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(54) Lubricating greases

(57) Lubricating greases comoprising:

A) from 65.1 to 95% by weight of a (per)fluoropolyether oil having a viscosity at 20°C in the range 20-2,000 cSt;
B) from 5 to 34.9% by weight of powder of polytetrafluoroethylene or of a tetrafluoroethylene copolymer with another monomer having an ethylene type unsaturation, said powder obtainable by coagulation with an electrolyte of an aqueous latex containing polymeric particles having sizes comprised between 5 and 100 nm,

wherein the grease has a surfactant content lower than 20 ppm and a water content lower than 100 ppm.

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Description

[0001] The present invention relates to lubricating grease compositions based on (per)fluoropolyethers, having low friction coefficients and reduced wears, particularly suitable to be used for example in bearings working at high speed in a wide range of temperatures.

[0002] (Per)fluoropolyethers having kinematic viscosities at 20°C between 20 and 2,000 cSt used as lubrificating oils, are known.

[0003] Greases obtained by said (per)fluoropolyethers by the addition of thickeners are also known, among which the most commonly used is polytetrafluoroethylene (PTFE) in powder.

[0004] In USP 4,472,290 it is described a process for preparing a grease based on a (per)fluoropolyether oil and PTFE in powder, in the form of aggregates having sizes from 1 to 200 micron, consisting in dispersing said PTFE in the (per)fluoropolyether oil by using a fluorinated surfactant. Said PTFE is obtained by tetrafluoroethylene (TFE) polymerization in aqueous dispersion and subsequent polymer separation from the aqueous medium. The greases obtained with this process show the following drawback, in particular at high temperatures: the surfactant contained therein decomposes thus modifying the good grease characteristics. In practice it is observed a corrosion of the bearing mechanical parts in contact with said lubricants.

[0005] In USP 6,025,307 it is described a fluorinated grease formed of: 15-50% of PTFE particles having sizes lower than 1 micron, 30-84% by weight of a perfluoropolyether oil and 0.5-10% by weight of a surfactant or of a dispersing agent having a perfluoroalkyl or perfluoropolyether chain. The preparation process of this grease is very complicate since it involves various steps:

- gel formation by addition of a strong electrolyte, for example nitric acid, to a PTFE latex, obtained by TFE emulsion polymerization, through slow percolation of the acid in a gelification column containing the latex;
- gradual gel neutralization by washing in column with slow flows of basic aqueous solutions having a decreasing concentration up to pH 6 and subsequent washings with water up to pH 7;
- redispersion in water of the gel obtained by using a fluorinated surfactant;
- addition of a light perfluoropolyether fluid to the above obtained aqueous redispersion and subsequent separation of the water and of the main part of the surfactant from the organic phase formed of the PTFE particles thus transferred in the light perfluoropolyether;
- addition of the separated organic phase to a lubricating perfluoropolyether oil and subsequent evaportion of the light fluorinated fluid.

[0006] Said process, even though preparing greases having good lubricating properties, is disadvantageous, since it requires several steps and significant amounts of acid and bases and light solvents to be stripped. Further it is extremely difficult to obtain on an industrial scale a grease having a constant quality.

[0007] Besides in the grease obtained with this process there are high amounts of surfactant and water. The drawback of these greases is that said components, in contact with metal surfaces and/or at high temperatures, give corrosion phenomena. In practice the use of said greases is limited to applications wherein oxidizable metal parts are absent.

[0008] In EP 856,570 antiseizing pastes are described, prepared by addition to a perfluoropolyether oil having a viscosity between 20 and 2,000 cSt at 20°C of a PTFE in powder having molecular weight between 100,000 and 700,000 and particle size from 2 to 7 micron, the PTFE being obtained by irradiation with gamma rays or with electron beam of PTFE powder and subsequent milling.

[0009] These pastes preferably containing 50-60% by weight of PTFE are not suitable to be used as lubricating greases in bearings working at high speed due to the remarkable friction coefficient owing to the high solid content (PTFE).

[0010] It was therefore desired to have available (per)fluoropolyether lubricating greases containing low amounts of the thickening agent PTFE, having a combination of low wear and friction values, suitable to be used in bearings working at high speed in a wide range of temperatures, preparable with a simple, inexpensive and insutrially reproducible process.

