Abstract:
The present invention relates to the use of certain (per)fluoropolyether polymers as anti-foam agents in compositions based on hydrogenated or fluorinated oils.
Description

Anti-foaming agents

Cross-reference to related applications

[0001] This application claims priority to European application No. 15177367.8 and to European application No. 15177365.2, both filed on 17 July 2015, the whole content of these applications being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention relates to the use of certain (per)fluoropolyether polymers as anti-foam agents in compositions based on hydrogenated or fluorinated oils.

Background Art

[0003] (Per)fluoropolyether (hereinafter also referred to as ‘PFPE’) oils are widely used as lubricants, hydraulic fluids, and the like as they are essentially immune to degradation by air and corrosive chemical agents, even at high temperatures. To this aim, neutral PFPE are notably used, i.e. PFPE having (per)fluoroalkyl end groups.

[0004] However, problems have arisen as neutral PFPE have the tendency to adsorb a lot of air during use, which results in foam formation. This problem is more important as the viscosity of the neutral PFPE increases. Foam formation is influenced by the chemical and physical properties of the oils and also by the operating conditions (e.g. temperature, viscosity, pressure, circulation rate) or can be caused by the presence of additives. However, foam does not circulate in the mechanical equipment and reduces the efficiency of the lubricating oils, resulting in drawbacks such as accelerated wear, overheating, cavitation and noise caused by entrained air in the system. Severe foaming could also lead to breakdown of the normal operation of the mechanical equipment.

[0005] Solutions to such a problem have been already proposed in the art. For example, US 3,445,392 (E.I. DU PONT DE NEMOURS AND COMPANY) discloses that the tendency of perfluorinated polyethers to foam can be overcome by providing a mixture of perfluorinated polyethers of the formula C3F7O[CF(CF3)CF2O]nCF2CF3 having a narrow molecular weight
distribution, as indicated by their volatility range no broader than 140 degrees on the centigrade scale.

[0006] As an alternative, foam control additives are conventionally used in industrial processes where foaming occurs. Foam control additives include both anti-foams, 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.

[0007] Among foam control additives, PFPE polymer derivatives are known in the art.

[0008] For example, US 201 1/0015420 relates to a perfluoropolyether-modified polysiloxane, which attains a good defoaming effect for organic solvents.

[0009] PFPE comprising salified carboxylate chain ends have been disclosed in the art as additives for neutral PFPE oils. For example, EP 0382224 A (AUSIMONT S.R.L.) discloses perfluoropolyethers having anti-rust properties, suitable for being used as components for lubricating greases or as antirust additives for lubricating oils and greases based on perfluoropolyethers. In particular, the products having antirust properties comprises a mixture of macromolecules having a perfluoropolyether chain of the following structure:

\[
T(CF2O)_{m}(CF2CF2O)_{n}[CF2CF(CF3)O]s[CF(CF3)O]pCF2T' (l)
\]

wherein the end groups T and T', the same or different from each other, are selected from CF2XO-, C2F4XO-, C3F6XO-, -COOH, -CONR1R2, -COO⁻HA⁺ carboxy group salified with an amine R1R2HN, -C(=O)CF3 and its hydroxylated derivative of formula -C(OH)(HO)(CF3),

wherein X is F or Cl.

However, this patent application only discloses PFPE comprising carboxylate chain ends salified with organic amine, notably morpholine, isobutylamine and triethanolamine.

[0010] In addition, metal salts of perfluorinated polyethers having at least one carboxylic acid end group have been disclosed in US 6638622 (HITACHI GLOBAL STORAGE TECHNOLOGIES) as anti-wetting and corrosion-protective agents for magnetic recording disks and magnetic
recording heads. More in particular, said compounds are also referred to as 'PFPE-COO -M+' wherein the PFPE is a perfluorinated polyether comprising monomers units having the structure -CF2O-, -CF2CF2O-, CF2 CF2CF2O-, -CF(CF3)O-, -CF(CF3)CF2O- or a combination thereof and M+ is the metal atom of the salt, preferably an alkali metal, e.g. sodium.

[0011] Further to the above, the phase behaviour of perfluoropolyether carboxylates having sodium, potassium or ammonium counter-ions in water to examine the effect of the aqueous binary systems, in terms of hydration and counter-ion binding has been investigated by CABOI, F., et al. Counterion effect on the phase behaviour of perfluoropolyether carboxylates: micelles and liquid crystals in water. Colloids and Surface. 1999, vol.160, p.47-56.

[0012] However, none of the abovementioned documents discloses or suggests the use of carboxylated PFPE as antifoam agents.

[0013] The Applicant perceived that foam formation is also a common problem in functional fluids.

[0014] 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.

[0015] 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, including notably the formation of foam, which has become more important in the last years, because of the diffusion of functional fluids having low and very low viscosity for
energy saving.

[0016] **US 7098173** (GENERAL MOTORS CORPORATION) relates to an anti-foam 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.

[0017] In the abovementioned patent and patent application in the name of General Motors Corporation, suitable PFPE compounds have the following formulae:

\[ R_1-(CF(CF_3)-CF_2-O)_n-R_2 \]
\[ R_1-(CF_2-CF_2-O)_n-R_2 \]
\[ R_1-(CF_2-CF_2-O)_n-(CF_2-O)_m-R_2 \]
\[ R_1-(CF_2-CF(CF_3)-O)_n-(CF_2-O)_m-R_2 \]

wherein \( R_1 \) and \( R_2 \) are functional or non-functional end groups. Among functional end groups, amide, alkoxy, silane, phosphate, carboxyl and \(-CF_2-CH2(OCH2CH2)pOH\) wherein \( p \) is from about 1 to about 20 are listed.

[0018] None of these documents however discloses PFPE polymers having at least one chain end comprising an acid group and a cationic counter ion as antifoaming additives for hydrogenated oils.

