United States Patent

Commichau

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[54] POLYGLYCOL BASE LUBRICANT

[72] Inventor: **Axel Klaus Commichau,** Hamburg-Rissen, Germany

[73] Assignee: **Mobil Oil Corporation,** New York, N.Y.

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[52] **U.S. Cl.** .....**252/34.7,** 252/52 A

[51] **Int. Cl.** **C10m 1/34**

[58] **Field of Search** 252/34.7, 50, 59

[56] **References Cited**

UNITED STATES PATENTS

2,839,468	6/1958	Stewart et al.	252/49.9 X
3,115,465	12/1963	Orloff et al.	252/49.9 X
3,413,227	11/1968	Howard et al.	252/50 X

Primary Examiner—Daniel E. Wyman
Assistant Examiner—W. Cannon
Attorney—Oswald G. Hayes, Andrew L. Gaboriault, Raymond W. Barclay and Benjamin I. Kaufman

[57] **ABSTRACT**

A polyglycol base lubricant is provided containing, in minor proportion, as a stabilizer, a mixture comprising: a substituted amine, an aliphatically substituted phenol, an organic phosphate, a polyhydroxyquinone, a benzotriazole, an amine salt and a substituted organic phosphite.

10 Claims, No Drawings

POLYGLYCOL BASE LUBRICANT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to improved lubricant compositions, and in one of its aspects, relates to polyglycol base lubricant compositions having improved oxidation and heat stability under sustained periods of operation. More particularly, in this aspect, the invention relates to polyglycol base lubricant compositions which effectively meet modern requirements in respect of oxidation stability at relatively high temperature operating conditions, affording good loading capacity and rust protection over long periods of time.

2. Description of the Prior Art

Prior to the present invention, polyglycol base lubricants have been suggested by the prior art. It has been found, however, that these lubricants have not always met the high demands made by modern industrial plant operations. Thus, these polyglycol lubricants have not succeeded in affording protection as lubricants in instances where oxidative stability, affording adequate rust protection, under sustained operation at relatively high temperatures is to be maintained. Hence, the ability to provide an effective polyglycol base lubricant, avoiding the aforementioned disadvantages, is highly desirable.

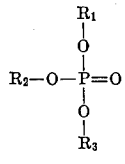
SUMMARY OF THE INVENTION

It has now been found, as more fully hereinafter described, that polyglycol base lubricants can be provided possessing improved oxidative stability under conditions of operation, containing, in minor proportion, as a stabilizer, a mixture comprising:

a. at least one substituted amine of the group consisting of aliphatically and aromatically substituted amines,

b. an aliphatically substituted phenol,

c. an organic phosphate having the general formula:



in which R_1, R_2 and R_3 are alkyl, aryl, alkaryl, alkoxyalkyl or halogen-alkyl groups,

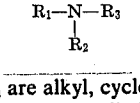
d. at least one compound of the group consisting of substituted and unsubstituted polyhydroxyquinones,

e. at least one compound of the group consisting of benzotriazole and its alkyl derivatives,

f. the reaction product of an organic acid and a substituted amine, and,

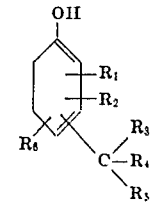
g. at least one compound of the group consisting of aliphatically and aromatically substituted organic phosphites.

In the aforementioned additive mixture, as hereinbefore indicated, substituted amine (a) may comprise an aliphatically or aromatically substituted amine, or mixtures of such amines. Exemplary thereof are: diphenyl amine, dinaphthyl amine, phenyl beta naphthyl amine, phenyl alpha naphthyl amine, naphthyl amine, phenothiazine, paraphenylene diamine and their alkyl and/or aryl substitution products, and polytrimethyl dihydroquinoline. In general, these substituted amines can be represented by the formula:



in which R_1 and/or R_3 are alkyl, cycloalkyl, phenyl, naphthyl, alkyl phenyl, alkyl naphthyl or alkyl aminophenyl and R_2 is hydrogen, alkyl or alkoxyalkyl.

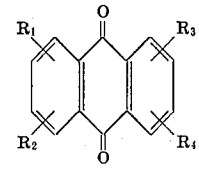
Exemplary of the aliphatically substituted phenol (b) are: 4-tertiarybutyl catechol, 2,4-ditertiarybutyl paracresol, 2,6-ditertiarybutyl-4-methyl phenol, 4,4'-methylene-bis-(2,6-ditertiarybutyl phenol) and alkylated bis phenols. In general, these substituted phenols can be represented by the formula:



in which R_1, R_2, R_3, R_4, R_5 and/or R_6 are hydrogen, alkyl cycloalkyl, hydroxyphenol or alkyl phenol.

