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(54) **Stabilisers for perfluoropolyether oils**

Stabilisatoren für Perfluoropolyetherölen

Stabilisateurs pour les huiles perfluoropolyetheriques

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EP 1 354 932 B1

Description

[0001] The present invention relates to the use of fluorinated compounds as stabilizing additives of perfluoropolyether oils for their use at high temperatures.

[0002] More specifically the present invention relates to the use of fluorinated compounds as stabilizing additives of perfluoropolyether oils for their use at high temperatures, in oxidizing environment and in the presence of metals.

[0003] It is known that perfluoropolyether fluids are lubricating oils used also at high temperatures. However, said fluids show the drawback that in oxidizing environment (for example oxygen, air) and in the presence of metals they have a limited thermal stability.

[0004] It is also known in the prior art that said drawback can be reduced by adding to perfluoropolyether fluids stabilizing additives. Said stabilizing additives are generally phosphor compounds wherein substituents of perfluoroalkyl, perfluorooxyalkyl and aromatic type are present. The synthesis of said compounds is generally complex or uses reactants at a high cost. The following patents can for example be mentioned. USP 4,681,693 describes stabilizers for perfluoropolyether fluids having a structure formed by arylphosphines, or derivatives thereof, linked to PFPE radicals through one oxygen or sulphur atom. Said compounds are synthesized by a more step process which includes intermediates difficult to be prepared. EP 597,369 describes stabilizers for perfluoropolyether fluids based on substituted phosphazene derivatives, where on the phosphazene ring both aromatic and (per)fluoropolyether radicals are contemporaneously present. The synthesis of said additives requires a double substitution on the phosphazene ring. Besides the starting phosphazene product has a high cost. This represents a further drawback from the industrial point of view.

[0005] USP 5,326,910 describes perfluoropolyether phosphotriazine derivatives as stabilizers for perfluoropolyether oils. Said derivatives are synthesized with several steps, using reactants of difficult preparation, such for example perfluorinated epoxides.

[0006] USP 5,550,277 describes stabilizers for perfluoropolyether fluids based on aromatic phosphates or phosphonates substituted by perfluoropolyether groups. The synthesis process is very complicated, it requires more steps and furthermore it employes the use of metallo-organic reactants, such for example butyl lithium, which are of difficult industrial use for the problems related to the plant safety.

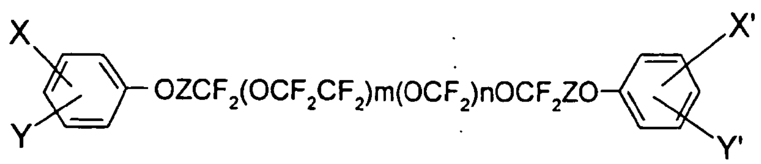
[0007] Patent application WO 99/51,612 describes new phosphoric esters, in particular substituted arylphosphates, where at least one of the substituents is a radical of perfluoropolyether type.

[0008] In the preparation method of said additives, aromatic phosphoric chloroesters, having a high cost, are used. As described in the Examples of the patent application, said esters are obtained by reacting aromatic alcohols with $POCl_3$, which is a toxic and scalding substance, requiring specific equipments for the use in an industrial scale.

[0009] According to the prior art the substances used as stabilizing additives for perfluoropolyether oils contain phosphor and are obtained by using, as seen, synthesis processes comprising various steps or, alternatively, using expensive reactants.

[0010] The Applicant has surprisingly found additives which even not containing phosphor in the molecule can be suitably used as perfluoropolyether oil stabilizers at high temperatures, even in oxidizing environment and in the presence of metals. Furthermore said additives can be obtained with simplified synthesis methods using cheap reactants.

[0011] An object of the present invention is the use as stabilizers of perfluoropolyether lubricating oils at high temperatures, higher than 200°C, of compounds having the following general formula (A):



(A)

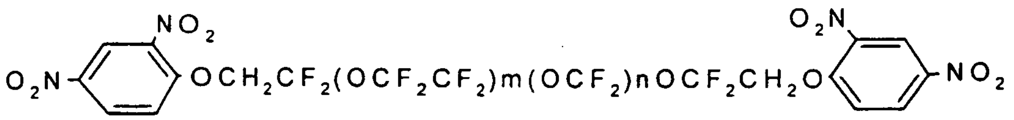
wherein:

- X, Y, X', Y', equal or different, are independently the one from the other H;. NO_2; C_1-C_4 alkyl; C_1-C_4 alkoxy, preferably methoxy group;
- Z = $-CH_2-$; >C=O (carbonyl);
- m and n are integers such that m is in the range 0-80, extremes included; n is in the range 0-20, extremes included; m+n being >1;

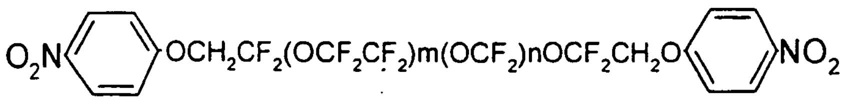
the molecular weight of the perfluoropolyether part (units with indexes m and n respectively) being from 500 to 10,000, preferably from 1,000 to 4,000.

[0012] Also mixtures of one or more formula (A) additives can be used.

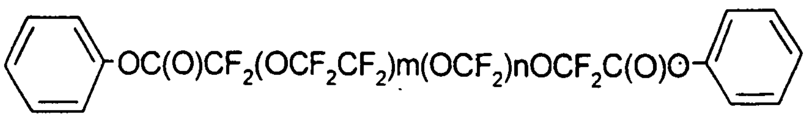
[0013] Preferably the general formula (A) products are selected from the following:



(I)



(II)



(III)

wherein m is in the range 0-80, extremes included; n is in the range 0-20, extremes included, m/n preferably being from 0.5 to 4 when n is different from zero and m+n is such to give the above molecular weight.

