



(43) International Publication Date
11 August 2016 (11.08.2016)

(10) International Publication Number
WO 2016/124579 A1

(51) International Patent Classification:

C10M 147/04 (2006.01) *C14C 11/00* (2006.01)
B41J 2/00 (2006.01) *D21C 3/28* (2006.01)
C08G 65/26 (2006.01) *D06B 3/28* (2006.01)

(21) International Application Number:

PCT/EP2016/052157

(22) International Filing Date:

2 February 2016 (02.02.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15154227.1 6 February 2015 (06.02.2015) EP

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(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, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, 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, SA, 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, ST, 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))

(54) Title: (PER)FLUOROPOLYETHER POLYMERS AS ANTIFOAM AGENTS

(57) Abstract: The present invention relates to the use of perfluoropolyether polymers as antifoam agents in functional fluid compositions, and compositions comprising the same.



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Description**(Per)fluoropolyether polymers as antifoam agents****Cross reference to related applications**

[0001] This application claims priority from European application No. 15154227.1, filed on 6th February 2015, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention relates to the use of (per)fluoropolyether polymers as antifoam agents in functional fluid compositions, and compositions comprising the same.

Background Art

[0003] Modern mechanical equipment such as a transmission, hydraulic, engine or gear all require a functional fluid to possess a number of different properties. These properties allow the equipment to operate in different harsh environments, including various regimes of soot/sludge formation, friction, corrosion, thermal decomposition, oxidation, extreme pressure and wear. In many instances the different properties of the functional fluids are unique to a component of the mechanical equipment. This unique properties may depend on chemical interactions between additives, component design, as well as the materials used. Consequently, a number of functional fluids are required to lubricate various components within the mechanical equipment.

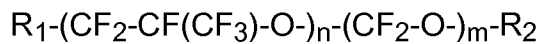
[0004] Functional fluids are known in the art as compositions comprising at least one oil in admixture with a further ingredient that is selected on the basis of the use intended for the specific functional fluid. However, functional fluids suffer of a number of disadvantages.

[0005] For example, bubbles (i.e., small gas particles entrained in the fluids) greatly influence the performance of functional fluids for hydraulic systems and may cause major problems, such as bulk modulus change, cavitation and aeration, degradation of lubrication, noise generation, oil temperature rise, and deterioration of fluid quality.

[0006] Foam formation is another common problem in functional fluids. The problem of foam formation has become more important in the last years,

because of the diffusion of functional fluids having low and very low viscosity for energy saving.

- [0007] Foam formation is influenced by the chemical and physical properties of the functional fluids and also by the operating conditions (e.g. temperature, viscosity, pressure, circulation rate) or can be caused by the presence of additives.
- [0008] Foam does not circulate in the mechanical equipment and reduces the efficiency of the functional fluid, resulting in drawbacks such as accelerated wear, overheating, cavitation and noise caused by entrained air in the system. Severe foaming can also lead to breakdown of the normal operation of the mechanical equipment.
- [0009] Foam control additives are thus conventionally used in industrial processes where foaming occurs. Foam control additives include both antifoams, i.e. chemical agents that are typically dispersed into the foaming solution to prevent the formation of excessive foam, and defoamers, i.e. substances that are sprayed over and rapidly collapse the existing foam.
- [0010] Among foam control additives, (per)fluoropolyether (PFPE) polymer derivatives are known in the art.
- [0011] For example, **US 2011/0015420** relates to a perfluoropolyether-modified polysiloxane, which attains a good defoaming effect for organic solvents.
- [0012] **US 7,098,173 (GENERAL MOTORS CORPORATION)** relates to an antifoam composition to be used in automatic transmission fluids (ATF), said composition comprising perfluoropolyether compounds. Also, **US 2004/0121921 (GENERAL MOTORS CORPORATION)** relates to a functional fluid comprising (a) a lubricating oil, (b) an antiwear agent and (c) an antifoam composition comprising a perfluoropolyether compound.
- [0013] In the abovementioned patent and patent application in the name of General Motors Corporation, suitable PFPE compounds have the following formulae:
- $$R_1-(CF(CF_3)-CF_2-O-)_n-R_2$$
- $$R_1-(CF_2-CF_2-CF_2-O-)_n-R_2$$
- $$R_1-(CF_2-CF_2-O-)_n-(CF_2-O-)_m-R_2$$



wherein R_1 and R_2 are functional or non-functional end groups, represented by A^1-CF_2O- and $-CF_2A^2$,

wherein at least one of A^1 and A^2 comprise functional groups including carboxyl, amide, silane, hydroxyl and phosphate, notably a group of formula $-CF_2-CH_2(OCH_2CH_2)_pOH$ wherein p is from about 1 to about 20.