[0019] Compositions containing (per)fluoropolyether polymers having two chain ends and comprising at one or both chain ends a carboxylic group in its acid form or in its salt form with monovalent organic and/or inorganic cations have been disclosed in **EP 1681339 A** (SOLVAY SOLEXIS S.P.A.), **EP 2025731 A** (SOLVAY SOLEXIS S.P.A.), **EP 0435062 A** (AUSIMONT S.P.A.) and **US 521 1861** (AUSIMONT S.P.A.).

**Summary of the invention**

[0020] The Applicant perceived that there is the industry of lubricants is always looking for novel anti-foam agents.

[0021] Thus, the Applicant faced the problem to provide novel anti-foam agents that can be used in both fluorinated and hydrogenated oils, notably in neutral (per)fluoropolyether oils (PFPE) and functional fluids.

[0022] The Applicant has surprisingly found that (per)fluoropolyether polymers
comprising at least one acid end group salified with organic or inorganic counter-ions can be used as anti-foam additives in neutral PFPE and functional fluids.

[0023] Thus, in a first aspect, the present invention relates to the use of a (per)fluoropolyether polymer [polymer (P)] as anti-foam agent, said polymer (P) comprising a (per)fluoropolyether chain [chain (Rpf)] having two chain ends, wherein at least one chain end comprises at least one anionic group [group -A'] selected from the group comprising, preferably consisting of, carboxylate, sulphate and phosphate, and a cationic group [group C+] selected from the group comprising, preferably consisting of, monovalent and divalent inorganic cations andonium compounds.

[0024] In a preferred embodiment, said polymer (P) is used as anti-foam agent for neutral (per)fluoropolyether polymers [neutral PFPE].

[0025] In another preferred embodiment, said polymer (P) is used as anti-foam agent in a functional fluid composition comprising at least one hydrogenated oil.

[0026] In a further aspect, the present invention relates to a method for reducing the formation of foam in a composition comprising at least one neutral PFPE [composition (C)] or in a functional fluid composition [composition (C')]., said method comprising

- providing a composition (C) comprising at least one neutral PFPE and adding at least one polymer (P) to said composition (C), wherein said polymer (P-1) comprises chain (Rpf) as defined above for polymer (P) having two chain ends, wherein at least one chain end comprises at least one group (-A') as defined above for polymer (P), and a cationic group [group C+] selected from the group comprising, preferably consisting of, monovalent inorganic cations andonium compounds; or

- providing a composition (C') comprising at least one hydrogenated oil, and adding at least one polymer (P) to said composition (C'), wherein said polymer (P2) comprises a chain (Rpf) as defined above for polymer (P) having two chain ends, wherein at least one chain end comprises at least one group (-A') as defined above for polymer (P), and a cationic group
[group C⁺] selected from the group comprising, preferably consisting of, monovalent and divalent inorganic cations andonium compounds.

**Description of embodiments**

[0027] For the purposes of the present description:

- the term "anti-foam" is intended to indicate the prevention of the formation of foam;
- the acronym "PFPE" is intended to indicate (per)fluoropolyether and, when used as substantive, is intended to mean either the singular or the plural from, depending on the context;
- the term "(per)fluoropolyether" is intended to indicate a fully or partially fluorinated polyether and the prefix "(per)" means that the polyether can be fully or partially fluorinated;
- the expression "neutral PFPE" is intended to indicate PFPE having chain ends comprising neutral groups, such as groups comprising for example (perhalo)alkyl chains;
- the expression "functional fluid composition" is intended to indicate a fluid composition comprising at least one hydrogenated 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 expression "monovalent inorganic cations" is intended to indicate an atom or small molecule with a positive charge and a valency of 1, that does not contain carbon in covalent linkage;
- the expression "monovalent and divalent inorganic cations" is intended to indicate an atom or small molecule with a positive charge and a valence of 1 and 2, respectively, that does not contain carbon in covalent linkage;
- the expression "onium compounds" is intended to indicate a cation formally obtained by the protonation of mononuclear parent hydride of a pnictogen (group 15 of the periodic table);
- the expression "composition based on neutral PFPE" is intended to
indicate lubricant (or oil) compositions comprising a neutral PFPE as the main component;
- 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.

[0028] In a preferred embodiment, said chain \((R_f)^p\) is a chain of formula

\[-(CFX)_aO(R_f)(CFX')_b-\]

wherein

- \(a\) and \(b\), equal or different from each other, are equal to or higher than 1, preferably from 1 to 10, more preferably from 1 to 3;
- \(X\) and \(X'\), equal or different from each other, are \(-F\) or \(-CF3\), provided that when \(a\) and/or \(b\) are higher than 1, \(X\) and \(X'\) are \(-F\);
- \((R_f)\) comprises, preferably consists of, repeating units \(R^o\), said repeating units being independently selected from the group consisting of:
  (i) \(-CFXO-\), wherein \(X\) is \(F\) or \(CF3\);
  (ii) \(-CFXCFXO-\), wherein \(X\), equal or different at each occurrence, is \(F\) or \(CF3\), with the proviso that at least one of \(X\) is \(-F\);
  (iii) \(-CF2CF2CW2O-\), wherein each of \(W\), equal or different from each other, are \(F\), \(Cl\), \(H\);
  (iv) \(-CF2CF2CF2O-\);
  (v) \(-(CF2)_j-CFZ-O-\) wherein \(j\) is an integer from 0 to 3 and \(Z\) is a group of general formula \(-O-R(f_{a})-T\), wherein \(R(f_{a})\) is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the following: \(-CFXO-\), \(-CF2CFXO-\), \(-CF2CF2CF2O-\), with each of each of \(X\) being independently \(F\) or \(CF3\) and \(T\) being a \(C1-C3\) perfluoroalkyl group.

[0029] Preferably, chain \((R_f)\) complies with the following formula:

\[\text{-}[\text{(CFX}^{1}O)\text{gi(CFX}^{2}3O)\text{g2(CF2CF2CF2O)g3(CF2CF2CF2CF2O)g4]}\]

wherein

- \(X^1\) is independently selected from \(-F\) and \(-CF3\),
- \(X^2, X^3\), equal or different from each other and at each occurrence, are
- $g_1$, $g_2$, $g_3$, and $g_4$, equal or different from each other, are independently integers $\geq 0$, such that $g_1+g_2+g_3+g_4$ is in the range from 2 to 300, preferably from 2 to 100; should at least two of $g_1$, $g_2$, $g_3$ and $g_4$ be different from zero, the different recurring units are generally statistically distributed along the chain.