[0014] The general formula (A) compounds can be prepared according to USP 3,810,874, EP 165,649, EP 165,650, USP 3,250,807. They are geneally obtainable in a single step by a reaction between a perfluoropolyether derivative of formula:

$$HOZCF_2(OCF_2CF_2)m(OCF_2)nOCF_2ZOH \qquad (B)$$

wherein Z, m and n are as above, with a suitable aromatic reactant having the substituents X, Y, X' and Y' as defined in formula (A). For example a nucleophilic substitution or esterification reaction can be used. In the former case the alcoholate of compound (B) ($Z = -CH_2-$), is used, in the latter case compound (B) with Z = >C=O. See the above patents.

[0015] The formula (A) compounds of the present invention are used as stabilizers for perfluoropolyether oils, available on the market as for example FOMBLIN® , marketed by Ausimont.

[0016] Said oils have perfluoroalkyl end groups, are liquid with a very low vapour pressure value and have a viscosity at 20°C generally in the range 10-100,000 cSt, preferably 30-2,000 cSt.

[0017] The perfluoropolyether oils are formed by repeating units statistically distributed along the chain, and have for example the following structures:

(1) $B\text{-}O\text{-}[C_3F_6O]_{m'}(CFT'O)_{n'}\text{-}B'$
wherein:

T' = F, CF_3;

B and B', equal to or different from each other, are selected from $-CF_3$, $-C_2F_5$ or $-C_3F_7$;
m' and n' are integers such that the m'/n' ratio is in the range 20-1,000, n' being different from zero, and the product viscosity is within the above limits;
said products can be obtained by photooxidation of the perfluoropropene as described in GB 1,104,432, and by subsequent conversion of the end groups as described in GB 1,226,566.

(2) $C_3F_7O-[C_3F_6O]_{o'}-D$
wherein:

D is equal to $-C_2F_5$ or $-C_3F_7$;
o' is an integer such that the product viscosity is in the above range;
said products can be prepared by ionic oligomerization of the perfluoropropylenoxide and subsequent treatment with fluorine as described in USP 3,242,218.

(3) $B-O-[CF(CF_3)CF_2O]_{q'}(C_2F_4O)_{r'}(CFT'O)_{s'}-B'$
wherein:

T' is as above;
B and B', equal to or different from each other, are selected from $-CF_3$, $-C_2F_5$ or $-C_3F_7$;
q', r' and s' are integers and can have also the value of zero, with the proviso that they are not all contemporaneously equal to zero, and are such that the product viscosity is in the above range, i.e. 10-100,000 sSt, preferably 30-2,000 cSt;
said products are obtainable a mixture photooxidation of
C_3F_6 and C_2F_4 and subsequent treatment with fluorine as described in USP 3,665,041.

(4) $B-O-(C_2F_4O)_{t'}(CF_2O)_{u'}-B'$
wherein:

B and B', equal to or different from each other, are selected from $-CF_3$, $-C_2F_5$ or $-C_3F_7$;
t' and u' are integers such that the t'/u' ratio is in the range 0.1-5, preferably 0.5-4, u' being different from zero, and the product viscosity is in the above range;
said products are obtained by photooxidation of C_2F_4 as reported in USP 3,715,378 and subsequent treatment with fluorine as described in USP 3,665,041.

(5) $B-O-(CF_2CF_2CF_2O)_{v'}-B'$
wherein:

B and B', equal to or different from each other, are selected from $-CF_3$, $-C_2F_5$ or $-C_3F_7$;
v' is a number such that the product viscosity is in the above range;
said products are obtained as reported in EP 148,482.

(6) $D-O-(CF_2CF_2O)_{z'}-D'$
wherein:

D and D', equal to or different from each other, are selected between $-C_2F_5$ or $-C_3F_7$;
z' is an integer such that the product viscosity is in the above range;
said products can be obtained as reported in USP 4,523,039.

[0018] The $-C_3F_6O-$ unit in the above formulas can have structure $-CF(CF_3)CF_2O-$ or $-CF_2CF(CF_3)O-$.

[0019] According to the present invention the class (4) perfluoropolyethers are preferably used.

[0020] The formula (A) compounds are mixed with perfluoropolyether oils in a percentage from 0.01 to 10% by weight, preferably from 0.2 to 5% with respect to the perfluoropolyether oil weight. Preferably the formula (I) compound is used.

[0021] To the aforesaid mixtures other additives commonly used in the perfluoropolyether lubricating compositions can be added.

[0022] The compositions comprising the invention additives can be used in the presence of metals and in the presence of air and oxygen at high tempertures, higher than 200°C, up to the oil decomposition temperature. In particular the invention additive can be used at temperatures of about 320°C, preferably up to 300°C.

[0023] The invention compositions, perfluoropolyether lubricating oil + additive, can be used for the above uses, preferably the additive has formula (I).

[0024] The following Examples are given for illustrative and not limitative purposes of the invention.

EXAMPLES

Microoxidation test

[0025] The microoxidation test used in the Examples has been carried out using the equipment described in the following publication: Carl E. Snyder, Jr. and Ronald E. Dolle, Jr., ASLE Transactions, 13(3), 171-180 (1975). The used operating conditions have been the following:

- Perfluoropolyether oil utilized: Fomblin® M30 having kinematic viscosity at 20°C of 270 cSt ($2.7 \cdot 10^8$ m^2/s) and acidity, determined with the method indicated hereinafter, lower than 0.01 mg KOH/g;
- Test temperature: 300°C;
- Test duration: 24 h;
- Air flow: 1 litre/h;
- Metals dipped in the fluid: stainless steel (AISI 304) and titanium alloy containing A1 6%, V 4% (Titanium 6A14V).