- [0014] The abovementioned PFPE compounds are said to work by being insoluble in ATF. However, said insolubility leads to some difficulties in formulating the ATF, such as the separation of the phase containing the PFPE compounds in the lubricating composition. This phase separation, on the one hand, affects the anti-foam properties of the lubricating composition and, on the other hand, results in a poor shelf-life of the formulation, that must be used immediately and cannot be storage. In practice, this limits the amount of antifoam agent that can be incorporated or dispersed in the ATF. Alternatively, the ATF may be re-dispersed, but the extra-steps creates additional expenses in the manufacturing process.
- [0015] The Applicant is not aware of other patents or patent applications disclosing the use of the PFPE polymers having chain ends comprising alkoxylated end groups as antifoaming additives in functional fluids other than ATF, such as for instance functional fluids for gear boxes, engines, compressors, hydraulics.
- [0016] **WO 2014/067715** (SICPA HOLDING SA) discloses radiation curable varnishes comprising one or more cationically curable compounds and one or more di-hydroxyl-terminated perfluoropolyether compounds of the general formula
- $$HO-(CH_2CH_2O)_c-CH_2CF_2O(CF_2CF_2O)_a(CF_2O)_bCF_2CH_2-(OCH_2CH_2)_dOH$$
- wherein a and b independently are integers in a range between 0 and 50, wherein $a+b \geq 1$ and
- wherein c and d may be the same or different and are in the range of 1-20.
- [0017] **JP 5780336** (DAINIPPON INK AND CHEMICALS) discloses a grease base oil diffusion preventing agent comprising a compound with an average molecular mass of 1000 to 3000 and general formula
- $$X-CF_2-(OCF_2CF_2)_p-(OCF_2)_q-OCF_2-X$$

wherein

X is a hydroxymethyl group, p is from 2 to 8, q is from 0 to 30, with p+1 being 3 or greater.

Summary of invention

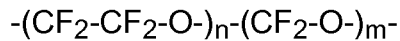
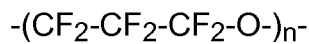
[0018] The Applicant has perceived that the problem of the separation of the phase containing the PFPE compound(s) in functional fluid compositions has not been solved in the art, not even in the abovementioned patent **US 7,098,173** and patent application **US 2004/0121921** .

[0019] Also, the Applicant has perceived that the insolubility of the PFPE compounds in functional fluid composition is a problem for both the manufacturers and the end-users of such functional fluid compositions, in particular in term of shelf-life.

[0020] Thus, the Applicant faced the problem to provide functional fluid compositions, wherein the foam formation is reduced and which do not show phase separation during storage, so as to provide compositions having longer shelf-life.

[0021] The Applicant has now surprisingly found that the above problem can be solved by using a PFPE polymer (polymer PFPE-PAGs) comprising a (per)fluoropolyether chain having two chain ends, wherein one or both chain ends bear a definite number of oxyalkylene units free from fluorine atoms, as anti-foam agent.

[0022] Thus, in a first aspect the present invention relates to the use of a (per)fluoropolyether polymer (polymer PFPE-PAGs) as anti-foam agent, said polymer (PFPE-PAGs) comprising a (per)fluoropolyoxyalkylene chain [chain (R_f)] having two chain ends, wherein one or both chain end(s) bear(s) a hydroxy-, alkoxy- or acyloxy- terminated polyoxyalkylene chain free from fluorine atoms [chain (R_a)], said chain (R_a) comprising from 4 to 50 fluorine-free oxyalkylene units, said units being the same or different each other and being selected from $-\text{CH}_2\text{CH}_2\text{O}-$ and $-\text{CH}_2\text{CH}(\text{J})\text{O}-$, wherein J is independently straight or branched alkyl or aryl, preferably methyl, ethyl or phenyl, provided that when said chain (R_f) is $-(\text{CF}(\text{CF}_3)-\text{CF}_2-\text{O})_n-$



$-(\text{CF}_2-\text{CF}(\text{CF}_3)-\text{O})_n-(\text{CF}_2-\text{O})_m-$, wherein n is at least 3 and the sum $n+m$ is at least 8, none of the two chain ends bears a hydroxy-terminated chain (R_a) comprising from 4 to 20 units of formula $-\text{CH}_2\text{CH}_2\text{O}-$.

- [0023] In a preferred embodiment, said polymer PFPE-PAGs is used as anti-foam agent in a functional fluid composition.
- [0024] In a second aspect, the present invention relates to a method for reducing the formation of foam in a functional fluid composition [composition (C)], said method comprising providing a composition (C) comprising at least one lubricant base oils, and adding at least one polymer PFPE-PAGs as defined above to said composition (C).
- [0025] The Applicant has surprisingly found that when the abovementioned polymer PFPE-PAGs are used as anti-foam agents in functional fluid compositions, no separation of the phase comprising the polymer PFPE-PAGs is observed during storage.
- [0026] The Applicant has also found that the abovementioned polymer PFPE-PAGs allow to reduce entrained air and hence bubbles formation, thus improving the air release properties of the functional fluid.
- [0027] In addition, the Applicant has found that the abovementioned polymer PFPE-PAGs can be easily added into the final functional fluid composition or into additive packages, without the need of further extra-steps in the manufacturing process.
- [0028] In a third aspect, the present invention relates a functional fluid composition [composition (C)] comprising at least one polymer PFPE-PAGs as defined above as anti-foam agent, and further ingredients.
- [0029] Polymer PFPE-PAGs will be herein after referred to as “mono- or bi-functional PFPE-PAGs”, depending on whether one or both chain ends bear a chain (R_a).

Description of embodiments

- [0030] For the purposes of the present description:
- the expression “functional fluid composition” is intended to indicate a fluid composition comprising at least one oil in admixture with a further

ingredient that is selected on the basis of the intended use, such as for example metal working fluids, such as cutting oils and coolants; engine oils; gear lubricants; hydraulic fluids; automatic transmission fluids; paints coating and inks; compositions for paper industry, oil recovery, construction industry, jet dyeing of textiles, leather processing, chemical processing;

- the term "anti-foam" is intended to indicate the prevention of the formation of foam;
- the term "(per)fluoropolyether" is intended to indicate a "fully or partially fluorinated polyether";
- the expression "(per)fluoropolyoxyalkylene chain" is intended to indicate a partially or fully fluorinated, straight or branched, polyoxyalkylene chain;
- the term "(halo)alkyl" is intended to indicate a hydrocarbon group wherein one or more hydrogens can be replaced by one or more halogen atoms, preferably fluorine atoms;
- the use of parentheses before and after symbols or numbers identifying compounds, chemical formulae or parts of formulae has the mere purpose of better distinguishing those symbols or numbers from the rest of the text and hence said parentheses can also be omitted.

