POLYPHENYL THIOETHER LUBRICATING COMPOSITIONS

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Int. Cl. C10M 1/48

U.S. Cl. 252—46.7

2 Claims

ABSTRACT OF THE DISCLOSURE

Lubricating compositions comprising polyphenyl thioethers, polyphenyl ethers-thioethers or mixtures thereof and containing small amounts of a polar organic compound and an organic phosphonic acid or ester have improved lubricating properties. These compositions are useful as lubricants over wide temperature ranges.

This is a division, of application Ser. No. 102,969, filed Dec. 30, 1970 (now U.S. Pat. 3,748,269 dated July 24, 1973).

IMPROVED POLYPHENYL THIOETHER LUBRICATING COMPOSITIONS

This invention relates to improved lubricating compositions comprising polyphenyl thioethers, mixed polyphenyl ethers-thioethers and mixtures thereof, containing from 3 to 8 aromatic groups and a small amount of a polar organic compound and an organic phosphonic acid as lubricating additives.

Polyphenyl thioethers and polyphenyl ether-thioether combinations have found wide application as functional fluids due to their excellent thermal stability and lubricity. For example they have been found to be valuable as hydraulic fluids and as lubricants in motor operation, particularly in jet engines.

Development of synthetic base stocks such as the polyphenyl thioether has provided lubricant fluids which are useful at elevated temperatures such as 400° to 500°F. It is known that one of the aspects in which the polyphenyl thioether base stocks are considered deficient is in their lubricating characteristics, especially for steel on steel or on chrome anodized aluminum. These lubricating characteristics include the load-carrying abilities and wear properties, especially under conditions of pumping the lubricant where the pump contains a chrome anodized aluminum bearing surface or gear box. Thus there is a demand for additives for polyphenyl thioethers which additives will improve the lubricity of the polyphenyl thioethers for steel on steel or on chrome anodized aluminum surfaces.

An object of the present invention is to provide for improved lubricating compositions employing polyphenyl thioethers, polyphenyl ether-thioethers, or mixtures thereof as base stocks for applications where at least one of the surfaces to be lubricated is chrome anodized aluminum.

This and other objects will become evident upon consideration of the following specification and examples.

It has now been found that compositions consisting essentially of a major amount of a polyphenyl thioether base fluid having the formula

(1) R—Y—(R'—Y)n—R

wherein R is a phenyl group, an alkyl-substituted phenyl group wherein the alkyl group contains 1 to 4 carbon atoms, an alkoxysubstituted phenyl group wherein the alkoxy group contains 1 to 4 carbon atoms or a halogenated phenyl group wherein the halogen is bromine, fluorine or chlorine, R' is a phenylene group, an alkyl or alkoxy-substituted phenylene group where the alkyl group contains 1 to 4 carbon atoms or a halogenated phenylene group wherein the halogen is fluorine, bromine or chlorine, and Y is selected from oxygen and sulfur but at least one of the Y's is sulfur and n is an integer having a value of from 1 to 6 and an additive amount of a polar organic compound and an organic phosphonic acid have unusual ability to lubricate steel on chrome anodized aluminum and steel on steel.

The amount of the polar organic compound employed in the compositions of this invention can range from 0.01 to about 0.5 percent by weight. It is preferred to employ the polar organic compound in the compositions of this invention in amounts of from 0.04 to 0.15 percent by weight based upon the total composition.

The amount of the organic phosphonic acid or ester employed in the compositions of this invention is from about 0.05 to about 1.0 percent by weight of the total composition. It is preferred to employ the organic phosphonic acid or ester in the compositions of this invention in amounts of from about 0.070 to about 0.2 percent by weight of the total composition.

The improvement in lubricity characteristics achieved by the addition of a perfluoro dibasic acid as the polar organic compound and the organic phosphonic acid or ester to the polyphenyl thioether base fluid is particularly unusual and surprising. Wear on a chrome anodized aluminum bearing surface is decreased at test temperatures of 200°F, whereas when the base fluid is tested without the additive the lubricity of the base fluid is not sufficient and the bearing surface fails after a short time.