[0026] The tested fluid is introduced into the glass test tube of the equipment, shown in Fig. 1 of the above reference, and the test tube charged with the fluid and the metal is weighed and brought to the test temperature. The established time elapsed, the glass test tube is cooled to room temperature and weighed again. The per cent weight loss of the tested fluid is determined by the difference of the weight before and after the thermal treatment. The fluid is then recovered and the kinematic viscosity and the acidity are determined. After the test the surface aspect of the metals which have been dipped in the tested fluid is visually evaluated.

Determination of the perfluoropolyether oil acidity number

[0027] The acidity number of the tested PFPE is measured by mixing under a light nitrogen flow, in the order, 5 ml of KOH 0,01 N, 10 g of sample to be tested, 30 ml of Freon 113 and 40 ml of MeOH. The base excess is titred with HCl 0.01 N by a potentiographic automatic titrator.

[0028] The acidity number N, is determined by the following formula:

$$N = 0{,}56 \cdot (B-A)/W,$$

wherein B = ml of HCl 0.01 N used for the control test (without sample), A = ml of HCl 0.01 N used in the titration of the base excess and W is the sample weight in grams. Therefore N is expressed in mg KOH/g fluid.

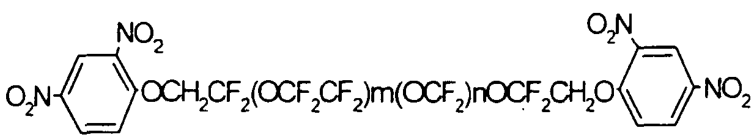
Determination of the kinematic viscosity of the perfluoropolyether oil

[0029] The kinematic viscosity has been determined by capillary viscosimeter Cannon-Fenske according to the ASTM D 445 method.

EXAMPLE 1

Synthesis of the bis(2,4-dinitro phenil) (per)fluoropoly-ether derivative

[0030]



(I)

[0031] 11.8 g of potassium terbutylate are dissolved in 200 ml of terbutanol in a 500 ml three necked flask, equipped with mechanical stirrer, water refrigerant, thermometer and nitrogen head. Subsequently, maintaining the reactor at room temperature by means of a water bath, 100 g of ZDOL® 2000 of formula $HOCH2CF_2(OCF_2CF_2)m(OCF2)nOCF_2CH_2OH$ MW = 1966 EW = 993, m/n = 1.2 are dripped. When dripping is over, the reaction mixture is left under stirring for two hours under nitrogen head.

[0032] Lastly a solution composed of 21.2 g of 2,4-dinitro chlorobenzene dissolved in 28 ml of dioxane is slowly dripped at room temperature. A yellow brownish precipitate mainly consisting of KCl immediately forms.

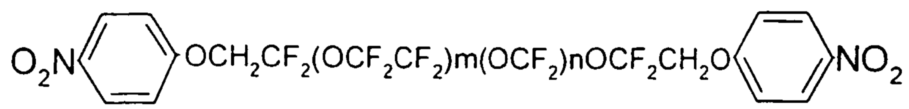
[0033] The reactor is left under stirring for one hour at room temperature, then for one hour at 65°C and lastly for another hour at 75°C. The reaction raw product is discharged in 600 ml of water. A turbid yellow brownish oil separates and the aqueous supernatant is extracted with two portions of 20 ml each of $CF_2Cl\text{-}CFCl_2$ having boiling point of 47.6°C.

[0034] The fluorinated phases are joined to the oil and the mixture is decoloured by mixing with active carbon. The mixture is filtered on porous septum and dried, it is washed with two portions of 10 ml each of ethanol to remove the unreacted 2,4-dinitrochlorobenzene, it is dried under vacuum at 60°C for one hour. 92 g of product are isolated.
Characterization of the product:
NMR ^{19}F spectrum in ppm (with respect to $CFCl_3$ =0):
-51/-56 (17F, $(OCF_2)_n$); -87/-91 (42F, $(OCF_2CF_2)_m$); -76/-80 (4F, OCF_2CH_2O);
NMR ^1H spectrum in ppm (with respect to TMS):
5.1 (4H, OCF_2CH_2); 8.8 (2H aromatic $CNO_2\text{-}CH\text{-}CNO_2$); 8.6 (2H aromatic $CNO_2\underline{CH}\text{-}CH\text{-}$); 7.8(2H aromatic $Rf\text{-}CH_2OC\text{-}\underline{CH}\text{-}CH\text{-}$);
IR spectrum (cm^{-1}) intensity: (w) = weak, (m) = mean, (s) = strong, (vs) = very strong
3092(w), 1612(w), 1542(w), 1351(m), 1207(vs), 1096(vs).
Said NMR peakds show that the product has formula (I) for 91% by weight.
NMR ^{19}F spectrum in ppm (with respect to the $CFCl_3$ =0): -81/-82 ($0\text{-}C\underline{F}_2\text{-}CH_2\text{-}OH$);
NMR ^1H spectrum in ppm (with respect to the TMS): 4.0 ($0\text{-}CF_2\text{-}C\underline{H}_2\text{-}OH$).

EXAMPLE 2

Synthesis of the bis(p-nitrophenyl) (per)fluoropolyether derivative

[0035]



(II)

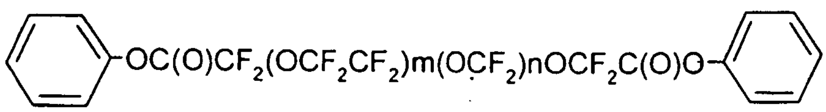
[0036] In a flask, equal to that used in Example 1, potassium terbutylate, terbutanol and ZDOL® 2000 are added under the same conditions and amounts described therein.