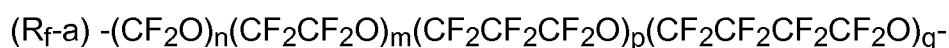
[0031] In a preferred embodiment, said chain (R_f) comprises recurring units, which may be equal to or different each other, selected from:

- (i) $-CFXO-$, wherein X is F or CF_3 ,
- (ii) $-CFXCFXO-$, wherein X, equal or different at each occurrence, is F or CF_3 , with the provision that at least one of X is $-F$,
- (iii) $-CF_2CF_2CW_2O-$, wherein each of W, equal or different from each other, are F or H,
- (iv) $-CF_2CF_2CF_2CF_2O-$,
- (v) $-(CF_2)_j-CFZ'-O-$ wherein j is an integer from 0 to 3 and Z' is a group of general formula $-OR_f'T$, wherein R_f' is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings : $-CFXO-$, $-CF_2CFXO-$, $-CF_2CF_2CF_2O-$, $-CF_2CF_2CF_2CF_2O-$, with each of each of X being independently F or CF_3 and T being a C_1 - C_3 perfluoroalkyl group.

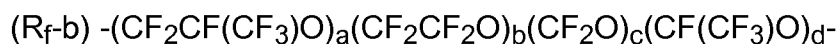
- [0032] Preferably, said chain (R_a) is terminated with a hydroxyl group, an alkyl group comprising from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, or an acyloxy group comprising from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms. In a preferred embodiment, said chain (R_a) is a hydroxyl group.
- [0033] As it will be apparent to the person skilled in the art, said chain (R_f) and said chain (R_a) are linked by a group of formula $-(CFX)_a-D-$ wherein
- a is an integer equal to or higher than 1, preferably from 1 to 10, more preferably from 1 to 3;
 - X is F or CF_3 , provided that when a is higher than 1, X is F;
 - D is a divalent alkyl chain comprising from 1 to 20, more preferably from 1 to 6 and even more preferably from 1 to 3 carbon atoms, said alkyl chain being optionally interrupted by at least one oxygen atom and/or optionally substituted with at least one hydroxy group and/or with a perfluoroalkyl group comprising from 1 to 3 carbon atoms.
- [0034] Thus, the general structural formula of polymer PFPE-PAGs can be represented as follows:
- $$-O-D-(CFX)_aO(R_f)(CFX')_b-D^*-$$
- wherein
- a, X and D are as defined above
 - b has the same meanings detailed for a,
 - X' has the same meanings detailed above for X and
 - D* has the same meanings detailed above for D.
- [0035] Preferably, polymer PFPE-PAGs for the use according to the present invention comply with formula (I) below:
- $$A-O-R_f-(CF_2)_x-CFZ-CH_2-O-R_a \quad (I)$$
- wherein:
- R_f is a (per)fluoropolyoxyalkylene chain having an average number molecular weight (M_n) ranging from 100 to 8,000, preferably from 500 to 6,000, more preferably from 1000 to 4,000, and comprising, preferably consisting of, repeating units, which may be equal to or different from one another, selected from those of formula (i) to (v) as defined above;

- Z is fluorine or CF₃;
- x is 0 or 1, with the proviso that, when, x is 1, Z is F;
- A is -(CF₂)_x-CFZ-CH₂-O-R_a, wherein x and Z are as defined above, or is a straight or branched C₁-C₄ perfluoroalkyl group wherein one fluorine atom can be substituted by one chlorine atom or one hydrogen atom, with the proviso that, if chlorine is present in group A, it is in a molar amount lower than 2% with respect to the overall amount of end groups and
- R_a is a hydroxy-, alkoxy- or acyloxy- terminated polyoxyalkylene chain free from fluorine atoms [chain (R_a)], said chain R_a being as defined above.

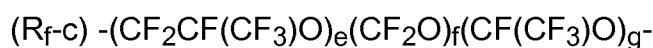
[0036] More preferably, in polymer PFPE-PAGs of formula (I) above, chain (R_f) is selected from the following formulae (R_f-a) to (R_f-c):



wherein m, n, p, q are 0 or integers selected in such a way as chain R_f meets the above number average molecular weight requirement, with the proviso that if, p and q are simultaneously 0, n is not 0; when m is other than 0, the m/n ratio is preferably between 0.1 and 20; when (m+n) is other than 0, (p+q)/(m+n) is preferably between 0 and 0.2;



wherein a, b, c, d are 0 or integers selected in such a way as chain R_f meets the above number average molecular weight requirement; with the proviso that, at least one of a, c and d is not 0; when b is other than 0, a/b is preferably between 0.1 and 10; when (a+b) is different from 0 (c+d)/(a+b) preferably is between 0.01 and 0.5, more preferably between 0.01 and 0.2;

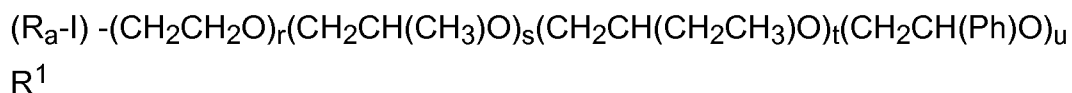


wherein e, f, g are 0 or integers selected in such a way as chain R_f meets the above number average molecular weight requirement; when e is other than 0, (f+g)/e is preferably between 0.01 and 0.5, more preferably between 0.01 and 0.2.