More preferably, chain (Rf) is selected from chains of formula: 

(Rf-IIA) $-[(\text{CF}_2\text{CF}_2\text{O})_a_i(\text{CF}_2\text{O})_a^2]$ - 

wherein:

- $a_1$ and $a_2$ are independently integers $\geq 0$ such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; both $a_1$ and $a_2$ are preferably different from zero, with the ratio $a_1/a_2$ being preferably comprised between 0.1 and 10; 

(Rf-IIIB) $-[(\text{CF}_2\text{CF}_2\text{O})_b_i(\text{CF}_2\text{O})_b^2(\text{CF}(\text{CF}_3)\text{O})_b^3(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_b^4]$ - 

wherein:

- $b_1$, $b_2$, $b_3$, and $b_4$, are independently integers $\geq 0$ such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; preferably $b_1$ is 0, $b_2$, $b_3$, $b_4$ are $>0$, with the ratio $b_4/(b_2+b_3)$ being $>1$; 

(Rf-IIIC) $-[(\text{CF}_2\text{CF}_2\text{O})_c^i(\text{CF}_2\text{O})_c^2(\text{CF}_2(\text{CF}_2)\text{cwCF}_2\text{O})_c^3]$ - 

wherein:

- $c_w = 1$ or 2; 
- $c_1$, $c_2$, and $c_3$ are independently integers $\geq 0$ chosen so that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; preferably $c_1$, $c_2$ and $c_3$ are all $>0$, with the ratio $c_3/(c_1+c_2)$ being generally lower than 0.2; 

(Rf-IIID) $-[(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_d]$ - 

wherein:

- $d$ is an integer $>0$ such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; 

(Rf-IIIE) $-[(\text{CF}_2\text{CF}_2(\text{Hal}^{*})\text{O})_e^i-(\text{CF}_2\text{CF}_2\text{CH}_2\text{O})_e^2-(\text{CF}_2\text{CF}_2\text{CH}(\text{Hal}^{*})\text{O})_e^3]$ - 

wherein:

- $\text{Hal}^{*}$, equal or different at each occurrence, is a halogen selected from
fluorine and chlorine atoms, preferably a fluorine atom;
- \( e_1, e_2, \) and \( e_3 \), equal to or different from each other, are independently integers \( \geq 0 \) such that the \( (e_1 + e_2 + e_3) \) sum is comprised between 2 and 300.

[0031] Still more preferably, chain \( (Rf) \) complies with formula \( (Rf-III) \):
\[
(Rf-III) -[(CF2O)\text{f1}(CF(CF3)O \text{f2})(CF2CF(CF3)O \text{f3})-]
\]
wherein:
\( \text{f1, f2 and f3 are independently integers } \geq 0 \) such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000.

[0032] Preferably, said group \( (A^-) \) is selected from carboxylate and phosphate. More preferably, said group \( (A^-) \) is carboxylate.

[0033] Preferably, said monovalent inorganic counter-ion is an alkaline metal, more preferably \( \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cs}^+ \).

[0034] Preferably, said divalent cations are selected in the group comprising, more preferably consisting of, alkaline earth metals such as \( \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+} \); and transition metals such as \( \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+} \). More preferably, said divalent cations are selected from \( \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Zn}^{2+} \) and \( \text{Cu}^{2+} \).

[0035] Preferably, said onium compounds are selected in the group comprising, preferably consisting of, quaternary ammonium cations, quaternary pyridinium cations and quaternary phosphonium cations.

[0036] More preferably, said onium compound is an ammonium cation, even more preferably an alkyl-ammonium cation. More preferably, it is selected in the group comprising tetrabutylammonium, tetrapropylammonium, tetraethylammonium, tetramethylammonium.

[0037] Preferably, said group \( (A^-) \) is bonded to said chain \( (Rf) \) through a bridging group \( [\text{group } (B)] \), said group \( (B) \) being a sigma bond or a linear or branched alkylene chain comprising from 1 to 6 carbon atoms, optionally interrupted by at least one heteroatom, preferably an oxygen atom. More preferably, said group \( (B) \) is a sigma bond or a linear or branched alkylene chain comprising from 1 to 3 carbon atom and interrupted by at least one oxygen atom. Even more preferably, said group \( (B) \) is a sigma bond or a
chain of formula \(-\text{CH}_2-\text{O}-\text{CH}_2-\).

[0038] In a preferred embodiment, said polymer (P) comprises one chain end comprising said group \((A^-)\) and said group \((C^+)\), the other chain end bearing a neutral terminal group \((T)\).

[0039] Preferably said group \((T)\) is selected in the group comprising \(-\text{H}, -\text{F}, -\text{Cl}, -(\text{O})\text{CF}_3\), a straight or branched (perhalo)alkyl group, more preferably perfluoroalkyl group, comprising from 1 to 3 carbon atoms.

[0040] Advantageously, the abovementioned polymer (P) allows to reduce entrained air and hence bubbles formation, thus improving the air release properties of the neutral PFPE or of the functional fluid.

[0041] Polymer (P) according to the present invention can be advantageously prepared according to methods known in the art, for example as disclosed in US 4814372 (AUSIMONT S.P.A.) and in EP 2004722 A (SOLVAY SOLEXIS S.P.A.) .

[0042] The Applicant found that polymer \((P^\ddagger)\) comprising chain \(\left(R_{p}\right)\) as defined above for polymer \((P)\) having two chain ends, wherein at least one chain end comprises at least one group \((-A^-)\) as defined above for polymer \((P)\), and a cationic group [group \(C^+\)] selected from the group consisting of, monovalent inorganic cations andonium compounds is particularly useful as anti-foam agent in oils based on neutral PFPEs.