[0037] Lastly a solution composed of 14.8 g of p-nitrofluorobenzene dissolved in 30 ml of dioxane is slowly dripped at room temperature. The reactor is left under stirring for one hour at room temperature, then for one hour at 65°C and lastly for two hours at 85°C. The reaction raw product is discharged in 600 ml of water. The oil is recovered as described in Example 1. The dried reaction raw product is then washed with two portions of 10 ml each of ethanol to remove the unreacted p-nitrofluorobenzene; it is dried under vacuum at 60°C for one hour. 85 g of product are isolated.
Characterization of the product:
NMR ^{19}F spectrum in p.p.m. (with respect to the $CFCl_3$ = 0): -51/-56 (17F, $(OCF_2)_n$); -87/-91 (42F, $(OCF_2CF_2)_m$); -76/-80 (4F, OCF_2CH_2O) ;
NMR ^1H spectrum in ppm (with respect to TMS): 4.8 (4H, OCF_2CH_2); 7.3 (4H aromatic in meta to NO_2); 8.3 (4H aromatic in ortho to NO_2);
IR spectrum (cm^{-1}) intensity: (w) = weak, (m) = mean, (s) = strong, (vs) = very strong
3090(w), 1789(w), 1596(m), 1596(m), 1522(m), 1456(w), 1350(s), 1200(vs), 1100(vs).
Said NMR peaks show that the product has formula (II) for 93% by weight.
NMR ^{19}F spectrum in ppm (with respect to $CFCl_3$ =0): -81/-82 ($0\text{-}C\underline{F}_2\text{-}CH_2\text{-}OH$).
NMR ^1H spectrum in ppm (with respect to TMS): 4.0 ($0\text{-}CF_2\text{-}C\underline{H}_2\text{-}OH$).

EXAMPLE 3

Synthesis of the (per)fluoropolyether phenyl ester having formula

[0038]



(III)

[0039] In a flask equal to that described in Example 1, 24 g of phenol, 200 g of an acylfluoride of formula:

$$FOC(O)CF_2(OCF_2CF_2)m(OCF_2)nOCF_2C(O)F$$

prepared according to USP 3,715,378, having molecular weight 2,400, m/n = 1.3 and 30 g of NaF, are introduced, in the order. The heterogeneous mixture is heated under stirring at 80°C for two hours. When heating is over, the product is filtered and heated at 135°C in a vacuum of 0.5 mm Hg (67 Pa) to remove the unreacted phenol. 198 g of the desired product are isolated.
Characterization of the product:
NMR ^{19}F spectrum in p.p.m. (with respect to $CFCl_3$ =0): -51/-56 (20F, $(OCF_2)_n$); -87/-91 (52F, $(OCF_2CF_2)_m$); -80/-84 (4F, $OCF_2(O)O$);
NMR ^1H spectrum in ppm (with respect to TMS):
7.5/7.3 (4H ortho); 7.3/7.2 (6H: 2H in para, 4H in meta); IR spectrum (cm^{-1}) intensity: (w) = weak, (m) = mean, (s) = strong, (vs) = very strong
3588(w), 2364(w), 1805(vs), 1593(m), 1494(s), 1204(vs).
[0040] Said NMR peaks show that the product has formula (I) for 100% by weight.

EXAMPLE 4

Microoxidation test of a perfluoropolyether oil added to the product obtained in Example 1.

[0041] 50 g of perfluoropolyether oil Fomblin® M30 are added with 0.5 g of the product obtained in Example 1 (1% by weight of the additive with respect to the oil) and then introduced into the glass test tube for the microoxidation test as above described. During the test the fluid has maintained limpid and no smoke development has been observed.
[0042] At the test end under the mentioned operating conditions a per cent loss ΔP% of fluid equal to 1.6% by weight has been measured. The kinematic viscosity has substantially remained unchanged ($\Delta\eta$= +0.84%).
[0043] The fluid acidity has not changed. The metals recovered from the fluid at the test end (stainless steel and Ti, Al, V alloy) did not show oxidation/corrosion signs, and their surface aspect was comparable with that of the specimens of the same metals not subjected to the treatment.

EXAMPLE 5

Microoxidation test of a perfluoropolyether oil added with the product obtained in Example 2.

[0044] Example 4 is repeated by using as additive 0.5 g of the product obtained in Example 2.
[0045] At the test end under the mentioned operating conditions a per cent loss ΔP% of fluid of 1.3% has been measured. The kinematic viscosity has substantially remained unchanged ($\Delta\eta$= +0.6%). The fluid acidity is not changed. The metals recovered from the fluid at the test end (stainless steel and Ti, Al, V alloy) did not show oxidation/corrosion signs, and their surface aspect was comparable with that of the specimens of the same metals not subjected to the treatment.

EXAMPLE 6

Microoxidation test of a perfluoropolyether oil added with the product obtained in Example 3.

[0046] Example 4 is repeated by using as additive 0.5 g of the product obtained in Example 3. At the test end under the mentioned operating conditions a per cent loss ΔP% of fluid equal to 1.7% and a kinematic viscosity variation equal to Δη= +2.1% have been measured.
[0047] The fluid acidity is not changed. The metals recovered from the fluid at the test end (stainless steel and Ti, Al, V alloy) did not show oxidation/corrosion signs, and their surface aspect was comparable with that of the specimens of the same metals not subjected to the treatment.

EXAMPLE 7 (comparative)

Microoxidation test of a not additivated perfluoropolyether oil in absence of metals.

