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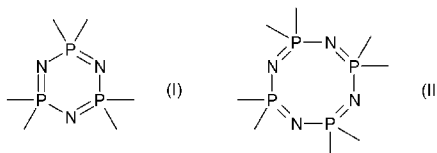
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(54) Title: LUBRICANT COMPOSITIONS FOR VACUUM PUMPS



(57) Abstract: The invention pertains to a lubricant composition comprising: (A) at least one non-functional (per)fluoropolyether oil (PFPE oil) comprising at least one (per)fluoropolyoxyalkylene chain (chain RF); (B) at least one cyclic phosphazene compound [compound (P)] comprising one or more cyclic moieties having formula (I) or (II) here below: said cyclic moieties comprising, bound to one or more phosphorus atoms, at least one substituent comprising at least one (per)fluoropolyoxyalkylene chain (chain R' F); (C) at least one functional (per)fluoropolyether derivative (functional PFPE derivative) different from compound (P) comprising at least one (per)fluoropolyoxyalkylene chain (chain R'F) and at least one functional group comprising at least one monocyclic or polycyclic aromatic ring, said aromatic ring optionally containing one or more heteroatoms selected from N, O and S and one or more substituents different from hydrogen atoms.

WO 2011/042374 A1

**Description****Lubricant compositions for vacuum pumps**

[0001] This application claims priority to European application No. 09172280.1 filed 06.10.2009, the whole content of this application being incorporated herein by reference for all purposes.

**Technical Field**

[0002] The present invention relates to (per)fluoropolyether lubricant compositions and use thereof for lubricating vacuum pumps.

**Background Art**

[0003] Fluoropolyether lubricants are known in the art for being used in vacuum pumps in highly demanding applications, e.g. in the semiconductor industry, in particular for lubricating compressors and pumps handling reactive and hazardous gases, typically in rotary pumps, turbomolecular pumps, roots pumps and diffusion pumps.

[0004] Actually, major requirements for fluoropolyether lubricants to be employed for high vacuum and ultra-high vacuum applications include high thermal-oxidative stability in the presence of metals, low evaporation weight loss and high lubrication performances.

[0005] Fluoropolyether oils substantially free from volatile fractions are typically used for lubricating vacuum pumps so that back migration of the volatile oil fractions into the vacuum chamber, which is commonly due to heat generated by friction among the moving metallic parts while operating, is generally reduced.

[0006] Thus, EP 0553768 B (AUSIMONT S.P.A.) 03.05.2000 discloses use in vacuum pumps of perfluoropolyethers having at most 0.1% by weight of fractions exhibiting a molecular weight lower than or equal to 1500 and at most 1.3% by weight of fractions exhibiting a molecular weight lower than or equal to 1800, said perfluoropolyethers being typically endowed with a viscosity ranging from about 140 cSt to about 270 cSt at 20°C and preferably complying with branched perfluoropolyethers having formulae  $CF_3(OCF(CF_3)CF_2)_m(OCF_2)_nOCF_3$ , wherein  $m/n$  is equal to or higher than 1000, and  $F(CF_2CF(CF_3)O)_qCF_2CF_3$ .

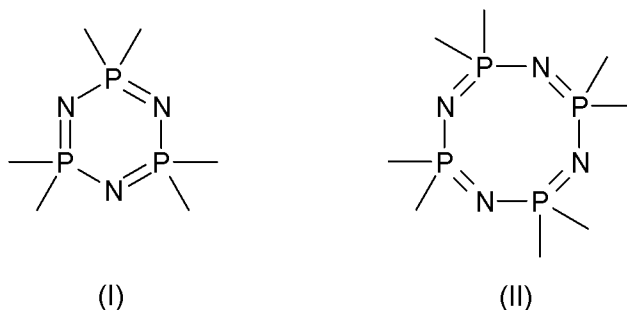
[0007] Nevertheless, fluoropolyether oils of the prior art, in particular linear

fluoropolyether oils generally suffer from low thermal-oxidative stability in the presence of metals to be advantageously used as lubricants in high vacuum and ultra-high vacuum pumps.

- [0008] EP 1454938 B (SOLVAY SOLEXIS S.P.A.) 05.10.2005 discloses linear perfluoropolyether oils comprising  $-\text{CF}_2\text{CF}_2\text{O}-$  and  $-\text{CF}_2\text{O}-$  recurring units, statistically distributed along the perfluoropolyoxyalkylene chain, in a  $-\text{CF}_2\text{CF}_2\text{O}-/-\text{CF}_2\text{O}-$  ratio comprised between 2 and 20, which exhibit improved thermal-oxidative stability in the presence of metals with respect to known linear perfluoropolyether oils having a lower  $-\text{CF}_2\text{CF}_2\text{O}-/-\text{CF}_2\text{O}-$  ratio, typically comprised between 0.1 and 10, while maintaining a high viscosity index and a low pour point value as compared with known linear perfluoropolyether oils. The stability of the novel linear perfluoropolyether oils when used as lubricants may be further increased by the addition of perfluoropolyether-based thermal stabilizers comprising functional groups like, e.g., phosphines, phosphates, phosphazenes, benzothiazoles, triazines, amines, substituted amines, nitroderivative compounds.
- [0009] The need was thus felt to provide for (per)fluoropolyether lubricants having improved thermal-oxidative stability in the presence of metals while maintaining low evaporation weight loss and high lubrication performances in terms of suitable kinematic viscosity and anti-wear and anti-rust properties, so as to be successfully used in high vacuum and ultra-high vacuum pumps by ensuring lower maintenance costs of the pumps due to a longer life-time of the lubricants and lower consumptions due to their high lubrication performances.

#### Disclosure of Invention

- [0010] It is thus an object of the invention a lubricant composition comprising:
- (A) at least one non-functional (per)fluoropolyether oil (non-functional PFPE oil) comprising at least one (per)fluoropolyoxyalkylene chain (chain  $R_F$ );
  - (B) at least one cyclic phosphazene compound [compound (P)] comprising one or more cyclic moieties having formula (I) or (II) here below:



said cyclic moieties comprising, bound to one or more phosphorus atoms, at least one substituent comprising at least one (per)fluoropolyoxyalkylene chain (chain R<sub>F</sub>);

(C) at least one functional (per)fluoropolyether derivative (functional PFPE derivative) different from compound (P) comprising at least one (per)fluoropolyoxyalkylene chain (chain R<sub>F</sub>) and at least one functional group comprising at least one monocyclic or polycyclic aromatic ring, said aromatic ring optionally containing one or more heteroatoms selected from N, O and S and one or more substituents different from hydrogen atoms.

[0011] The Applicant has surprisingly found that the lubricant composition of the invention advantageously exhibits improved thermal-oxidative stability in the presence of metals while maintaining low evaporation weight loss and high lubrication performances to be successfully used for high vacuum and ultra-high vacuum applications.

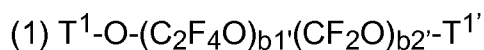
[0012] To the purpose of the present invention, “(per)fluoropolyether” is intended to denote either a fully fluorinated perfluoropolyether or a partially fluorinated fluoropolyether.

[0013] To the purpose of the present invention, “(per)fluoropolyoxyalkylene chain” is intended to denote either a fully fluorinated perfluoropolyoxyalkylene chain or a partially fluorinated fluoropolyoxyalkylene chain.

[0014] The (per)fluoropolyoxyalkylene chain (chain R<sub>F</sub>) of the non-functional (per)fluoropolyether oil (non-functional PFPE oil) of the invention typically comprises one or more recurring units R<sup>o</sup> having general formula -(CJJ')<sub>j</sub>-CKK'-O-, wherein J and J', equal to or different from each other, independently represent a fluorine atom or a C<sub>1</sub>-C<sub>6</sub> (per)fluoro(oxy)alkyl group, K and K', equal to or different from each other, independently

represent a hydrogen atom, a fluorine atom, a chlorine atom or a C<sub>1</sub>-C<sub>6</sub> (per)fluoro(oxy)alkyl group and j is an integer comprised between 0 and 3, said recurring units being generally statistically distributed along the (per)fluoropolyoxyalkylene chain.

