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SEMI-FLUID LUBRICANT COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Lubricant compositions comprising a synthetic base fluid of a polyoxy-alkylene compound gelled to a semi-fluid consistency, having a penetration value within the range of about 350 to about 450, reduce lubricant loss from imperfect gear-box seals etc. and possess good oxidation and good slip properties.

BACKGROUND OF THE INVENTION

The invention relates to semi-fluid lubricant compositions and more particularly to synthetic base semi-fluid lubricant compositions comprising copolymers of oxyalkylene compounds.

Lubricant compositions containing naturally occurring hydrocarbon base oils gelled to a grease consistency are well known. It is also well known that such greases are frequently unstable under working conditions and often undergo changes in their basic nature over the temperature range in which they are to be used. Consequently they require many varied and expensive additives if they are to meet minimal desirable lubricant standards. Furthermore, hydrocarbon base greases are not sufficiently fluid to provide adequate lubrication for today's advanced machinery. Conversely, the synthetic lubricant compositions of the invention are inherently stable over a wide range of working conditions and temperatures, providing excellent lubrication coupled with good oxidation and slip properties while requiring only minimal additives at elevated temperatures or where particularized characteristics are desired. They are particularly applicable as lubricants for gear sets, especially those in gear boxes which are commonly described as being "filled for life," they have also been found suitable for a wide range of other applications discussed hereinafter.

SUMMARY OF THE INVENTION

The present lubricant compositions comprise a synthetic base fluid gelled to a semi-fluid consistency and have penetrations of about 350 to 450. The synthetic base is a polyoxyalkylene compound obtained by condensing a plurality of alkylene oxide molecules with an organic compound containing from 2 to about 20 carbon atoms, and one or more suitably reactive hydrogen atoms, said organic compound can be alkyl, aryl, alkaryl, or aralkyl. Typical examples of some well known synthetic fluids are polyoxyalkylene glycols (e.g. polyoxyethylene glycol, polyoxypropylene glycol and mixed oxyethylene-oxypropylene glycols), the mono-ethers obtained by condensing an alkylene oxide with a monohydric alcohol or a phenol, and the mono-esters obtained by condensing an alkylene oxide with a mono-basic carboxylic acid. Other such synthetic fluids are the conjugated sequential condensation products of propylene and ethylene oxides with compounds containing a singly reactive hydrogen atom.

These compounds have the following formula:

$$Y(C_3H_6O)_n(C_2H_4O)_mH$$

wherein Y is the residue of an organic compound having from 2 to about 20 carbon atoms and one reactive hydrogen atom, n has an average value of at least 6.4 as determined by hydroxyl number, and m has a value such that the oxyethylene group constitute about 15–90% by weight of the compound with n and m having an upper limit of about 300. Many other percentage variations of the oxyalkylene constituents of these compounds or any compounds of the invention are possible and can be used in the lubricant compositions.

A further class of compounds included within the group of synthetic base fluids are the conjugated sequential condensation products of propylene and ethylene oxides with an organic compound containing a plurality of reactive hydrogen atoms.

The preferred class of synthetic compounds for use in the lubricant composition of the invention are copolymers of ethylene oxide and propylene oxide and have the generalized formula:

$$RO(C_2H_4O)_x—(C_3H_6O)_yH$$

wherein R can be either a hydrogen atom or an alkyl radical having from 1 to about 20 carbon atoms and x and y are respectively the number of ethylene oxide and propylene oxide monomers present in the copolymer each having a range from 5 to about 300 and preferably about 10 to 100. If the polymerization initiator used is water then R is a hydrogen atom and if the polymerization initiator is an alcohol R is the corresponding alkyl radical. These synthetic base media have properties that are desirable in lubricants, including good lubricity, high viscosity index, low pour point and volatility and good thermal stability. Representatives of this class of compound are available commercially under the trade name "Oxilube."

Preferred base fluids for lubricants according to the present invention are those designated "Oxilube 85/140" and "Oxilube 85/230" both of which are obtained from the polymerization of about 85% propylene oxide monomer and about 15% ethylene oxide monomer and have, respectively, viscosities of approximately 140 and 230 centistokes at 38° C.

As previously stated the lubricant compositions of the invention are of semi-fluid consistency, having a penetration value within the range of about 350 to about 450 (as determined by I.P. 167/59T method), however, compositions having a rather narrower range of 385 to 450, and preferably of 420 to 450 may be particularly suitable when they are used in "filled for life" worm gear boxes. Hydrocarbon base greases will generally have lower penetration values and lower dropping points. Thus indicating a tendency toward unsatisfactory lubrication at a lower temperature.

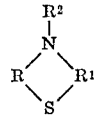
The specific penetration range (385 to 450) of the invention has proven extremely satisfactory over a wide range of uses and diverse applications. It is particularly important and vital to the invention that the lubricant have a semi-fluid consistency within such a penetration value range if the reduced leakage loss of the lubricant is to be realized.