[0043] Preferably, said neutral PFPE oils have a kinematic viscosity equal to or higher than 10 cSt at 20°C, more preferably of from 30 to 5000 cSt at 20°C, and even more preferably of from 50 to 1000 cSt at 20°C, measured according to ASTM D445.

[0044] Neutral PFPE oils are preferably selected from the following groups:

\(1)\) \(\text{B-O-}[\text{CF(CF}_3\text{)}\text{CF}_2\text{O}]_b^{+}\text{[CFXO]}_b^{-}\text{B}'\)

wherein:

- \(X\) is equal to \(-\text{F} \) or \(-\text{CF}_3\);
- \(B\) and \(B'\), equal to or different from each other, are selected from \(-\text{CF}_3\), \(-\text{C}_2\text{F}_5\) or \(-\text{C}_3\text{F}_7\);
- \(b1'\) and \(b2'\), equal or different from each other, are independently integers \(\geq 0\) selected such that the \(b17b2'\) ratio is comprised between 20 and 1,000 and \(b1'+b2'\) is in the range 5 to 250; should \(bV\) and \(b2'\) be both
different from zero, the different recurring units are generally statistically
distributed along the chain. Said products can be obtained by
photooxidation of the hexafluoropropylene as described in CA 786877
(MONTEDISON S.P.A.) 06.04.1968, and by subsequent conversion of the
everrecurring units as described in GB 1226566 (MONTECATINI EDISON S.P.A.)
31.03.1971;
(2) $C_3F_7O-[CF(CF3)CF2O]_o'-D$
wherein
- D is equal to -C2F5 or -C3F7,
- o' is an integer from 5 to 250,
said products can be prepared by ionic hexafluoropropylene epoxide
oligomerization and subsequent treatment with fluorine as described in US
3242218 (DU PONT) 22.03.1966;
(3) $\{C_3F_7O-[CF(CF3)CF_2O]_{dd'}-CF(CF3)\}_2$
wherein
- dd' is an integer between 2 and 250,
said products can be obtained by ionic telomerization of the
hexafluoropropylene epoxide and subsequent photochemical dimerization
as reported in US 3214478 (DU PONT) 26.10.1965;
(4) $C'_1-O-[CF(CF3)CF2O]_{cr(C2F_4O)_{cz(CFX)c3}}-C''$
wherein
- X is equal to -F or -CF3;
- C' and C", equal to or different from each other, are selected from -CF3,
-C2F5 or -C3F7;
- c1', c2' and c3' equal or different from each other, are independently
integers ≥0, such that and c1' + c2' + c3' is in the range 5 to 250; should at
least two of c1', c2' and c3' be different from zero, the different recurring
units are generally statistically distributed along the chain; said products
can be manufactured by photooxidation of a mixture of C3F6 and C2F4 and
subsequent treatment with fluorine as described in US 3665041
(MONTEDISON S.P.A.) 23.05.1972;
(5) $D-O-(C_2F_4O)_{d'}(CF_2O)_{d''}^-D'$
wherein
- D and D', equal to or different from each other, are selected from -CF3, -C2F5 or -C3F7;
- d1' and d2' equal or different from each other, are independently integers >0, such that the d1'/d2' ratio is comprised between 0.1 and 5 and d1'+d2' is in the range 5 to 250; should d1' and d2' be both different from zero, the different recurring units are generally statistically distributed along the chain; said products can be produced by photooxidation of C2F4 as reported in US 3715378 (MONTEDISON S.P.A.) 06.02.1973 and subsequent treatment with fluorine as described in US 3665041 (MONTEDISON S.P.A.) 23.05.1972;
(6) G-0-(CF2CF2C(Hal')20)gr-(CF2CF2CH20)g2'-(CF2CF2CH(Hal')0)g3' -G'
wherein
- G and G', equal to or different from each other, are selected from -CF3, -C2F5 or -C3F7;
- Hal', equal or different at each occurrence, is a halogen chosen among F and Cl, preferably F;
- g1', g2', and g3' equal or different from each other, are independently integers ≥0, such that g 1'+ g2' + g3' is in the range 5 to 250; should at least two of g 1', g2' and g3' be different from zero, the different recurring units are generally statistically distributed along the chain; said products may be prepared by ring-opening polymerizing 2,2,3,3-tetrafluorooxethane in the presence of a polymerization initiator to give a polyether comprising repeating units of the formula: -CH2CF2CF2O-, and optionally fluorinating and/or chlorinating said polyether, as detailed in EP 148482 A (DAIKIN INDUSTRIES) 17.07.1985;
(7) L-O-(CF2CF2O)r-L'
wherein
- L and L', equal to or different from each other, are selected from -C2F5 or -C3F7,
- r is an integer in the range 5 to 250,
said products can be obtained by a method comprising fluorinating a polyethyleneoxide, e.g. with elemental fluorine, and optionally thermally
fragmentating the so-obtained fluorinated polyethyleneoxide as reported in

US 4523039 (THE UNIVERSITY OF TEXAS) 11.06.1985 ;

(8) $R^1f$-[C(CF)3]-2-O-[C(R2f)2]-kkCrC(R2f)2-O]-kk2-R1f

wherein

- $R^1f$ is a perfluoroalkyl group having from 1 to 6 carbon atoms;
- $R^2f$ is equal to -F or perfluoroalkyl group having from 1 to 6 carbon atoms;
- kk1' is an integer from 1 to 2;
- kk2' represents a number in the range 5 to 250;

said products can be produced by the copolymerization of

hexafluoroacetone with an oxygen-containing cyclic comonomer selected from ethylene oxide, propylene oxide, epoxy-butane and/or trimethylene oxide (oxethane) or substituted derivatives thereof and subsequent perfluorination of the resulting copolymer, as detailed in patent application


[0045] Preferred compositions (C) suitable for the purposes of the invention are lubricant compositions comprising PFPE oils of formulae (1), (4) and (5) cited above.

[0046] More preferably, compositions (C) suitable for the purposes of the invention comprise notably:

- lubricants commercially available under the trade name FOMBLIN® (type Y, M, W, or Z) from Solvay Specialty Polymers Italy, S.p.A. .