The polar organic compounds which are employed in the compositions of this invention include aliphatic perfluoro dibasic acids, carboxy substituted polyphenyl thioethers, substituted phenols and aryl substituted fatty acids, acetylene dicarboxylic acids, and the like.

Illustrative of aliphatic perfluoro dibasic acids which can be employed in the compositions of this invention are the perfluorinated dibasic acid containing 5 to 10 carbon atoms and represented by the formula

\[ \text{HOOC—C}_n\text{F}_{2n—1}—\text{COOH} \]

wherein n is an integer from 1 to 8. It is particularly preferred to employ perfluorinated dibasic acid of formula II wherein n is an integer from 2 to 6.

Illustrative of the carboxy substituted polyphenyl thioethers which are employed in the compositions of this invention are those having the formula

\[ (\text{R—Y—(R'—Y)n—R})\text{(COOH)}_2 \]

wherein R, R', Y and n are as above defined with the proviso that at least one Y is sulfur and that from one to two of R and R' is substituted with a carboxy group and x is an integer of 1 or 2. Such carboxy substituted polyphenyl thioethers are for example m-(m-phenylnaphthylmercapto) benzolic acid, m-(phenylmercapto)benzolic acid, m-(phenylnaphthylmercapto) benzolic acid, and the other carboxy substituted polyphenyl thioethers.

Illustrative of the substituted phenols which are useful in the compositions of this invention are the 2,6-(alkyl) phenols such as for example 2,6-di-i-butyl-4-methyl phenol and the like. It is preferred that the alkyl groups on the phenol contain from 1 to 12 carbon atoms.

Illustrative of the aryl substituted fatty acids which are useful in the compositions of this invention are those having the general formula

\[ \text{Ar—C}_n\text{H}_{2n—1}—\text{COOH} \]

wherein Ar is an aryl group containing from 6 to 16 carbon atoms and n is an integer from 8 to 24. Illustrative of these aryl substituted fatty acids are, for example, phenolyladecanoic acid, phenooctanoic acid, tolyldodecanoic acid, xylyltetracosanoic acid and the like.
Illustrative of the acetylenic dibasic acids useful in the compositions of this invention are those having the general formula

$$\text{HOOC-}C_9H_{22}-C-C-C_9H_{22}-\text{COOH}$$

where $b$ and $c$ are integers of from 0 to 10 inclusive. Acetylene dicarboxylic acid is especially preferred for use in the compositions of this invention.

Illustrative of the aryl phosphate esters useful in the compositions of this invention are those having the formula

$$O-\text{R'-PO(OR')}_2$$

wherein $R'$ is an aryl group containing from 6 to 16 carbon atoms and $R''$ and $R'''$ are alkyl groups containing from 1 to 12 carbon atoms or an $R''$ group. It is preferred that when $R''$ and $R'''$ are alkyl groups that at least one of the aryl groups be an alkyl substituted aryl group. Illustrative of the phosphate esters are for example, tricresyl phosphate, dibutyl phenyl phosphate, cresyl diphenyl phosphate, xylyl di cresyl phosphate, cresyl diocyl phosphate and the like.

Illustrative of the perfluorinated dibasic acids represented by formula II are, for example, perfluoro malonic acid, perfluoro succinic acid, perfluoro azelaic acid and perfluoro sebacic acid.

The organic phosphinic acids or esters which are employed in the compositions of this invention are those of the formula

$$O-C-\text{R''}-\text{PO(OR''')}_2$$

wherein $R''$ is an aryl group containing from 6 to 16 carbon atoms, a halogenated aryl group or an alkyl group containing from 1 to 12 carbon atoms, and $R'''$ is hydrogen or an $R''$ group. Illustrative of the groups represented by $R''$ and $R'''$ are, for example, phenyl, tolyl, xylyl, napthyl, $a$-methyl napthyl and diphenyl, and such aryl groups substituted with halogen or with alkyl groups containing up to 10 carbon atoms. Further alkyl substituted aryl groups are nonylphenyl, ethylphenyl, butylphenyl, t-butylphenyl and the like. Such halogen substituted aryl groups are p-chlorophenyl, o-bromophenyl, m-fluorophenyl, p-iodophenyl, chlorotolyl, bromoxylol, chloronaphthyl, and the like. Illustrative of the alkyl groups represented by $R''$ and $R'''$ are, for example, methyl, ethyl, propyl, isobutyl, pentyl, $t$-butyl, hexyl, isocetyl, nonyl, decyl, dodecyl, and the like. Such alkyl groups are, for example, phenylphosphinic acid, nonylphenylphosphinic acid, tolylphosphinic acid, xylylphosphinic acid, naphthyloxyphosphinic acid, diphenylphosphinic acid and the like. It is especially preferred to employ in the compositions of this invention compounds of formula III wherein $R''$ is an aryl group and $R'''$ is hydrogen.

