example perfluoropolyether oils, a sudden viscosity increase is observed.

[0005] To lower the pour point, it is also known to use "pour point depressant" additives. For example non fluorinated additives, have been developed for hydrogenated paraffins, for mineral oils and petroleum. Such additives are generally hydrogenated polymers miscible with the lubricating oil preventing the oil from crystallizing as the temperature decreases without altering the lubricating characteristics, and therefore the lubricant performances of the oil. Examples of said additives are polyalkylmethacrylates, polyacrylates, phthalates. For example, patent application WO 89/01507 describes the use of "pour point depressant" additives consisting of polymethacrylates having molecular weight in the range 10,000-300,000 to lower the pour point of paraffinic oils down to about −35° C.

[0006] However the use of non fluorinated additives in fluorinated oils, for example, perfluoropolyether oils, is not viable as said additives are not miscible with fluorinated lubricants.

[0007] In the field of fluorinated oils, in particular of perfluoropolyether oils, pour point depressant additives allowing to lower the pour point are not available on the market.

[0008] The need was therefore felt to have available additives:

[0009] capable to lower the pour point of fluorinated lubricants, in particular perfluoropolyether oils;

[0010] soluble in fluorinated oils, in particular perfluoropolyether oils;

[0011] not substantially altering the lubricating characteristics of the fluorinated oil, in particular of the perfluoropolyether oil, for example viscosity, evaporation loss, chemical stability, viscosity index, in particular not altering the viscosity index;

so as to widen the thermal rating at low temperatures of said fluorinated lubricants, preferably perfluoropolyether lubricants.

[0012] The Applicant has unexpectedly and surprisingly found that the addition of particular fluorinated compounds, to perfluoropolyether oils, allows to lower the pour point temperature of said oils and to solve the above technical problem.

[0013] It is-an object of the present invention the use as pour point depressant additives for fluorinated oils, preferably perfluoropolyether oils, of compounds having the following structure:

$$X_1—O(CF_{2O})_n(CF_2CF_2O)_m(CF_2CF_2CF_2O)_p(CF_2CF_2CF_2CF_2O)_q—X_2 \quad (I)$$

wherein:

[0014] the repeating units $—CF_2O—$, $—CF_2CF_2O—$, $—CF_2CF_2CF_2O—$, $—CF_2CF_2CF_2CF_2O—$ are statistically distributed along the chain;

[0015] $—X_1$ and $—X_2$ are perfluoroalkyl chain end groups equal to or different from each other, having formula $—(CF_2)_zCF_3$ wherein z is an integer from 0 to 3;

[0016] n is an integer from 1 to 200,

[0017] m is an integer from 0 to 200,

[0018] p, q are integers from 0 to 10, preferably from 0 to 5, more preferably from 0 to 1, still more preferably 0,

with the proviso that:

[0019] the ratio (p+q)/(p+q+m+n) is lower than or equal to 0.05, being also equal to 0, (p+q+m+n) being different from 0;

[0020] the ratio m/n, when n is different from 0, is lower than or equal to 0.7, preferably lower than 0.5, more preferably lower than 0.35;

[0021] the number average molecular weight of the compounds (I) ranges from 1,000 to 10,000, preferably from 2,000 to 8,000, more preferably from 2,400 to 5,000.

[0022] The additives of the invention at ^{19}F NMR analysis do not show chlorine atoms, the latter being substantially absent. With compounds of formula (I) wherein the chlorine atoms, determined by ^{19}F NMR, are substantially absent, compounds are meant wherein the chlorine atoms are lower than the sensitivity limit of the analytical method ^{19}F NMR.

[0023] The additives of formula (I) are added to fluorinated oils, preferably perfluoropolyether oils having viscosity at 20° C. between 10 and 4,000 cSt, preferably between 30 and 2,000 cSt, and containing one or more of the following repeating units: $—CFXO—$, wherein X is equal to F or CF_3; $—CF_2CF_2O—$, $—(C_3F_6O)—$, $—CF_2CF_2CF_2O—$, $—CF_2CF_2CF_2CF_2O—$, said units being statistically distributed along the backbone.