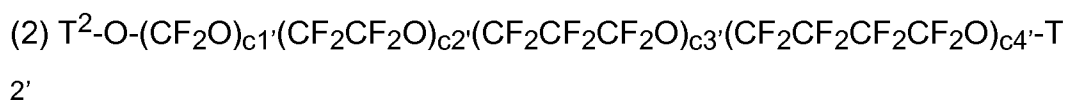
- [0015] The non-functional PFPE oil of the invention may be a linear non-functional PFPE oil or a branched non-functional PFPE oil.
- [0016] By "linear non-functional PFPE oil" it is meant a non-functional PFPE oil comprising at least one (per)fluoropolyoxyalkylene chain (chain R<sub>F</sub>) as defined above, wherein J and J' both represent a fluorine atom and K and K', equal to or different from each other, independently represent a hydrogen atom, a fluorine atom or a chlorine atom.
- [0017] By "branched non-functional PFPE oil" it is meant a non-functional PFPE oil comprising at least one (per)fluoropolyoxyalkylene chain (chain R<sub>F</sub>) as defined above, wherein at least one of J, J', K and K' represents a C<sub>1</sub>-C<sub>6</sub> (per)fluoro(oxy)alkyl group.
- [0018] Representative examples of suitable non-functional PFPE oils according to the invention include, notably, the followings:



wherein:

- T<sup>1</sup> and T<sup>1'</sup>, equal to or different from each other, are independently selected from -CF<sub>3</sub>, -C<sub>2</sub>F<sub>5</sub> and -C<sub>3</sub>F<sub>7</sub> groups;
- b<sup>1'</sup> and b<sup>2'</sup>, equal to or different from each other, are independently integers ≥ 0 such that the b<sup>1'</sup>/b<sup>2'</sup> ratio is comprised between 0.1 and 5 and the (b<sup>1'</sup>+b<sup>2'</sup>) sum is comprised between 5 and 250; should b<sup>1'</sup> and b<sup>2'</sup> be both different from zero, the different recurring units are generally statistically distributed along the perfluoropolyoxyalkylene chain.

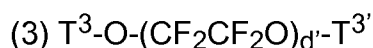
Said products can be produced by photooxidation of C<sub>2</sub>F<sub>4</sub> as reported in **US 3715378** (MONTECATINI EDISON S.P.A.) 06.02.1973 and subsequent treatment with fluorine as described in **US 3665041** (MONTECATINI EDISON S.P.A.) 23.05.1972 .



wherein:

- $T^2$  and  $T^{2'}$ , equal to or different from each other, are independently selected from  $-CF_3$ ,  $-C_2F_5$ ,  $-C_3F_7$ ,  $-C_4F_9$ ,  $-CF_2Cl$ ,  $-CF_2CF_2Cl$  groups;
  - $c_1'$ ,  $c_2'$ ,  $c_3'$  and  $c_4'$ , equal to or different from each other, are independently integers  $\geq 0$  such that the number average molecular weight is comprised between 700 and 100000;
  - the  $c_2'/c_1'$  ratio is comprised between 2 and 20;
  - the  $(c_3'+c_4')/(c_1'+c_2'+c_3'+c_4')$  ratio is comprised between 0.05 and 0.2;
  - the  $c_1'/(c_1'+c_2'+c_3'+c_4')$  ratio is comprised between 0.05 and 0.4;
- should at least two of  $c_1'$ ,  $c_2'$ ,  $c_3'$  and  $c_4'$  be different from zero, the different recurring units are generally statistically distributed along the perfluoropolyoxyalkylene chain.

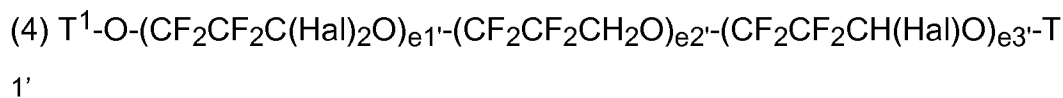
Said products can be produced as described in EP 1454938 B (SOLVAY SOLEXIS S.P.A.) 05.10.2005 .



wherein:

- $T^3$  and  $T^{3'}$ , equal to or different from each other, are independently selected from  $-C_2F_5$  and  $-C_3F_7$  groups;
- $d'$  is an integer comprised between 5 and 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 .



wherein:

- $T^1$  and  $T^{1'}$ , equal to or different from each other, have the same meaning as defined above;
- 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 5 and 250; should at least two of  $e_1'$ ,  $e_2'$  and  $e_3'$  be different from zero, the different recurring units are generally statistically distributed along the

(per)fluoropolyoxyalkylene chain.

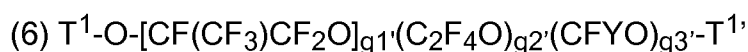
Said products may be prepared by ring-opening polymerizing 2,2,3,3-tetrafluorooxethane in the presence of a polymerization initiator to give a polyether comprising repeating units of the formula:  $-\text{CH}_2\text{CF}_2\text{CF}_2\text{O}-$ , and optionally fluorinating and/or chlorinating said polyether, as detailed in EP 148482 B (DAIKIN INDUSTRIES LTD.) 25.03.1992 .



wherein:

- $\text{T}^1$  and  $\text{T}^1'$ , equal to or different from each other, have the same meaning as defined above;
- Y, equal or different at each occurrence, is selected from a fluorine atom or a  $-\text{CF}_3$  group;
- $f1'$  and  $f2'$ , equal to or different from each other, are independently integers  $\geq 0$  such that the  $f1'/f2'$  ratio is comprised between 20 and 1000 and the  $(f1'+f2')$  sum is comprised between 5 and 250; should  $f1'$  and  $f2'$  be both different from zero, the different recurring units are generally statistically distributed along the perfluoropolyoxyalkylene chain.

Said products can be obtained by photooxidation of  $\text{C}_3\text{F}_6$  as described in CA 786877 (MONTEDISON S.P.A.) 04.06.1968 and by subsequent conversion of the end groups as described in GB 1226566 (MONTECATINI EDISON S.P.A.) 31.03.1971 .

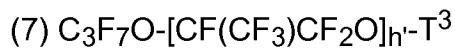


wherein:

- $\text{T}^1$  and  $\text{T}^1'$ , equal to or different from each other, have the same meaning as defined above;
- Y, equal or different at each occurrence, has the same meaning as defined above;
- $g1'$ ,  $g2'$  and  $g3'$ , equal to or different from each other, are independently integers  $\geq 0$  such that the  $(g1'+g2'+g3')$  sum is comprised between 5 and 250; should at least two of  $g1'$ ,  $g2'$  and  $g3'$  be different from zero, the different recurring units are generally statistically distributed along the perfluoropolyoxyalkylene chain.

Said products can be manufactured by photooxidation of a mixture of  $\text{C}_3\text{F}_6$

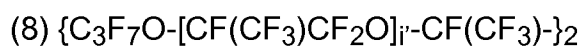
and C<sub>2</sub>F<sub>4</sub> and subsequent treatment with fluorine as described in **US 3665041** (MONTECATINI EDISON S.P.A.) 23.05.1972 .



wherein:

- T<sup>3</sup> has the same meaning as defined above;
- h' is an integer comprised between 5 and 250.

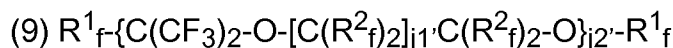
Said products can be prepared by ionic hexafluoropropylene epoxide oligomerization and subsequent treatment with fluorine as described in **US 3242218** (E. I. DU PONT DE NEMOURS AND CO.) 22.03.1966 .



wherein:

- i' is an integer comprised 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** (E. I. DU PONT DE NEMOURS AND CO.) 26.10.1965 .



wherein:

- R<sup>1</sup><sub>f</sub>, equal or different at each occurrence, is a C<sub>1</sub>-C<sub>6</sub> perfluoroalkyl group;
- R<sup>2</sup><sub>f</sub>, equal or different at each occurrence, is selected from a fluorine atom and a C<sub>1</sub>-C<sub>6</sub> perfluoroalkyl group;
- j1' is equal to 1 or 2;
- j2' is an integer comprised between 5 and 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 **WO 87/00538** (LAGOW ET AL.) 29.01.1987 .