[0037] Polymers PFPE-PAGs of formula (I) wherein chain (R_f) complies with formula (R_f-a) as defined above are particularly preferred in the method of the invention.

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[0038] More preferably, in polymer PFPE-PAGs of formula (I) above, chain (R_a) complies with the following formula (R_a-I):



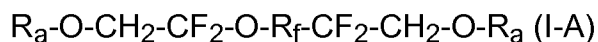
wherein r, s, t and u are independently selected from 0 and a positive number, with r+s+t+u ranging from 4 to 50, preferably from 4 to 15, more preferably from 4 to 10, and R¹ is selected from hydrogen, C₁-C₄ straight or branched alkyl, preferably methyl, and -C(O)R², wherein R² is C₁-C₄ straight or branched (halo)alkyl.

[0039] In one preferred embodiment, in the above chain (R_a-I), r is a positive number ranging from 4 to 15, preferably from 4 to 10, s is a positive number ranging from 2 to 10, preferably from 4 to 8, t and u are 0, and R¹ is selected from hydrogen or methyl. More preferably, r and s are positive numbers and t and u are 0, r+s ranges from 4 to 20, preferably from 10 to 15, and R¹ is selected from hydrogen or methyl.

[0040] In another preferred embodiment, r, t and u are 0, s is a positive number ranging from 4 to 15, preferably from 4 to 10, and R¹ is selected from hydrogen or methyl.

[0041] When two or more of the -CH₂CH₂O-, -CH₂CH(CH₃)O-, -CH₂CH(CH₂CH₃)O- and -CH₂CH(Ph)O- units are present in chain (R_a-I), they can be arranged in blocks or they can be disposed at random.

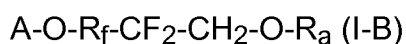
[0042] According to one preferred embodiment, polymer PFPE-PAGs are bifunctional PFPE-PAGs complying with formula (I-A) below:



wherein:

- R_a is as defined above and
- R_f complies with formula (R_f-a) as defined above.

[0043] According to another preferred embodiment, polymer PFPE-PAGs are monofunctional PFPE-PAGs complying with formula (I-B) below:



wherein:

- A is a straight or branched C₁-C₄ perfluoroalkyl group wherein one fluorine atom can be substituted by one chlorine atom or one hydrogen

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atom, with the proviso that, if chlorine is present in group A, it is in a molar amount lower than 2% with respect to the overall amount of end groups,

- R_a is as defined above and

- R_f complies with formula (a) as defined above.

[0044] In the method of the invention, bifunctional PFPE-PAGs of formula (I-A) are preferred.

[0045] A preferred group of polymers PFPE-PAGs of formula (I) complies with formula (I*) below:



wherein:

- R_f is a (per)fluoropolyoxyalkylene chain having an average number molecular weight M_n ranging from 100 to 8,000, preferably from 500 to 6,000, more preferably from 1,000 to 4,000, and comprising, preferably consisting of, repeating units, which may be equal to or different from one another, selected from

(i) $-CFXO-$, wherein X is F or CF_3 ,

(ii) $-CFXCFXO-$, wherein X, equal or different at each occurrence, is F or CF_3 , with the proviso that at least one of X is $-F$,

(iii) $-CF_2CF_2CW_2O-$, wherein each of W, equal or different from each other, are F or H,

(iv) $-CF_2CF_2CF_2CF_2O-$,

(v) $-(CF_2)_j-CFZ'-O-$ wherein j is an integer from 0 to 3 and Z' is a group of general formula $-OR_f'T$, wherein R_f' is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings : $-CFXO-$, $-CF_2CFXO-$, $-CF_2CF_2CF_2O-$, $-CF_2CF_2CF_2CF_2O-$, with each of each of X being independently F or CF_3 , and T being a C_1 - C_3 perfluoroalkyl group;

- Z is fluorine or CF_3 ;

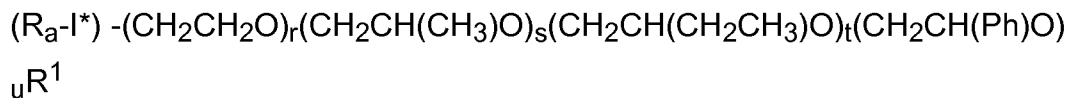
- x is 0 or 1, with the proviso that, when, x is 1, Z is F;

- A is $(CF_2)_x-CFZ-CH_2-O-R_a$, wherein x and Z are as defined above, or is selected from straight or branched C_1 - C_4 perfluoroalkyl groups wherein one fluorine atom can be substituted by one chlorine atom or one hydrogen atom, with the proviso that, if chlorine is present in group A, it is

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in a molar amount lower than 2% with respect to the overall amount of end groups and

- R_a complies with the following formula (R_a-I^*):

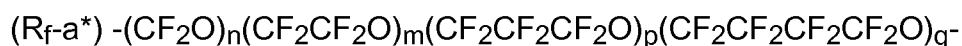


wherein:

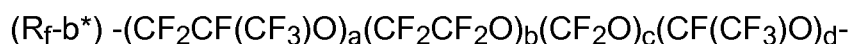
- r , s , t and u are independently selected from 0 and a positive number and $r+s+t+u$ is a positive number ranging from 4 to 50, preferably from 4 to 15, more preferably from 4 to 10; and

- R^1 is selected from hydrogen, C_1 - C_4 straight or branched alkyl, and $-C(O)R^2$, wherein R^2 is C_1 - C_4 straight or branched (halo)alkyl, with the proviso that, when R^1 is hydrogen, at least one of s , t and u is not 0.

