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(54) **Use of a fluid perfluoropolyether having a very high viscosity as a lubricant.**

(57) Use as the basic component of lubricating oils and greases, of a fluid perfluoropolyether, with linear structure, having a kinematic viscosity at 20°C not lower than 8,000 cSt, and constituted by sequences of perfluorooxyalkylene units selected from $-CF_2CF_2O-$, $-CF_2O$, $-CF_2CF_2CF_2O-$units.

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USE OF A FLUID PERFLUOROPOLYETHER HAVING A VERY HIGH VISCOSITY AS A LUBRICANT

The object of the invention is the use of fluid perfluoropolyethers having a very high kinematic viscosity, comprised within the range of from 8,000 cSt to 40,000 cSt at 20°C, and preferably of at least 10,000 cSt, as lubricating oils, and as the basic components of perfluorinated lubricating greases.

The use is well-known of fluid perfluoropolyethers, of neutral type, as lubricating oils endowed with high performance characteristics relating to the resistance to the atmospheric and chemical agents in general, even at high temperatures.

The products presently available from the market, suitable for use as lubricants, are low-or medium viscosity oils, with maximum viscosity values of the order of 2,000 cSt at 20°C.

It has been suprisingly found now that the perfluoropolyethers having such a high kinematic viscosity as indicated above, show surprisingly improved characteristics of use, as lubricants, over the lower viscosity perfluoropolyethers used up to date.

The improvement in some specific properties is not attributale simply to the high viscosity of the product, and should be regarded as unforeseeable.

The perfluoropolyethers according to the invention, having viscosity values comprised within the above specified range, are constituted of linear chains of oxyperfluoroalkylene units selected from the following units:

$-CF_2CF_2O-$, $-CF_2O-$, $-CF_2CF_2CF_2O-$.

The chain end groups are of perfluorinated, neutral type.

In particular, the products belonging to the following classes are suitable:

1) $R'_FO(CF_2CF_2O)_m(CF_2O)_nR_f$

wherein R_f and R'_f, equal to, or different from each other, are either $-CF_3$ or $-C_2F_5$, the perfluorooxyalkylene units being randomly distributed along the chain, and indices m, n are such integers that the viscosity (which is a function of the average molecular weight) is within the indicated ranges. Products of this type are disclosed in U.S. patent No. 3,665,041 and are known on the market under the trade name "Fomblin Z®";

2) $R'_fO(CF_2CF_2O)_pR_f$

wherein R_f and R'_f, equal to, or different from each other, are either $-CF_3$ or $-C_2F_5$ and index p is such an integer that the viscosity falls within the above indicated limits. Products of this type are disclosed in U.S. patent No. 4,523,039;

3) $R'_fO(CF_2CF_2CF_2O)_sR_f$

wherein R_f and R'_f, equal to, or different from each other, are $-CF_3$, or $-C_2F_5$ or $-C_3F_7$, and index s is an integer such that the viscosity is comprised within the above indicated ranges. Products of this type are disclosed in European patent No 148 482.

On considering the very high viscosity of the products, and that such a viscosity, because of their linear structure, varies to a considerably low degree with varying temperature, as well as their very low volatility, the products of the invention can be advantageously used as lubricants for high temperatures.

It is known that a relationship, exists which allows the friction coefficient μ to be expressed as a function of Stribeck number $\eta N/P$, wherein η = dynamic viscosity; N = revolution speed; P = applied load per surface unit. Such a relationship, reported on a diagram allows the areas to be evidenced in which the system works under boundary lubrication, mixed lubrication and elastohydrodynamic lubrication conditions; on this regard, reference is made to "Lubricants", by D. Klamann (Verlag Chemie 1984), pages 38-foll..

The perfluoropolyether according to the present invention shows a surprising and unexpected improvement as relates to the wear rate under "mixed" lubrication conditions, as compared to the up to date commonly used perfluoropolyethers, having a much lower viscosity. This improvement cannot be simply explained by taking into account the difference in viscosity; it could be thought as being in some way connected with the molecular structure of the product.

The equipment used for measuring the wear rate is essentially constituted by a a pin-on-rig system, consisting of a carbon steel (c 15) pin resting, for a surface area of 12 mm^2, on the cylindrical surface, revolving at a rate of 350 rpm, of a specimen of the same material, having an average surface roughness of 0.15 microns, and a diameter of 45 mm. The pin is loaded with a weight of 15 kg.

The procedure used in the test was as follows.

The specimens and the pins are cleaned in 1,1,2-trichloro-2,2,1-trifluoroethane, let dry and weighed. The specimen is assembled on the equipment in such a way that it can dip inside a tray containing the lubricating oil. After 1,000 revolutions, the specimen is drawn from the equipment, is cleaned in 1,1,2-trichloro-2,2,1-trifluoroethane, let dry and weighed again, and is then assembled again on the equipment. The measurement is repeated after 10,000 rpm. Then the difference in weight is computed relatively to the number of run metres (ΔW/L):

Test Time (Minutes)	Z 1600 ΔW/L (g/m)	Z 25 ΔW/L (g/m)	Z 03 ΔW/L (g/m)
3	0.1×10^{-5}	3×10^{-5}	3.1×10^{-5}
30	1×10^{-5}	2×10^{-5}	2.5×10^{-5}

Z 1600 Perfluoropolyether belonging to Class (1), a commercial product Fomblin® Z by Montedison, having a kinematic viscosity of 16,000 cSt at 20°C.

Z 25 Ditto, with a viscosity of 250 cSt

Z 03 Ditto, with a viscosity of 30 cSt.

The difference in the values measured between the investigated products evidences a lower wear rate in the high-viscosity oil. Above all, the necessary times for wear to be obtained are much higher for the highest-viscosity oil.

The perfluoropolyethers of the invention are particularly fit for the formulation of perfluorinated greases endowed with enhanced characteristics as compared to analogous products manufactured from lower-viscosity perfluoropolyether oils. Because of the very low value of high-temperature oil separation which was observed (even at a much higher oil percentage in the grease, than in the products of the prior art), the novel grease type results particularly suitable for high temperature uses.

A very meaningful characterizing property of the new grease type formulated with the perfluoropolyether oil according to the invention is the low static friction coefficient (measured as the starting resistent torque).

The method of preparation of the greases according to the invention is similar to the method as reported in European patent application No. EP 0 095 825, with the difference that, because of the high viscosity of the perfluoropolyether, the kneading and the following homogenizing have to be performed under high temperature conditions (70°C).

The oil amounts used for formulating polytetrafluoroethylene (PTFE)-thickened greases vary within the range of from 60% to 90%.

EXAMPLE OF PREPARATION OF A PERFLUORINATED GREASE

Oil used is Fomblin® Z 1600, an above-mentioned product, having a kinematic viscosity of 16,000 cSt at 20°C.

It is introduced in the percentage of 74.1% by weight, relatively to the grease.

The thickening agent is a granular PTFE (average particle diameter 4-5 μm; m.w. 40,000), used in the percentage of 25.9% by weight, relatively to the grease.

The kneading and homogenizing method is reported in the above-cited patent.

For comparative purposes, a perfluorinated grease was prepared by using the same PTFE type, and Fomblin ® Z 25 oil, having a viscosity of 250 cSt.

The formulation comprises 68.5% by weight of Fomblin® Z 25 and 31.5% by weight of PTFE.

CHEMICAL-PHYSICAL CHARACTERIZATION OF THE FORMULATED GREASE

Consistency	With Fomblin Z 1600	With Fomblin Z 25
Macropenetration mm/10 (ASTM D 217)	283	286
Macropenetration after 10,000 double shots, mm/10 (ASTM D 217)	270	298
Oil separation @ 204°C/30 h (FTMS 791-321)	1.6 %	10 %
Oil evaporation @ 204°C/22 h (ASTM D 972)	0.06%	0.1%

Relatively to the perfluorinated greases of the prior art, the very low degree of oil separation and evaporation results evident.

TRIBO-RHEOLOGICAL CHARACTERISTICS OF THE FORMULATED GREASE

The rheological characterization of the grease was carried out by means of measurements of its dynamic viscosity by using the plate/cone system mounted on a Rotovisco HAAKE 12 system, with M150 head (PKII/0.3°).

The first type of measurements was carried out at 25°C with increasing $\dot{\gamma}$ (flow gradient) values (20; 40; 80 sec^{-1}), with the viscosity of the grease being measured at start-up, and after 15 minutes. At each measurement, the used grease was replaced by fresh grease.

For a grease according to the invention, formulated with Fomblin® Z 1600, an early transient period was observed, the duration of which increases with decreasing $\dot{\gamma}$ (from 5 to 6 minutes within the selected $\dot{\gamma}$ range). During this period, the grease shows a rheopexic behaviour, followed by a stabilization of the signal at an equilibrium value higher than the initial values. The oscillations of the signal are, under these conditions, lower than of Z greases having a lower viscosity. The dynamic viscosity of the investigated grease at 80 sec^{-1} is equal to about 1,100 p (poises)whilst that of a grease formulated with Fomblin® Z 25 oil is of about 260 p under the same conditions.

The behaviour of the viscosity over time, with constant $\dot{\gamma}$ values, shows hence that the grease according to the invention does not offer, at start-up, a higher resistance than under equilibrium conditions. This result, important in connection with the power that the molar will have to apply at start-up, never occurred with greases containing lower-viscosity PFPE-based oils.

The limited range of signal oscillation is indicative of a better constancy of lubricating performance.

A second type of measurement was carried out under constant $\dot{\gamma}$ conditions of 40 sec^{-1}, at temperatures of 25°C; 50°C; 100°C. The endurance of the lubricating grease, at 100°C, is exceptionally good, whilst, under the same conditions, a grease formulated with a lower-viscosity oil (Fomblin® Z 25) shows a trend to unhomogeneousness.

On the grease formulated according to the invention a tribological evaluation was carried out, by determining the welding load according to ASTM D 2596 Standard.

The welding load results higher than 700 kg (device measurement limit).

Claims

1. Use of a perfluoropolyether of the neutral type, having a linear structure constituted of the sequence of one or more of the following oxyperfluoroalkylene units:
$-CF_2CF_2O-$, $-CF_2O-$, $-CF_2CF_2CF_2O-$,
and having a kinematic viscosity within the range of from 8 000 to 40 000 cSt at 20°C as a lubricating oil.

2. Use according to claim 1, wherein the kinematic viscosity is at least 10 000 cSt.

3. Use according to claim 1, wherein the perfluoropolyether hasthe structure:
$R'_fO(CF_2CF_2O)_m(CF_2O)_nR_f$
wherein R_f and R'_f, equal to, or different from, each other, are $-CF_3$ or $-C_2F_5$, the perfluorooxyalkylene units being randomly distributed along the chain, and indices m, n are such integers that the viscosity of perfluoropolyether is within the indicated ranges.

4. Perfluorinated lubricating grease based on polytetrafluoroethylene and on a perfluoropolyether lubricating oil according to anyone of claims 1 to 3, said grease containing from 60% to 90% by weight of oil, based on the total weight of the grease.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 87 10 6528

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.4)
D,X L	EP-A-0 095 825 (MONTEDISON S.p.A.) * Claims 1,2; page 7, lines 24-26; page 13, line 20 - page 14, line 3; page 16, line 28 - page 15, line 14; examples 4-6 *	4	C 10 M 107/38 C 10 M 169/02 // (C 10 M 169/02 C 10 M 107:38 C 10 M 119:22)
Y		1-3	

Y	EP-A-0 089 820 (MONTEDISON S.p.A.) * Claims 1-3; page 7, lines 12-28; page 8, line 15 - page 9, line 6; page 11, lines 17-26 *	1-4	

D,Y	EP-A-0 148 482 (DAIKIN INDUSTRIES LTD) * Claim 4; page 12, lines 14-24; example 20; page 10, line 17 - page 11, line 3 *	1-3	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 10 M

Y	US-A-4 438 006 (C.E. SNYDER et al.) * Column 2, line 18 - column 3, line 3; column 1, lines 15-18; column 4, lines 24-30 *	3,4	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29-07-1987	FISCHER W.H.F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y,D	US-A-3 665 041 (D. SIANESI) * Abstract; column 1, lines 40-75; column 2, line 64 - column 4, line 41 * & GB-A-1 226 566	1-4	
A	US-A-3 242 218 (W.T. MILLER) * Column 1, lines 10-27,45-56; column 4, lines 18-22 *	1-4	
A	US-A-4 438 007 (C.E. SNYDER Jr.) * Column 2, line 24 - column 3, line 3; column 4, lines 17-21 *		
P,X	EP-A-0 180 996 (DAIKIN INDUSTRIES, LTD) * Page 2, line 25 - page 3, line 4; in particular page 3, line 3; example 1 *	4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)

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THE HAGUE	29-07-1987	FISCHER W.H.F.

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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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