[0019] Preferred non-functional PFPE oils suitable for the purpose of the invention include, notably, the followings:

- (i) non-functional PFPE oils complying with formula (2) as described

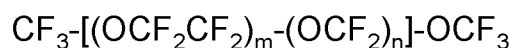


above, wherein:

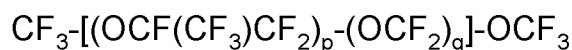
- T<sup>2</sup> and T<sup>2'</sup> are -CF<sub>3</sub> groups;
- c<sup>1'</sup>, c<sup>2'</sup>, c<sup>3'</sup> and c<sup>4'</sup>, equal to or different from each other, are independently integers > 0 such that the number average molecular weight is comprised between 1000 and 20000;
- the c<sup>2'</sup>/c<sup>1'</sup> ratio is comprised between 2 and 5;
- the (c<sup>3'</sup>+c<sup>4'</sup>)/(c<sup>1'</sup>+c<sup>2'</sup>+c<sup>3'</sup>+c<sup>4'</sup>) ratio is comprised between 0.07 and 0.2;
- the c<sup>1'</sup>/(c<sup>1'</sup>+c<sup>2'</sup>+c<sup>3'</sup>+c<sup>4'</sup>) ratio is comprised between 0.1 and 0.3;

the different recurring units being generally statistically distributed along the perfluoropolyoxyalkylene chain;

(ii) non-functional PFPE oils commercially available from Solvay Solexis S.p.A. under the trade name FOMBLIN<sup>®</sup> (type M, Z or Y), said oils generally comprising at least one oil complying with either of formulae here below:

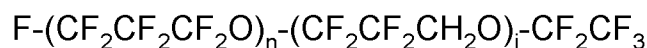


$$m+n = 40 - 180; m/n = 0.5 - 2$$



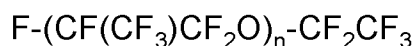
$$p+q = 8 - 45; p/q = 20 - 1000$$

(iii) non-functional PFPE oils commercially available from Daikin under the trade name DEMNUM<sup>®</sup>, said oils generally comprising at least one oil complying with formula here below:



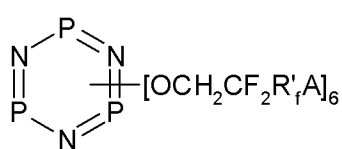
$$j = 0 \text{ or integer } > 0; n+j = 10 - 150$$

(iv) non-functional PFPE oils commercially available from Du Pont de Nemours under the trade name KRYTOX<sup>®</sup>, said oils generally comprising at least one low-molecular weight, fluorine end-capped, homopolymer of hexafluoropropylene epoxide complying with formula here below:

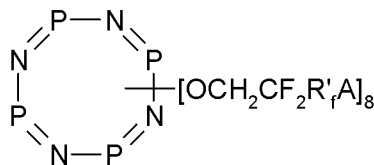


$$n = 10 - 60$$

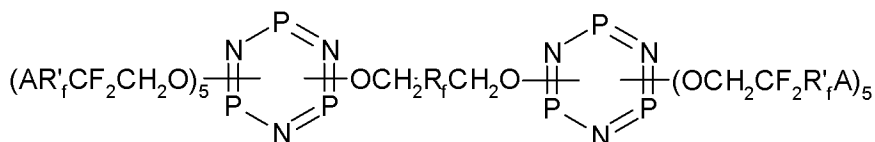
- [0020] More preferred non-functional PFPE oils suitable for the purpose of the invention include, notably, non-functional PFPE oils complying with formula (2) as described hereinabove and non-functional PFPE oils commercially available from Solvay Solexis S.p.A. under the trade name FOMBLIN<sup>®</sup> (type M, Z or Y) as described hereinabove.
- [0021] A mixture of more than one non-functional PFPE oil as defined above may also be used in the lubricant composition of the invention.
- [0022] Preferred mixtures of more than one non-functional PFPE oil as defined above include, notably, mixtures of at least one linear non-functional PFPE oil as defined above with at least one branched non-functional PFPE oil as defined above. Representative examples of suitable mixtures of at least one linear non-functional PFPE oil as defined above with at least one branched non-functional PFPE oil as defined above include, notably, those commercially available from Solvay Solexis S.p.A. under the trade name FOMBLIN<sup>®</sup> W.
- [0023] The (per)fluoropolyoxyalkylene chain (chain R'<sub>F</sub>) of the cyclic phosphazene compound [compound (P)] of the invention typically comprises one or more recurring units R<sup>1</sup> having general formula -(CF<sub>2</sub>)<sub>j</sub>-CFK-O-, wherein K is selected from a fluorine atom and a C<sub>1</sub>-C<sub>5</sub> (per)fluoro(oxy)alkyl group and j is an integer comprised between 0 and 3, said recurring units being generally statistically distributed along the (per)fluoropolyoxyalkylene chain.
- [0024] According to a first embodiment of the invention, the compound (P) complies with formula (I-A), (I-A bis) or (II-A) here below:



(I-A)



(II-A)



(I-A bis)

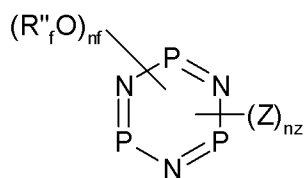
wherein:

- R<sub>f</sub> is a (per)fluoropolyoxyalkylene chain comprising one or more recurring units having formula -CF<sub>2</sub>O(CF<sub>2</sub>CF<sub>2</sub>O)<sub>p'</sub>(CF<sub>2</sub>O)<sub>q'</sub>CF<sub>2</sub>-, wherein p' and q' are integers such that the number average molecular weight of the chain is comprised between 1000 and 2000, the q'/p' ratio being comprised between 0.2 and 2;

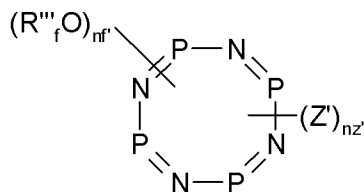
- R'<sub>f</sub> is a (per)fluoropolyoxyalkylene chain comprising one or more recurring units having formula -(C<sub>3</sub>F<sub>6</sub>O)<sub>q</sub>(CF(CF<sub>3</sub>)O)<sub>r</sub>-, wherein q and r are integers such that the number average molecular weight of the chain is comprised between 500 and 700, the q/r ratio being ≥ 2.

[0025] Compounds (P) complying with formula (I-A), (I-A bis) or (II-A) as described in this first embodiment of the invention are notably disclosed in EP 1336614 A (SOLVAY SOLEXIS S.P.A.) 20.08.2003 .

[0026] According to a second embodiment of the invention, the compound (P) complies with formula (I-B) or (II-B) here below:



(I-B)



(II-B)

wherein:

- R''<sub>f</sub> and R'''<sub>f</sub>, equal to or different from each other, independently represent a (per)fluoropolyoxyalkylene chain comprising one or more recurring units selected from:

- (i) -CFYO-, wherein Y is a fluorine atom or a -CF<sub>3</sub> group,
- (ii) -CF<sub>2</sub>CFYO-, wherein Y has the same meaning as defined above,
- (iii) -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-,
- (iv) -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-,

said recurring units being generally statistically distributed along the (per)fluoropolyoxyalkylene chain;

- Z and Z', equal to or different from each other, independently represent a polar group of formula -O<sup>-</sup>M<sup>+</sup>, wherein M is selected from hydrogen, a monovalent metal, preferably an alkaline metal, and an ammonium radical having formula -NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>, wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> is, independently, a hydrogen atom or a C<sub>1</sub>-C<sub>12</sub> hydrocarbon group, optionally fluorinated, or a polar group of formula -O<sup>-</sup>)<sub>2</sub>M'<sup>2+</sup>, wherein M' is a divalent metal, preferably an alkaline earth metal;

- n<sub>Z</sub> is an integer comprised between 1 and 3, preferably equal to 1;
- n<sub>Z'</sub> is an integer comprised between 1 and 4, preferably equal to 1;
- n<sub>f</sub> is an integer such that n<sub>Z</sub> + n<sub>f</sub> is equal to 6;
- n<sub>f'</sub> is an integer such that n<sub>Z'</sub> + n<sub>f'</sub> is equal to 8.