Lubricants of this family generally comprise at least one oil (i.e. only one or mixture of more than one oil) complying with either of formulae here below:

\[
\begin{align*}
F_{3}C&\:\:\\ 0\:\\ CF_{2} \:\:\:\:\:\:\:\: m\:\:\\ 0\:\\ CF_{2} \:\:\:\:\:\:\:\: n\:\:\\ OCF_{3} \\
F_{3}C&\:\:\\ 0\:\\ CF_{2} \:\:\:\:\:\:\:\: p\:\:\\ 0\:\\ CF_{2} \:\:\:\:\:\:\:\: q\:\:\\ OCF_{3}
\end{align*}
\]

wherein

m/n is preferably from 20 to 10000, more preferably from 30 to 5000; and
p/q is preferably 0.1/10, more preferably 0.2/5 and even more preferably 0.5/1.5.

[0047] Advantageously, said composition (C) or said composition (C*) is a
lubricant composition, which can be used for example as 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.

[0048] Even more preferably, said composition (C) comprises the neutral PFPE as the main component, preferably in an amount of at least 60 wt.%, more preferably at least 80 wt %, even more preferably at least 85 wt % based on the total weight of the composition.

[0049] Also, the Applicant found that polymer (P2) comprising a chain \((R_p)^l\) as defined above for polymer (P) having two chain ends, wherein at least one chain end comprises at least one group \((-A^-)\) as defined above for polymer (P), and a cationic group \([\text{group C}^+]\) selected from the group comprising, preferably consisting of, monovalent and divalent inorganic cations andonium compounds, is particularly useful as anti-foam agent in hydrogenated oils and notably functional fluids.

[0050] Preferably, said composition \((C^-)\) comprises at least one hydrogenated base oil, which is preferably a mineral oil or a synthetic oil, such as polyalphaolefins (PAO) and PAGs; esters; silicon oils; polyphenylethers; etc.

[0051] Said at least one hydrogenated base oil can be in admixture with different hydrogenated base oils or with water. In the latter case, the composition \((C^-)\) is in the form of a water-in-oil emulsion.

[0052] Even more preferably, said composition \((C^-)\) comprises the hydrogenated base oil(s) as the main component, preferably in an amount of at least 60 wt.%, more preferably at least 80 wt %, even more preferably at least 85 wt % based on the total weight of the composition.

[0053] In addition to the neutral PFPE or to the hydrogenated oil, said composition (C) and said composition \((C^-)\) can comprise further additives, such as for example antirust agents, antioxidants, thermal stabilizers, pour-point depressants, antiwear agents, including those for high pressures, dispersants, tracers, dyestuffs and fillers.

[0054] Examples of dispersants are for example surfactants, preferably non-ionic
surfactants, more preferably (per)fluoropolyether surfactants and (per)fluoroalkyl surfactants.

[0055] Examples of fillers are organic fillers such as polytetrafluoroethylene (PTFE) and inorganic fillers such as silica and talc.

[0056] Embodiments wherein the composition (C) or the composition (C*) are essentially made of the said neutral PFPE in combination with an amount of up to 1 % wt of any of the additives listed above are also encompassed by the present invention.

[0057] Preferably, polymer (P) according to the present invention can be added to said composition (C) or to said composition (C*) in an amount of from 0.0001 wt.% (1 ppm) to 10 wt.% based on the total weight of said composition,

[0058] More preferably, polymer (P-) is added to composition (C) in an amount of from 0.05 to 8 wt.% and even more preferably from 1 to 5.5 wt.%.

[0059] More preferably, polymer (P2) is added to composition (C*) in an amount of from 0.0001 wt.% (1 ppm) to 10 wt.% based on the total weight of said composition (C), more preferably, from 0.0005 wt.% (5 ppm) to 5 wt.% and even more preferably from 0.001 wt.% (10 ppm) to 1 wt.%.

[0060] Preferably, polymer (P) is added to said composition (C) or to said composition (C*) and then a mixing step is performed, for example by high shear mixing.

[0061] Thus, in a further aspect, the present invention relates to a composition [composition (C#)] comprising at least one neutral PFPE oil, at least one polymer (P-) as defined above and optionally further additives, as defined above.

[0062] Preferably, said composition (C#) comprises the neutral PFPE as the main component, i.e. from 60 to 99.9999 wt.% based on the total weight of the composition, more preferably from 70 to 99.95 wt.% and even more preferably from 90 to 99 wt.%.

[0063] Preferably, said composition (C#) comprises polymer (P-) in an amount of from 0.0001 wt.% (1 ppm) to 10 wt.% based on the total weight of said composition, more preferably from 0.05 to 8 wt.% and even more preferably from 1 to 5.5 wt.%.
[0064] When present, said composition (C#) comprises the further additives in an amount of from 0.1 to 30 wt.% based on the total weight of the composition.

[0065] In a further aspect, the present invention relates to a functional fluid composition [composition (C$)] comprising at least one hydrogenated base oil as defined above, at least one polymer (P2) as defined above and optionally further additives.

[0066] Preferably, said composition (C$) comprises the hydrogenated base oil(s) as the main component, i.e. from 60 to 99.9999 wt.% based on the total weight of the composition, more preferably from 70 to 99.9995 wt.% and even more preferably from 90 to 99.999 wt.%.

[0067] Preferably, said composition (C$) comprises said polymer (P2) in an amount of from 0.0001 wt.% (1 ppm) to 10 wt.% based on the total weight of said composition (C), more preferably, from 0.0005 wt.% (5 ppm) to 5 wt.% and even more preferably from 0.001 wt.% (10 ppm) to 1 wt.%.

[0068] When present, said composition (C$) comprises the further additives in an amount of from 0.1 to 30 wt.% based on the total weight of the composition.

[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 now described in more detail with reference to the following examples whose purpose is merely illustrative and not limitative of the scope of the invention.

Examples

[0071] MATERIALS

[0072] Base oils 1 to 3 and polymers A to C were obtained by Solvay Specialty Polymers Italy S.p.A.