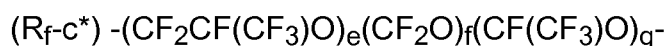
[0046] Preferred chain (R_f) in the PFPE-PAGs of formula (I^*) are those selected from formulae (R_f-a^*) - (R_f-c^*) here below:



wherein m , n , p , q are 0 or integers selected in such a way as chain R_f meets the above number average molecular weight requirement; when m is other than 0, the m/n ratio is preferably between 0.1 and 20, more preferably between 0.2 and 10 and even more preferably between 0.5 and 5; when $(m+n)$ is other than 0, $(p+q)/(m+n)$ is preferably between 0 and 0.2;



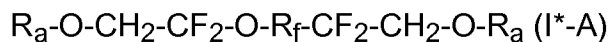
wherein a , b , c , d are 0 or integers selected in such a way as chain R_f meets the above number average molecular weight requirement; with the proviso that, at least one of a , c and d is not 0; when b is other than 0, a/b is preferably between 0.1 and 10; when $(a+b)$ is different from 0 $(c+d)/(a+b)$ preferably is between 0.01 and 0.5, more preferably between 0.01 and 0.2;



wherein e , f , g are 0 or integers selected in such a way as chain R_f meets the above number average molecular weight requirement; when e is other than 0, $(f+g)/e$ is preferably between 0.01 and 0.5, more preferably between 0.01 and 0.2.

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[0047] A first group of preferred compounds (I*) complies with formula (I*-A) below:



in which:

- R_f complies with formulae (R_{f-a^*}) – (R_{f-c^*}) as defined above; and
- R_a complies with formula (R_{a-l^*}) as defined above.

[0048] Preferably, in compounds (I*-A), chain R_f complies with formula (R_{f-a^*}).

[0049] A second group of compounds (I*) complies with formula (I*-B) below:



in which:

- R_f complies with formulae (R_{f-a^*}) – (R_{f-c^*}) as defined above; and
- R_a complies with formula (R_{a-l^*}) as defined above, and A is a straight or branched C_1 - C_4 perfluoroalkyl group wherein one fluorine atom can be substituted by one chlorine atom or one hydrogen atom, with the proviso that, if chlorine is present in group A, it is in a molar amount lower than 2% with respect to the overall amount of end groups.

[0050] Preferably, in compounds (I*-B), chain R_f complies with formula (R_{f-a^*}).

[0051] Preferred compounds (I*-A) and (I*-B) are those wherein $r+s$ is a positive number ranging from 2 to 20, preferably from 4 to 15, and t and u are 0.

[0052] Further preferred compounds (I*-A) and (I*-B) are those wherein r , t and u are 0 and s is a positive number ranging from 4 to 15, preferably from 4 to 10.

[0053] Preferably, in compounds (I*-A) and (I*-B), R^1 is hydrogen or methyl.

[0054] The PFPE-PAGs for the use according to the present invention can be obtained for example by reaction of a mono- or bi-functional PFPE alcohol with an alkoxylating agent in such an amount as to obtain from 4 to 50, preferably from 4 to 15, more preferably from 4 to 10, oxyalkylene units at one or both chain ends.

[0055] Preferably, the functionality (F) of PFPE-PAGs, i.e. the average number of functional groups per molecule of polymer, is from 1 to 2. Bifunctional PFPE-PAGs are more preferred, which have a functionality (F) from 1.5 to 1.95, more preferably from 1.7 to 1.9. The functionality (F) can be calculated for example as disclosed in EP 1810987 A (SOLVAY SOLEXIS

S.P.A.) .

- [0056] Preferably, the PFPE-PAGs for use in the present invention are synthesised following the process (or “method”) disclosed in international patent application **WO 2014/090649** (SOLVAY SPECIALTY POLYMERS ITALY S.P.A.) , which comprises the use of a boron-based catalytic species, wherein said species is prepared by first providing a mixture of a PFPE alcohol containing a catalytic amount of the corresponding alkoxide and then bringing into contact such mixture with a catalytic amount of a boric acid triester of the same PFPE alcohol.
- [0057] Preferably, said composition (C) is selected from the group comprising metal working fluids, such as cutting oils and coolants; engine oils; gear lubricants; hydraulic fluids; automatic transmission fluids; shock absorber oils; paints coating and inks; compositions for paper industry, oil recovery, construction industry, jet dyeing of textiles, leather processing, chemical processing.
- [0058] In a third aspect, the present invention relates to a functional fluid composition [composition (C)] comprising at least one polymer PFPE-PAGs as defined above as anti-foam agent and further ingredients.
- [0059] Preferably, said polymer PFPE-PAGs is added to said composition (C) and then a mixing step is performed, for example by high shear mixing.
- [0060] Preferably, said composition (C) comprises said at least one polymer PFPE-PAGs in an amount of from 0.0001 wt.% (1 ppm) to 3 wt.% based on the total weight of said composition (C), more preferably from 0.0001 wt.% (1 ppm) to less than 2.5 wt.% and even more preferably from 0.0005 wt.% (5 ppm) to 2 wt.%.
- [0061] Preferably, said polymer PFPE-PAGs complies with formula (I) as defined above.
- [0062] Preferably, said further ingredients are selected from those commonly used in lubricant compositions, such as lubricant base oils and optionally further additives.
- [0063] Non-limiting examples of lubricant base oils comprise mineral oils, in particular those belonging to Group III (according to American Petroleum Institute – API – classification); to Group (IV) such as polyalphaolefins

(PAO) and PAGs; silicon oils; polyphenylethers; etc...