The polyphenyl thioethers employed in the composition of this invention have from 3 to 8 benzene rings and from 1 to 7 sulfur atoms with the sulfur atoms joining the benzene rings in chains as ether linkages. By the term "polyphenyl thioether" as used herein is meant a compound or physical mixture of compounds represented by formula I. The term includes compounds wherein all of the Y's in formula I are sulfur. The term also includes those compounds which contain both oxygen and sulfur linkages between the benzene rings.

The compositions of this invention contain a major amount of the polyphenyl thioether base stock, i.e., at least 50 percent by weight of the total composition comprises a polyphenyl thioether. It is preferred that at least 60 percent by weight of the composition be a polyphenyl thioether base stock and even more preferred that at least 85 percent by weight of the total composition comprise a polyphenyl thioether.
3,3'-bis(m-phenoxyphenylmercapto)diphenyl ether and
3-(m-phenoxyphenylmercapto)-3'-(m-phenoxyphenoxy) diphenyl sulfide.

In addition to the foregoing compounds, the phenyl and phenylene groups of such compounds can contain
substituents, such as alkyl of 1 to 4 carbon atoms, alkoxy
of 1 to 4 carbon atoms and halogen such as chlorine,
bromine and fluorine. Examples of such compounds are
as follows:
4,4'-bis(m-tolylmercaptoc) diphenyl ether
3,3'-bis(m-tolylmercapto) diphenyl ether
2,4'-bis(m-tolylmercapto) diphenyl ether
3,3'-bis(m-tolylmercaptoc) phenyl ether
5,5'-bis(m-tolylmercaptoc) phenyl ether
4,4'-bis(m-isopropylmercapto) diphenyl ether
3,3'-bis(m-isopropylmercapto) diphenyl ether
2,4'-bis(m-isopropylmercapto) diphenyl ether
3,3'-bis(p-tert-butylmercapto) phenyl ether
4,4'-bis(p-t tert-butylmercaptoc) phenyl ether
3,3'-bis(2,4-di-tert-butylmercapto) phenyl ether
3,3'-bis(3-chlorophenylmercapto) diphenyl ether
4,4'-bis(3-chlorophenylmercapto) diphenyl ether
3,3'-bis(trifluoromethylmercapto) phenyl ether
4,4'-bis(trifluoromethylmercaptoc) phenyl ether
3,3'-bis(m-methylmercapto) phenyl ether
4,4'-bis(m-methylmercapto) phenyl ether
3,3'-bis(3,4'-bism-(p-methylphenylmercapto)phenoxydiphenyl sulfide
3-(p-methylmercapto)phenoxylphenyl mercaptoc) diphenyl sulfide
and the like and mixtures thereof. It is also contemplated
within the scope of this invention to employ mixtures of
polyphenyl ether-thioethers as base stocks.

The compositions of this invention are useful as lubricants
under extreme conditions. The compositions are especially useful for steel on chrome anodized aluminum
lubrication.

The following examples serve to further illustrate
the invention. All parts are parts by weight unless otherwise
expressly set forth.

**EXAMPLE 1**

A polyphenyl thioether - polyphenyl ether - thioether
lubricant composition is prepared by combining perfluoro-
glutaric acid (0.1 gram) and phenylphosphonic acid
(0.075 gram) with 100 grams of a thioether of the fol-
lowing composition:

<table>
<thead>
<tr>
<th>Percent by wt.</th>
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<tbody>
<tr>
<td>meta-bis(phenylmercaptoc)benzene</td>
</tr>
<tr>
<td>bis(phenoxophenyldiphenyl sulfide)</td>
</tr>
<tr>
<td>(p-methylmercapto)phenoxydiphenyl sulfide</td>
</tr>
<tr>
<td>bis(phenylmercaptoc)phenyl ether</td>
</tr>
<tr>
<td>3 ring and 5 ring thioethers</td>
</tr>
</tbody>
</table>

This mixture is stirred for about 12 hours at 40-45°
C. After cooling to room temperature the mixture is
filtered to remove a small amount of insoluble material.