[0027] The compound (P) of this second embodiment of the invention preferably complies with formula (I-B) or (II-B) here above, wherein R''<sub>f</sub>O<sup>-</sup> and R'''<sub>f</sub>O<sup>-</sup> are selected from:

(a) T<sup>4</sup>-O- (CF<sub>2</sub>CF<sub>2</sub>O)<sub>p'</sub>(CF<sub>2</sub>O)<sub>q'</sub>-J-

wherein:

- T<sup>4</sup> is selected from -CF<sub>3</sub>, -CF<sub>2</sub>CF<sub>3</sub>, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>, -(CF<sub>2</sub>)<sub>f</sub>-CF<sub>2</sub>(T<sub>1</sub>) and -(CF<sub>2</sub>)<sub>f</sub>-CF(T<sub>1</sub>)(T<sub>2</sub>), wherein f is 0 or 1, T<sub>1</sub> and T<sub>2</sub>, equal to or different from each other, are independently selected from chlorine, bromine and hydrogen atoms;
- J is selected from groups having formulae -CE'(Y)CE<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>s1</sub>- and -CE'YO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>s2</sub>-, wherein E and E', equal to or different from each other, are independently selected from a fluorine atom, a hydrogen atom and a -CF<sub>3</sub> group, E being preferably a hydrogen atom and E' being

preferably selected from a fluorine atom and a  $-CF_3$  group, Y is selected from a fluorine atom and a  $-CF_3$  group, s1 and s2, equal to or different from each other, are integers comprised between 0 and 5;

- p' and q' are numbers such that the (p'+q') sum is comprised between 1 and 100 and the q'/p' ratio is comprised between 0.1 and 10;

(b)  $T^5-O-(CF_2CF(CF_3)O)_r-(CF_2CF_2O)_s-(CFYO)_t-J-$

wherein:

-  $T^5$  is selected from  $-CF_3$ ,  $-CFYCF_3$ ,  $-CF(Y)CF(Y)CF_3$ ,  $-(CFY)_f-CFY(T'_1)$  and  $-(CFY)_f-CY(T'_1)(T'_2)$ , wherein f is 0 or 1,  $T'_1$  and  $T'_2$ , equal to or different from each other, are independently selected from chlorine, bromine and hydrogen atoms;

- Y, equal or different at each occurrence, has the same meaning as defined above;

- J has the same meaning as defined above;

- r', s' and t' are numbers such that the (r'+ s'+ t') sum is comprised between 1 and 100, the t'/(r'+ s') ratio being comprised between 0.01 and 0.1;

(c)  $T^5-(OCFY)_{t1''}(OC_3F_6)_{u1''}-OR^*_fO-(C_3F_6O)_{u2''}(CFYO)_{t2''}-J-$

wherein:

-  $T^5$  has the same meaning as defined above;

- Y, equal or different at each occurrence, has the same meaning as defined above;

- J has the same meaning as defined above;

-  $R^*_f$  is a  $C_1-C_8$  perfluoroalkylene group;

- t1'', u1'', t2'', u2'' are numbers such that the (t1''+ u1''+ t2''+ u2'') sum is comprised between 1 and 100, the (t1''+ t2'')/(u1''+ u2'') ratio being comprised between 0.01 and 0.1;

(d)  $T^4-CF_2CF_2O-(CF_2-(CF_2)_x-CF_2O)_v-J-$

wherein:

-  $T^4$  has the same meaning as defined above;

- J has the same meaning as defined above;

- x' is equal to 1 or 2;

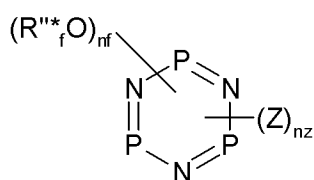
- v' is a number comprised between 1 and 100;

(e)  $T^4\text{-CF}_2\text{CH}_2\text{-(OCF}_2\text{CF}_2\text{CH}_2\text{)}_{w'}\text{-OR}^*_f\text{O-(CH}_2\text{CF}_2\text{CF}_2\text{O)}_{w'}\text{-J-}$

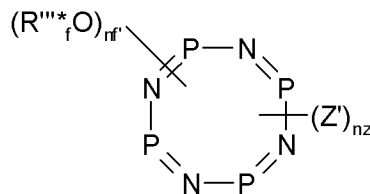
wherein:

- $T^4$  has the same meaning as defined above;
- J has the same meaning as defined above;
- $R^*_f$  has the same meaning as defined above;
- $w'$  is a number comprised between 1 and 100.

[0028] The compound (P) of this second embodiment of the invention more preferably complies with formula (I-B\*) or (II-B\*) here below:



(I-B\*)



(II-B\*)

wherein:

- Z, Z',  $n_z$ ,  $n_{z'}$ ,  $n_f$  and  $n_{f'}$  have the same meaning as defined above;
- $R''*_f\text{O-}$  and  $R''''*_f\text{O-}$ , equal to or different from each other, represent a fluoropolyoxyalkylene chain having formula:

$T^*\text{-O-(CF}_2\text{CF}_2\text{O)}_{p^*}\text{(CF}_2\text{O)}_{q^*}\text{-CF}_2\text{-CH}_2\text{O(CH}_2\text{CH}_2\text{O)}_{s^*}\text{-}$

wherein:

- $T^*$  is selected from  $\text{-CF}_3$ ,  $\text{-CF}_2\text{CF}_3$  and  $\text{-CF}_2\text{CF}_2\text{CF}_3$  groups;
- $p^*$  and  $q^*$  are numbers such that the  $(p^*+q^*)$  sum is comprised between 1 and 50 and the  $q^*/p^*$  ratio is comprised between 0.1 and 10;
- $s^*$  is a number comprised between 0 and 5.

[0029] The compound (P) of this second embodiment of the invention most preferably complies with formula (III-B) or (III-B bis) here below:



(i) -QR groups, wherein Q is a divalent group selected from -O-, -S-, -NR<sub>1</sub>- and -NH-NH-, wherein R<sub>1</sub> is a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group, and R is a C<sub>6</sub>-C<sub>12</sub> aryl group, preferably a phenyl group, optionally substituted by one or more, preferably 1 or 2 groups selected from C<sub>1</sub>-C<sub>4</sub> alkyl groups, -OR<sub>2</sub>-, -NR<sub>3</sub>R<sub>4</sub>-, -NO<sub>2</sub>, fluorine and chlorine atoms, wherein R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are hydrogen atoms or C<sub>1</sub>-C<sub>4</sub> alkyl groups;

(ii) R<sub>F</sub>CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>s</sub>-, wherein R<sub>F</sub> is a (per)fluoropolyoxyalkylene chain (chain R'<sub>F</sub>) as defined above and s is equal to 0, 1 or 2;

- m is equal to 3 or 4;

- n is equal to 0.

[0032] Compounds (P) complying with formula (IV-C) as described in this third embodiment of the invention are notably disclosed in **EP 0597369 A** (AUSIMONT S.P.A.) 16.09.1998 .

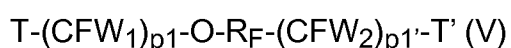
[0033] Preferred lubricant compositions of the invention comprise one or more compounds (P) according to the first and/or the second embodiment of the invention as detailed above.

[0034] More preferred lubricant compositions of the invention comprise one or more compounds (P) according to the second embodiment of the invention as detailed above.

[0035] Most preferred lubricant compositions of the invention comprise one or more compounds (P) complying with either of formulae (III-B) or (III-B bis) as described above.

[0036] The functional (per)fluoropolyether derivative (functional PFPE derivative) of the invention comprises at least one (per)fluoropolyoxyalkylene chain (chain R'<sub>F</sub>) as defined above and at least one functional group typically comprising at least one ether, thioether, ester or amine group comprising at least one monocyclic or polycyclic aromatic ring, said aromatic ring optionally containing one or more heteroatoms selected from N, O and S and one or more substituents different from hydrogen atoms.

[0037] The functional (per)fluoropolyether derivative (functional PFPE derivative) of the invention preferably complies with formula (V) here below:

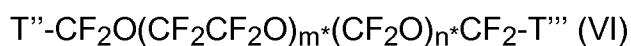


wherein:



- R<sub>F</sub> is a (per)fluoropolyoxyalkylene chain (chain R'<sub>F</sub>) as defined above;
- T and T', equal to or different from each other, are selected from:
  - i) functional end-groups comprising at least one ether, thioether, ester or amine group comprising at least one monocyclic or polycyclic aromatic ring, said aromatic ring optionally containing one or more heteroatoms selected from N, O and S and one or more substituents different from hydrogen atoms,
  - ii) non-functional end-groups selected from a fluorine atom, a chlorine atom and a C<sub>1</sub>-C<sub>3</sub> (per)fluoroalkyl group optionally containing one or more chlorine atoms,
 with the proviso that at least one of T and T' is a functional end-group as defined hereinabove;
- W<sub>1</sub> and W<sub>2</sub>, equal to or different from each other, independently represent a fluorine atom or a -CF<sub>3</sub> group;
- p<sub>1</sub> and p'<sub>1</sub>, equal to or different from each other, are independently integers comprised between 1 and 3, preferably being equal to 1 when W<sub>1</sub> and/or W<sub>2</sub> are -CF<sub>3</sub> groups.