Exemplary of the organic phosphate (c) are: diphenyl cresyl phosphate and other alkyl, aryl, alkaryl, alkoxyalkyl or halogen-alkyl containing groups of cresol phosphatic compounds.

Exemplary of the substituted and unsubstituted polyhydroxy quinones (d) are: quinizarin or the isomers 1,2; 1,3; 1,5 or 1,8 dihydroxy anthraquinone compounds and their alkyl substitution products. Included are substituted or unsubstituted polyhydroxyquinones of the formula:



in which R_1, R_2, R_3 and/or R_4 represent hydrogen, alkyl groups and/or hydroxy groups.

Component (e) as hereinbefore indicted is exemplified by benzotriazole, itself, or alkyl derivatives of benzotriazole.

Exemplary of the reaction product (f) of an organic acid and a substituted amine are: amine salts formed by neutralization of an organic acid such as butyric acid, benzoic acid, sulfamidoacetic acid, heptane carboxylic acid, cyclohexane sulfonic acid with a substituted amine such as butyl amine, cyclohexyl amine, octyl amine, monoethanol amine, diethanolamine, dicyclohexyl amine, morpholine, piperidine and octyl ammonium caprylate. In general, the amine salt (f) can be formed by the neutralization of an organic acid R_1COOH or R_1SO_3H with an amine NHR_2R_3, with R_1, R_2 and/or R_3 representing hydrogen, alkyl, cycloalkyl, aryl and/or alkyl aryl and R_1 in addition representing alkyl sulfamidomethyl and R_2 and R_3 also representing hydroxyalkyl or part of an alicyclic or heterocyclic saturated or unsaturated ring.

Exemplary of the organic phosphite (g) are dialkyl or diaryl phosphites, including, di-n-octyl phosphite and dinonyl phenyl phosphite. Representative thereof is an additive of the formula $(R_1O)(R_2O)POH$, in which R_1 and/or R_2 represent hydrogen, alkyl, cycloalkyl, aryl and/or alkyl aryl.

The aforementioned components (a) through (g) are employed in minor proportion with respect to the total weight of the lubricant composition, and are preferably employed in an amount from about 0.001 to about 5 percent by weight. The additive mixture preferably is added to the polyglycol base lubricant by intimate admixture at a temperature between about 40° C. and about 150° C.

The polyglycol base oil, employed in the lubricant compositions of the present invention, preferably comprise the addition products of alkylene oxides (oxiranes) on water or on univalent or multivalent alcohols and the reaction products, wholly or partly etherified and/or esterified on the free hydroxyl groups of these addition products. These reaction products, comprising the aforementioned polyglycol base, have the general formula:

$$R_1—[O—(CHR_2—CR_3R_4—O—)_xR_5]_y$$

in which: y has a value of from 1 to 6; when y has a value of 1, R_1 and R_5 are hydrogen, alkyl-cycloalkyl, or acyl; R_2, R_3 and R_4 are hydrogen, alkyl or cycloalkyl; and when y has a value of from 2 to 6, R_1 represents the rest of a multivalent alcohol, the other substituents being the same as hereinbefore defined.

Suitable initial products for the aforementioned addition, include, for example, water, the univalent alcohols such as methanol, ethanol, propanol, butanol, 2-ethyl hexanol, isononanol, the bivalent alcohols such as ethylene glycol, propylene glycol, neopentyl glycol, cyclohexylene glycol, the trivalent alcohols such as glycerine, trimethylol ethane, trimethylol propane and, as examples, the alcohols with higher valence such as pentaerythritol, dipentaerythritol and sorbitol. Examples of the alkylene oxides added to hydroxyl groups of these compounds are ethylene oxide, propylene oxide, butylene oxide, cyclohexene oxide and decene oxide, it being possible for one or more of these oxiranes to be present as units in the end product.

Substitution of hydrogen atoms of the hydroxyl groups by etherization can be carried out by methyl, ethyl, butyl or cyclohexyl groups, for example; the same applies to esterization of hydrogen atoms on the hydroxyl groups to, for example, acetyl, propionyl or butyryl groups.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The following data and examples will serve to illustrate the preparation of the novel polyglycol base lubricants of the present invention and their efficacy is meeting commercial requirements with respect to oxidative stability at relatively high operating conditions, and also their ability in affording adequate rust protection over relatively long periods of time.

Polyglycol Base Oil

A polyglycol base oil was prepared by the addition reaction of propylene oxide to trimethylol propane, to produce a corresponding reaction product containing components having an average molecular weight of up to 3,000.

Polyglycol base lubricant

A polyglycol base lubricant was prepared employing the above-described polyglycol base oil, in which this polyglycol base lubricant had the following composition:

		wt. %
Polyglycol base oil		93.48
Phenyl-α-naphthyl amine	(a)	3.00
4,4'-methylene-bis-(2,6-di-tert.-butylphenol)	(b)	2.00
Diphenyl cresyl phosphate	(c)	1.00
Quinzarin	(d)	0.02
Benzotriazole	(e)	0.05
Octyl ammonium caprylate	(f)	0.20
Di-n-octyl phosphite	(g)	0.25

Example 1

The above-described polyglycol base lubricant was subjected to a heat and oxidation test, as were also the aforementioned polyglycol base oil and an additional oil, which differed from the polyglycol base lubricant only in that they did not contain the phenyl-α-naphthyl amine (3 percent) (a). 25 ml. of the respective lubricants were individually placed in a glass tube and were maintained at a temperature of 347° F. (175° C.). 10 liters of air were blown through the individual samples hourly in the presence of lead, aluminum, copper and iron catalysts. Oxidation or decomposition of the respective lubricants was indicated by increasing substance loss of the sample and the time was noted which elapsed before the sample showed no significant evaporation loss.

It was noted that while this time lapse was only 18 hours in the case of the polyglycol base oil, and 25 hours in the case of the oil without the aforementioned component (a), it was 69 hours in the case of the polyglycol base lubricant, prepared in accordance with the invention.

Example 2

The aforementioned polyglycol base lubricant was maintained in a glass tube with a bronze strip at 338° F. (170° C.) for a period of 10 days. At the end of this time 10 liters of air per hour were blown through the oil for a period of 47 hours. The same procedure was conducted with another oil which differed from the aforementioned polyglycol base lubricant only in that it did not contain the aforementioned phenol derivative (b), but in which the phenyl-α-naphthyl amine content, component (a), amounted to 5 percent. Following the above-described test, there were no apparent signs of sludge of precipitation on the bronze in the case of the polyglycol base lubricant. It was noted, however, that there was a brown precipitation in the case of the comparison sample. Surprisingly, it was noted that the component (b) did have such effect.

Example 3

Experimentation was conducted in accordance with German Industrial Standard DIN 51 354 gear test. This test refers to the mechanical testing of gear oils in a gear rig by the FZG method which is described in the "Journal of the Institute of Petroleum," Vol. 52, No. 507, pp. 98–107 Mar. 1966. The object of the test is the prior examination and checking of gear oils by establishing their ultimate load-carrying capacity and the weight change on the teeth surfaces. In this test, selected gear wheels are run using the splash lubrication method in the gear oil to be tested at a constant speed and fixed initial oil temperature. The load on the teeth surfaces is gradually increased. After every change in the load, the weight changes on the tested wheels are measured by weighing, and a record is made of the changes in the teeth surfaces (surface damage).

In accordance with the above-described test, the polyglycol base lubricant and a comparison oil were tested. The comparison oil differed from the polyglycol base lubricant only in that it did not contain the phosphorus component (c). The results of the test revealed that the polyglycol base lubricant successfully met all of the requirements of the test in all of a series of 12 stages, while the comparison oil failed to do so in the ninth stage.

Example 4

The amount of corrosion protection afforded by two lubricating oils was determined in accordance with Standard ASTM Specification No. D 665. Different results were obtained with respect to the above-described polyglycol base lubricant and another oil, which differed from the former only in that it did not contain the amine salt component (g). The test objects in the polyglycol base lubricant oil, prepared in accordance with the present invention, were found to be entirely free from corrosion, while those in the comparison oil were found to be severely corroded.

Example 5

Examination of the catalysts employed in accordance with the test procedure described in Example 1 above, clearly revealed the metal protecting qualities of components (e) and (f) of the polyglycol base lubricant oil prepared in accordance with the present invention. In the case of the polyglycol base lubricant, it was found that the lead and copper catalyst exhibit no signs of wear after an operating time of 60 hours. However, employing another oil, differing from the polyglycol base lubricant only in that it did not contain components (e) and (f), it was found that there was pitting on the lead catalyst and coating and discoloration on the copper catalyst under the same conditions.