- [0064] Preferably, said composition (C) comprises said at least one lubricant base oil in an amount of from 90 to 99.9999 wt.% based on the total weight of said composition (C).
- [0065] Non-limiting examples of additives comprise antirust agents, antioxidants, thermal stabilizers, pour-point depressants, antiwear agents, including those for high pressures, dispersants, tracers, dyestuffs and fillers.
- [0066] Examples of dispersants are, for example, surfactants, preferably non-ionic surfactants, more preferably (per)fluoropolyether surfactants and (per)fluoroalkyl surfactants.
- [0067] Examples of fillers are organic fillers such as polytetrafluoroethylene (PTFE) and inorganic particles such as silica and talc.
- [0068] Each of the abovementioned additives is preferably present in composition (C) in an amount of from 0.0001 to 8 wt.% based on the total weight of said composition (C).
- [0069] Should the disclosure of any patents, patent applications and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.
- [0070] The invention will be herein after illustrated in greater detail by means of the Examples contained in the following Experimental Section; the Examples are merely illustrative and are by no means to be interpreted as limiting the scope of the invention.

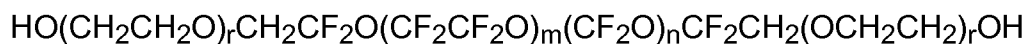
Experimental Section

[0071] Materials

- [0072] Polyethoxy-propoxy-perfluoropolyether PFPE-PAG (hereinafter "PFPE-PAG EO/PO") used in the Example 1 and complying with formula:
- $$\text{HO}(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_s(\text{CH}_2\text{CH}_2\text{O})_r\text{CH}_2\text{CF}_2\text{O}-(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n\text{CF}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_r(\text{OCH}_2\text{CH}(\text{CH}_3))_s\text{OH}$$
- wherein $r = 8.5$, $s = 4.5$, $m/n \sim 1$, average number molecular weight (M_n) 2,900 and $F = 1.8$ was manufactured according to the procedure disclosed in WO 2014/090649 .

- [0073] Polyethoxy-perfluoropolyether (hereinafter "PFPE-PAG nEO=7) used in

Comparative Example 2 and complying with formula:



wherein $r = 7$, $m/n \sim 1$, average number molecular weight (M_n) 2,200 and $F = 1.8$ was manufactured according to the procedure disclosed in the aforementioned international patent application **WO 2014/090649**. PFPE-PAG $n_{EO}=7$ is representative of the PFPE disclosed in prior art document **US 7,098,173** (GENERAL MOTORS CORPORATION) cited above.

[0074] Branched perfluoropolyether Fomblin ®Y25/6 used in Comparative Example 3 complying with formula:



wherein $m/n=40/1$, average number molecular weight (M_n) 2,400 and kinematic viscosity at 20°C 250 cSt (measured according to ASTM D445).

[0075] YUBASE4 from SK lubricants - mineral oil belonging to Group III and having a kinematic viscosity of 5 cSt at 100°C (measured according to ASTM D445).

[0076] **Example 1**

[0077] A solution containing 300 ppm (0.03% by weight) of PFPE-PAG EO/PO was prepared by magnetic stirring 3 g of PFPE-PAG EO/PO in 100 g of mineral oil in a glass vessel over an hotplate at 60°C for 1 h.

[0078] The solution was analysed by visual inspection after stirring ($t=0$) and after 24 hours ($t=24h$). The results are reported in the following Table 1.

[0079] **Example 2 (comparative example)**

[0080] A solution containing 300 ppm (0.03% by weight) of PFPE PAG (EO, $n=7$) was prepared by magnetic stirring 3 g of PFPE PAG (EO, $n=7$) in 100 g of mineral oil in a glass vessel over an hotplate at 60°C for 1 h.

[0081] The solution was analysed by visual inspection after stirring ($t=0$) and after 24 hours ($t=24h$). The results are reported in the following Table 1.

[0082] **Example 3 (comparative example)**

[0083] A solution containing 300 ppm (0.03% by weight) of Fomblin® Y25/6 was

prepared by magnetic stirring 3 g of Fomblin® Y25/6 in 100 g of mineral oil in a glass vessel over an hotplate at 60°C for 1 h.

[0084] The solution was analysed by visual inspection after stirring (t=0) and after 24 hours (t=24h). The results are reported in the following Table 1.

Table 1

	t=0	t=24h
Example 1	Clear 1 phase	Clear 1 phase
Example 2(*)	Slight opalescent 1 phase	2 phases
Example 3(*)	Opalescent 1 phase	2 phases

[0085] (*) comparative

[0086] The above results show that no sediments or phase separation was observed in the solution obtained in Example 1 according to the present invention. Differently, phase separation was observed after 24 hours in the solution obtained according to comparative Example 2 and comparative Example 3.