[0024] Said perfluoropolyether oils are preferably selected from the following classes:

$$E—O—(CF_2CF(CF_3)\ O)_{m'}(CFXO)_{n'}—E' \quad (1)$$

[0025] wherein:

[0026] X is equal to F or CF_3;

[0027] E and E', equal to or different from each other, are selected from CF_3, C_2F_5 or C_3F_7, one fluorine atom of one or both the end groups being replaceable with Cl and/or H; m' and n' are integers such that the ratio m'/n' is between 20 and 1,000, n' being different from zero; the units being statistically distributed along the backbone, the viscosity of the product being within the above range.

[0028] These polymers can be obtained by perfluoropropene photooxidation as described in GB 1,104,432, and by subsequent conversion of the end groups as described in GB 1,226,566;

$$C_3F_7O(CF(CF_3)CF_2O)_{o'}—D \quad (2)$$

[0029] wherein:

[0030] D is equal to $—C_2F_5$ or $—C_3F_7$, one fluorine atom of one or both the end groups being replaceable with Cl and/or H; o' is an integer such that the viscosity of the product is within the above range.

[0031] These polymers can be prepared by ionic oligomerization of the perfluoropropylenoxide and subsequent treatment with fluorine as described in U.S. Pat. No. 3,242,218;

$$\{C_3F_7O—(CF(CF_3)CF_2O)_{p'}—CF(CF_3)—\}_2 \quad (3)$$

[0032] wherein:

[0033] p' is an integer such that the viscosity of the product is within the above range, one F atom of one or both the end groups C_3F_7 being replaceable with Cl and/or H. These products can be prepared by ionic telomerization of the perfluoropropylenoxide and subsequent photochemical dimerization as reported in U.S. Pat. No. 3,214,478;

$$E—O—(CF_2CF(CF_3)O)_{q'}(C_2F_4O)_{r'}(CFX)_{s'}—E' \quad (4)$$

[0034] wherein:

[0035] X is equal to F or CF_3;

[0036] E and E', equal to or different from each other, are as above;

[0037] q', r' and s' are integers including 0, and such that the viscosity of the product is within the above range.

[0038] These polymers are obtainable by photooxidation of a mixture of C_3F_6 and C_2F_4 and subsequent treatment with fluorine as described in U.S. Pat. No. 3,665,041;

$$E—O—(C_2F_4O)_{t'}(CF_2O)_{u'}—E' \quad (5)$$

[0039] wherein:

[0040] E and E', equal to or different from each other, are as above;

[0041] t' and u' are integers such that the ratio t'/u' is between 0.1 and 5, u' being different from 0 and the viscosity of the product is within the above range.

[0042] These polymers are obtained by photooxidation of C_2F_4 as reported in U.S. Pat. No. 3,715,378 and subsequent treatment with fluorine as described in U.S. Pat. No. 3,665,041;

$$E—O—(CF_2CF_2CF_2O)_{v'}—E' \quad (6)$$

[0043] wherein:

[0044] E and E', equal to or different from each other, are as above';

[0045] v' is a number such that the viscosity of the product is, within the above range.