[0038] The functional PFPE derivative of the invention more preferably complies with formula (VI) here below:



wherein:

- T'' and T''', equal to or different from each other, are selected from:
  - i) functional end-groups selected from those having formulae -CH<sub>2</sub>-A-Y, -CH(CF<sub>3</sub>)-A-Y, -CHW'-B-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m'</sub>-Y and -COOY, wherein:
    - (a') A is selected from oxygen and sulphur atoms,
    - (b') B is selected from an oxygen atom, a sulphur atom and a -NH group,
    - (c') W' is selected from a hydrogen atom and a -CF<sub>3</sub> group,
    - (d') m' is an integer comprised between 0 and 6,
    - (e') Y is selected from phenyl, pyridine, triazine, benzoxazole, benzothiazole and benzopyrazine groups optionally substituted with one or more substituents different from hydrogen atoms,
  - ii) non-functional end-groups selected from a fluorine atom, a chlorine atom, a -CF<sub>3</sub> group, a -C<sub>2</sub>F<sub>5</sub> group and a -(CF<sub>2</sub>)<sub>n</sub>Cl group, wherein n is an

integer comprised between 1 and 3,  
with the proviso that at least one of T'' and T''' is a functional end-group as defined hereinabove;

- m\* and n\* are integers such that the number average molecular weight of the functional PFPE derivative is comprised between 400 and 10000, the m\*/n\* ratio being comprised between 0.1 and 10.

[0039] Preferred lubricant compositions of the invention comprise one or more functional PFPE derivatives selected from:

- functional PFPE derivatives complying with formula (V) as described above wherein at least one of T and T' is a functional end-group comprising at least one ether or thiether group comprising at least one pyridine group optionally substituted with one or more substituents different from hydrogen atoms, notably disclosed in EP 1479753 A (SOLVAY SOLEXIS S.P.A.) 24.11.2004 ;

- functional PFPE derivatives complying with formula (V) as described above wherein at least one of T and T' is a functional end-group comprising at least one ether or ester group comprising at least one phenyl group optionally substituted with one or more substituents different from hydrogen atoms, notably disclosed in EP 1354932 B (SOLVAY SOLEXIS S.P.A.) 14.06.2006 ;

- functional PFPE derivatives complying with formula (V) as described above wherein at least one of T and T' is a functional end-group comprising at least one ether, thioether or amine group comprising at least one 1,3,5-triazine group optionally substituted with one or more substituents different from hydrogen atoms, notably disclosed in EP 1712580 B (SOLVAY SOLEXIS S.P.A.) 10.12.2008 ;

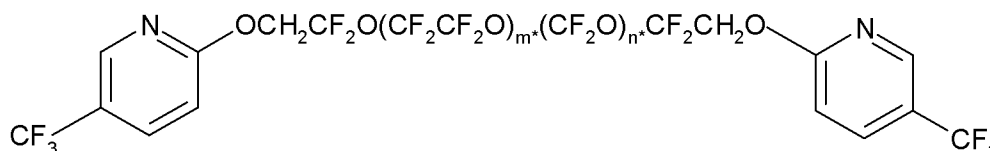
- functional PFPE derivatives complying with formula (V) as described above wherein at least one of T and T' is a functional end-group comprising at least one ether or thioether group comprising at least one benzoxazole, benzothiazole or benzopyrazine group optionally substituted with one or more substituents different from hydrogen atoms, notably disclosed in EP 1659164 A (SOLVAY SOLEXIS S.P.A.) 24.05.2006 .

[0040] Most preferred lubricant compositions of the invention comprise one or

more functional PFPE derivatives complying with formula (VI) as described above wherein both T'' and T''' are functional end-groups as defined above (bifunctional PFPE derivatives).

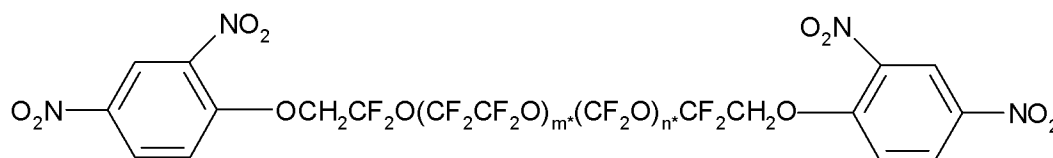
[0041] Non-limitative examples of suitable bifunctional PFPE derivatives include, notably, the followings:

- bifunctional PFPE derivatives complying with formula here below:



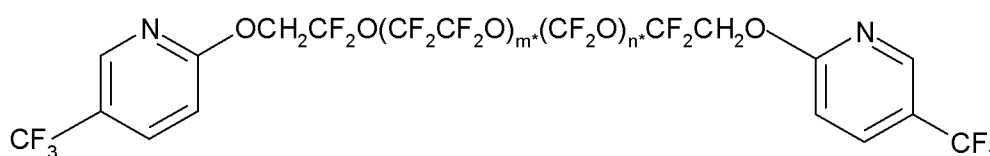
wherein  $m^*$  and  $n^*$  are integers such that the number average molecular weight of the bifunctional PFPE derivative is comprised between 1000 and 6000, preferably between 2000 and 4000, the  $m/n$  ratio being comprised between 0.1 and 5;

- bifunctional PFPE derivatives commercially available from Solvay Solexis S.p.A. under the trade name FOMBLIN<sup>®</sup> DA 410, said bifunctional PFPE derivatives complying with formula here below:



wherein  $m^*$  and  $n^*$  are integers such that the number average molecular weight of the bifunctional PFPE derivative is comprised between 1000 and 6000, preferably between 2000 and 4000, the  $m/n$  ratio being comprised between 0.1 and 5.

[0042] Very good results have been obtained with lubricant compositions comprising one or more bifunctional PFPE derivatives complying with formula here below:



wherein  $m^*$  and  $n^*$  are integers such that the number average molecular weight of the bifunctional PFPE derivative is comprised between 1000 and 6000, preferably between 2000 and 4000, the  $m/n$  ratio being comprised between 0.1 and 5.

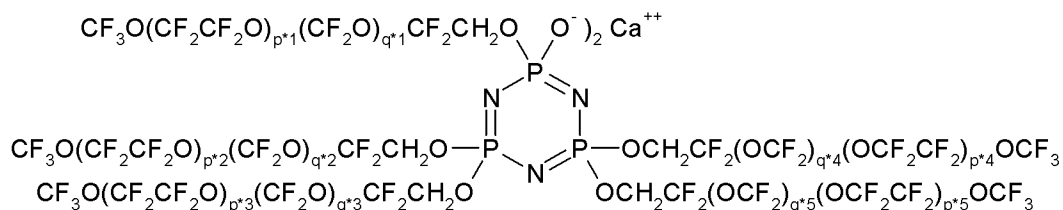
- [0043] The lubricant composition of the invention typically comprises at least one cyclic phosphazene compound [compound (P)] as defined above in an amount of at least 0.1% by weight, preferably at least 0.2% by weight, more preferably at least 0.3% by weight with respect to the weight of the non-functional PFPE oil.
- [0044] The lubricant composition of the invention typically comprises at least one cyclic phosphazene compound [compound (P)] as defined above in an amount of at most 15% by weight, preferably at most 10% by weight, more preferably at most 5% by weight with respect to the weight of the non-functional PFPE oil.
- [0045] The lubricant composition of the invention typically comprises at least one functional PFPE derivative different from compound (P) as defined above in an amount of at least 0.5% by weight, preferably at least 1% by weight, more preferably at least 2% by weight with respect to the weight of the non-functional PFPE oil.
- [0046] The lubricant composition of the invention typically comprises at least one functional PFPE derivative different from compound (P) as defined above in an amount of at most 15 % by weight, preferably at most 10% by weight, more preferably at most 6% by weight with respect to the weight of the non-functional PFPE oil.
- [0047] Very good results have been obtained with lubricant compositions comprising at least one cyclic phosphazene compound [compound (P)] in an amount ranging from 0.3% to 5% by weight with respect to the weight of the non-functional PFPE oil and at least one functional PFPE derivative different from compound (P) as defined above in an amount ranging from 2% to 6% by weight with respect to the weight of the non-functional PFPE oil.
- [0048] The lubricant composition of the invention typically has a kinematic viscosity ( $\eta$ ) ranging from 100 to 350, preferably from 120 to 300, as

measured at 20°C by ASTM D445.

- [0049] The lubricant composition can also further comprise other additives notably including one or more anti-rust additives, oxidation inhibitors, antifoam agents, anti-wear additives and anti-scuff additives. Representative examples of anti-rust additives which can be advantageously added to the lubricant composition of the invention include, notably, functional PFPEs commercially available from Solvay Solexis S.p.A. under the trade names FOMBLIN<sup>®</sup> DA305, FOMBLIN<sup>®</sup> DA306 and FOMBLIN<sup>®</sup> DA308.
- [0050] Another object of the invention is use of the lubricant composition as described above for lubricating vacuum pumps, in particular high vacuum and ultra-high vacuum pumps, especially in the semiconductor industry where high-purity lubricants are typically required.
- [0051] 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.
- [0052] 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.
- [0053] **Raw materials**
- [0054] The non-functional PFPE oil (1) is a linear non-functional PFPE oil having formula  $\text{CF}_3\text{O}-(\text{CF}_2\text{O})_n(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_r(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_s-\text{CF}_3$ , wherein m, n, r and s are integers such that the number average molecular weight is about 11000, the m/n ratio being about 2.7.
- [0055] The non-functional PFPE oil (2) is a FOMBLIN<sup>®</sup> M15 linear non-functional PFPE oil having formula  $\text{CF}_3\text{O}-(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n-\text{CF}_3$ , wherein m and n are integers such that the number average molecular weight is about 10600, the m/n ratio being about 0.9.
- [0056] The non-functional PFPE oil (3) is a FOMBLIN<sup>®</sup> M30 linear non-functional PFPE oil having formula  $\text{CF}_3\text{O}-(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n-\text{CF}_3$ , wherein m and n are integers such that the number average molecular weight is about 13000, the m/n ratio being about 0.9.

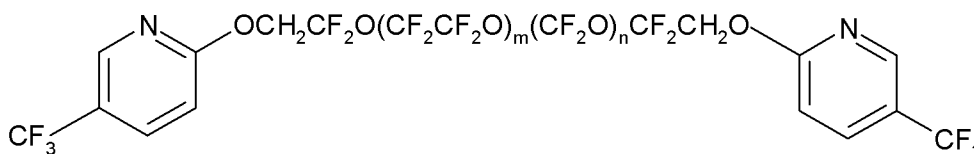
[0057] The non-functional PFPE oil (4) is a FOMBLIN<sup>®</sup> Y25/6 branched non-functional PFPE oil having formula  $\text{CF}_3\text{O}-(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_p(\text{CF}_2\text{O})_q-\text{CF}_3$ , wherein p and q are integers such that the number average molecular weight is about 3800.

[0058] The compound (P1) is a cyclic phosphazene compound having formula



wherein p\*i (i = 1 to 5) and q\*i (i = 1 to 5) indexes are integers such that the number average molecular weight is about 8300.

[0059] The functional PFPE derivative (1) has formula



wherein m and n are integers such that the number average molecular weight is about 3800, the m/n ratio being about 0.9.

[0060] **Thermal-oxidative stability test method**

Thermal-oxidative stability tests were conducted on a sintered metal bearing of Fe-Cu-Sn-C type.

The sintered metal bearing of Fe-Cu-Sn-C type was impregnated with the lubricant composition of the invention at 30°C, under vacuum (7 mbar), for 25 minutes. The sintered metal bearing so treated was then allowed to drain for about 15 minutes, so that the amount of lubricant composition impregnated in the sintered metal bearing was about 0.05 g.

The sintered metal bearing so impregnated was placed in a ventilated oven set at 200°C and weighted every 48-72 hours.

Weight loss of the lubricant composition was checked as a function of time.

An induction time was measured until complete degradation of the lubricant composition.

[0061] **Tribological test method**

Sliding wear tests were conducted with a ball-on-disk tribometer at 140°C during 6 hours under the following operating conditions:

- ball diameter: 10 mm;
- applied load: 200 N;
- amplitude of oscillation: 1 mm;
- frequency of oscillation: 50 Hz.

The wear volume (V) on the disk [mm<sup>3</sup>] has been calculated as follows:

$$V = \frac{(d1)^2 \cdot (d2)^2 \cdot 3.14}{64R}$$

wherein:

- d1 represents the diagonal of the disk wear parallel to the oscillating motion;
- d2 represents the diagonal of the disk wear perpendicular to the oscillating motion;
- R represents the ball radius (5 mm).

[0062] **Example 1**

A lubricant composition was prepared by mixing non-functional PFPE oil (3) with 0.5% by weight of non-functional PFPE oil (3) of compound (P1) and 5% by weight of non-functional PFPE oil (3) of functional PFPE derivative (1).

The results for the thermal-oxidative stability test of said lubricant composition are set forth in Table 1 here below.

[0063] **Example 1C (comparative)**

A composition was prepared by mixing non-functional PFPE oil (3) with 0.5% by weight of non-functional PFPE oil (3) of compound (P1).

The results for the thermal-oxidative stability test of said composition are set forth in Table 1 here below.

[0064] **Example 2C (comparative)**

A composition was prepared by mixing non-functional PFPE oil (3) with 5% by weight of non-functional PFPE oil (3) of functional PFPE derivative (1).

The results for the thermal-oxidative stability test of said composition are set forth in Table 1 here below.

Table 1

Example	Non-functional PFPE oil	Induction time [hours]
1	PFPE oil (3)	1104
1C	PFPE oil (3)	816
2C	PFPE oil (3)	744

[0065] The thermal-oxidative stability tests performed with the lubricant composition of Example 1 of the invention showed a substantial increase of the induction time to degradation with respect to compositions of comparative Examples 1C and 2C, that is to say that the lubricant composition of the invention showed improved thermal-oxidative stability with respect to compositions comprising at least one non-functional PFPE oil as defined above and either at least one compound (P) as defined above or at least one functional PFPE derivative as defined above.

[0066] **Example 2**

A lubricant composition was prepared by mixing non-functional PFPE oil (1) with 3% by weight of non-functional PFPE oil (1) of compound (P1) and 3% by weight of non-functional PFPE oil (1) of functional PFPE derivative (1).

The results for the tribological test and the evaporating constant at 150°C  $[(\text{mm}^3 \text{ of evaporated lubricant} / \text{mm}^2 \text{ of exposed surface area}) \cdot \text{h}] ([*])$  of said lubricant composition are set forth in Table 2 here below.

[0067] **Example 3**

A lubricant composition was prepared by mixing non-functional PFPE oil (2) with 3% by weight of non-functional PFPE oil (2) of compound (P1) and 3% by weight of non-functional PFPE oil (2) of functional PFPE derivative (1).

The results for the tribological test and the evaporating constant at 150°C  $[(\text{mm}^3 \text{ of evaporated lubricant} / \text{mm}^2 \text{ of exposed surface area}) \cdot \text{h}] ([*])$  of said lubricant composition are set forth in Table 2 here below.

[0068] **Example 4**

A lubricant composition was prepared by mixing non-functional PFPE oil



(4) with 3% by weight of non-functional PFPE oil (4) of compound (P1) and 3% by weight of non-functional PFPE oil (4) of functional PFPE derivative (1).

The results for the tribological test and the evaporating constant at 150°C [(mm<sup>3</sup> of evaporated lubricant / mm<sup>2</sup> of exposed surface area) · h] ([\*]) of said lubricant composition are set forth in Table 2 here below.

[0069] **Example 3C (comparative)**

A composition was prepared by mixing non-functional PFPE oil (2) with 3% by weight of non-functional PFPE oil (2) of compound (P1).

The results for the tribological test and the evaporating constant at 150°C [(mm<sup>3</sup> of evaporated lubricant / mm<sup>2</sup> of exposed surface area) · h] ([\*]) of said composition are set forth in Table 2 here below.

The thermal-oxidative stability tests performed with the composition of Example 3C showed a substantial decrease of the induction time to degradation with respect to the lubricant composition of Example 4 of the invention.

[0070] **Example 4C (comparative)**

A composition was prepared by mixing non-functional PFPE oil (2) with 3% by weight of non-functional PFPE oil (2) of functional PFPE derivative (1).