The lubricant compositions of the invention are gelled to the semi-fluid condition by the addition to the synthetic base fluid of an appropriate quantity of a gelling agent such as an alkali metal or alkaline earth metal soap of a fatty acid or substituted fatty acid (e.g. a hydroxy fatty acid). Mixtures of such soaps may be employed if desired. The acids from which the soaps are derived preferably contain from 12 to 24 carbon atoms and particularly from 16 to 22 carbon atoms in the molecule. Selection of an appropriate gelling agent is made in the light of knowledge, of particular properties required in the lubricant. The metal may be, for example, lithium,

sodium, potassium or calcium; lithium salts are generally preferred because of their heat stability, and lithium 12-hydroxystearate is a particularly suitable gelling agent.

Other gelling agents which may be employed instead of, or in conjunction with soaps to give the desired degree of fluidity are, for example, inorganic clays and silicas which have been rendered olephilic, as by a suitable coating procedure. The "Bentone" series of clays may be mentioned in this connection (treated bentonites).

A disadvantage of the polyalkylene compounds used as base fluids in the present invention is that at the elevated temperatures encountered in gearboxes they produce odiferous and highly corrosive break-down products, which tend also to adversely affect the viscosity characteristics of the lubricant. It is, therefore, usual to incorporate in the base fluids of compositions of the invention, before they are subjected to high temperatures, such as during formulation of the lubricant compositions, an anti-oxidant. The anti-oxidant is commonly present in amounts up to about 5%, preferably up to 2.5% by weight of the total composition. A particularly suitable anti-oxidant is one selected from the group of compounds having the general formula:



wherein R and R^1 are the same or different aromatic radicals having from 12 to about 40 carbon atoms, and R^2 can be hydrogen or an alkyl, aryl alkaryl, aralkyl or cyanoalkyl radical having from 1 to about 20 carbon atoms. This group comprises three main sub-groups, viz: phenothiazine and substituted phenothiazines, thiophenlynaphthylamine and substituted thiophenylnaphthylamines, and thio-dinaphthylamine and substituted thiodinaphthylamines. The first mentioned sub-group, and especially phenothiazine, is the preferred anti-oxidant. The aryl radicals contained in these materials may be substituted, for example, by alkyl, alkoxy or amino groups, and any amino groups in the compound may be substituted by alkyl, aryl, hydroxy or amino groups. Such anti-oxidants are well known in the art.

When the lubricant compositions of the invention are used in gear lubrication, and particularly for the lubrication of worm gears, it has been found to be advantageous to include in the composition a friction-reducing additive. Any suitable additive which does not unduly impair the oxidation stability of the composition can be used. For example, sorbitan mono-oleate ("Span 80") when used at concentrations of the order of 1% by weight of the total composition can give a substantial reduction in friction at very low speed, without any undue disadvantage as regards oxidation life. Surprisingly, it has also been found that a very different class of additives, the N-acyl sarcosines, which compounds are available under the trade name "Sarkosyl" give good improvement in frictional properties coupled with good rusting resistance when used in quite low concentrations (of the

order of 0.5% and preferably of the order of 0.3% by weight of the total composition). The preferred compound of this class in N-oleyl sarcosine ("Sarkosyl O") which is N-oleylmethylamino acetic acid and is a liquid which is readily soluble in the composition of the invention. Such additives are conveniently added after any heat treatment to which the composition of the invention is subjected during formulation since they tend to be somewhat thermolabile.

It has already been mentioned that the compositions of the invention are particularly useful as gear box lubricants because, as a consequence of their semi-fluid nature, loss of the lubricant from the gearbox by leakage from imperfect seals is significantly less than the loss that occurs when the ungelled synthetic base lubricant is employed, and indeed if seals are efficiently designed and well fitted retention of the lubricant is sufficiently good for the gearbox to be described as "filled for life."

It is thought that this occurs as a consequence of separation of the oil and thickening components of the composition in the gearbox, the thickening agent contributing to the sealing effect.

However, the novel compositions of the invention, because of their semi-fluid nature, good oxidation and good slip properties, have found application in, for example, packed universal joins (e.g. in vehicle steering mechanisms), in packed wheel bearings and in gear couplings, and they have also been found particularly advantageous as lubricants for metal drawing processes, such as in the drawing of copper tubing. A further advantage of the compositions of the invention is that being semi-fluid, they may be easily pumpable to constantly lubricated bearing surfaces.

When the lubricant composition of the invention is employed in certain gearboxes having a high power rating the incorporation into the lubricant of an extreme pressure additive has been found beneficial. The additive selected must, of course, be soluble in the synthetic fluid base. Many such additives are available and the expert will have no difficulty in selecting a suitable additive for this purpose. A primary C_{18}–C_{22} amine salt of monochloromethyl phosphonic acid is particularly suitable. Such an additive is available commercially as "MCMPA/JMT." The proportion of the extreme pressure additive usually employed is small, commonly of the order of 0.1–0.5%, preferably about 0.3% by weight of the total composition.

The use of a metal deactivator with such extreme pressure additives is desirable, and for this purpose it is preferred to use a small proportion of a 1,2,4-triazole. Particularly suitable is a 3-amino-1,2,4-triazole as described in U.K. patent specification No. 1,124,904. Such triazoles may be used in a proportion of 0.001 to 2%, preferably 0.1–0.5% by weight of the total composition.

In the performance of the experimental work described hereinafter, most of the testing, where suitable, was carried out on lubricant compositions from which the gelling agent was omitted. This is no way influences the findings with regard to oxidation stability, rust resistance and improvement in frictional properties.

Typical properties of a suitable polyalkylene base fluid are shown in the table below with and without the addition of 2% by weight of an anti-oxidant.

TABLE 1

Composition	Toxicity	Sp. gr. 60/60° F.	Vis. cs. at— 100° F.	210° F.	VIE	Flash point, ° F.*	Pour point, ° F.
Copolymer of ethylene oxide-propylene oxide (Oxilube 85/140)	Nil	1.025	140	23.5	209	355	−25
Copolymer of ethylene oxide-propylene oxide (Oxilube 85/140+2%) wt. phenathiazine.	Nil	1.025	144	23.1	200	405	−25

*The flash points were determined by the Pensky Martins Closed Cup Method ASTM D 93.

From the above data it can be recognized that this fluid has suitable properties for use as a base oil for the present invention. It can also be seen that the addition of 2% by weight of phenothiazine anti-oxidant does not have any noticeable effect on the fluid's properties, except that it effectively raises its flashpoint by inhibiting oxidation during the determination, which would normally produce compounds giving rise to a lowered flash point.

As stated earlier polyoxyalkylene fluids, even when inhibited against oxidation, tend to show very high coefficients of friction, particularly when starting from rest. In order to illustrate this point and to show how it is overcome by the compositions of the present invention the following examples were prepared and tested on a disc machine which was modified for measurements at very low rotational speeds. The test machine consists essentially of a 4 inch diameter bronze disc in loaded contact with a 2-inch diameter steel disc. The two discs rotate on parallel shafts in the same direction and at the same angular speed of rotation. The results are given in Table 2 below.

EXAMPLE A

A mineral gear oil containing an anti-frothing agent, having a viscosity at 100° F. of 140 centistokes.

EXAMPLE B

Ethylene oxide-propylene oxide copolymer (Oxilube 85/140)+2% wt. phenothiazine.

EXAMPLE C

Ethylene oxide-propylene oxide copolymer (Oxilube 85/140)+2% wt. phenothiazine+0.3% wt. N-oleylmethylamino acetic acid.

EXAMPLE D

Pure castor oil reference fluid.

Test conditions

Oil temperature—80° C.
Disc loading—2500 Sc. [1]
Oil flow rate—3 pints/min.

[1] $Sc = \frac{\text{load/inch face width}}{\text{rel. radius of curvature of the discs.}}$

TABLE 2

Example	Coefficient of friction at— 2.4 ft./min.	15.7 ft./min.	78.5 ft./min.
A	0.10	0.08	0.06
B	0.20	0.15	0.10
C	0.08	0.06	0.04
D	0.11	0.08	0.04

It will be apparent from these results that the inclusion of only 0.3% by weight of the N-acyl sarcosine additive to the polyoxyalkylene/phenothiazine combination gives a fluid with greatly improved frictional properties, being even superior to castor oil in this respect.

The addition of the N-acyl sarcosine additive as well as improving the frictional properties of the composition as demonstrated above, has the added advantage that the anti-rusting ability is similarly improved as shown in Table 3 which gives the results of rusting tests carried out according to an International Harvester Corporation (I.H.C.) method. The apparatus for this test is similar to that for ASTM D665 except that the cylindrical test piece is made entirely of steel instead of steel and plastic as in the latter. The test pieces have a temperature differential of 5.5° C. maintained along them so that water condenses. They are immersed in the oil for 30 minutes, then placed in the apparatus. The times taken for the first specks of rust to appear are recorded. Similar results were obtained using ASTM D665. The collected results are given in Table 3. The N-acyl sarcosine is added to a polyoxyalkylene base fluid (Oxilube 85/140) having 2% wt. of anti-oxidant (phenothiazine).