The aluminum lubricity of the composition of Exam-
ple 1 was shown using a chrome anodized oil pump. This
is a Pratt & Whitney T3D-3B main engine pump. This
type of pump is commonly used in jet engine gear boxes.
The gear box oil pump is a compound pump composed
of the pressure oil pump and the gear box scavenging pump
operating from a single shaft. Both drive gears of the
pumps and the rotating shaft are hung from two out-
board journals with a journal in the middle separating
the two pumps. Rotating drive for both pumps is pro-
vided by a single axially located splined shaft which ex-
tends through one side of the pump housing to a power
source. The driven or idler mating gears in these pumps
rotate on a fixed shaft. The rotating shaft is steel, the
pumps and journals are chrome anodized aluminum. Design
loading is 50 p.s.i. for the pressure pump.

Normally, the journals are part of the pump case.
For testing purposes, the housing is widened and chrome
anodized bushings are placed between the shaft and the
bushings. These are then replaced allowing continual
testing with one pump.

A shock cycle test was used to evaluate fluids. The oil
was circulated in the pump under no load while being
heated to 200° F. The output of the pump was throttled
until a discharge pressure of 20 p.s.i. was reached. This
pressure was held for ten seconds, then lowered to zero
p.s.i. for five seconds. This off-on shock cycle was re-
peated twenty times at 20 p.s.i., twenty times at 30 p.s.i.,
40 p.s.i., 50 p.s.i., 60 p.s.i., and 75 p.s.i. This final load
is 50 percent excess load above the design load. Com-
pletion of 120 cycles without wear or seizure of the
bushings constitutes a successful test.

The composition of Example 1 was able to complete
120 testing cycles without failure of the bushings. The
base oil containing 0.1 percent disopropyl hydrogen
phosphate failed the test after 60 cycles. The base oil with
only phenylphosphonic acid (0.1 percent) failed at 62
cycles. The thioethers containing only perfluoroglutaric
acid (0.08 percent) failed after 84 cycles.

The lubricating ability of the fluids of this invention
was shown with a slow speed four ball machine. A slow
speed four ball machine measures the boundary lubricity
action of additives. This test is a variation of the well
known Shell Four Ball Test in which a ball is rotated
against three stationary balls. Wear scars and/or seizure
3,843,532

EXAMPLE 2

To 100 grams of the base fluid of thioethers from Example 1 was added 0.075 gram phenylphosphinic acid and 0.05 gram of acetylene dicarboxylic acid. After heating at 45° C. for about twenty hours, the blend was cooled to room temperature and filtered.

A boundary friction-temperature curve for the fluid from Example 2 was run on M50 steel. The boundary friction for the blend was significantly lowered relative to the base stock containing only phenylphosphinic acid over a temperature range of 400° to 700° F.

EXAMPLE 3

To 100 grams of the base fluid of the thioethers as set forth in Example 1 was added 0.075 gram phenylphosphinic acid and 0.05 gram of m- (m-phenylmercaptophenylmercapto)benzoid acid. After heating at 45° for about twenty hours, the blend was cooled to room temperature and filtered.

A boundary friction-temperature curve for the fluid from Example 3 was run on M50 steel. The boundary friction for the blend from 500° to 700° F. was significantly lower than a blend containing only phenylphosphinic acid.

EXAMPLE 4

To 100 grams of the base fluid of thioethers from Example 1 was added 0.075 gram phenylphosphinic acid and 0.05 gram of 2,6-di-t-butyl-4-methyl phenol. After heating at 45° C. for about three hours the blend was cooled to room temperature and filtered.