[0046] These polymers are obtained as described in EP 148,482;

$$D—O—(CF_2CF_2O)_{z'}—D' \quad (7)$$

[0047] wherein:

[0048] D and D', equal to or different from each other, are selected from C_2F_5 or C_3F_7, one fluorine atom of one or both the end groups being replaceable with Cl and/or H; z' is an integer such that the viscosity of the product is within the above range. These polymers can be obtained as reported in U.S. Pat. No. 4,523,039;

$$E_1—O(CF_2O)_n(CF_2CF_2O)_m—(CF_2CF_2CF_2O)_p(CF_2CF_2CF_2CF_2O)_q—E_2 \quad (8)$$

[0049] wherein:

[0050] E_1 and E_2 are perfluoroalkyl end groups, equal to or different from each other, having formula $—(CF_2)_zCF_3$ wherein z is an integer from 0 to 3;

[0051] n, m, p, q are integers equal to or different from each other comprised between 0 and 100 and selected so that the viscosity of the oil is within the above range and such that the ratio m/n is between 2 and 20, n being different from 0; (p+q)/(n+m+p+q) is between 0.05 and 0.2, (n+m+p+q) being different from 0; n/(n+m+p+q) is between 0.05 and 0.40 (n+m+p+q) being different from 0. These polymers can be obtained according to EP 1,454,938.

[0052] The preferred perfluoropolyether oils are those of the classes (1), (4), (5), (8) or their mixtures and are available on the market as FOMBLIN® marketed by Solvay Solexis and those of the classes (2), (6).

[0053] The additives of the present invention are used in amounts ranging from 0.1% to 30% by weight with respect to the final composition, preferably from 1% to 20%, more preferably from 5% to 10%.

[0054] A further object of the present invention are lubricating compositions comprising (% by weight) from:

[0055] A) 70% to 99.9% by weight of at least a fluorinated oil, preferably a perfluoropolyether oil having viscosity at 20° C. between 10 and 4,000 cSt, preferably between 30 and 2,000 cSt, and comprising one or more of the following repeating units:

[0056] —CFXO—wherein X is equal to F or CF_3;—CF_2CF_2O—,—(C_3F_6O)—, —$CF_2CF_2CF_2O$—, —$CF_2CF_2CF_2CF_2O$—, said units being statistically distributed along the backbone; and

[0057] B) 0.1% to 30% by weight of at least an additive of formula

In these compositions mixtures of perfluoropolyether oils and mixtures of additives of general formula (I) can be used.

[0058] The compositions comprising an additive of formula (I) and at least an oil of the classes (1), (5) are particularly preferred; the compositions comprising the oils of the class (5) having a viscosity at 20° C. between 30 cSt and 300 cSt are more preferred.

[0059] The lubricating compositions of the present invention show a pour point lower than that of the non additivated oil.

[0060] The lubricating compositions of the present invention having a pour point lower than −950° C. are particularly useful in aerospace applications; this low pour point represents an improvement with respect to the perfluoropolyether oils available on the market.

[0061] The compositions of the present invention show a pour point temperature preferably lower of at least 4° C. with respect to the one of the perfluoropolyether lubricant contained therein, corresponding to a decrease of at least St with respect to the pour point temperature of the non additived oil (see the comparative Examples).

[0062] Furthermore the compositions of the invention are limpid as it has been found that the additives of formula (I) are completely soluble in the perfluoropolyether oils and therefore said compositions are thermodynamically stable. This is particularly advantageous as there are no phase separation problems during the storage.

[0063] The invention lubricating compositions can also comprise the additives commonly used in perfluoropolyether oils, such as for example antirust, antiwear, antioxidant additives, thermal stabilizers.

[0064] The use of the lubricating compositions of the invention, as said, is particularly advantageous in applications wherein a lubricating capability at a very low operating temperature is required, for example in aerospace applications, in the refrigeration and in equipments under vacuum used at low temperatures.

[0065] The Applicant has furthermore found that the additives of the present invention, besides being liquid at the temperature of 20° C. and having a low vapour pressure, also show a high viscosity index and a pour point lower than −90° C., preferably lower than −95° C., more preferably lower than −100° C. Therefore said additives can be used also as lubricating oils per se.

[0066] A further object of the present invention is the use of compounds (I) as lubricating oils having a low pour point.