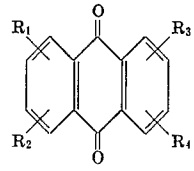
Example 6

In accordance with the heat and oxidation test described in Example 1 above, the following polyglycol oils were subjected to aging at a temperature of 347° F. (175° C.):

Example	Composition	Number of hours until occurrence of severe evaporation loss
1	100% polyglycol base oil	18
2	95% polyglycol base oil 5% phenyl-α-naphthyl amine (a)	39
3	99% polyglycol base oil 1% diphenyl cresyl phosphate (c)	18
4	94% polyglycol base oil 5% phenyl-α-naphthyl amine 1% diphenyl cresyl phosphate (a) + (c)	70

From the foregoing data, it will be noted that a synergistic effect with respect to components (a) and (c) exists in the polyglycol base oil, although as Example 3 reveals, component (c) alone cannot be regarded as an additive affording protection against heat and oxidation.

From the following table it will become apparent that only a combination of all of the aforementioned additives (a) through (g) can produce a polyglycol base lubricant oil.



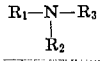
TABLE

	Polyglycol base oil	Polyglycol base oil plus--							Polyglycol base lubricant
		3% (a)	2% (b)	1% (c)	0.05% (d)	0.05% (e)	0.25% (f)	0.25% (g)	
Oxidation stability	Poor	Mediocre	Poor	Poor	Poor	Poor	Poor	Poor	Very good.
Loading capacity	Mediocre	do	Mediocre	Satisfactory	Mediocre	Mediocre	Mediocre	Good	Do.
Corrosion protection against water in the liquid phase.	Poor	Poor	Poor	Poor	Poor	Poor	Good	Mediocre	Good.
Corrosion protection in the steam phase.	do	do	do	do	do	do	do	Poor	Do.
Protection against wear	do	do	do	Mediocre	do	do	Poor	Mediocre	Do.
Stability at high temperatures	do	do	do	Poor	do	do	do	Poor	Do.

I claim:

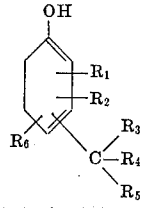
1. A polyglycol base lubricant in major proportion containing a minor stabilizing proportion of a mixture comprising:

a. a substituted amine represented by the formula:



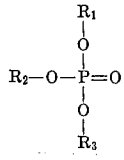
in which R_1 and/or R_3 are alkyl, cycloalkyl, phenyl, naphthyl, alkyl phenyl, alkyl naphthyl or alkyl aminophenyl and R_2 is hydrogen, alkyl or alkoxyalkyl,

b. a substituted phenol represented by the formula:



in which R_1, R_2, R_3, R_4, R_5 and/or R_6 are hydrogen, alkyl, cycloalkyl, hydroxyphenol or alkyl phenol,

c. an organic phosphate having the general formula:



in which R_1, R_2 and R_3 are alkyl, aryl, alkaryl, alkoxyalkyl or halogen-alkyl groups,

d. a polyhydroxyquinone represented by the formula:

in which R_1, R_2, R_3 and/or R_4 represent hydrogen, alkyl groups and/or hydroxy groups,

e. at least one compound of the group consisting of benzotriazole and its alkyl derivatives,

f. the reaction product of an organic acid and an amine, and

g. an organic phosphite represented by the formula:

$$(R_1O)(R_2O)POH$$

in which R_1 and/or R_2 represent hydrogen, alkyl, cycloalkyl, aryl and/or alkyl aryl.

2. A lubricant as defined in claim 1 wherein each of (a) through (g) is present in an amount of from about 0.001 to about 5 percent, by weight, based on the total weight of said lubricant.

3. A lubricant as defined in claim 1 wherein (a) comprises phenyl alpha naphthyl amine.

4. A lubricant as defined in claim 1 wherein (b) comprises 4,4'-methylene-bis-(2,6-ditertiary butyl phenol).

5. A lubricant as defined in claim 1 wherein (c) comprises diphenyl cresyl phosphate.

6. A lubricant as defined in claim 1 wherein (d) comprises quinizarin.

7. A lubricant as defined in claim 1 wherein (e) comprises benzotriazole.

8. A lubricant as defined in claim 1 wherein (f) comprises octyl ammonium caprylate.

9. A lubricant as defined in claim 1 wherein (g) comprises di-n-octyl phosphite.

10. A lubricant as defined in claim 1 wherein said polyglycol base has the general formula:

$$R_1-[O-(CHR_2-CR_3R_4-O-)_x R_5]_y$$

in which: y has a value of from 1 to 6; when y has a value of 1, R_1 and R_5 are hydrogen, alkyl-cycloalkyl, or acyl; R_2, R_3 and R_4 are hydrogen, alkyl or cycloalkyl; and when y has a value of from 2 to 6, R_1 represents the rest of a multivalent alcohol, the other substituents being the same as hereinbefore defined.

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