United States Patent Office 3,249,543 Patented May 3, 1966

3,249,543

LUBRICANT COMPOSITION CONTAINING A RHODANINE COMPOUND

Glenn R. Wilson, Cambridge, Mass., assignor to Monsanto Research Corporation, St. Louis, Mo., a corporation of Delaware

No Drawing. Filed Apr. 30, 1963, Ser. No. 276,987
3 Claims. (Cl. 252—47.5)

This invention relates to liquid fluids of high thermal stability, and more particularly, provides functional fluids comprising polyphenyl ethers and certain rhodanine compounds as additives therefor.

Polyphenyl ethers have found wide application as functional fluids owing to their very good thermal stability, lubricity, and resistance to foam. For example, they have been found to be valuable as hydraulic fluids, as heat-exchange media, as atomic reactor coolants, as diffusion pump fluids, as lubricants in motor operation generally, and particularly as jet engine lubricants.

As is known in the art, petroleum lubricants, in addition to the petroleum base stock, generally include additives which impart specific desired properties to the base stock, such as rust inhibitors, anti-oxidants, extreme pressure resisting agents, lubricity improvers, detersives and the like. The additives proposed heretofore have been designed to provide petroleum base compositions for lubrication in conventional equipment such as internal combustion engines of the automotive type, diesel engines and the like, in which the temperature of use is not excessive, not exceeding about 400° F. Advanced designs such as jet aircraft design have called for effective lubrication at higher temperatures, such as 500° F. and above, and for these designs, it was found that neither the petroleum base stock nor the conventional additives used therewith were practical. The temperatures of operation exceeded the boiling point of some lubricant composition components, and generally were in a range at which both lubricant and additives were thermally unstable and decomposed.

Development of synthetic base stocks like the polyphenyl ethers has provided lubricant fluids stable at temperatures above the useful range of the mineral oils. There is now a demand for compositions in which such functional fluids, with thermal stability superior to that of the mineral oils, are compounded with additives enhancing desirable properties thereof. Many materials known as useful mineral oil additives are, as stated, excluded from utility in this connection by volatility and lack of thermal stability at the temperatures of use of the polyphenyl ethers. Furthermore, it has been found that additives conventional in mineral oil lubricants do not perform predictably upon combination with synthetic base stocks. There are significant differences in chemical structure of the stocks which can affect the response to additives: for example, whereas the mineral oils consist of aliphatic hydrocarbons, the polyphenyl ethers are, by contrast, aromatic ethers. Indeed, base stocks chemically different from the mineral oils may actually suffer chemical attack by certain additives, with deleterious effects on their superior high temperature properties. Temperature of operation can also affect the performance of additives, and so forth. Thus an empirical approach has been required for the provision of improved lubricants including the polyphenyl ethers as base stocks.

One of the aspects in which the properties of the polyphenyl ether base stocks are considered deficient consists in their lubricity characteristics. The lubricity characteristics of a lubricant include its load-carrying abilities and its wear properties. Compared to other synthetic high temperature lubricant fluids, the polyphenyl ethers rank high in lubricity characteristics. However, severe design requirements for applications such as aircraft engines include effective lubrication under high pressures as well as at high temperatures which the uncompounded polyphenyl ethers do not meet. Thus there is a demand for polyphenyl ether base compositions having improved lubricity properties.

An object of the present invention is the provision of improved lubricant compositions employing polyphenyl ether fluids as base stocks.

A particular object of the present invention is to provide polyphenyl ether base compositions having improved lubricity properties.

These and other objects will become evident upon consideration of the following specification and claims.

It has now been found that compositions consisting essentially of a polyphenyl ether base fluid and an additive amount of a 3-aminorhodanine Schiff base have unusual ability to lubricate under ultra high loads at high temperatures.

The improvement in lubricity characteristics achieved by addition of a compound of the stated kind to the polyphenyl ether base fluids is unusual and surprising. Wear is decreased at each of the test temperatures of 167° F., 400° F. and 600° F., whereas the effect of wear diminishing additives on polyphenyl ether base fluids is frequently temperature-dependent, apparent at only one or two points in this temperature range, and activity at one temperature is often accompanied by an actual increase in wear at another of the temperature points. The load-carrying ability of the base fluid is also raised.