[0067] The compounds of formula (I) can be prepared, for example, according to the following process comprising the following steps:

[0068] a) synthesis of a peroxidic perfluoropolyether, obtainable by one of the following reactions:

[0069] a1) tetrafluoroethylene (TFE) photooxidation, in the presence of UV light, at a temperature between −40° C. and −100° C., in solvents liquid under the reaction conditions, of formula:

$$C_yF_{(2y+2-x)}H_x \qquad \text{(II)}$$

[0070] wherein y is an integer from 2 to 4; x is an integer equal to 0 or 1;

[0071] in the presence of elemental fluorine as chain transfer agent, diluted with an inert gas; or

[0072] a2) TFE oxidation by using as radical initiator fluorine or hypofluorites of formula

$$R_fOF \qquad \text{(III)}$$

[0073] R_f being a perfluoroalkyl radical from 1 to 3 carbon atoms,

[0074] by operating in the temperature range from −40° C. to −100° C. at a pressure between 0 and 12 bar, in an inert solvent;

[0075] preferably a2) is used;

[0076] b) thermal treatment of the peroxidic product obtained in step a) at a temperature from 150° C. to 250° C., optionally in the presence of chain transfer agent selected from elemental fluorine, and one or more hypofluorites of formula (III);

[0077] c) treatment with elemental fluorine of the polymer obtained in b) at temperatures from 100° C. to 250° C., or by treatment with fluorine in the presence of UV radiations, by operating at temperatures between −50° C. and 120° C.

In step a1) generally the fluorine is added in amounts such that the molar ratio fluorine/tetrafluoroethylene is between $2\cdot10^{-2}$ and $1.2\cdot10^{-3}$, preferably between $1.2\cdot10^{-2}$ and $1.7\cdot10^{-3}$ and is diluted with an inert gas in ratios by volume from 1/50 to 1/1,000.

[0078] In step a1) preferably the solvents are the following: perfluoropropane (C_3F_8), hydropentafluoroethane (C_2F_5H) and 2-hydroheptafluoropropane (CF_3CFHCF_3), C_4F_9H (for example CF_3C -$FHCF_2CF_3$, $(CF_3)_3CH$, $HCF_2CF_2CF_2CF_3$).

[0079] The solvent used in step al) is liquid at the synthesis temperatures (−40°÷−80° C.) and solubilizes the peroxidic polymer even in high molecular weights forming a homogeneous solution. This represents a remarkable advantage since there is no separation of the peroxidic polymer. This makes possible the industrial use of said process as no cloggings of the industrial plant piping due to uncontrolled viscosity increase take place. Further the thermal exchanges are extremely effective and this avoids uncontrolled degradation of the peroxidic polymer.

[0080] Besides the solvents used in step a1) allow a high reaction kinetics, so to maintain high productivities combined with a low peroxidic content in the polymer, lower than 4-5 g of active oxygen/100 g of product, to avoid explosion risks.

[0081] As said, the fluorine used in step a1) must be diluted with a gas. Generally an inert gas, such as nitrogen or helium is used. Oxygen can also be used as diluent. In fact, when undiluted fluorine is used, the fluorine produces uncontrolled. local reactions and gaseous decomposition products. The latter cause stopping of the process due to the fouling of the reactor and of the optical system (UV lamp), in case of polymerization in the presence of UV radiations. Besides, in these cases, an uncontrolled increase of the P.O., higher than 4-5 g of active oxygen/100 g of product can take place, bringing to explosion risks in the system. When it is used diluted, the fluorine acts in step a1) as chain transfer agent with a very high selectivity, of the order of 90%. The fluorine furthermore, in step a1), reduces and substantially eliminates the reaction induction times avoiding the use of reaction activators.

[0082] In step a2), wherein the TFE oxidation is carried out without using the UV light, the solvents can be those above mentioned, or chlorinated solvents. For example CF_2Cl_2, optionally in admixture with COF_2 can be mentioned.

[0083] In step a2) the molar ratio TFE/chemical initiator ranges from 10 to 200, preferably from 40 to 120.

[0084] In step b) the use of chain transfer agents can be omitted when the control of the molecular weight is not necessary. This happens, for example, when the viscosity of the peroxidic product is lower than 5,000 cSt at 20° C.

[0085] In step b) generally the fluorine or the hypofluorites of formula (III), when present, are used with a flow-rate from $1\cdot10^{-2}$ to 3 moles ·h/Kg polymer, preferably from $2\cdot10^{-2}$ to 2.

[0086] Step a) and step b) of the process of the present invention can be carried out in a discontinous, semicontinuous or continuous way.

[0087] Step b) ends when the peroxidic content in the polymer is substantially absent. This means that the P.O. value is equal to or lower than the sensitivity limit of the analytical method used (1 ppm) which consists in the titration with thiosulphate of the iodine developed by the reaction of the peroxidic polymer with sodium iodide. Generally the thermal treatment times are from 10 to 30 hours, depending on the P.O. and the temperature used in this step.

[0088] Step c) is usually carried out in a discontinuous way. The reaction ends when, at ^{19}F NMR analysis, the functional end groups (mainly $—OCF_2COF$ and —OCOF) have been transformed into perfluoroalkyl end groups (method sensitivity limit: 1 meq/Kg polymer).

[0089] In step c) the fluorine is fed in amounts so to have a concentration in the perfluoropolyether generally corresponding to the fluorine solubility limit. At the temperature used in this step, it is of the order of 10^{-2} moles of fluorine/litre of polymer.

[0090] Optionally, the product can be distilled to obtain fractions having a given number average molecular weight and a determined distribution of the molecular weights.

[0091] Some illustrative but not limitative Examples of the present invention follow.

EXAMPLES

Characterization:

[0092] Determination of the Pour Point Temperature:

[0093] It has been carried out by using the ASTM D 97 method.

[0094] The reported results are the average of 5 tests.

[0095] Determination of the Kinematic Viscosity:

[0096] It has been carried out according to the ASTM D 445 method.

[0097] Determination of the Viscosity Index:

[0098] It has been carried out according to the ASTM D 2270 method. The higher the viscosity index, the lower is the viscosity variation as the temperature changes.

Example 1

[0099] 95 g of a perfluoropolyether oil of the class (5), commercially known with the name Fomblin® Z25, having kinematic viscosity at 20°C. of 255 cSt, viscosity index equal to 356 and pour point of −74° C., are additioned with 5 g of an additive of formula (I) having number average molecular weight of 2,467, m/n=0.33 and p+q/(p+q+m+n)=0.016.

[0100] The pour point of the obtained composition is determined according to the above method and is equal to −82° C. The viscosity index of said composition is equal to 348.

[0101] Therefore the obtained lubricating composition shows a pour point of SOC lower than that of the basic perfluoropolyether oil, corresponding to a pour point temperature decrease of about 11%.

[0102] It is to be noted that the addition of the additive (I) of the present invention to the perfluoropolyether oil does not alter the lubricant nature since the viscosity index of the obtained lubricating composition is subsantially equal to that of the basic oil.

Example 2

[0103] The Example 1 was repeated by using an additive of formula (I) having number average molecular weight of 3,777, m/n=0.31 and p+q/(p+q+m+n)=0.016.

[0104] The pour point of the obtained mixture is determined according to the above method and is equal to −80° C.

[0105] Therefore the obtained lubricting composition shows a pour point of 6° C. lower than that of the basic perfluoropolyether oil corresponding to a pour point temperature decrease equal to about 8%.

Example 3 (Comparative)

[0106] The Example 1 was repeated by using as an additive a compound having formula (I) and number average molecular weight of 4,000 but having m/n=0.8.

[0107] The pour point of the obtained mixture is determined according to the above method and is equal to −76° C.

[0108] Therefore the obtained lubricating composition shows a pour point of only 3° C. lower than that of the basic perfluoropolyether oil. Such temperature variation corresponds to a decrease of about 3%.

Example 4

[0109] 90 g of a perfluoropolyether oil of class (5), commercially known as Fomblin® Z03, having kinematic viscosity at 20° C. of 30 cSt and pour point of −93° C., are additioned with 10 g of an additive having formula (I), wherein the number average molecular weight is 2,467, m/n=0.33 and p+q/(p+q+m+n)=0.016.

[0110] The pour point of the obtained mixture is determined according to the above method and is equal to −102° C.

[0111] Therefore the obtained lubricating composition shows a pour point of 11° C. lower than that of the basic perfluoropolyether oil corresponding to a decrease of 10%.

Example 5

[0112] The Example 1 was repeated by using an additive having formula (I) wherein the number average molecular weight is 3,777; m/n=0.31 and p+q/(p+q+m+n)=0.016.

[0113] The pour point of the obtained mixture is determined according to the above method and is equal to −99° C.

[0114] Therefore the lubricating composition of the Example shows a pour point of 6° C. lower than that of the basic perfluoropolyether oil corresponding to a decrease of 6%.

Example 6

[0115] The Example 1 was repeated but by using as lubricant the perfluoropolyether oil of structure (6) and commercially known as Demnum® S-20, having a viscosity of 53 cSt and a pour point of −75° C. determined with the above method.

[0116] The pour point of the obtained mixture is determined according to the above method and is equal to −79° C.

[0117] Therefore the obtained lubricating composition shows a pour point of 4° C. lower than that of the basic perfluoropolyether oil corresponding to a decrease of 6%.

Example 7 (Comparative)

[0118] The Example 6 was repeated but by using as additive a compound having formula (I) and number average molecular weight of 4,000 but wherein m/n=0.8.

[0119] The pour point of the obtained mixture is determined according to the above method and is equal to −75° C.

[0120] Therefore the obtained lubricating composition shows a pour point equal to that of the basic perfluoropolyether oil.

Example 8

[0121] The Example 4 was repeated but by using as lubricating oil the perfluoropolyether oil of structure (6) and commercially known as Demnum® S-200, having a viscosity of 500 cSt and a pour point of −53° C. determined with the above method.

[0122] The pour point of the obtained mixture is determined according to the above method and is equal to −63° C.

[0123] Therefore the obtained lubricating composition shows a pour point of 10° C. lower than that of the basic perfluoropolyether oil corresponding to a decrease of 19%.

Example 9

[0124] The Example 1 was repeated but by using as lubricant the perfluoropolyether oil of structure (2) and commercially known as Krytox® 1506, having a viscosity of 60 cSt and a pour point of −47° C. determined with the above method.

[0125] The pour point of the obtained mixture is determined according to the above method and is equal to −51° C.

[0126] Therefore the obtained lubricating composition shows a pour point of 4° C. lower than that of the basic perfluoropolyether oil corresponding to a decrease of 9%.

Example 10

[0127] The Example 9 was repeated but changing the mixture composition by using 90 g of oil and 10 g of additive.

[0128] The pour point of the obtained mixture is determined according to the above method and is equal to −56° C.

[0129] Therefore the obtained lubricating composition shows a pour point of 90° C. lower than that of the basic perfluoropolyether oil corresponding to a decrease of 19%.

Example 11

[0130] The Example 1 additive was subjected to characterization from which the following properties resulted:

viscosity at 20° C.:	13 cSt;
viscosity at −60° C.:	344 cSt;
viscosity index:	381;
pour point:	−111° C.

[0131] From the above reported data it is evident that the compounds of formula (I) can also be used as lubricating oils per se, in particular in applications wherein a lubrication at a very low temperature is required.

TABLE 1

EXAMPLE	OIL Commercial Name	OIL Pour Point (PP) (° C.)	OIL % wt. oil	ADDITIVE % wt. oil	ADDITIVE Type	Pour Point (PP) Composition (° C.)	PP Reduction (in %)
1	Fomblin ® Z 25	−74	95	5	(I)	−82	11
2	Fomblin ® Z 25	−74	95	5	(I)	−80	8
3 (comp)	Fomblin ® Z 25	−74	95	5	(I) with m/n > 0.7	−76	3

TABLE 1-continued

	OIL			ADDITIVE			
EXAMPLE	Commercial Name	Pour Point (PP) (° C.)	% wt. oil	% wt. oil	Type	Pour Point (PP) Composition (° C.)	PP Reduction (in %)
4	Fomblin ® Z 03	−93	90	10	Ex. 1	−102	10
5	Fomblin ® Z 03	−93	90	10	Ex. 2	−99	6
6	Demnum S20	−75	95	5	Ex. 1	−79	6
7 (comp)	Demnum S20	−75	95	5	Ex. 3	−75	0
8	Demnum S200	−53	90	10	Ex. 1	−63	19
9	Krytox 1506	−47	95	5	Ex. 1	−51	9
10	Krytox 1506	−47	90	10	Ex. 1	−56	19

1. Use as "pour point depressant" additives for fluorinated oils, of compounds having the following structure:

$$X_1—O(CF_2O)_n(CF_2CF_2O)_m(CF_2CF_2CF_2O)_p(CF_2CF_2CF_2CF_2O)_q—X_2 \quad (I)$$

wherein:

the repeating units $—CF_2O—$, $—CF_2CF_2O—$, $—CF_2CF_2CF_2O—$, $—CF_2CF_2CF_2CF_2O—$, are statistically distributed along the chain;

$—X_1$ and $—X_2$ are perfluoroalkyl chain end groups equal to or different from each other, having formula $—(CF_2)_zCF_3$ wherein z is an integer from 0 to 3;

n is an integer from 1 to 200,

m is an integer from 0 to 200,

p, q are integers from 0 to 10, preferably from 0 to 5, more preferably from 0 to 1, still more preferably 0,

with the proviso that:

the ratio (p+q)/(p+q+m+n) is lower than or equal to 0.05, being also equal to 0, (p+q+m+n) being different from 0;

the ratio m/n, when n is different from 0, is lower than or equal to 0.7, preferably lower than 0.5, more preferably lower than 0.35;

the number average molecular weight of the compounds

(I) ranges from 1,000 to 10,000, preferably from 2,000 to 8,000, more preferably from 2,400 to 5,000; the chlorine atoms in the compounds of formula (I) determined by ^{19}F NMR analysis are substantially absent.

2. Use according to claim 1, wherein the fluorinated oils are perfluoropolyether oils having viscosity at 20° C. between 10 and 4,000 cSt, preferably between 30 and 2,000 cSt, and containing one or more of the following repeating units: —CFXO— wherein X is equal to F or CF_3; $—CF_2CF_2O—$, $—(C_3F_6O)—$, $—CF_2CF_2CF_2O—$, $—CF_2CF_2CF_2CF_2O—$, said units being statisticall distributed along the backbone.

3. Use according to claim 2, wherein the perfluoropolyether oils are selected from the following classes:

$$E—O—(CF_2CF(CF_3)O)_{m'}(CFXO)_{n'}—E' \quad (1)$$

wherein:

X is equal to F or CF_3;

E and E', equal to or different from each other, are selected from CF_3, C_2F_5 or C_3F_7, one fluorine atom of one or both the end groups being replaceable with Cl and/or H; m' and n' are integers such that the ratio m'/n' is between 20 and 1,000, n' being different from zero; the units being statistically distributed along the backbone, the viscosity of the product being within the above range;

$$C_3F_7O(CF(CF_3)CF_2O)_{o'}—D \quad (2)$$

wherein:

D is equal to $—C_2F_5$ or $—C_3F_7$, one fluorine atom of one or both the end groups being replaceable with Cl and/or H; o' is an integer such that the viscosity of the product is within the above range;

$$\{C_3, F_70—(CF(CF_3)CF_2O)_{p'}—CF(CF_3)—\}_2 \quad (3)$$

wherein:

p' is an integer such that the viscosity of the compound is within the above range, one F atom of one or both the end groups C_3F_7 being replaceable with Cl and/or H;

$$E—O—(CF_2CF(CF_3)O\ )_{q'}(C_2F_4O)_{r'}(CFX)_{s'}—E' \quad (4)$$

wherein:

X is equal to F or CF_3;

E and E', equal to or different from each other, are as above; q', r' and s' are integers including 0, and such that the viscosity of the product is within the above range;

$$E—O—(C_2F_4O)_{t'}(CF_2O)_{u'}—E' \quad (5)$$

wherein:

E and E', equal to or different from each other, are as above; t' and u' are integers such that the ratio t'/u' is between 0.1 and 5, u' being different from 0 and the viscosity of the product is within the above range;

$$E—O—(CF_2CF_2CF_2O)_{v'}—E' \quad (6)$$

wherein:

E and E', equal to or different from each other, are as above; v' is a number such that the viscosity of the product is within the above range;

$$D—O—(CF_2CF_2O)_{z'}—D' \quad (7)$$

wherein:

D and D', equal to or different from each other, are selected from C_2F_5 or C_3F_7, one fluorine atom of one or both the end groups being replaceable with Cl and/or H; z' is an integer such that the viscosity of the product is within the above range

$$E_1—O(CF_2O)_n(CF_2CF_2O)_m—(CF_2CF_2CF_2O)_p(CF_2CF_2CF_2CF_2O)_q—E_2 \quad (8)$$

wherein:

E_1 and E_2 are perfluoroalkyl end groups equal to or different from each other, having formula $—(CF_2)_zCF_3$ wherein z is an integer from 0 to 3; n, m, p, q are integers equal to or different from each other comprised between 0 and 100 and selected so that the viscosity of the oil is within the above range and such that the ratio m/n is between 2 and 20, n being different from 0; (p+q)/(n+m+p+q) is between 0.05 and 0.2, (n+m+p+q) being different from 0; n/(n+m+p+q) is between 0.05 and 0.40, (n+m+p+q) being different from 0.

4. Use according to claim 3, wherein the perfluoropolyether oils are those of the classes (1), (4), (5), (8) or their mixtures and those of the class (2) and (6).

5. Use according to claim 1, wherein the pour point depressant additives are used in amounts ranging from 0.1% to 30% by weight with respect to the final composition, preferably from 1% to 20%, more preferably from 5% to 10%.

6. Use according to claim 1, wherein mixtures of additives of general formula (I) and mixtures of perfluoropolyether oils are used.

7. Lubricating compositions comprising from:

A) 70% to 99.9% by weight of at least a fluorinated oil, preferably a perfluoropolyether oil having viscosity at 20° C. between 10 and 4,000 cSt, preferably between 30 and 2,000 cSt, and comprising one or more of the following repeating units: —CFXO— wherein X is equal to F or CF_3; $—CF_2CF_2O—$, $—(C_3F_6O—$, $—CF_2CF_2CF_2O—$, $—CF_2CF_2CF_2CF_2O—$, said units being statistically distributed along the backbone; and

B) 0.1% to 30% by weight of at least an additive of formula (I).

8. Compositions according to claim 3 comprising at least an additive of formula (I) and at least an oil of the classes (1), (5); preferably an oil of class (5) having a viscosity between 30 cSt and 300 cSt.

9. Lubricating compositions according to claim 7 comprising antirust, antiwear, antioxidant additives, suitable thermal stabilizers for perfluoropolyether oils.

10. Use of the compounds (I) of claim 1 as lubricating oils having a low pour point.

11. Perfluoropolyether lubricating oils of claim 10.

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