The results for the tribological test and the evaporating constant at 150°C [(mm<sup>3</sup> of evaporated lubricant / mm<sup>2</sup> of exposed surface area) · h] ([\*]) of said composition are set forth in Table 2 here below.

The thermal-oxidative stability tests performed with the composition of Example 4C showed a substantial decrease of the induction time to degradation with respect to the lubricant composition of Example 4 of the invention.

**Table 2**

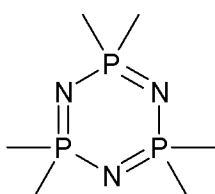
Example	Non-functional PFPE oil	Wear volume [mm <sup>3</sup> ]	Evaporating constant [*]
2	PFPE oil (1)	0.075	4.89 · 10 <sup>-3</sup>
3	PFPE oil (2)	0.071	3.77 · 10 <sup>-3</sup>

4	PFPE oil (4)	0.067	$1.13 \cdot 10^{-2}$
3C	PFPE oil (2)	0.069	$2.83 \cdot 10^{-3}$
4C	PFPE oil (2)	0.087	$1.36 \cdot 10^{-3}$

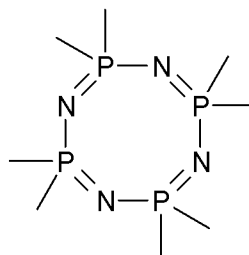
[0071] Substantially low wear volumes and low evaporating constants were measured for the lubricant compositions of Examples 2, 3 and 4 of the invention, that is to say that the lubricant compositions of the invention exhibited substantially high lubrication performances in terms of anti-wear properties and low evaporation weight loss. In particular, the tribological tests performed with the lubricant composition of Example 3 of the invention showed that substantially low or even slightly decreased wear volumes were measured with respect to compositions of comparative Examples 3C and 4C, that is to say that the lubricant composition of the invention showed good or slightly improved anti-wear properties with respect to compositions comprising at least one non-functional PFPE oil as defined above and either at least one compound (P) as defined above or at least one functional PFPE derivative as defined above.

## Claims

1. A lubricant composition comprising:
  - (A) at least one non-functional (per)fluoropolyether oil (non-functional PFPE oil) comprising at least one (per)fluoropolyoxyalkylene chain (chain R<sub>F</sub>);
  - (B) at least one cyclic phosphazene compound [compound (P)] comprising one or more cyclic moieties having formula (I) or (II) here below:



(I)



(II)

said cyclic moieties comprising, bound to one or more phosphorus atoms, at least one substituent comprising at least one (per)fluoropolyoxyalkylene chain (chain R'<sub>F</sub>);

(C) at least one functional (per)fluoropolyether derivative (functional PFPE derivative) different from compound (P) comprising at least one (per)fluoropolyoxyalkylene chain (chain R'<sub>F</sub>) and at least one functional group comprising at least one monocyclic or polycyclic aromatic ring, said aromatic ring optionally containing one or more heteroatoms selected from N, O and S and one or more substituents different from hydrogen atoms.

2. The lubricant composition of claim 1, wherein the non-functional PFPE oil is selected from the followings:
  - (1) T<sup>1</sup>-O-(C<sub>2</sub>F<sub>4</sub>O)<sub>b1'</sub>(CF<sub>2</sub>O)<sub>b2'</sub>-T<sup>1'</sup>
 wherein:
  - T<sup>1</sup> and T<sup>1'</sup>, equal to or different from each other, are independently selected from -CF<sub>3</sub>, -C<sub>2</sub>F<sub>5</sub> and -C<sub>3</sub>F<sub>7</sub> groups;
  - b1' and b2', equal to or different from each other, are independently integers

$\geq 0$  such that the  $b1'/b2'$  ratio is comprised between 0.1 and 5 and the  $(b1'+b2')$  sum is comprised between 5 and 250; should  $b1'$  and  $b2'$  be both different from zero, the different recurring units are generally statistically distributed along the perfluoropolyoxyalkylene chain.

(2)  $T^2-O-(CF_2O)_{c1'}(CF_2CF_2O)_{c2'}(CF_2CF_2CF_2O)_{c3'}(CF_2CF_2CF_2CF_2O)_{c4'}-T^2'$   
wherein:

- $T^2$  and  $T^2'$ , equal to or different from each other, are independently selected from  $-CF_3$ ,  $-C_2F_5$ ,  $-C_3F_7$ ,  $-C_4F_9$ ,  $-CF_2Cl$ ,  $-CF_2CF_2Cl$  groups;
  - $c1'$ ,  $c2'$ ,  $c3'$  and  $c4'$ , equal to or different from each other, are independently integers  $\geq 0$  such that the number average molecular weight is comprised between 700 and 100000;
  - the  $c2'/c1'$  ratio is comprised between 2 and 20;
  - the  $(c3'+c4')/(c1'+c2'+c3'+c4')$  ratio is comprised between 0.05 and 0.2;
  - the  $c1'/(c1'+c2'+c3'+c4')$  ratio is comprised between 0.05 and 0.4;
- should at least two of  $c1'$ ,  $c2'$ ,  $c3'$  and  $c4'$  be different from zero, the different recurring units are generally statistically distributed along the perfluoropolyoxyalkylene chain.

(3)  $T^3-O-(CF_2CF_2O)_{d'}-T^3'$

wherein:

- $T^3$  and  $T^3'$ , equal to or different from each other, are independently selected from  $-C_2F_5$  and  $-C_3F_7$  groups;
- $d'$  is an integer comprised between 5 and 250.

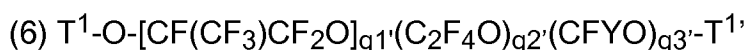
(4)  $T^1-O-(CF_2CF_2C(Hal)_2O)_{e1'}-(CF_2CF_2CH_2O)_{e2'}-(CF_2CF_2CH(Hal)O)_{e3'}-T^1'$   
wherein:

- $T^1$  and  $T^1'$ , equal to or different from each other, have the same meaning as defined above;
- Hal, equal or different at each occurrence, is a halogen selected from fluorine and chlorine atoms, preferably a fluorine atom;
- $e1'$ ,  $e2'$ , and  $e3'$ , equal to or different from each other, are independently integers  $\geq 0$  such that the  $(e1'+e2'+e3')$  sum is comprised between 5 and 250; should at least two of  $e1'$ ,  $e2'$  and  $e3'$  be different from zero, the different recurring units are generally statistically distributed along the (per)fluoropolyoxyalkylene chain.



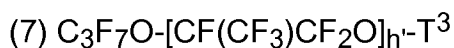
wherein:

- $T^1$  and  $T^1'$ , equal to or different from each other, have the same meaning as defined above;
- Y, equal or different at each occurrence, is selected from a fluorine atom or a  $-CF_3$  group;
- $f1'$  and  $f2'$ , equal to or different from each other, are independently integers  $\geq 0$  such that the  $f1'/f2'$  ratio is comprised between 20 and 1000 and the  $(f1'+f2')$  sum is comprised between 5 and 250; should  $f1'$  and  $f2'$  be both different from zero, the different recurring units are generally statistically distributed along the perfluoropolyoxyalkylene chain.



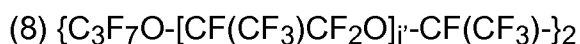
wherein:

- $T^1$  and  $T^1'$ , equal to or different from each other, have the same meaning as defined above;
- Y, equal or different at each occurrence, has the same meaning as defined above;
- $g1'$ ,  $g2'$  and  $g3'$ , equal to or different from each other, are independently integers  $\geq 0$  such that the  $(g1'+g2'+g3')$  sum is comprised between 5 and 250; should at least two of  $g1'$ ,  $g2'$  and  $g3'$  be different from zero, the different recurring units are generally statistically distributed along the perfluoropolyoxyalkylene chain.



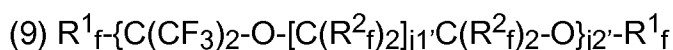
wherein:

- $T^3$  has the same meaning as defined above;
- h' is an integer comprised between 5 and 250.



wherein:

- i' is an integer comprised between 2 and 250.



wherein:

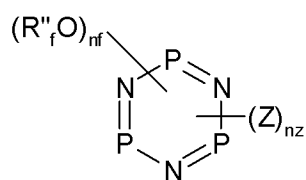
- $R^1_f$ , equal or different at each occurrence, is a  $C_1$ - $C_6$  perfluoroalkyl group;
- $R^2_f$ , equal or different at each occurrence, is selected from a fluorine atom

and a C<sub>1</sub>-C<sub>6</sub> perfluoroalkyl group;

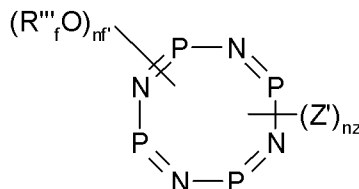
- j1' is equal to 1 or 2;

- j2' is an integer comprised between 5 and 250.

3. The lubricant composition of claims 1 and 2, wherein a mixture of more than one non-functional PFPE oil is used.
4. The lubricant composition of anyone of claims 1 to 3, wherein the cyclic phosphazene compound [compound (P)] complies with formula (I-B) or (II-B) here below:



(I-B)



(II-B)

wherein:

- R''<sub>f</sub> and R'''<sub>f</sub>, equal to or different from each other, independently represent a (per)fluoropolyoxyalkylene chain comprising one or more recurring units selected from:

- (i) -CFYO-, wherein Y is a fluorine atom or a -CF<sub>3</sub> group,
- (ii) -CF<sub>2</sub>CFYO-, wherein Y has the same meaning as defined above,
- (iii) -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-,
- (iv) -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-,

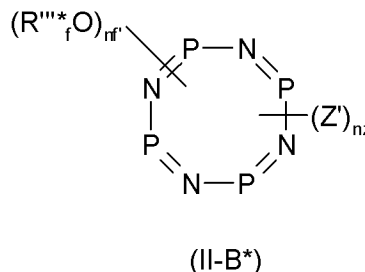
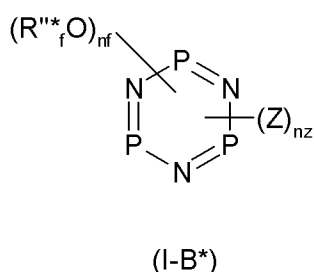
said recurring units being generally statistically distributed along the (per)fluoropolyoxyalkylene chain;

- Z and Z', equal to or different from each other, independently represent a polar group of formula -O<sup>-</sup>M<sup>+</sup>, wherein M is selected from hydrogen, a monovalent metal, preferably an alkaline metal, and an ammonium radical having formula -NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>, wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> is, independently, a hydrogen atom or a C<sub>1</sub>-C<sub>12</sub> hydrocarbon group, optionally

fluorinated, or a polar group of formula  $(-O^-)_2M'^{2+}$ , wherein  $M'$  is a divalent metal, preferably an alkaline earth metal;

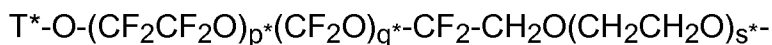
- $n_Z$  is an integer comprised between 1 and 3, preferably equal to 1;
- $n_{Z'}$  is an integer comprised between 1 and 4, preferably equal to 1;
- $n_f$  is an integer such that  $n_Z + n_f$  is equal to 6;
- $n_{f'}$  is an integer such that  $n_{Z'} + n_{f'}$  is equal to 8.

5. The lubricant composition of claim 4, wherein the cyclic phosphazene compound [compound (P)] complies with formula (I-B\*) or (II-B\*) here below:



wherein:

- $Z$ ,  $Z'$ ,  $n_Z$ ,  $n_{Z'}$ ,  $n_f$  and  $n_{f'}$  have the same meaning as defined in claim 4;
- $R''*_f O-$  and  $R''''*_f O-$ , equal to or different from each other, represent a (per)fluoropolyoxyalkylene chain having formula:



wherein:

- $T^*$  is selected from  $-CF_3$ ,  $-CF_2CF_3$  and  $-CF_2CF_2CF_3$  groups;
- $p^*$  and  $q^*$  are numbers such that the  $(p^*+q^*)$  sum is comprised between 1 and 50 and the  $q^*/p^*$  ratio is comprised between 0.1 and 10;
- $s^*$  is a number comprised between 0 and 5.

6. The lubricant composition of claims 4 and 5, wherein the cyclic phosphazene compound [compound (P)] complies with formula (III-B) or (III-B bis) here below:





aromatic ring optionally containing one or more heteroatoms selected from N, O and S and one or more substituents different from hydrogen atoms,

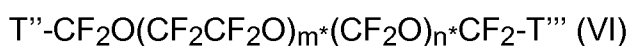
ii) non-functional end-groups selected from a fluorine atom, a chlorine atom and a C<sub>1</sub>-C<sub>3</sub> (per)fluoroalkyl group optionally containing one or more chlorine atoms,

with the proviso that at least one of T and T' is a functional end-group as defined hereinabove;

- W<sub>1</sub> and W<sub>2</sub>, equal to or different from each other, independently represent a fluorine atom or a -CF<sub>3</sub> group;

- p<sub>1</sub> and p<sub>1</sub>', equal to or different from each other, are independently integers comprised between 1 and 3, preferably being equal to 1 when W<sub>1</sub> and/or W<sub>2</sub> are -CF<sub>3</sub> groups.

8. The lubricant composition of claim 7, wherein the functional PFPE derivative complies with formula (VI) here below:



wherein:

- T'' and T''', equal to or different from each other, are selected from:

i) functional end-groups selected from those having formulae -CH<sub>2</sub>-A-Y, -CH(CF<sub>3</sub>)-A-Y, -CHW'-B-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m'</sub>-Y and -COOY, wherein:

(a') A is selected from oxygen and sulphur atoms,

(b') B is selected from an oxygen atom, a sulphur atom and a -NH group,

(c') W' is selected from a hydrogen atom and a -CF<sub>3</sub> group,

(d') m' is an integer comprised between 0 and 6,

(e') Y is selected from phenyl, pyridine, triazine, benzoxazole, benzothiazole and benzopyrazine groups optionally substituted with one or more substituents different from hydrogen atoms,

ii) non-functional end-groups selected from a fluorine atom, a chlorine atom, a -CF<sub>3</sub> group, a -C<sub>2</sub>F<sub>5</sub> group and a -(CF<sub>2</sub>)<sub>n</sub>Cl group, wherein n is an integer comprised between 1 and 3,

with the proviso that at least one of T'' and T''' is a functional end-group as defined hereinabove;

- m\* and n\* are integers such that the number average molecular weight of the functional PFPE derivative is comprised between 400 and 10000, the m\*/n\*

ratio being comprised between 0.1 and 10.

9. The lubricant composition of anyone of claims 1 to 8, wherein at least one cyclic phosphazene compound [compound (P)] is comprised in an amount ranging from 0.3% to 5% by weight with respect to the weight of the non-functional PFPE oil and at least one functional PFPE derivative different from compound (P) is comprised in an amount ranging from 2% to 6% by weight with respect to the weight of the non-functional PFPE oil.
10. Use of the lubricant composition of anyone of claims 1 to 9 for lubricating vacuum pumps.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2010/064686

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C10M169/04  
ADD. C10N40/00

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

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX, 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	EP 1 659 164 A2 (SOLVAY SOLEXIS SPA [IT]) 24 May 2006 (2006-05-24) paragraph [0009] - paragraph [0018] claims; examples -----	1, 2, 4, 7-9
Y	EP 1 336 614 A1 (SOLVAY SOLEXIS SPA [IT]) 20 August 2003 (2003-08-20) paragraph [0010] - paragraph [0023] claims; examples -----	1-10
Y	DATABASE WPI Week 198948 Thomson Scientific, London, GB; AN 1989-353232 XP002576837, & JP 1 265049 A (NIPPON MEKTRON KK) 23 October 1989 (1989-10-23) * abstract -----	1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

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\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

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\*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

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\* & \* document member of the same patent family

Date of the actual completion of the international search

30 November 2010

Date of mailing of the international search report

07/12/2010

Name and mailing address of the ISA/

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No  
PCT/EP2010/064686

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1659164	A2	24-05-2006	CA	2527421 A1	19-05-2006
			JP	2006144007 A	08-06-2006
			US	2006111250 A1	25-05-2006
-----					
EP 1336614	A1	20-08-2003	IT	MI20020281 A1	14-08-2003
			JP	2004002308 A	08-01-2004
			US	2003176738 A1	18-09-2003
-----					
JP 1265049	A	23-10-1989	JP	2614740 B2	28-05-1997
-----					