Claims

1. Use of a (per)fluoropolyether polymer (polymer PFPE-PAGs) as anti-foam agent, said polymer PFPE-PAGs comprising a (per)fluoropolyoxyalkylene chain [chain (R_f)] having two chain ends, wherein one or both chain end(s) bear(s) a hydroxy-, alkoxy- or acyloxy- terminated polyoxyalkylene chain free from fluorine atoms [chain (R_a)], said chain (R_a) comprising from 4 to 50 fluorine-free oxyalkylene units, said units being the same or different each other and being selected from $-\text{CH}_2\text{CH}_2\text{O}-$ and $-\text{CH}_2\text{CH}(\text{J})\text{O}-$, wherein J is independently straight or branched alkyl or aryl, provided that when said chain (R_f) is
 - $-(\text{CF}(\text{CF}_3)-\text{CF}_2-\text{O})_n-$
 - $-(\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{O})_n-$
 - $-(\text{CF}_2-\text{CF}_2-\text{O})_n-(\text{CF}_2-\text{O})_m-$
 - $-(\text{CF}_2-\text{CF}(\text{CF}_3)-\text{O})_n-(\text{CF}_2-\text{O})_m-$, wherein n is at least 3 and the sum $n+m$ is at least 8, none of the two chain ends bears a hydroxy-terminated chain (R_a) comprising from 4 to 20 units of formula $-\text{CH}_2\text{CH}_2\text{O}-$.
2. The use according to claim 1, wherein said chain (R_f) comprises recurring units, which may be equal to or different each other, selected from:
 - (i) $-\text{CFXO}-$, wherein X is F or CF_3 ,
 - (ii) $-\text{CFXCFXO}-$, wherein X, equal or different at each occurrence, is F or CF_3 , with the provision that at least one of X is $-\text{F}$,
 - (iii) $-\text{CF}_2\text{CF}_2\text{CW}_2\text{O}-$, wherein each of W, equal or different from each other, are F or H,
 - (iv) $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$,
 - (v) $-(\text{CF}_2)_j-\text{CFZ}'-\text{O}-$ wherein j is an integer from 0 to 3 and Z' is a group of general formula $-\text{OR}_f'\text{T}$, wherein R_f' is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings : $-\text{CFXO}-$, $-\text{CF}_2\text{CFXO}-$, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$, with each of each of X being independently F or CF_3 and T being a $\text{C}_1\text{-C}_3$ perfluoroalkyl group.
3. The use according to claim 1 or 2, wherein said chain (R_f) and said chain (R_a)

are linked by a group of formula $-(CFX)_a-D-$
wherein

a is an integer equal to or higher than 1, preferably from 1 to 10, more preferably from 1 to 3;

X is F or CF_3 , provided that when a is higher than 1, X is F;

D is a divalent alkyl chain comprising from 1 to 20, more preferably from 1 to 6 and even more preferably from 1 to 3 carbon atoms, said alkyl chain being optionally interrupted by at least one oxygen atom and/or optionally substituted with at least one hydroxy group and/or with a perfluoroalkyl group comprising from 1 to 3 carbon atoms.

4. The use according to any one of the preceding claims, wherein said polymer PFPE-PAGs complies with formula (I):



wherein:

- R_f is a (per)fluoropolyoxyalkylene chain having an average number molecular weight (M_n) ranging from 100 to 8,000 and comprising repeating units, which may be equal to or different from one another, selected from those of formula (i) to (v) as defined in claim 2;

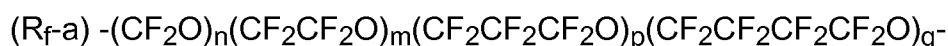
- Z is fluorine or CF_3 ;

- x is 0 or 1, with the proviso that, when, x is 1, Z is F;

- A is $-(CF_2)_x-CFZ-CH_2-O-R_a$, wherein x and Z are as defined above, or is a straight or branched C_1 - C_4 perfluoroalkyl group wherein one fluorine atom can be substituted by one chlorine atom or one hydrogen atom, with the proviso that, if chlorine is present in group A, it is in a molar amount lower than 2% with respect to the overall amount of end groups and

- R_a is a hydroxy-, alkoxy- or acyloxy- terminated polyoxyalkylene chain free from fluorine atoms [chain (R_a)], said chain R_a being as defined in claim 1.

5. The use according to claim 4, wherein in said formula (I) said chain (R_f) is selected from the following formulae (R_f -a) to (R_f -c):



wherein m, n, p, q are 0 or integers selected in such a way as chain R_f meets

the above number average molecular weight requirement, with the proviso that if, p and q are simultaneously 0, n is not 0; when m is other than 0, the m/n ratio is preferably between 0.1 and 20; when (m+n) is other than 0,

$(p+q)/(m+n)$ is preferably between 0 and 0.2;

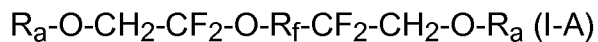
$(R_f-b) -(CF_2CF(CF_3)O)_a(CF_2CF_2O)_b(CF_2O)_c(CF(CF_3)O)_d-$

wherein a, b, c, d are 0 or integers selected in such a way as chain R_f meets the above number average molecular weight requirement; with the proviso that, at least one of a, c and d is not 0; when b is other than 0, a/b is preferably between 0.1 and 10; when (a+b) is different from 0 $(c+d)/(a+b)$ preferably is between 0.01 and 0.5, more preferably between 0.01 and 0.2;

$(R_f-c) -(CF_2CF(CF_3)O)_e(CF_2O)_f(CF(CF_3)O)_g-$

wherein e, f, g are 0 or integers selected in such a way as chain R_f meets the above number average molecular weight requirement; when e is other than 0, $(f+g)/e$ is preferably between 0.01 and 0.5, more preferably between 0.01 and 0.2.