A boundary friction-temperature curve for the fluid from Example 4 was run on M50 steel. The boundary friction for the blend was either significantly lower than, or equal to the boundary friction of the base stock containing only phenylphosphinic acid over a temperature range of from room temperature to 700° F. From 300° F. to 700° F. the boundary friction of the blend of Example 4 was significantly lower than that of the blend containing only phenylphosphinic acid.

EXAMPLE 5

To 100 grams of the base fluid of thioethers from Example 1 was added 0.075 gram phenylphosphinic acid and 0.05 gram of triacetylphosphate. After heating at 40° to 45° C. for about 3 hours the blend was cooled to room temperature and filtered.

A boundary friction-temperature curve for the fluid from Example 5 was run on M50 steel. The boundary friction for the blend was lower than for a base stock containing only the phenylphosphinic acid over a temperature range of from room temperature to 700° F.

EXAMPLE 6

To 100 grams of the base fluid of thioethers from Example 1 was added 0.075 gram phenylphosphinic acid and 0.05 gram of phenoloctadecanoic. After heating at 40° to 45° C. for about 3 hours the blend was cooled to room temperature.

A boundary friction-temperature curve for the fluid from Example 6 was run on M50 steel. The boundary friction for the blend was lower than for a base stock containing only the phenylphosphinic acid over a temperature range of from 600° to 700° F.

It will be appreciated that the composition of the invention, in addition to the polyphenyl thioether base fluid and the organic phosphinic acid additive, may also contain other additives, such as oxidation inhibitors, rust and corrosion inhibitors, anti-foaming agents, detergents, viscosity index improvers such as polymeric materials for example, polycarboxylate alkyl esters, polymethacrylate alkyl esters, polynonylketene compounds, polyurethanes and the like. Such additives are usually employed in amounts as low as 10 parts per million for anti-foaming agent to as much as 15 parts by weight of the total compositions for viscosity index improvers.

While this invention has been described with respect to various specific examples and embodiments, it is understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A lubricant composition consisting essentially of a major amount of a polyphenyl thioether having the formula

   \[ R - Y(R')_n - R \]

   wherein \( R \) is a phenyl group or a substituted phenyl group, \( R' \) is a phenylene group or substituted phenylene group, in which the substituents on said phenyl and phenylene groups are halogen, alkyl or alkoxy containing from 1 to 4 carbon atoms, \( n \) is an integer of from 1 to 6, \( Y \) is sulfur or oxygen provided that at least one of the groups represented by \( Y \) is sulfur, and mixtures of such thioethers and from about 0.05 to about 10.0 percent by weight of an organic phosphinic acid of the formula

   \[ \text{R}'' - \text{R} - \text{OR}''\text{R}'' \]

   wherein \( \text{R}'' \) is an aryl group of from 6 to 16 carbon atoms, a halogen substituted aryl group of from 6 to 16 carbon atoms, an alkyl substituted aryl group containing from 6 to 16 carbon atoms or an alkyl group containing 1 to 12 carbon atoms, \( \text{R}'' \) is hydrogen or an \( \text{R}'' \) group and from 0.01 to 0.5 percent by weight of monocyclic, monohydric alkyl-substituted phenols.
2. A composition of Claim 1 wherein the substituted phenol is 2,6-di-t-butyl-4-methylphenol.

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<th>Date</th>
<th>Inventor(s)</th>
<th>Class</th>
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<td>Great Britain</td>
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W. H. CANNON, Primary Examiner

U.S. Cl. X.R.
PO-1050 UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION


Inventor(s) Frank S. Clark

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 25, delete the word "IMPROVED" from the subtitle.

Column 2, line 56, "o-(m-phenylmercapto)phenylmercapto-benzoic"
should be -- o-(m-phenylmercaptophenylmercapto)benzoic --.

Column 3, line 4, formula reads

"HOOC—C\textsubscript{b}H\textsubscript{2b}—C≡C—C\textsubscript{c}H\textsubscript{2c}—COOH"
should be

-- HOOC—C\textsubscript{b}H\textsubscript{2b}—C≡C—C\textsubscript{c}H\textsubscript{2c}—COOH -- .

Column 7, line 50, "benzoid" should be -- benzoic --.

Column 7, line 69, "bounary" should be -- boundary --.

Signed and sealed this 18th day of February 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks