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

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EP-A- 0 089 820	EP-A- 0 095 825
EP-A- 0 148 482	EP-A- 0 180 996
US-A- 3 242 218	US-A- 3 665 041
US-A- 4 438 006	US-A- 4 438 007
US-A- 4 523 039	

"Lubricants" by D. Klamann (Verlag Chemie 1984) p.38-42

(73) Proprietor: **AUSIMONT S.p.A.**
Foro Buonaparte, 31
I-20121 Milano(IT)

(72) Inventor: **Zanini, Giovanni**
Setagaya-ku Setagaya - 4-4-25 Setagaya
House 401
154 Tokyo(JP)
Inventor: **Alfieri, Mario**
8, via Casoretto
I-20131 Milan(IT)

(74) Representative: **Barz, Peter, Dr. et al**
Patentanwälte Dipl.-Ing. G. Dannenberg Dr.
P. Weinhold, Dr. D. Gudel Dipl.-Ing. S. Schu-
bert, Dr. P. Barz Siegfriedstrasse 8
W-8000 München 40(DE)

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Description

The present invention relates to the use of fluid linear perfluoropolyethers having a very high kinematic viscosity, comprised within the range of from 8,000 mm²/s (cSt) to 40,000 mm²/s (cSt) at 20° C, and preferably of at least 10,000 mm²/s (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.

EP-A-95825 discloses lubricating greases based on polytetrafluoroethylene and certain perfluoropolyethers which may have a linear or branched structure. In the former case the viscosity of the polyether ranges from 40 to 6000 mm²/s. EP-A-89820 describes a process for the preparation of perfluoropolyethers of high viscosity but without linear structure. US-A-4 438 006 is directed to lubricant compositions which contain perfluoropolyethers having a viscosity at 38° C of from about 15 to about 1000 mm²/s.

It has been found now that the linear perfluoropolyethers having such a high kinematic viscosity is 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 attributable simply to the high viscosity of the product, and should be regarded as unforeseeable.

Accordingly, the present invention provides a process for lubricating under "mixed" lubrication conditions, characterized in that a perfluoropolyether of the neutral type, having a linear structure composed of a sequence of one or more of the following oxyperfluoroalkylene units:

-CF₂CF₂O-, CF₂O-, -CF₂CF₂CF₂O-,

and having a kinematic viscosity of from 8000 to 40000 mm²/s (cSt) at 20° C is used as lubricant.

Also provided is a perfluorinated lubricating grease based on polytetrafluoroethylene (PTFE) and a perfluoropolyether as defined above, said grease containing from 60% to 90% by weight of oil, based on the total weight of the grease.

The chain end groups are of perfluorinated, neutral type.

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

1) R_f'O(CF₂CF₂O)_m(CF₂O)_nR_f

wherein R_f and R_f', equal to, or different from each other, are either -CF₃ or -C₂F₅, the perfluoroalkylene 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 US-A-3,665,041 and are known on the market under the trade name "Fomblin Z^(R)";

2) R_f'O(CF₂CF₂O)_pR_f

wherein R_f and R_f', equal to, or different from each other, are either -CF₃ or -C₂F₅ and index p is such an integer that the viscosity falls within the above indicated limits. Products of this type are disclosed in US-A-4,523,039;

3) R_f'O(CF₂CF₂CF₂O)_sR_f

wherein R_f and R_f', equal to, or different from each other, are -CF₃, or -C₂F₅ or -C₃F₇, and index s is an integer such that the viscosity is comprised within the above indicated ranges. Products of this type are disclosed in EP-A-148 482.

In consideration of the very high viscosity of the above products, and of the fact that such a viscosity, because of their linear structure, varies to a considerably low degree with varying temperature, as well as of 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 η 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 38-42.

According to said monography mixed friction (lubrication) consists of fluid and non-fluid friction terms:

$$\mu_{\text{mixed}} = x \cdot \mu_{\text{fluid}} + y \cdot \mu_{\text{dry}}$$

where $x + y = 1$ and the contribution of the individual type of friction depends on the conditions.

The perfluoropolyethers used according to the present invention show 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 essentially comprises a a pin-on-rig system, consisting of a carbon steel (c 15) pin resting, for a surface area of 12 mm², 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 μm (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 relative to the number of run metres ($\Delta W/L$):

Test Time (Minutes)	Z 1600 $\Delta W/L$ (g/m)	Z 25 $\Delta W/L$ (g/m)	Z 03 $\Delta W/L$ (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 ^(R) Z by Montedison, having a kinematic viscosity of 16,000 mm ² /s (cSt) at 20 ° C. Z 25 Ditto, with a viscosity of 250 mm ² /s (cSt) Z 03 Ditto, with a viscosity of 30 mm ² /s (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 used according to 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 grease according to the present invention is particularly suitable for high temperature uses.

A very meaningful characterizing property of the grease according to the invention is the low static friction coefficient (measured as the starting resistant torque).

The method of preparation of the greases according to the invention is similar to the method reported in EP-A-95 825, 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).

EXAMPLE OF PREPARATION OF A PERFLUORINATED GREASE

The oil used is Fomblin^(R) Z 1600, an above-mentioned product, having a kinematic viscosity of 16,000 mm²/s (cSt) at 20 ° C.

It is introduced in an amount of 74.1% by weight, relative to the grease.

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

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

For comparative purposes, a perfluorinated grease was prepared by using the same PTFE type, and Fomblin^(R) Z 25 oil, having a viscosity of 250 mm²/s (cSt).