[0073] Base oil 1: Fomblin®M30 PFPE - linear PFPE oil having chemical formula CF3-{[(CF2CF2O)p-(CF2O)q]-CF3 with p/q between 0.9 and 1 average molecular weight about 16,000 Da kinematic viscosity (measured according to ASTM D445): 280 cSt at 20°C,
45 cSt at 100°C
viscosity index (measured according to ASTM S2270): 338

[0074] Base oil 2: Fomblin®M60 PFPE - linear PFPE oil having chemical formula
\(\text{CF}_3-[(\text{CF}_2\text{CF}_2\text{O})_p-(\text{CF}_2\text{O})_q]-\text{CF}_3\) with \(p/q\) between 0.9 and 1
average molecular weight 18,700 Da
kinematic viscosity (measured according to ASTM D445): 550 cSt at 20°C,
86 cSt at 100°C
viscosity index (measured according to ASTM S2270): 343

[0075] Base oil 3: Fomblin®Y25 PFPE - branched PFPE oil having chemical formula
\(\text{CF}_3\text{O}-[(\text{CF}_2\text{CF}_3\text{O})_n-(\text{CF}_2\text{O})_m]-\text{CF}_3\) with \(m/n = 40/1\)
average molecular weight 3,700 Da
kinematic viscosity (measured according to ASTM D445): 250 cSt at 20°C,
10 cSt at 100°C
viscosity index (measured according to ASTM S2270): 108

[0076] Polymer A: branched mono-carboxylic acid PFPE having general formula
\(\text{T(CF}_2\text{O)}_m(\text{CF}_2\text{CF}_3\text{O})_s(\text{CF}_3\text{O})_p\text{CF}_2\text{T}'\)
and average molecular weight (Mn) about 3,300 Da.

[0077] Polymer B: branched mono-carboxylic acid PFPE having general formula
\(\text{T(CF}_2\text{O)}_m(\text{CF}_2\text{CF}_3\text{O})_s(\text{CF}_3\text{O})_p\text{CF}_2\text{T}'\)
and average molecular weight (Mn) about 2,200 Da.

[0078] Polymer C: branched mono-carboxylic acid PFPE having general formula
\(\text{T(CF}_2\text{O)}_m(\text{CF}_2\text{CF}_3\text{O})_s(\text{CF}_3\text{O})_p\text{CF}_2\text{T}'\)
and average molecular weight (Mn) about 1,300 Da.

[0079] Commercial RENOLIN UNISYN CLP 320 - fully-synthetic industrial gear
and lubricating oil-based on polyalphaolefin (PAO) having low foaming
tendency.

[0080] Polymer P-I: PFPE carboxylate monofunctional salt of potassium, having
the following structure:
\(\text{CF}_3\text{O}(\text{CF}_2\text{CF}_3\text{O})_p(\text{CF}_2\text{O})_q\text{CF}_2\text{COO- K}^+\)
average molecular weight (Mn) about 3,500 Da by NMR analysis.

[0081] Polymer P-II: Commercial Fomblin® DA305 PFPE obtained from Solvay
Specialty Polymers Italy S.p.A - monofunctional carboxylic acid having the
following structure:
\[ \text{CF}_3\text{O(CF}_2\text{CF(CF}_3\text{O)}_p\text{CF}_2\text{O) q CF}_2\text{COOH} \]
average molecular weight (Mn) about 3,500 Da by NMR analysis.

[0082] METHODS

[0083] ASTM D892 - Standard test method for foaming characteristics of Lubricating Oils

[0084] This test method is used to determine the foaming characteristics of lubricating oils at 24°C and 93.5°C. The test consists of three sequences performed at different temperatures. A portion of lubricants is aerated by the use of a gas diffuser with air at a flow rate of 94±5 ml/minute (corresponding to 5.64 l/h) at the test temperature of 24°C (Sequence I). The sample is aerated for 5 minutes and the amount of foam generated after disconnecting the gas diffuser is reported. At the end of a 10 minutes settling time, the amount of foam left is recorded. The test is repeated for fresh sample at 93.5°C (Sequence II), and then, after collapsing the foam, at 24°C (Sequence III).

[0085] Formulations with good antifoaming performances show sequence foam results in the range of 0 ml/0 ml, and the maximum foam tolerated is 50 ml/0 ml.

[0086] Preparation of potassium salts

An aqueous solution containing KOH (1.85 grams, equal to 33.0 mmoles, in 1.85 g of distilled H2O) was added, under stirring at room temperature to a 100 g of polymer C (32.5 meq of -COOH chain ends). The solution was then heated up to 40°C and this temperature was kept while stirring for 5 hours. The reaction mixture was then cooled to room temperature and the unreacted KOH was carbonated by bubbling carbon dioxide into the solution, until the pH was lower than 7. Water was then evaporated at reduced pressure and the resulting liquid mixture was filtered on PTFE membrane thus removing the potassium carbonate. 99.7 g of liquid product were obtained.

FTIR analysis show a complete conversion of the carboxylic acid groups to
the correspondent potassium salt.
The potassium salts of polymers A and B were prepared following the same procedure disclosed above.

[0087] **Preparation of sodium salts**
Sodium salts of polymers A, B and C were prepared following a procedure similar to that described for potassium salt using NaOH instead of KOH, in the same mol amount.

[0088] **Preparation of calcium salts**
100 g of polymer C (32.5 meq of -COOH chain ends) were diluted with 100 ml of perfluorohexane. Then, 0.91 g (16.2 mmoles) of CaO powder were added under stirring at room temperature. The mixture was then heated up to 40°C and this temperature was kept while stirring for 5 hours. The reaction mixture was then cooled to room temperature and the resulting solution was filtered on PTFE membrane thus removing the unreacted CaO. The solvent was evaporated at reduced pressure and 98.2 g of colourless liquid product were obtained. The FTIR analysis show a complete conversion of the carboxylic acid groups to the correspondent calcium salt.

The calcium salts of polymers A and B were prepared following the same procedure disclosed above.