[0011] (Per) fluoropolyether-based greases have been surprisingly and unexpectedly found, satisfying the above requirements.

[0012] An object of the present invention are (per)fluoropolyether lubricating greases comoprising:

A) from 65.1 to 95% by weight of a (per)fluoropolyether oil having a viscosity at 20°C in the range 20-2,000 cSt;

B) from 5 to 34.9% by weight of polytetrafluoroethylene or of a tetrafluoroethylene copolymer powder with another monomer having an ethylene type unsaturation, said polymers having a number average mclecular weight in the range 20,000-1,000,000, preferably 40,000-800,000, said powder obtainable by coagulation with an electrolyte of an aqueous latex containing polymeric particles having sizes in the range 5-100 nm, preferably 10-60 nm formed

of polytetrafluoroethylene or of a tetrafluoroethylene copolymer with another monomer having an ethylene type unsaturation, having a number average molecular weight in the range 20,000-1,000,000, preferably 40,000-800,000, and subsequent drying,

wherein the grease has a surfactant content lower than 20 ppm and a water content lower than 100 ppm, preferably lower than 60 ppm.

[0013] The surfactant content of 20 ppm represents the sensitivity limit of the analytical determination as described in the characterization of the Examples.

[0014] The drying to obtain component B) is carried out at a temperture in the range 105°C-190°C, preferably 110-140°C. Generally powder particle aggregates are obtained having an average size between 10 and 30 micron.

[0015] The perfluoropolyether oils of component A) are selected from the following classes:

$$(1) \qquad E\text{-}O\text{-}(CF(CF_3)CF_2O)_{m'}(CFXO)_{n'}\text{-}E'$$

wherein:

X is equal to F or CF_3;
E and E', equal to or different from each other, are selected from CF_3, C_2F_5 or C_3F_7, one fluorine atom of one or of both end groups can be substituted by Cl and/or H;
m' and n' are integers such that the m'/n' ratio is in the range 20-1,000 and the product viscosity be between 10 and 4,000 cSt; the various units are statistically distributed along the chain.

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

$$(2) \qquad C_3F_7O(CF(CF_3)CF_2O)_{o'}\text{-}D$$

wherein:

D is equal to $-C_2F_5$ or $-C_3F_7$, one fluorine atom of one or of both end groups can be substituted by Cl and/or H;
o' is an integer such that the product viscosity is within 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;

$$(3) \qquad \{C_3F_7O\text{-}(CF(CF_3)CF_2O)_{p'}\text{-}CF(CF_3)\text{-}\}_2$$

wherein:

p' is an integer such that the compound viscosity is within the above range, one F atom of one or of both end groups C_3F_7 can be substituted by Cl and/or H.

These products can be obtained by ionic telomerization of the perfluoropropylenoxide and subsequent photochemical dimerization as reported in USP 3,214,478;

$$(4) \qquad E\text{-}O\text{-}(CF(CF_3)CF_2O)_{q'}(C_2F_4O)_{r'}(CFX)_{s'}\text{-}E'$$

wherein:

X is equal to F or CF_3;
E and E', equal to or different from each other, are as above;
q', r' and s' are integers and can also have the 0 value, and such that the product viscosity is within the above range.

These products are obtainable by photooxidation of a mixture of C_3F_6 and C_2F_4 and subsequent treatment with

fluorine as described in USP 3,665,041;

$$(5) \qquad E\text{-}O\text{-}(C_2F_4O)_{t'}\,(CF_2O)_{u'}\text{-}E'$$

wherein:

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

These 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;

$$(6) \qquad E\text{-}O\text{-}(CF_2CF_2CF_2O)_{v'}\text{-}E'$$

wherein:

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

These products are obtained as described in EP 148,482;

$$(7) \qquad D\text{-}O\text{-}(CF_2CF_2O)_{z'}\text{-}D'$$

wherein:

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

These products can be obtained as reported in USP 4,523,039.

[0016] The preferred perfluoropolyether oils are those of the classes (1), (4), (5) or their mixtures and are available on the market with the trademark FOMBLIN® marketed by Solvay Solexis.