TABLE 3

N-acyl sarcosine, percent wt.	I.H.C. time to rust	ASTM D 665 percent area rust covered
0	15 minutes	100
0.1	60 minutes	95
0.2		20
0.3	3 hours	5
0.4	>18 hours	
0.5	>20 hours	11

In order to provide a composition having sufficient consistency, particularly so as to alleviate the problem of leakage from or around the seals when polyoxyalkylene fluids are used as lubricants, we have chosen to provide by our present invention semi-fluid lubricant compositions prepared by the gelling of the polyoxyalkylene-based fluids with alkali metal soaps of normal or substituted fatty acids or oleophilic clays or silicas. Due to the possibility of variations in conditions during large scale manufacture it is usual not to incorporate into a grease a definite quantity of the gelling agent but rather to add a slight excess in the first place and then to adjust the final grease by addition of extra oil to give a penetration value within a required range. This range is chosen according to the purpose to which the final composition is to be used.

For purposes of comparison, semi-fluid lubricating compositions having different penetration values were prepared, and tested in a David Brown (DB) Industries Type 3 (No. 337) Radicon gearbox unit modified by the addition of thermocouples at strategic positions within the casting.

The heat generated in the working gearbox is an important factor in lubricant effectiveness and the cooler running of boxes filled with a lubricant having a penetration value within the range of 420–450 is shown by the results summarized in the following table. The unit was run at various loads to allow the temperature to stabilize. The following compositions were tested:

EXAMPLE E

	Percent
Ethylene oxide-propylene oxide copolymer (Oxilube 85/140)	93.7
Phenothiazine	2.0
N-oleylmethylamino acetic acid	0.3
Lithium hydroxystearate	3.0

EXAMPLE F

	Percent
Ethylene oxide-propylene oxide copolymer (Oxilube 85/140)	95
Phenothiazine	2
N-oleylmethylamino acetic acid	0.3
Lithium hydroxystearate	2.7

EXAMPLE G

	Percent
Ethylene oxide-propylene oxide copolymer (Oxilube 85/140)	94.7
Phenothiazine	2
N-oleylmethylamino acetic acid	0.3
Lithium hydroxystearate	3.0

TABLE 4

Example	Worked penetration, IP 167/59T	Percent load	Temp. rise ° C. (above ambient)
E	368	85	83
F	430	100	62
G	450	100	62

EXAMPLE H

A semi-fluid lubricant containing an extreme pressure additive was prepared having the following composition:

	Percent
Ethylene oxide-propylene oxide copolymer (Oxilube 85/140)	94.6
Phenothiazine	2.0
N-oleylmethylamino acetic acid	0.3
Amine salt of mono chloro methyl phosphonic acid (MCMPA/JMT)	0.3
3-amino-1,2,4-triazole	0.1
Lithium hydroxystearate	2.7

and a worked penetration (I.P. 167/59T) of 425.

This lubricant was used satisfactorily in a Bauer motorized industrial reduction gearbox, of a type having hardened steel on steel gears which is usually run under very severe conditions of speed and load.

EXAMPLE I

	Percent
Ethylene oxide-propylene oxide copolymer (Oxilube 85/230)	94
Lithium-12-hydroxystearate	3.8
Phenothiazine	1.9
N-oleylmethylamino acetic acid	0.3

This lubricant was employed satisfactorily in a worm reduction gearbox having hardened steel on bronze gears.

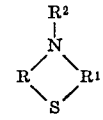
We claim as our invention:

1. A semi-fluid lubricant composition, adapted for use in filled for life gear boxes, consisting essentially of (1) a major amount of a synthetic base fluid which is a copolymer of ethylene oxide and propylene oxide having the following general formula:

$$RO(C_2H_4O)_x(C_3H_6O)_y$$

in which R is hydrogen or an alkyl radical having from one to about 20 carbon atoms and x and y respectively are the number of ethylene oxide and propylene oxide

monomers present in the copolymer with each having a range from 2 to about 300, (2) a minor amount, sufficient to inhibit oxidation, of an antioxidant of the general formula



where R and R^1 are the same or different aromatic radicals having from 12 to about 40 carbon atoms, and R^2 is hydrogen or an alkyl, aryl, alkaryl, aralkyl or cyanoalkyl radical having from 1 to about 20 carbon atoms, and (3) a minor amount of a suitable gelling agent selected from the group consisting of alkali metal soap, alkaline earth metal soap, clay, and silica, said lubricant having a penetration value of from 350 to about 450.

2. The composition of claim 1 wherein the anti-oxidant is thiodiarylamine.

3. The composition of claim 1 in which the anti-oxidant is phenothiazine or a hydrocarbon substituted phenothiazine.

References Cited

UNITED STATES PATENTS

2,425,755	8/1947	Roberts et al.	252—52
2,522,155	9/1950	Ballard et al.	252—52
3,158,574	11/1964	Greenwood et al.	252—42
3,171,812	3/1965	Horth et al.	252—52
3,200,073	8/1065	Criddle	252—42
3,428,562	2/1969	Crouch et al.	252—56

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