[0048] Example 4 is repeated without adding the additives of the present invention and in absence of metals in the perfluoropolyether oil.
[0049] During the test the development of white smokes has been observed.
[0050] At the test end under the mentioned operating conditions a per cent loss ΔP% of fluid of 4.6% by weight and a kinematic viscosity variation equal to Δη= +0.5% have been measured. The measured final fluid acidity has been 0.07 mg KOH/g.

EXAMPLE 8 (comparative)

Microoxidation test of a not additivated perfluoropolyether oil in the presence of metals.

[0051] Example 4 is repeated without adding the additives of the present invention.
[0052] During the test the intense development of white smokes has been observed.
[0053] At the test end under the mentioned operating conditions a very high per cent loss ΔP% of fluid equal to 82.8% by weight has been measured.
[0054] The measured final fluid acidity has been of 5.5 mg KOH/g. The surface aspect of the metals has resulted modified for the presence of evident oxidation signs (browning).

EXAMPLE 9

Microoxidation test of a perfluoropolyether oil added with the product obtained in Example 1.

[0055] Example 4 has been repeated but by using 0.125 g of the product obtained in Example 1 (0.25% by weight of the additive with respect to the oil).
[0056] During the test the fluid has maintained limpid and no smoke development has been observed.
[0057] At the test end under the mentioned operating conditions a per cent loss ΔP% of fluid of 0.18% has been measured, while the kinematic viscosity has substantially remained unchanged (Δη= +1.33%).
[0058] The fluid acidity is not changed. The metals recovered from the fluid at the test end (stainless steel and Ti, Al, V alloy) did not show oxidation/corrosion signs, and their surface aspect was comparable with that of the specimens of the same metals not subjected to the treatment.
[0059] The following Table 1 summarizes the results obtained in Examples 4-9.

Table 1

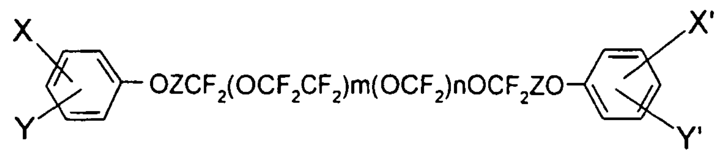
Ex.	Metal treatment	Concentration and used compounds of formula (A)		Final fluid after microoxidation test		
		% by weight	formula	Fluid weight variation ΔP %	Kinematic viscosity variation Δη %	Acidity mg KOH/g
4	Yes	1	(I)	-1.6	0.84	< 0.01
5	Yes	1	(II)	-1.3	0.60	< 0.01
6	Yes	1	(III)	-1.7	2.1	< 0.01

Table continued

Ex.	Metal treatment	Concentration and used compounds of formula (A)		Final fluid after microoxidation test		
		% by weight	formula	Fluid weight variation ΔP %	Kinematic viscosity variation Δη %	Acidity mg KOH/g
7 comp	No	-	-	-4.6	0.5	0.07
8 comp	Yes	-	-	-82.8	-	5.5
9	Yes	0.25	(I)	-0.2	1.33	< 0.01

Claims

1. Use as stabilizers of perfluoropolyether lubricating oils at high tempertures, higher than 200°C, of compounds having the following general formula (A):



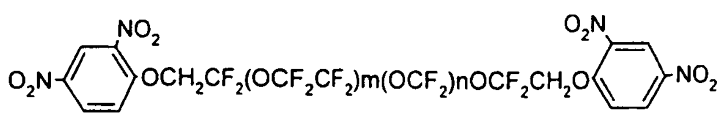
(A)

wherein:

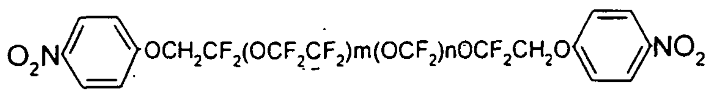
- X, Y, X', Y', equal to or different, are independently the one from the other H; NO_2; C_1-C_4 alkyl; C_1-C_4 alkoxy, preferably methoxy group;
- Z = $-CH_2-$; >C=O (carbonyl);
- m and n are integers such that m is in the range 0-80, extremes included; n is in the range 0-20, extremes included, m+n being >1;

the molecular weight of the perfluoropolyether part (units with indexes m and n) being from 500 to 10,000, preferably from 1,000 to 4,000.

2. Use according to claim 1, wherein the general formula (A) compounds are selected from the following:



(I)



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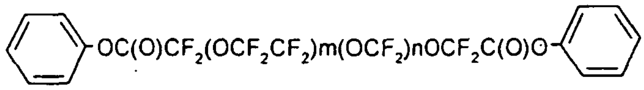


(III)

wherein m is in the range 0-80, extremes included; n is in the range 0-20, extremes included, m/n preferably being from 0.5 to 4 when n is different from zero and m+n is such to give the above molecular weight.

3. Use according to claims 1-2, wherein the perfluoropoly-ether oils have perfluoroalkyl end groups and have a viscosity at 20°C in the range 10-100,000 cSt, preferably 30- 2,000 cSt.

4. Use according to claim 3, wherein the perfluoropolyether oils have the repeating units statistically distributed along the chain and have the following structures:

(1) $B\text{-}O\text{-}[C_3F_6O]_{m'}(CFT'O)_{n'}\text{-}B'$
wherein:

T' = F, CF_3;
B and B', equal to or different from each other, are selected from $-CF_3$, $-C_2F_5$ or $-C_3F_7$;
m' and n' are integers such that the m'/n' ratio is in the range 20-1,000, n' being different from zero, and the product viscosity is in the above limits;

(2) $C_3F_7O\text{-}[C_3F_6O]_{o'}\text{-}D$
wherein:

D is equal to $-C_2F_5$ or $-C_3F_7$;
o' is an integer such that the product viscosity is in the above range;

(3) $B\text{-}O\text{-}[CF(CF_3)CF_2O]_{q'}(C_2F_4O)_{r'}(CFT'O)_{s'}\text{-}B'$
wherein:

T' is as above;
B and B', equal to or different from each other, are selected from $-CF_3$, $-C_2F_5$ or $-C_3F_7$;
q', r' and s' are integers and can take also the value of zero, with the proviso that they are not all contemporaneously equal to zero, and are such that the product viscosity is in the above range;

(4) $B\text{-}O\text{-}(C_2F_4O)_{t'}(CF_2O)_{u'}\text{-}B'$
wherein:

B and B', equal to or different from each other, are selected from $-CF_3$, $-C_2F_5$ or $-C_3F_7$;
t' and u' are integers such that the t'/u' ratio is in the range 0.1-5, preferably 0.5-4, u' being different from zero, and the product viscosity is in the above range;

(5) $B\text{-}O\text{-}(CF_2CF_2CF_2O)_{v'}\text{-}B'$
wherein:

B and B', equal to or different from each other, are selected from $-CF_3$, $-C_2F_5$ or $-C_3F_7$;
v' is a number such that the product viscosity is in the above range;

(6) $D-O-(CF_2CF_2O)_{z'}-D'$
wherein:

D and D', equal to or different from each other, are selected between $-C_2F_5$ or $-C_3F_7$;
z' is an integer such that the product viscosity is in the above range.
The $-C_3F_6O-$ unit in the above formulas can have the structure $-CF(CF_3)CF_2O-$ or $-CF_2CF(CF_3)O-$.

5. Use according to claim 4, wherein the perfluoropolyether oils have structure (4).

6. Use according to claims 1-5, wherein the compounds of formula (A) are mixed with the perfluoropolyether oils in a percentage from 0.01 to 10% by weight, preferably from 0.2 to 5% by weight, with respect to the perfluoropoly-ether oil weight.

7. Use according to claims 1-6, wherein the formula (I) compound is used.

8. Use according to claims 1-7, wherein to the mixtures of the formula (A) compounds with perfluoropolyether oils, additives selected from those used in the perfluoro-polyether lubricating compositions are added.

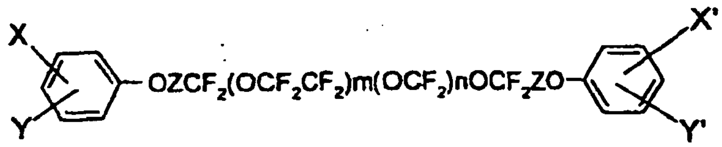
9. Use according to claims 1-8, wherein the compositions are used in the presence of metals and in the presence of air and oxygen at high temperatures, higher than 200°C, up to the oil decomposition temperature, preferably up to about 320°C, still more preferably up to 300°C.

10. Compositions comprising perfluoropoly ether lubricating oils and the compound of formula (A) as defined in claim 1.

11. Compositions according to claim 10 wherein the additive (A) has formula (I), as defined in claim 2.

Patentansprüche

1. Verwendung von Verbindungen der folgenden allgemeinen Formel (A):



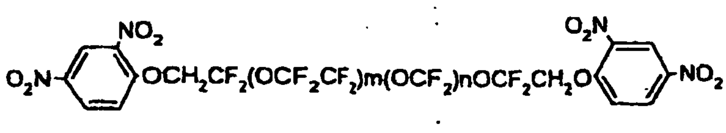
(A)

worin:

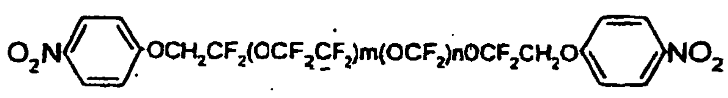
- X, Y, X', Y' gleich oder verschieden und unabhängig voneinander H; NO_2; C_1-C_4-Alkyl; C_1-C_4-Alkoxy, vorzugsweise eine Methoxygruppe sind;
- Z = $-CH_2-$; > C = O (Carbonyl) ist;
- m und n ganze Zahlen sind, derart, dass m im Bereich von 0 - 80 liegt, die Grenzwerte eingeschlossen; n im Bereich von 0 - 20 liegt, die Grenzwerte eingeschlossen, m + n > 1 ist; wobei

das Molekulargewicht des Perfluorpolyetherteils (Einheiten mit den Inidizes m und n) von 500 bis 10.000, vorzugsweise von 1.000 bis 4.000 beträgt, als Stabilisatoren für Perfluorpolyether-Schmieröle bei hohen Temperaturen, höher als 200 °C.

2. Verwendung nach Anspruch 1, wobei die Verbindungen der allgemeinen Formel (A) ausgewählt werden aus den folgenden:



(I)



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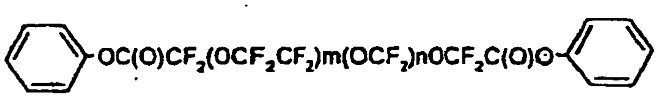


(III)

wobei m im Bereich von 0 - 80 liegt, Grenzwerte eingeschlossen; n im Bereich von 0 - 20 liegt, Grenzwerte eingeschlossen; m/n vorzugsweise 0,5 bis 4 beträgt, wenn n nicht Null ist, und m + n derart ist, dass sich das obige Molekulargewicht ergibt.

3. Verwendung nach Ansprüchen 1 - 2, wobei die Perfluorpolyetheröle Perfluoralkyl-Endgruppen aufweisen und eine Viskosität bei 20 °C im Bereich von 10 - 100.000 cST, vorzugsweise 30 - 2.000 cSt, besitzen.