[0017] Component B) is selected between the TFE homopolymer (PTFE) and the TFE copolymers with 0.01-1% by weight of a comonomer having an ethylene type unsaturation.

[0018] As comonomers having an ethylene type unsaturation, those olefinic, acrylic and styrene can be mentioned as, for example, ethylene, propylene, methylmethacrilate, (metha)acrylic acid, butylacrylate, hydroxyethylhexylacrylate, styrene, C_3-C_8 pefluoroolefins, as hexafluoropropene (H-FP) ; C_2-C_8 fluoroolefins containin hydrogen, as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, hexafluoroisobutene, CH_2=CH-R_f perfluoroalkylethylene, wherein R_f is a C_1-C_6 perfluoroalkyl; C_2-C_8 chloro- and/or bromo- and/or iodo-fluoroolefins, as chlorotrifluoroethylene (CTFE); CF_2=$CFOR_f$ (per)fluoroalkylvinylethers (PAVE), wherein R_f is a C_1-C_6 (per)fluoroalkyl, for example CF_3, C_2F_5, C_3F_7, preferably perfluoropropylvinylether (PVE); CF_2=CFOX (per)fluorooxyalkylvinylethers, wherein X is: a C_1-C_{12} alkyl, or a C_1-C_{12} oxyalkyl, or a C_1-C_{12} (per)fluorooxyalkyl having one or more ether groups, for example perfluoro-2-propoxy-propyl; fluorodioxoles, preferably perfluorodioxoles; fluorovinylethers CFX=CXOCF_2OR (MOVE) wherein R is a C_2-C_6 (per) fluoroalkyl or a C_5-C_6 cyclic group, or a C_2-C_6 (per)fluorooxyalkyl group containing from one to three oxygen atoms and X = F, H, preferably perfluoro-3,5-dioxa-1-heptene CF_2=CF-O-CF_2-O-CF_2CF_3 (MOVE 1) and perfluoro-3,5,8-trioxa-1-nonene $CF_3OCF_2CF_2OCF_2OCF$ =CF_2 (MOVE 2).

[0019] The preferred comonomers are perfluoropropyl-vinylether (PVE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD).

[0020] The aqueous latex of polytetrafluoroethylene or of the tetrafluoroethylene copolymer with another monomer having an ethylene type unsaturation, used to prepare component B), is known and is prepared according to what described in USP 6,297,334 herein incorporated by reference,

[0021] The preparation of the TFE polymer latex comprises the following steps:

- preparation of an aqueous microemulsion of perfluoropolyethers;
- feeding of the microemulsion in a polymerization reactor;

- feeding in the polymerization reactor of demineralized water, reactor vent, addition of stabilizers, chain transfer agents, optional comonomers and reactor pressurization with TFE;
- addition of the polymerization initiator;
- discharge of the latex.

[0022] The microemulsion used in the latex preparation is described in USP 4,864,006 and USP 4,990,283.

[0023] As above said, the latex is coagulated and the obtained polymer particles are dried. The coagulation is carried out by addition of an electrolyte.

[0024] The electrolyte can be an inorganic acid or an inorganic salt. Among the acids, it can be mentioned nitric acid, hydrochloric acid, sulphuric acid; among the salts, it can be mentioned potassium nitrate, ammonium carbonate, magnesium sulphate, aluminum sulphate, potassium carbonate, calcium nitrate, sodium chloride.

[0025] Preferably nitric acid or ammonium carbonate are used.

[0026] As said the drying of the coagulated latex is carried out at a temperature in the range 105°C-190°C, preferably 110°-140°C, for a time between 20 and 60 hours.

[0027] A further object of the present invention is a process for the preparation of the invention (per)fluoropolyether greases comprising the following steps:

a) introduction of the lubricating oil A) in a mixer;
b) gradual addition in a continuous way or by steps of the powder of component B) to the oil;
c) slurry stirring;
d) discharge and refining of the obtained grease.

[0028] In step a), after the (per)fluoropolyether oil A) introduction in the mixer, generallly a degassing under vacuum at 60°C for 2 hours at 0.1 mbar is carried out.

[0029] In step b), the addition of the powder of component B) to the oil is generally carried out in at least 3 hours until reaching the desired composition.