6. The use according to claim 5, wherein in said formula (I) said chain (R_a) complies with the following formula (R_a-I):
 $(R_a-I) -(CH_2CH_2O)_r(CH_2CH(CH_3)O)_s(CH_2CH(CH_2CH_3)O)_t(CH_2CH(Ph)O)_uR^1$
 wherein r, s, t and u are independently selected from 0 and a positive number, with $r+s+t+u$ ranging from 4 to 50, and R^1 is selected from hydrogen, C_1 - C_4 straight or branched alkyl, preferably methyl, and $-C(O)R^2$, wherein R^2 is C_1 - C_4 straight or branched (halo)alkyl.
7. The use according to claim 6, wherein in chain (R_a-I), r is a positive number ranging from 4 to 15, s is a positive number ranging from 2 to 10, t and u are 0, and R^1 is selected from hydrogen or methyl.
8. The use according to any one of claims 1 to 7, wherein said polymer PFPE-PAGs is a bifunctional PFPE-PAGs.
9. The use according to claim 8, wherein said bifunctional PFPE-PAGs complies with formula (I-A) below:

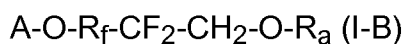


wherein:

- R_a is as defined in any one of claims 1, 3 or 5 and
- R_f complies with formula (R_f -a) as defined in claim 4.

10. The use according to any one of claim 1 to 7, wherein said polymer PFPE-PAGs is a monofunctional PFPE-PAGs.

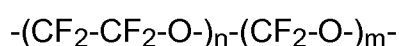
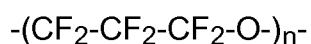
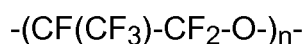
11. The use according to claim 10, wherein said monofunctional PFPE-PAGs complies with formula (I-B) below:



wherein:

- A is a straight or branched C_1 - C_4 perfluoroalkyl group wherein one fluorine atom can be substituted by one chlorine atom or one hydrogen atom, with the proviso that, if chlorine is present in group A, it is in a molar amount lower than 2% with respect to the overall amount of end groups,
- R_a is as defined in any one of claims 1, 3 or 5 and
- R_f complies with formula (R_f -a) as defined in claim 4.

12. A method for reducing the formation of foam in a functional fluid composition [composition (C)], said method comprising providing a composition (C) comprising at least one lubricant base oils, and adding to said functional fluid composition at least one polymer PFPE-PAGs comprising a (per)fluoropolyoxyalkylene chain [chain (R_f)] having two chain ends, wherein one or both chain end(s) bear(s) a hydroxy-, alkoxy- or acyloxy- terminated polyoxyalkylene chain free from fluorine atoms [chain (R_a)], said chain (R_a) comprising from 4 to 50 fluorine-free oxyalkylene units, said units being the same or different each other and being selected from $-CH_2CH_2O-$ and $-CH_2CH(J)O-$, wherein J is independently straight or branched alkyl or aryl, provided that when said chain (R_f) is



$-(\text{CF}_2\text{-CF}(\text{CF}_3)\text{-O})_n\text{-(CF}_2\text{-O)}_m\text{-}$, wherein n is at least 3 and the sum $n+m$ is at least 8, none of the two chain ends bears a hydroxy-terminated chain (R_a) comprising from 4 to 20 units of formula $-\text{CH}_2\text{CH}_2\text{O-}$.

13. The method according to claim 12, wherein said functional fluid composition (C) is selected in the group comprising metal working fluids; engine oils; gear lubricants; hydraulic fluids; automatic transmission fluids; shock absorber oils; paints coating and inks; compositions for paper industry, oil recovery, construction industry, jet dyeing of textiles, leather processing, chemical processing.
14. A composition [composition (C)] comprising at least one polymer PFPE-PAGs as defined in any one of claims 1 to 11 as antifoam agent and optionally further ingredients, wherein said at least one polymer PFPE-PAGs is in an amount of from 0.0001 wt.% (1 ppm) to 3 wt.% based on the total weight of said composition (C).
15. The composition according to claim 14, wherein said further ingredients are selected in the group lubricant base oils and further additives.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/052157

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10M147/04 B41J2/00 C08G65/26 C14C11/00 D21C3/28
D06B3/28

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)

C10M B41J C08G C14C D21C D06B C10N

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/121921 A1 (CALCUT BRENT D [US] ET AL) 24 June 2004 (2004-06-24) cited in the application paragraphs [0026], [0033] - [0035]; claims 1,18	1-15
X	WO 2014/090649 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 19 June 2014 (2014-06-19) cited in the application examples	14,15
X	WO 2014/067715 A1 (SICPA HOLDING SA [CH]) 8 May 2014 (2014-05-08) cited in the application table 1	14,15
	----- -/-	



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

12 April 2016

Date of mailing of the international search report

20/04/2016

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/052157

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2014 156606 A (DAINIPPON INK & CHEMICALS) 28 August 2014 (2014-08-28) cited in the application paragraph [0016] -----	12-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/052157

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004121921	A1	24-06-2004	NONE
WO 2014090649	A1	19-06-2014	CN 104884502 A 02-09-2015 EP 2931785 A1 21-10-2015 JP 2016500373 A 12-01-2016 KR 20150094707 A 19-08-2015 US 2015329453 A1 19-11-2015 WO 2014090649 A1 19-06-2014
WO 2014067715	A1	08-05-2014	AU 2013339747 A1 02-04-2015 CA 2884872 A1 08-05-2014 CN 104870582 A 26-08-2015 CO 7400863 A2 30-09-2015 EA 201590832 A1 31-08-2015 EP 2912125 A1 02-09-2015 JP 2015533904 A 26-11-2015 KR 20150073978 A 01-07-2015 PH 12015500656 A1 11-05-2015 SG 11201501959W A 28-05-2015 TW 201425401 A 01-07-2014 US 2015259565 A1 17-09-2015 WO 2014067715 A1 08-05-2014
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