[0089] **Preparation of magnesium salts**
Magnesium salts were prepared following a procedure similar to that described for calcium salts using MgO instead of CaO, in the same mol amount.

[0090] **Preparation of organic salts with TEA and TBA**
[0091] Triethanolamine (TEA) salts were prepared following the procedure disclosed in EP 0382224 cited above. TEA salts are representative of EP 0 382 224 cited above.

[0092] Following a similar procedure, tetrabutylammonium (TBA) salts were prepared using tetrabutyl ammonium hydroxide.

[0093] **Example 1**
[0094] 1a) Compositions based on neutral PFPE oils according to the present
invention

[0095] Each base oil 1, 2 and 3 was added with a PFPE carboxylate comprising monovalent organic and inorganic counter-ions, in the concentration as listed in the following Table 1.

[0096] The compositions were then submitted to the test for the evaluation of foam formation, according to ASTM D892.

[0097] The results are reported in the following Table 1.

[0098] 1b) Compositions based on neutral PFPE oils as comparison

[0099] Base oils 1, 2 and 3 were submitted to the test for the evaluation of foam formation, according to ASTM D892.

[0100] As further comparative examples, base oils 1 to 3 were added with PFPE carboxylate comprising divalent organic and inorganic counter-ions, in the concentrations listed in the following Table 1. These compositions were also submitted to the test for the evaluation of foam formation, according to ASTM D892.

[0101] The results of the comparative examples are reported in the following Table 1 and are identified with the symbol (*)

Table 1

<table>
<thead>
<tr>
<th>No. Ex.</th>
<th>Base oil</th>
<th>Polymer -COO-</th>
<th>Counter ion</th>
<th>Cone. (wt.%)</th>
<th>ASTM D892 (3 cycles, foam volume ml/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Seq. 1</td>
<td>Seq. 2</td>
</tr>
<tr>
<td>1(*)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>510/190</td>
</tr>
<tr>
<td>2(*)</td>
<td>1</td>
<td>A</td>
<td>Ca(^{2+})</td>
<td>5</td>
<td>0/0</td>
</tr>
<tr>
<td>3(*)</td>
<td>1</td>
<td>B</td>
<td>Mg(^{2+})</td>
<td>5</td>
<td>90/30</td>
</tr>
<tr>
<td>4(*)</td>
<td>1</td>
<td>B</td>
<td>TEA</td>
<td>5</td>
<td>10/0</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>B</td>
<td>Na(^+)</td>
<td>5</td>
<td>0/0</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>B</td>
<td>TBA</td>
<td>5</td>
<td>50/0</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>B</td>
<td>K(^+)</td>
<td>5</td>
<td>0/0</td>
</tr>
<tr>
<td>8(*)</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>530/120</td>
</tr>
<tr>
<td>9(*)</td>
<td>2</td>
<td>C</td>
<td>Ca(^{2+})</td>
<td>1.5</td>
<td>205/0</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>C</td>
<td>K(^+)</td>
<td>1.5</td>
<td>0/0</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>C</td>
<td>TBA</td>
<td>3</td>
<td>0/0</td>
</tr>
</tbody>
</table>
Example 2

2a) Composition No. 15 (comparative)

RENOLIN was left aging for more than 2 years. The properties of this lubricant, including the formation of foam, were evaluated after this aging time.

The kinematic viscosity of the aged oil at 40°C was 325 cSt, measured according to ASTM D445 standard method.

The antifoaming properties of the aged oil were evaluated according to ASTM D892 standard method Sequence I (at 24°C).

This result are reported in Table 1.

The foam volume was 520/250 ml, indicating that probably the antifoaming agent was separated from the composition and loosed its effectiveness.

2b) Composition No. 16

RENOLIN was formulated by adding 50 ppm of polymer P-I.

The antifoaming properties were evaluated according to ASTM D892 standard method Sequence I (at 24°C).

The results are reported in Table 1.

2c) Composition No. 17 (comparative)

RENOLIN was formulated by adding 100 ppm of polymer P-II.

The antifoaming properties were evaluated according to ASTM D892 standard method Sequence I (at 24°C). The results are reported in Table 2.
The above results clearly demonstrate the excellent anti-foam properties of polymer (P2) according to the present invention, notably when compared to the PFPE having carboxylate end groups. Indeed, while the amount of the foam was acceptable, the foam was dense and it did not decrease even after the end of the test.

[0113]  (`) comparative
Claims

1. A method for reducing the formation of foam in a composition comprising at least one neutral PFPE [composition (C)] or in a functional fluid composition [composition (C*)], said method comprising

- providing a composition (C) comprising at least one neutral PFPE and adding at least one polymer (P) to said composition (C), wherein said polymer (P-) comprises a (per)fluoropolyether chain [chain (Rpf)] having two chain ends, wherein at least one chain end comprises at least one anionic group [group -A-] selected from the group comprising carboxylate, sulphate and phosphate, and a cationic group [group C+] selected from the group comprising, preferably consisting of, monovalent inorganic cations and onium compounds;

or

- providing a composition (C*) comprising at least one hydrogenated oil, and adding at least one polymer (P) to said composition (C*), wherein said polymer (P2a (per)fluoropolyether chain [chain (Rpf)] having two chain ends, wherein at least one chain end comprises at least one anionic group [group -A-] selected from the group comprising carboxylate, sulphate and phosphate, and a cationic group [group C+] selected from the group comprising, preferably consisting of, monovalent and divalent inorganic cations and onium compounds.