[0030] In step c) the stirring is carried out in a constant way, for about 8 hours, under vacuum.

[0031] The refining of step d) is generally carried out in a three-cylindrical refiner.

[0032] The grease obtainable with this process has, as said, an amount of water lower than 100 ppm, preferably lower than 60 ppm and a surfactant amount lower than 20 ppm.

[0033] The greases of the present invention can be used as such or can be additioned with the known additives of the prior art, as, for example, antirust, antiwear, antioxidants, stabilizers.

[0034] The invention greases can be formulated depending on the amounts of A) and B) so to have different penetration degrees.

[0035] The penetration is determined according to the ASTM D-217 method and the greases are classified according to the NLGI scale from 000 degree, corresponding to a penetration value of 475 mm/10', to 6 degree, corresponding to 85 mm/10'.

[0036] The greases of the present invention result more stable, in applications requiring high temperatures, since the thickener is directly formulated with (per)fluoropolyether oil without using surfactants.

[0037] The greases of the present invention contain, the penetration being equal, compared with the known (per) fluorinated greases, a much lower amount of thickening agent (PTFE).

[0038] Unexpectedly and surprisingly the invention greases show very low friction coefficient values and a very reduced wear with respect to the known (per)fluorinated greases.

[0039] The invention greases are used in the lubrication of mechanical parts and their combination of very good properties makes them particularly suitable in the lubrication of bearings working at high speed and in a wide range of temperatures.

[0040] Even operating under these conditions, the bearings have improved peformances since the stress values are reduced and a lower heat generation is obtained (see the Examples, stress and maximum temperature reached).

[0041] Furthermore it has been found that the greases of the present invention, considering their low solid content, are applicable with significant advantages in the lubrication of microbearings, microgears, preferably in plastic, for example mechanical actuators, extending their life and significantly reducing the running noise.

[0042] The invention greases show furthermore a very low toxicity since they are formed of substantially stable and inert (per)fluoropolyether oils and PTFE.

[0043] Some Examples follow for illustrative and not limitative purposes of the invention.

EXAMPLES

CHARACTERIZATION

[0044] The following characterizations have been carried out on the components and on the greases of the invention.

Determination of the polymer molecular weight

[0045] The number average molecular weight of PTFE is calculated from the first melting temperature, if lower than 327°C, as described in EP 481,509, or by the absolute specific weight datum according to what described by Doban R.C., Knight A.C., Peterson J.H, Sperati C.A. in " Meeting of the American Chemical Society" Atlantic City, September 1956.

Determination of the average particle diameter in the latex

[0046] The average particle diameter is measured by Laser Light Scattering based on the laser light diffusion (Photon Correlation Spectroscopy). The used instrument consists of an Argon laser light source having a wave length of 514.5 nm by Spectra-Physics and in a photocorrelator by Brookhaven 2030 AT model. The scattering measurement is carried out at 25°C on latex samples diluted with filtered water and at an angle of 90°. The particle diameter in the latex is calculated by applying the cumulant method.

Determination of the polymer content in the latex (expressed in g/l H_2O)

[0047] About 20 grams of latex are weighed in a glass beaker and put in a stove to dry for 1 hour at 150°C. The latex dry content, expressed as g PTFE/l water, is obtained by applying the formula:

$$g\ PTFE/l\ water = (Wess-Wtara)/(Winiz-Wess)*1000$$

wherein

Wess = beaker weight with the dry residue after drying;
Wtara = weight of the empty beaker;
Winiz = beaker weight with the initial latex.

Quantitative determination of the surfactant in the polymeric powder B)

[0048] 0.5 g of powder are wet with ethanol and brought to basic pH with a NH_4OH solution. The powder is dried under nitrogen flow, to the dried powder 2 ml of acidified methanol with some drops of concentrated H_2SO_4 are added, the whole is brought into a hermetically sealed test tube heated at 70°C for 70 hours to carry out the surfactant esterification. To the obtained mixture 5 ml of Delifrene A 113 and 4 ml of water are then added. It is let stand. Two phases are separated, a μlitre of the lower fluorinated phase containing the surfactant ester is taken.