4. Verwendung nach Anspruch 3, wobei die Perfluorpolyetheröle entlang der Kette statistisch verteilte, wiederkehrende Einheiten aufweisen und folgende Strukturen besitzen:

(1) $B\text{-}O[C_3F_6O]_{m'}(CFT'O)_{n'}\text{-}B'$,
worin:

T' = F, CF_3 ist;
B und B' gleich oder verschieden voneinander sind und ausgewählt werden aus $-CF_3$, $-C_2F_5$ oder $-C_3F_7$;
m' und n' ganze Zahlen sind, so dass das m'/n'-Verhältnis im Bereich von 20 - 1.000 liegt, n' nicht Null ist und die Produktviskosität innerhalb der obigen Grenzen liegt;

(2) $C_3F_7O\text{-}[C_3F_6O]_{o'}\text{-}D$
worin:

D gleich $-C_2F_5$ oder $-C_3F_7$ ist;
o' eine ganze Zahl ist, so dass die Produktviskosität innerhalb des obigen Bereichs liegt;

(3) $B\text{-}O\text{-}[CF(CF_3)CF_2O]_{q'}(C_2F_4O)_{r'}(CFT'O)_{s'}\text{-}B'$
worin:

T' die obige Bedeutung hat;
B und B' gleich oder verschieden voneinander sind und ausgewählt werden aus $-CF_3$, $-C_2F_5$ oder $-C_3F_7$;
q', r' und s' ganze Zahlen sind und auch Null sein können, unter der Voraussetzung, dass sie nicht alle gleichzeitig Null sind, und derart sind, dass die Produktviskosität in dem obigen Bereich liegt;

(4) B-O- $(C_2F_4O)_{t'}(CF_2O)_{u'}$-B'
worin:

B und B' gleich oder verschieden voneinander sind und ausgewählt werden aus $-CF_3$, $-C_2F_5$ oder $-C_3F_7$; t' und u' ganze Zahlen sind, so dass das Verhältnis t'/u' im Bereich von 0,1 bis 5, vorzugsweise 0,5 bis 4 liegt, u' nicht Null ist und die Produktviskosität in dem obigen Bereich liegt;

(5) B-O- $(CF_2CF_2CF_2O)_{v'}$-B'
worin:

B und B' gleich oder verschieden voneinander sind und ausgewählt werden aus $-CF_3$, $-C_2F_5$ oder $-C_3F_7$; v' eine Zahl ist, derart, dass die Produktviskosität in dem obigen Bereich liegt;

(6) D-O- $(CF_2CF_2\text{-}O)_{z'}$-D'
worin:

D und D' gleich oder verschieden voneinander sind und ausgewählt werden aus $-C_2F_5$ oder C_3F_7; z' eine ganze Zahl ist, derart, dass die Produktviskosität in dem obigen Bereich liegt,

wobei die $-C_3F_6O$-Einheit in den obigen Formeln die Struktur $-CF(CF_3)CF_2O-$ oder $-CF_2CF(CF_3)O-$ haben kann.

5. Verwendung nach Anspruch 4, wobei die Perfluorpolyetheröle die Struktur (4) aufweisen.

6. Verwendung nach Ansprüchen 1 - 5, wobei die Verbindungen der Formel (A) mit den Perfluorpolyetherölen in einem Anteil von 0,01 bis 10 Gew.-%, vorzugsweise 0,2 bis 5 Gew.-%, bezogen auf das Gewicht des Perfluorpolyetheröls, gemischt werden.

7. Verwendung nach Ansprüchen 1 - 6, wobei die Verbindung der Fromel (I) verwendet wird.

8. Verwendung nach Ansprüchen 1 - 7, wobei den Gemischen der Formel (A) - Verbindungen mit Perfluorpolyetherölen Additive zugesetzt werden, die aus jenen ausgewählt werden, die in den Perfluorpolyether-Schmierzusammensetzungen verwendet werden.

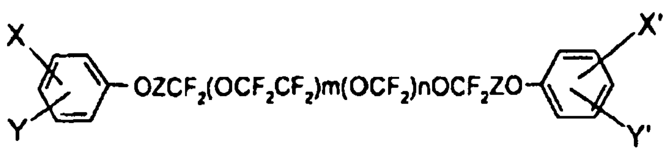
9. Verwendung nach Ansprüchen 1 - 8, wobei die Zusammensetzungen in Gegenwart von Metallen und in Gegenwart von Luft und Sauerstoff bei hohen Temperaturen, höher als 200 °C, bis zur Ölzersetzungstemperatur, vorzugsweise bis zu etwa 320 °C, noch bevorzugter bis 300 °C, verwendet werden.

10. Zusammensetzungen, welche Perfluorpolyether-Schmieröle und Verbindungen der Formel (A), wie im Anspruch 1 definiert, enthalten.

11. Zusammensetzungen nach Anspruch 10, wobei das Additiv (A) die Formel (I) aufweist, wie im Anspruch 2 definiert.

Revendications

1. Utilisation comme stabilisateurs d'huiles lubrifiantes de perfluoropolyéther à des températures élevées, supérieures à 200 °C, de composés ayant la formule générale (A) suivante :

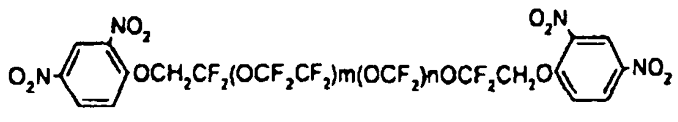


(A)

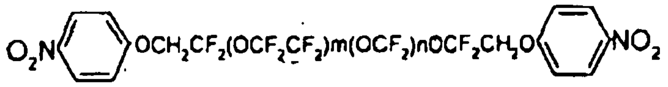
dans laquelle :

X, Y, X', Y', égaux ou différents, sont indépendamment les uns des autres H ; NO_2 ; un groupe alkyle en C_1-C_4 ; un groupe alcoxy en C_1-C_4, de préférence un groupe méthoxy ;
Z = $-CH_2-$; >C=O (carbonyle) ;
m et n sont des entiers tels que m est compris dans la plage allant de 0 à 80, extrêmes inclus ; n est compris dans la plage allant de 0 à 20, extrêmes inclus, m+n étant > 1 ;
le poids moléculaire de la partie perfluoropolyéther (motifs avec les indices m et n) étant de 500 à 10 000, de préférence de 1 000 à 4 000.