2. The method according to claim 1, wherein said chain (Rpf) is a chain of formula

\[-(CFX)_aO(Rf)(CFX')_b-\]

wherein

a and b, equal or different from each other, are equal to or higher than 1, preferably from 1 to 10, more preferably from 1 to 3;

X and X', equal or different from each other, are -F or -CF3, provided that when a and/or b are higher than 1, X and X' are -F;

(Rf) comprises, preferably consists of, repeating units R°, said repeating units being independently selected from the group consisting of:

(i) -CFXO-, wherein X is F or CF3;

(ii) -CFXCFXO-, wherein X, equal or different at each occurrence, is F or CF3, with the proviso that at least one of X is -F;

(iii) -CF2CF2CW2O-, wherein each of W, equal or different from each other, are
F, Cl, H;
(iv) -CF2CF2CF2CF2O-;
(v) -(CF2)j-CFZ-O- wherein j is an integer from 0 to 3 and Z is a group of

general formula -O-R(f.a)-T, wherein R(f.a) is a fluoropolyoxyalkene chain

comprising a number of repeating units from 0 to 10, said recurring units being

chosen among the following: -CFXO-, -CF2CFXO-, -CF2CF2CF2O-, -CF2CF2CF2CF2O-, with each of each of X being independently F or CF3 and T being a

C1-C3 perfluoroalkyl group.

3. The method according to claim 1 or 2, wherein said group (A⁻) is selected from
carboxylate and phosphate.

4. The method according to claim 1, wherein said monovalent inorganic cation is
an alkaline metal.

5. The method according to claim 4, wherein said alkaline metal is selected from
Li⁺, Na⁺, K⁺, Cs⁺.

6. The method according to claim 1, wherein said onium compounds are selected
in the group comprising quaternary ammonium cations, quaternary pyridinium
cations and quaternary phosphonium cations.

7. The method according to claim 6, wherein said onium compound is an
ammonium cation, even more preferably an alkyl-ammonium cation.

8. The method according to claim 1, wherein said divalent inorganic cations is
selected from alkaline-earth metals and transition metals.

9. The method according to claim 8, wherein said alkaline earth metal is Mg²⁺,
Ca²⁺, Sr²⁺, Ba²⁺.

10. The method according to claim 8, wherein said transition metal is Zn²⁺, Cu²⁺,
Mn²⁺, Ni²⁺.
11. The method according to any one of claims 1 to 6, wherein said group \((A^-)\) is bonded to said chain \((R_p,f)\) through a bridging group \([group (B)]\), said group \((B)\) being a sigma bond or a linear or branched alkylene chain comprising from 1 to 6 carbon atoms, optionally interrupted by at least one heteroatom, preferably an oxygen atom.

12. The method according to claim 1, wherein said polymer \((P)\) comprises one chain end comprising said group \((A^-)\) and said group \((C^+)\), the other chain end bearing a neutral terminal group \((T)\).

13. The method according to claim 1, wherein said neutral PFPEs oils have a kinematic viscosity equal to or higher than 10 cSt at 20°C, according to ASTM D445.
**INTERNATIONAL SEARCH REPORT**

**PCT/EP2016/066486**

### A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D19/04 C10M171/00 C10M147/00

**ADD.**

According to International Patent Classification (IPC) or to both national classification and IPC:

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
<th>Patent Number</th>
<th>Date</th>
<th>Page</th>
<th>Paragraphs</th>
<th>Relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td>B01D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI0M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10M171/00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10M147/00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols):

B01D CI0M C10G D21C D21H C11D

**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

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
</tr>
</thead>
</table>

**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(s) which may throw doubts on priority claim(s) one(s) which 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 as 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

**A** document of the same patent family

---

* 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(s) which may throw doubts on priority claim(s) one(s) which 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 as 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
- "A" document of the same patent family

---

**Date of the actual completion of the international search**

6 October 2016

**Date of mailing of the international search report**

17/10/2016

**Name and mailing address of the ISA**

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

**Authorized officer**

Hi l genga, Kl aas

---

Form PCT/ISA210 (second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 3 250 808 A (MOORE JR EARL PHILLI P ET AL) 10 May 1966 (1966-05-10) the whol e document</td>
<td>1-13</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>US 2004097384 AI</td>
<td>20-05-2004</td>
<td>DE 10348584 AI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2004097384 AI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69002724 T2</td>
</tr>
<tr>
<td>US 3775324 A</td>
<td>27-11-1973</td>
<td>NONE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2006188693 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2006163532 AI</td>
</tr>
<tr>
<td>EP 2025731 AI</td>
<td>18-02-2009</td>
<td>CN 101809114 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2025731 AI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2183334 A2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2010535880 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2010187469 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wo 2009019267 A2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2032023 AI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 1052502 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69002744 DI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69002744 T2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0435062 AI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IT 1237887 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP H04108896 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 5124058 A</td>
</tr>
<tr>
<td>US 5211861 A</td>
<td>18-05-1993</td>
<td>NONE</td>
</tr>
<tr>
<td>Wo 9319142 AI</td>
<td>30-09-1993</td>
<td>AU 3646793 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2109504 AI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0583462 AI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP H07500142 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NZ 249578 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SG 48697 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 5435927 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wo 9319142 AI</td>
</tr>
<tr>
<td>US 3250808 A</td>
<td>10-05-1966</td>
<td>NONE</td>
</tr>
<tr>
<td>Wo 9532174 AI</td>
<td>30-11-1995</td>
<td>CA 2190116 AI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 1148377 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69527527 DI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69527527 T2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 076809 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1170275 A2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 3590067 B2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 3971389 B2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2004203889 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2007186679 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RU 2177934 C2</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>US 5658962 A</td>
<td>19-08-1997</td>
<td></td>
</tr>
<tr>
<td>us 6024176 A</td>
<td>15-02-2000</td>
<td></td>
</tr>
<tr>
<td>us 6204299 BI</td>
<td>20-03-2001</td>
<td></td>
</tr>
<tr>
<td>us 6214253 BI</td>
<td>10-04-2001</td>
<td></td>
</tr>
<tr>
<td>us 6361713 BI</td>
<td>26-03-2002</td>
<td></td>
</tr>
<tr>
<td>us 2001027172 AI</td>
<td>04-10-2001</td>
<td></td>
</tr>
<tr>
<td>us 2003166487 AI</td>
<td>04-09-2003</td>
<td></td>
</tr>
<tr>
<td>Wo 9532174 AI</td>
<td>30-11-1995</td>
<td></td>
</tr>
<tr>
<td>US 2004121921 AI</td>
<td>24-06-2004</td>
<td>NONE</td>
</tr>
</tbody>
</table>