[0049] The fluorinated phase is gaschromatographically analyzed by injecting it in a 3 m long glass column, with a diameter of 3 mm, filled with a stationary phase constituted by Carbovax 20M absorbed at 25% by weight on Chromosorb W 80-100 mesh.

[0050] The method sensitivity limit is 20 ppm.

Quantitative determination of the water in the grease

[0051] The ASTM E 1064-85 method has been used.

Penetration

[0052] The test is carried out according to the ASTM D 217 method.

Four-ball Wear Test

[0053] For the wear evaluation the ASTM D 2266 method has been followed using a 40±0.2 kgf (392N) load at a

test temperature of 75°±2°C.

Evaluation friction test for ball bearings

[0054] A ball bearing (SKF 6303 model), cleaned with n-hexane and dried, is filled at 30% by weight, with respect to the grease weight required for the total filling, with the grease to be tested and the suitable screens are inserted to avoid the material coming out. The so assembled bearing is mounted on a shaft, connected to an engine, equipped with suitable housing couple and tightened. The cup wherein the bearing is placed is equipped with a loading cell which allows to measure the bearing stress during the running. On the outer race of the bearing a thermocouple is positioned detecting the temperature evolution during the test. The test is carried out by making the bearing to start at 5,000 rpm and maintaining such speed for 2 hours. The test result is given by the initial take-off value in mN•m, stress after steady conditions of 2 hours in mN•m, oscillation of the steady condition value and maximum temperature reached at the end of the test.

Test for friction (stress) evaluation at high speed

[0055] The same equipment and filling modalities of the bearing described in the previous test are used.

[0056] The test conditions are the following: a speed gradient is set from 0 to 16,000 rpm with step of 2000 rpm, each lasting 1 hour. The test duration is of total 8 hours and the stress value after 1 hour at 16,000 rpm and the maximum temperature reached are evaluated.

EXAMPLE 1A

Preparation of component B) formed of PTFE modified with 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD)

[0057] In a glass vessel there are added in sequence:

- 5 parts by weight of the ammonium salt of an acid having the following structure:

$$ClC_3F_6O(C_3F_6O)_nCF_2COOH \quad (I)$$

wherein n ranges from 0 to 6 and the average value is such to give an acidimetrical molecular weight equal to 530;

- 3 parts by weight of a perfluoropolyether having a structure of type:

$$R_f(C_3F_6O)_n{}^I(CF_2O)_m{}^IR^I{}_f \quad (II)$$

wherein n^I and m^I are integers, R_f, R^I_f equal to or different from each other are C_1-C_3 perfluoroalkyls, n^I, m^I, R_f, R^I_f being such to give a number average molecular weight of about 700;

- 8 parts by weight of demineralized water.

[0058] A perfectly clear microemulsion is obtained in the temperature range from 2°C to 46°C.

[0059] In a 400 l reactor equipped with stirring system wherein vacuum has been made (-660 mmHg), 9,500 g of the microemulsion prepared according to the described process, 2 kg of a paraffin having a softening point 52°-54°C and 270 l of demineralized water are introduced.

[0060] The reactor is maintained under mechanical stirring. 1,200 g of 2,2,4-trifluoro-5-trifluoro-methoxy-1,3-dioxole (TTD) and 100 mmHg of ethane are fed into the reactor. The reactor is pressurized at 20 bar with C_2F_4 and heated to 90°C. At this point 700 cc of a solution of ammonium persulphate (initiator) equal to 14 g are fed into the reactor.

[0061] After a first pressure decrease of 0.5 bar, the pressure is maintained at 20 bar by feeding C_2F_4.

[0062] After 30 minutes the tetrafluoroethylene (TFE) feeding is stopped, it is cooled and the reactor is discharged.

[0063] The so obtained latex has a concentration of 440 g/l and an average particle diameter of 50 nm.

[0064] The latex is diluted until bringing the polymer concentration to 7% by weight and 20 litres of said latex are introduced at a temperature of 24°C in a 50 litre reactor. The latex is additioned under stirring with an aqueous solution of $(NH_4)_2CO_3$ at 15% so to bring the pH to 8.