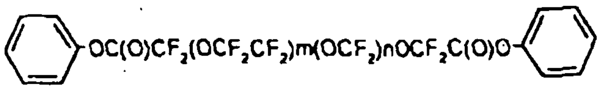
2. Utilisation selon la revendication 1, dans laquelle les composés de formule générale (A) sont choisis parmi les suivants :



(I)



(II)



(III)

dans lesquels m est compris dans la plage allant de 0 à 80, extrêmes inclus ; n est compris dans la plage allant de 0 à 20, extrêmes inclus, m/n étant de préférence de 0,5 à 4 lorsque n est différent de 0 et m+n est tel qu'il donne le poids moléculaire ci-dessus.

3. Utilisation selon les revendications 1 à 2, dans laquelle les huiles de perfluoropolyéther ont des groupes terminaux perfluoroalkyles et ont une viscosité à 20 °C comprise dans la plage allant de 10 à 100 000 cst, de préférence de 30 à 2000 cst.

4. Utilisation selon la revendication 3, dans laquelle les huiles de perfluoropolyéther ont les motifs répétitifs distribués statistiquement le long de la chaîne et ont les structures suivantes :

(1) $B\text{-}O\text{-}[C_3F_6O]_{m'}(CFT'O)_{n'}\text{-}B'$
dans laquelle
T' = F, CF_3 ;
B et B', égaux ou différents l'un de l'autre, sont choisis parmi - CF_3, $-C_2F_5$ ou $-C_3F_7$;
m' et n' sont des entiers tels que le rapport m'/n' est compris dans la plage allant de 20 à 1 000, n' étant différent de 0, et la viscosité du produit est dans les limites ci-dessus ;
(2) $C_3F_7O\text{-}(C_3F_6O)_{o'}\text{-}D$
dans laquelle
D est égal à $-C_2F_5$ ou $-C_3F_7$;

o' est un entier tel que la viscosité du produit est dans la plage ci-dessus ;
(3) B-O-[CF(CF_3)CF_2O]$_{q'}$(C_2F_4O)$_{r'}$(CFT'O)$_{s'}$-B'
dans laquelle
T' est comme ci-dessus ;
B et B', égaux ou différents l'un de l'autre, sont choisis parmi - CF_3, -C_2F_5 ou -C_3F_7 ;
q', r' et s' sont des entiers et peuvent également prendre la valeur 0, à condition qu'ils ne soient pas tous en même temps égaux à 0, et sont tels que la viscosité du produit est dans la plage ci-dessus ;
(4) B-O-(C_2F_4O)$_{t'}$(CF_2O)$_{u'}$-B'
dans laquelle
B et B', égaux ou différents l'un de l'autre, sont choisis parmi - CF_3, -C_2F_5 ou -C_3F_7 ;
t' et u' sont des entiers tels que le rapport t'/u' est dans la plage allant de 0,1 à 5, de préférence de 0,5 à 4, u' étant différent de 0, et la viscosité du produit est dans la plage ci-dessus ;
(5) B-O-($CF_2CF_2CF_2$O)$_{v'}$-B'
dans laquelle
B et B', égaux ou différents l'un de l'autre, sont choisis parmi - CF_3, -C_2F_5 ou -C_3F_7 ;
v' est un nombre tel que la viscosité du produit est dans la plage ci-dessus ;
(6) D-O-(CF_2CF_2O)$_{z'}$-D'
dans laquelle
D et D', égaux ou différents l'un de l'autre, sont choisis parmi - C_2F_5 ou -C_3F_7 ;
z' est un entier tel que la viscosité du produit est dans la plage ci-dessus ;
le motif -C_3F_6O- dans les formules ci-dessus peut avoir la structure -CF(CF_3)CF_2O- ou -CF_2CF(CF_3)O-.

5. Utilisation selon la revendication 4, dans laquelle les huiles de perfluoropolyéther ont la structure (4).

6. Utilisation selon les revendications 1 à 5, dans laquelle les composés de formule (A) sont mélangés avec les huiles de perfluoropolyéther selon un pourcentage de 0,01 à 10 % en poids, de préférence de 0,2 à 5 % en poids, par rapport au poids d'huile de perfluoropolyéther.

7. Utilisation selon les revendications 1 à 6, dans laquelle on utilise le composé de formule (I).

8. Utilisation selon les revendications 1 à 7, dans laquelle aux mélanges des composés de formule (A) avec des huiles de perfluoropolyéther, on ajoute des additifs choisis parmi ceux utilisés dans les compositions de lubrifiant de perfluoropolyéther.

9. Utilisation selon les revendications 1 à 8, dans laquelle les compositions sont utilisées en présence de métaux et en présence d'air et d'oxygène à des températures élevées, supérieures à 200 °C, jusqu'à la température de décomposition de l'huile, de préférence jusqu'à environ 320 °C, encore plus préférablement jusqu'à 300 °C.

10. Compositions comprenant des huiles lubrifiantes de perfluoropolyéther et le composé de formule (A) comme défini dans la revendication 1.

11. Compositions selon la revendication 10, dans lesquelles l'additif (A) a la formule (I), comme défini dans la revendication 2.