The formulation comprised 68.5% by weight of Fomblin^(R) Z 25 and 31.5% by weight of PTFE.

CHEMICO-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%

Relative to the perfluorinated greases of the prior art, the very low degree of oil separation and evaporation is 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^(R) Z 1600, an early transient period was observed, the duration of which increased with decreasing $\dot{\gamma}$ (from 5 to 6 minutes within the selected $\dot{\gamma}$ range). During this period, the grease showed a rheopexic behaviour, followed by a stabilization of the signal at an equilibrium value higher than the initial values. The oscillations of the signal were, under these conditions, lower than of Z greases having a lower viscosity. The dynamic viscosity of the investigated grease at 80 sec^{-1} was equal to about 110 Pa·s (1,100 poises) whilst that of a grease formulated with Fomblin^(R) Z 25 oil was about 26 Pa·s (260 poise) 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 show, at start-up, a higher resistance than under equilibrium conditions. This result, important in connection with the power that the motor 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.

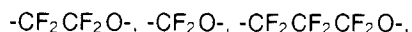
A second type of measurement was carried out under constant $\dot{\gamma}$ conditions of 40 sec^{-1} , at temperatures of 25 ° C; 50 ° C; 100 ° C. The endurance of the lubricating grease, at 100 ° C, is exceptionally good, whilst, under the same conditions, a grease formulated with a lower-viscosity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

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 was higher than 700 kg (device measurement limit).

Claims

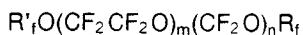
1. Process for lubricating under "mixed" lubrication conditions, characterized in that a perfluoropolyether of the neutral type, having a linear structure composed of a sequence of one or more of the following oxyperfluoroalkylene units:



and having a kinematic viscosity of from 8000 to 40000 mm^2/s (cSt) at 20 ° C is used as lubricant.

2. Process according to claim 1, wherein the kinematic viscosity of the perfluoropolyether is at least 10000 mm^2/s (cSt).

3. Process according to claim 1, wherein the perfluoropolyether has the structure:



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 m and n are integers such that the viscosity of the perfluoropolyether is within the indicated range.

- 5 4. Perfluorinated lubricating grease based on polytetrafluoroethylene and a perfluoropolyether as defined in any one of claims 1 to 3, said grease containing from 60% to 90% by weight of oil, based on the total weight of the grease.

Revendications

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1. Procédé de lubrification dans des conditions dites de lubrification "mixtes", caractérisé en ce qu'on utilise en tant que lubrifiant un perfluoropolyéther de type neutre, présentant une structure linéaire, formé d'une séquence d'un ou de plusieurs des motifs oxyperfluoroalkylènes suivants:

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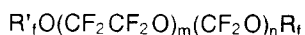
$-CF_2CF_2O-$, $-CF_2O-$, $-CF_2CF_2CF_2O-$,

et présentant une viscosité cinématique comprise entre 8000 et 40 000 mm^2/s (cSt) à 20 °C.

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2. Procédé selon la revendication 1, dans lequel la viscosité cinématique du perfluoropolyéther est d'au moins 10 000 mm^2/s (cSt).

3. Procédé selon la revendication 1, dans lequel le perfluoropolyéther présente la structure:



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dans laquelle R_f et R'_f , identiques ou différents l'un de l'autre, sont $-CF_3$ ou $-C_2F_5$, les motifs perfluorooxyalkylènes étant distribués de façon statistique le long de la chaîne, et m et n étant des nombres entiers tels que la viscosité du perfluoropolyéther soit comprise dans les valeurs indiquées.

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4. Graisse lubrifiante perfluorée à base de polytétrafluoroéthylène et d'un perfluoroéther tel que défini dans l'une quelconque des revendications 1 à 3, ladite graisse contenant de 60 à 90% en poids d'huile, exprimés par rapport au poids total de la graisse.

Patentansprüche

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1. Verfahren zur Schmierung unter "gemischten" Schmierungsbedingungen, dadurch gekennzeichnet, daß ein Perfluoropolyether vom neutralen Typ mit einer linearen Struktur aus einer Sequenz von einer oder mehreren der folgenden Oxyperfluoralkylen-Einheiten:

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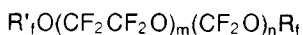
$-CF_2CF_2O-$, $-CF_2O-$, $-CF_2CF_2CF_2O-$,

und mit einer kinematischen Viskosität von 8000 bis 40 000 mm^2/s (cSt) bei 20 °C als Schmiermittel verwendet wird.

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2. Verfahren nach Anspruch 1, worin die kinematische Viskosität des Perfluoropolyethers mindestens 10 000 mm^2/s (cSt) beträgt.

3. Verfahren nach Anspruch 1, worin der Perfluoropolyether die Struktur:



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aufweist, worin R_f und R'_f , gleich oder verschieden voneinander, $-CF_3$ oder $-C_2F_5$ sind, wobei die Perfluorooxyalkylen-Einheiten statistisch entlang der Kette verteilt sind, und m und n ganze Zahlen sind, derart, daß die Viskosität des Perfluoropolyethers im angegebenen Bereich liegt.

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4. Perfluoriertes Schmierfett auf der Basis von Polytetrafluorethylen und eines Perfluoropolyethers nach irgendeinem der Ansprüche 1 bis 3, welches Fett 60 bis 90 Gewichtsprozent Öl enthält, bezogen auf das Gesamtgewicht des Fetts.