[0065] Stirring is continued by applying specific power of 3 KW/m^3 until powder flotation. Stirring is then stopped and the water is discharged by separating it from the wet powder.

[0066] The wet powder is then subjected to two washings with 20 litres of water at the temperature of 24°C, under stirring for 5 minutes. The wet powder is then discharged and dried in a static oven at 120°C for 48 hours.
[0067] The dry powder analyzed with the above described method resulted free from surfactant.

EXAMPLE 1B

Lubricating grease preparation

[0068] In a grease mixer (2,7 litre Apinox model) 1,200 g of oil (Fomblin® Y04) are introduced, having the following structure:

$$CF_3\text{-}[(O\text{-}CF(CF_3)\text{-}CF_2)_n\text{-}(O\text{-}CF_2)_m]\text{-}O\text{-}CF_3$$

with n/m = 40 and kinematic viscosity at 40°C of 15 cSt, and it is degassed for two hours at 0.1 mbar. 300 g of modified PTFE prepared in the Example 1A are then added, by successive steps of about 100 g at a time, starting the mixer at least 30' after every addition. When the additions are over, the slurry is left under vacuum, mixing for 8 hours.
[0069] Said time elapsed, 1,500 g of grease are discharged, and is refined by one passage through the three cylinder refiner.
[0070] The analyzed grease shows a water content of about 50 ppm.
[0071] On the refined grease the following characterizations are carried out: penetration, wear test, steady condition test and high speed test the results of which are reported in Table 1.

EXAMPLE 2 (comparative)

[0072] The Example 1B is repeated but by introducing 900 g of the oil described in the Example 1B and 600 g of a commercial PTFE Algoflon® L203 having a number average molecular weight of 500,000, obtained from a latex having a particle diameter of 200-300 nm, by successive steps of about 100 g at a time.
[0073] On the refined grease the same characterizations of the Example 1B are carried out and the results are reported in Table 1.
[0074] From the comparison of the Example 1B with the Example 2 it results that with the invention grease remarkably improved performances are obtained (see the Table) the consistency (penetration degree) being equal.

EXAMPLE 3

[0075] The Example 1B is repeated but by using 1,200 g of oil (Fomblin® Z15), having the following structure:

$$CF_3\text{-}[(O\text{-}CF_2CF_2)_n\text{-}(O\text{-}CF_2)_m]\text{-}O\text{-}CF_3$$

with n/m ≈ 1 and kinematic viscosity at 40°C of 92 cSt, and 300 g of PTFE of the Example 1A.
[0076] The analyzed grease shows a water content of about 50 ppm.
[0077] On the refined grease the following characterizations are carried out: penetration, wear test, steady condition test and high speed test, the results of which are reported in Table 2.

EXAMPLE 4 (comparative)

[0078] The Example 3 is repeated by introducing 900 g of the oil described in the Example 3 and 600 g of a commercial PTFE Algoflon® L203 described in the Example 2.
[0079] On the refined grease the same characterizations of the Example 3 are carried out and the results are reported in Table 2.
[0080] From the comparison of the Example 3 with the Example 4 it results that with the invention grease remarkably improved performances are obtained (see the Table) the consistency (penetration degree) being equal.

EXAMPLE 5 (comparative)

[0081] The Example 1B has been repeated but by using as PTFE the commercial PTFE of the Example 2 (comparative). The obtained grease has shown a penetration degree higher than 400.

[0082] The performances and the uses of such very fluid grease are not absolutely comparable with those of the grease according to the invention.

Table 1

Example No.	Penetration (mm/10')	Wear (mm)	Friction test for ball bearings (5,000 rpm)				High speed Test (16,000 rpm)	
			initial take-off (mN.m)	stress after 2h (mN.m)	oscillation (mN.m)	Final T max (°C)	stress after 1 h (mN.m)	Final T max (°C)
1B	265	0.6	182	60	±6	94	7	119
2(comp)	263	1.2	186	90	±20	117	40	150

Table 2

Example No.	Penetration (mm/10')	Wear (mm)	Friction test for ball bearings (5,000 rpm)				High speed Test (16.000 rpm)	
			initial take-off (mN.m)	stress after 2h (mN.m)	oscillation (mN.m)	Final T max (°C)	stress after 1 h (mN.m)	Final T max (°C)
3	240	1.1	177	40	±3	80	26	160
4(comp)	238	1.5	224	70	±20	100	63	200

Claims

1. (Per)fluoropolyether lubricating greases comoprising:

A) from 65.1 to 95% by weight of a (per) fluoropolyether oil having a viscosity at 20°C in the range 20-2,000 cSt;
B) from 5 to 34.9% by weight of polytetrafluoroethylene or of a tetrafluoroethylene copolymer powder with another monomer having an ethylene type unsaturation, said polymers having a number average molecular weight in the range 20,000-1,000,000, preferably 40,000-800,000, said powder obtainable by coagulation with an electrolyte of an aqueous latex containing polymeric particles having sizes in the range 5-100 nm, preferably 10-60 nm formed of polytetrafluoroethylene or of a tetrafluoroethylene copolymer with another monomer having an ethylene type unsaturation, having a number average molecular weight in the range 20,000-1,000,000, preferably 40,000-800,000, and subsequent drying,

wherein the grease has a surfactant content lower than 20 ppm and a water content lower than 100 ppm, preferably lower than 60 ppm.

2. Greases according to claim 1, wherein the drying to obtain component B) is carried out at a temperature in the range 105°C-190°C, preferably 110-140°C.

3. Greases according to claims 1-2, wherein component B) is in the form of powder particle aggregates having an average size between 10 and 30 micron.

4. Greases according to claims 1-3, wherein the perfluoropolyether oils of component A) are selected from the following classes:

$$(1) \qquad E\text{-}O\text{-}(CF(CF_3)CF_2O)_{m'}(CFXO)_{n'}\text{-}E'$$

wherein:

X is equal to F or CF_3;

E and E', equal to or different from each other, are selected from CF_3, C_2F_5 or C_3F_7, one fluorine atom of one or of both end groups can be substituted by Cl and/or H;
m' and n' are integers such that the m'/n' ratio is in the range 20-1,000 and the product viscosity be between 10 and 4,000 cSt; the various units are statistically distributed along the chain;

(2) $C_3F_7O(CF(CF_3)CF_2O)_{o'}$-D

wherein:

D is equal to -C_2F_5 or -C_3F_7, one fluorine atom of one or of both end groups can be substituted by Cl and/or H;
o' is an integer such that the product viscosity is within the above range;

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

wherein:

p' is an integer such that the compound viscosity is within the above range, one F atom of one or of both end groups C_3F_7 can be substituted by Cl and/or H.

(4) E-O-$(CF(CF_3)CF_2O)_{q'}(C_2F_4O)_{r'}(CFX)_{s'}$-E'

wherein:

X is equal to F or CF_3;
E and E', equal to or different from each other, are as above defined;
q', r' and s' are integers and can also have the 0 value, and such that the product viscosity is within the above range.

(5) E-O- $(C_2F_4O)_{t'}(CF_2O)_{u'}$-E'

wherein:

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

(6) E-O-$(CF_2CF_2CF_2O)_{v'}$-E'

wherein:

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

(7) D-O-$(CF_2CF_2O)_{z'}$-D'

wherein:

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

5. Greases according to claim 4, wherein the perfluoropolyether oils of component A) are selected from the classes

(1), (4), (5) or their mixtures.

6. Greases according to claims 1-5, wherein component B) is a TFE copolymer with 0.01-1% by weight of a comonomer having an ethylene type unsaturation.

7. Greases according to claim 6, wherein the comonomer having an ethylene type unsaturation is selected from the olefinic, acrylic and styrene comonomers, preferably ethylene, propylene, methylmethacrylate, (metha)acrylic acid, butylacrylate, hydroxyethylhexylacrylate, styrene; C_3-C_8 pefluoroolefins, preferably hexafluoropropene (HFP); C_2-C_8 fluoroolefins containing hydrogen, preferably vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, hexafluoroisobutene, perfluoroalkylethylene CH_2=CH-R_f, wherein R_f is a C_1-C_6 perfluoroalkyl; C_2-C_8 chloro- and/or bromo- and/or iodo-fluoroolefins, preferably chlorotrifluoroethylene (CTFE); (per)fluoroalkylvinylethers (PAVE) CF_2=CFOR_f, wherein R_f is a C_1-C_6 (per)fluoroalkyl, for example CF_3, C_2F_5, C_3F_7, preferablyperfluoropropyl-vinylether (PVE) ; (per) fluorooxyalkylvinylethers CF_2=CFOX, wherein X is: a C_1-C_{12} alkyl, or a C_1-C_{12} oxyalkyl, or a C_1-C_{12} (per)fluorooxyalkyl having one or more ether groups, preferably perfluoro-2-propoxy-propyl; fluorodioxoles, preferably perfluorodioxoles; fluorovinylethers CFX=CXOCF_2OR (MOVE) wherein X = F, H, and R is a C_2-C_6 (per)fluoroalkyl or C_5-C_6 cyclic group, or a C_2-C_6 (per)fluorooxyalkyl group containing from one to three oxygen atoms, preferably perfluoro-3,5-dioxa-1-heptene CF_2=CF-O-CF_2-O-CF_2CF_3 (MOVE 1) and perfluoro-3,5,8-trioxa-1-nonene $CF_3OCF_2CF_2OCF_2OCF$ =CF_2 (MOVE 2).

8. Greases according to claim 7, wherein the comonomer is selected from perfluoropropyl-vinylether (PVE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD).

9. Greases according to claims 1-8, wherein the coagulation electrolyte to obtain component B) is an inorganic acid or an inorganic salt selected from nitric acid, hydrochloric acid, sulphuric acid, potassium nitrate, ammonium carbonate, magnesium sulphate, aluminum sulphate, potassium carbonate, calcium nitrate, sodium chloride, preferably nitric acid or ammonium carbonate.

10. A process for the preparation of the (per) fluoropolyether greases of claims 1-9, comprising the following steps:

    a) introduction of the lubricating oil A) in a mixer;
    b) gradual addition in a continuous way or by step of the powder of component B) to the oil;
    c) slurry stirring;
    d) discharge and refining of the obtained grease.

11. A process according to claim 10, wherein in step a), after the introduction of the (per) fluoropolyether oil A) in the mixer, a degassing under vacuum at 60°C for 2 hours at 0.1 mbar is carried out.

12. A process according to claim 10, wherein in step b), In the addition of the powder of component B) to the oil is carried out in at least 3 hours.

13. A process according to claim 10, wherein in step c), In the stirring is carried out in a constant way, for about 8 hours, under vacuum.

14. A process according to claim 10, wherein the refining of step d) is carried out in a three cylinder refiner.

15. Use of the greases according to claims 1-9 in the lubrication of mechanical parts.

16. Use of the greases according to claim 15, in the lubrication of bearings working at high speed and in a large temperature range.

17. Use of the greases according to claim 15 in the lubrication of microbearings, microgears, in plastic, preferably mechanical actuators.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 02 2779

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A,D	US 4 472 290 A (CAPORICCIO GERARDO ET AL) 18 September 1984 (1984-09-18) * abstract *	1	C10M169/02
A,D	EP 0 856 570 A (AUSIMONT SPA) 5 August 1998 (1998-08-05) * abstract *	1	
A,D	US 6 025 307 A (CALUSO LUCA ET AL) 15 February 2000 (2000-02-15) * abstract *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	7 January 2005	Kazemi, P

CATEGORY OF CITED DOCUMENTS

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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07-01-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4472290 A	18-09-1984	IT 1152230 B	31-12-1986
		CA 1204426 A1	13-05-1986
		DE 3382829 D1	28-10-1999
		DE 3382829 T2	18-05-2000
		EP 0095825 A2	07-12-1983
		EP 0605403 A2	06-07-1994
		ES 8402613 A1	01-05-1984
		JP 1706821 C	27-10-1992
		JP 3073599 B	22-11-1991
		JP 58215495 A	14-12-1983
EP 0856570 A	05-08-1998	IT MI970174 A1	30-07-1998
		EP 0856570 A2	05-08-1998
US 6025307 A	15-02-2000	IT MI970656 A1	21-09-1998
		EP 0866114 A2	23-09-1998
		JP 10273684 A	13-10-1998

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