The effectiveness of these 3-aminorhodanine Schiff bases as lubricity-improving additives is particularly surprising since it has been observed in mineral oil studies that substitution of the 3-position of the rhodanine ring suppresses its activity as a lubricity improver. A further contra-indication of the utility of the stated compounds as additives for enhancing the lubricating qualities of a polyphenyl ether base fluid is that 3-aminorhodanine is found to exert a pro-oxidant effect on such fluids. The polyphenyl ether base fluids are chiefly used in environments where they are exposed to temperatures of 500° F. and above, in the presence of air. At temperatures above about 550° F., the polyphenyl ethers become rather readily oxidizable, and formation of oxidation products is accompanied by an undesirable increase in viscosity. Thus pro-oxidants must be avoided. However, it has now been found that the Schiff bases of 3-aminorhodanine do not have the pro-oxidant activity of the free amine, and indeed, may have a beneficial antioxidant effect on the base fluid.

To provide the lubricant compositions of this invention, the 3-aminorhodanine Schiff bases are combined with a high temperature, oxygenated carbonaceous lubricant base fluid comprising a polyphenyl ether. This will be a base fluid of lubricating viscosity having a chemical structure made up of C, H and O, and characterized by thermal stability at temperatures up to at least about 500° F. In general, the lubricant composition of this invention will be designed for lubrication of the moving parts of mechanisms operating in temperature ranges of 400° F. to 700° F. A particularly advantageous base fluid for use under these conditions comprises the above-mentioned polyphenyl ethers.

The polyphenyl ethers employed in the compositions of this invention have from 3 to 7 benzene rings and from 1 to 6 oxygen atoms, with the stated oxygen atoms joining the benzene rings in chains as ether linkages. One or more of the benzene rings in these polyphenyl ethers may be hydrocarbyl substituted. The hydrocarbyl substituents, for thermal stability, must be free of CH_2 and aliphatic CH, so that preferred aliphatic substituents are lower saturated hydrocarbon radicals (1 to 6 carbon

atoms) like methyl and tert-butyl, and preferred aromatic substituents are aryl radicals like phenyl, tolyl, t-butylphenyl and α-cumyl. In the latter case, the benzene ring supplied in the hydrocarbyl substituent contributes to the total number of benzene rings in the molecule. Polyphenyl ethers consisting exclusively of chains from 3 to 7 benzene rings with at least one oxygen atom joining the stated benzene rings in the chains as an ether linkage have particularly desirable thermal stability.

Exemplary of the polyphenyl ethers containing aliphatic carbon which are suitable for high temperature base fluids are 3-ring polyphenyl ethers like 1-(p-methylphenoxy)-4-phenoxybenzene and 2,4-diphenoxy-1-methylbenzene, 4-ring polyphenyl ethers like bis[p-(p-methylphenoxy)phenyl] ether and bis[p-(p-tert-butylphenoxy) phenyl] ether, and so forth.

Polyphenyl ethers consisting exclusively of benzene rings and including ether oxygen atoms linking said rings are exemplified by the triphenoxy benzenes and aryl-substituted polyphenyl ethers such as biphenylyl phenoxyphenyl ether, biphenylyloxyphenyl phenoxyphenyl ether, dibiphenylyl ether, dibiphenylyloxybenzene, bis(biphenylyloxyphenyl) ether, and the like.

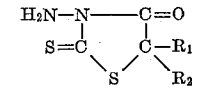
A preferred class of the polyphenyl ethers are those consisting of benzene rings joined in a chain by oxygen atoms as ether linkages between each ring, of the formula $C_6H_5O—(C_6H_4O—)_n—C_6H_5$ where n is an integer of from 1 to 5.

Examples of the polyphenyl ethers contemplated in this class are the bis(phenoxyphenyl) ethers (4 benzene rings joined in a chain by 3 oxygen atoms), illustrative of which is bis(m-phenoxyphenyl)ether. The bis(phenoxyphenoxy) benzenes are particularly valuable in the present connection. Illustrative of these are m-bis(m-phenoxyphenoxy)benzene, m-bis(p-phenoxyphenoxy)benzene, o-bis(o-phenoxyphenoxy)benzene, and so forth. Further, the polyphenyl ethers contemplated herein include the bis(phenoxyphenoxyphenyl) ethers such as bis[m-(m-phenoxyphenoxy)phenyl] ether, bis[p-(p-phenoxyphenoxy)phenyl] ether, and m-(m-phenoxyphenoxy)phenyl m-(o-phenoxyphenoxy)phenyl ether, and the bis(phenoxyphenoxyphenoxy)benzenes such as m-bis[m-(m-phenoxyphenoxy)phenoxy]benzene, p-bis[p-(m-phenoxyphenoxy)phenoxy]benzene and m-bis[m-(p-phenoxyphenoxy)phenoxy]benzene.

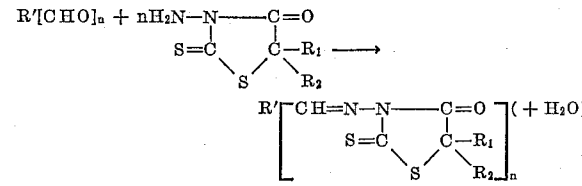
The preferred polyphenyl ethers are those having all their ether linkages in the meta-positions since the all-meta-linked ethers are particularly advantageous because of their wide liquid range and high thermal stability. However, mixtures of the polyphenyl ethers, either isomeric mixtures or mixtures of homologous ethers, can also advantageously be used in some applications, especially where particular properties such as lower solidification points are required. Mixtures of polyphenyl ethers in which the non-terminal phenylene rings are linked through oxygen atoms in the meta and para positions have been found to be particularly suitable to provide compositions with wide liquid ranges. Of the mixtures having only meta and para linkages, a preferred polyphenyl ether mixture of this invention is the mixture of bis (phenoxyphenoxy)benzenes wherein the non-terminal phenylene rings are linked through oxygen atoms in the meta and para position, and composed by weight of about 65% m-bis[m-phenoxyphenoxy]benzene, 30% m-[(m-phenoxyphenoxy)(p-phenoxyphenoxy)]benzene and 5% m-bis(p-phenoxyphenoxy)benzene. Such a mixture solidifies at below room temperature (that is, below about 70° F.) whereas the three components solidify individually at temperatures above normal room temperatures.

The aforesaid polyphenyl ethers can be obtained by known procedures such as, for example, the Ullmann ether synthesis, which broadly relates to ether-forming reactions wherein alkali metal phenoxides such as sodium and potassium phenoxide are reacted with aromatic halides such as bromobenzene in the presence of a copper catalyst such as metallic copper, copper hydroxides, or copper salts.

The additives combined with the above-described base fluids in accordance with this invention are Schiff bases of a 3-aminorhodanine. The stated amine is a compound of the structure

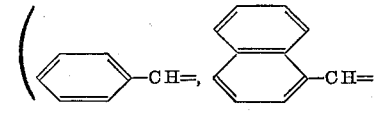


where each of R_1 and R_2 is a substituent selected from the class consisting of hydrogen and hydrocarbon radicals, and its Schiff bases are condensation products with aldehydes in accordance with the equation

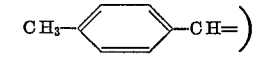


where R′ is a hydrocarbon radical and n is an integer of from 1 to 2. The resulting compound is a hydrocarbylideneaminorhodanine which is the Schiff base of the 3-aminorhodanine.

The presently useful Schiff bases can and generally will be prepared by the condensation of a hydrocarbyl mono- or dicarboxaldehyde with 3-aminorhodanine, which is a known compound, or with a 5-hydrocarbyl-substituted 3-aminorhodanine, which may be prepared from the corresponding rhodanine by the method used for synthesis of 3-aminorhodanine. The hydrocarbon radicals in the presently contemplated Schiff bases will be free of aliphatic (olefinic and acetylenic) unsaturation, and may be aromatic (including aryl, alkaryl and aralkyl) or saturated aliphatic (straight chain, branched and alicyclic), and contain up to 14 carbon atoms. One or both of the substituents of the 5-position of the rhodanine ring may be monovalent hydrocarbon radicals, or the substituents shown in the formula above as R_1 and R_2 may be, taken together, a divalent hydrocarbylidene radical. Arylmethylene



and alkaryl methylenes such as



substituents are especially preferred.

Thus, illustrative of presently contemplated Schiff bases are

3-(benzylideneamino)rhodanine,
3-(4-methylbenzylideneamino)rhodanine,
3-(4-t-butylbenzylideneamino)rhodanine,
3-(4-t-butylbenzylideneamino)rhodanine,
3-(4-i-propylbenzylideneamino)rhodanine,
3-(4-phenylbenzylideneamino)rhodanine,
3-(α-naphthylmethyleneamino)rhodanine,
3-(benzylideneamino)-5-ethylrhodanine,
3-(benzylideneamino)-5,5-dimethylrhodanine,
3-(benzylideneamino)-5-phenylrhodanine,
3-(benzylideneamino)-5,5-(2-ethylhexyl)rhodanine,
3-(4-methylbenzylideneamino)-5-octylidenerhodanine,
3-(benzylideneamino)-5-benzylidenerhodanine,
3,3′-methylenebis(benzylideneaminorhodanine),
3,3′-o-phenylenebis(methylideneaminorhodanine),

3,3'-o-phenylenebis(methylideneamino-5-methylrhodanine),
3-(cyclohexylideneamino)rhodanine,
3-(cyclohexylmethylideneamino)-5-cyclohexylidenerhodanine,
3-(butylideneamino)rhodanine,
3-(ethylideneamino)-5-butylrhodanine,
3,3'-ethanediylidenedi(aminorhodanine) and so forth.

The 3-aminorhodanine Schiff base is combined with the fluid polyphenyl ether base fluid to the extent of, generally, between about 0.01% and 10% by weight of the fluid. Particular effective amounts depend on the nature of the individual additive and of the ether fluid. In most cases the ability of the agent with respect to extreme pressure lubrication improvement increases as the concentration is increased. For puposes of supplying additive concentrates, adapted for convenient formulation of finished lubricant compositions, useful compositions may comprise up to about 1:1 weight ratio of the additives of this invention and the polyphenyl ether base fluid.

It will be appreciated that the compositions of this invention, in addition to the polyphenyl ether base fluid and the Schiff base, may additionally include any of a wide variety of further additives. For example, these may include sludge inhibitors and detergents such as the oil-soluble petroleum sulfonates, to loosen and suspend products of decomposition and counteract their effect. Other agents such as viscosity index improvers, as exemplified by alkyl methacrylate polymers, pour point depressants, oiliness agents, and so forth, may also be present in these compositions if desired.

The invention is illustrated but not limited by the following examples, in which the tests employed to determine the reported adjuvant effects of the Schiff bases when employed with the polyphenyl ether lubricant base fluid are conducted as follows:

The antiwear and extreme pressure lubrication characteristics of the lubricant compositions are evaluated by means of the well known "Shell 4-Ball Extreme Pressure Tester" and the "Shell 4-Ball Wear Machine," as described, for exampe, in the "Lubrication Engineers Manual" (U.S. Steel Corp., 1960). These testers include 4 balls of stainless steel arranged in the form of an equilateral tetrahedron. The three lower balls are held immovably clamped in a holder to form a cradle in which the fourth upper ball is caused to rotate at 1200–1800 r.p.m. about a vertical axis in contact with the three lower stationary balls. The contacting surfaces of the balls are immersed in the test fluid which is held in a cup surrounding the assembly. A modified cup and heater assembly is used to evaluate lubricants at elevated temperature and provisions are made to permit high temperature testing under an inert atmosphere: see the "The Study of Lubrication Using the 4-Ball Type Machine" by R. G. Larsen, Lubrication Engineering, 1, 35–43, 59 (August, 1945).

For determination of the extreme pressure properties in the 4-Ball EP tester, the upper ball is rotated while the load is gradually increased by increments of 10 kg. until the balls are welded together in a 1-minute test period.

For measurement of wear in the Wear Machine, the upper ball is rotated under a load of 40 kg. for one hour at each of the temperatures for which wear scar diameters worn in the surface of the three stationary balls are reported.

For determination of the effect of the presently employed additives on oxidation resistance, air is bubbled through duplicate samples at 600° F. for 48 hours at a rate of 1 liter per hour of air, in the presence of silver, aluminum, copper and stainless steel wires. The percent change in viscosity (at 100° F.) from before to after oxidation is an index of antioxidant activity.

Example 1

A lubricant composition is prepared by combining 3-(benzylideneamino)rhadanine with a polyphenyl ether of the following composition, by weight:

65% m-bis(m-phenoxyphenoxy)benzene,
30% m-[(m-phenoxyphenoxy)(p-phenxoyphenoxy)]benzene,
5% m-bis(p-phenoxyphenoxy)benzene,

in a proportion of 1 gram (g.) of the Schiff base to 100 g. of the base fluid.

A portion of the base fluid used to provide the above-described compositon is reserved, free of additive, and run through the same sequence of tests, to provide a basis for comparison.

Using the base fluid alone, in the extreme pressure test, the balls weld at a pressure of 150 kg.

Employing the lubricant composition described above, consisting of 1% of the stated Schiff base combined with the same polyphenyl ether, the weld point is 240 kg.

Using the Shell 4-Ball Wear Tester, the wear scar diameter determined for the lubricant composition of this example including the Schiff base and for the base fluid without additive are as follows:

	Wear Scar Diameter, mm.		
	167° F.	400° F.	600° F.
With additive	1.73	1.03	1.61
Without additive	1.82	1.17	2.92

Example 2

This example provides an illustration of the oxidation stability of compositions of this invention.

The additive-containing lubricant composition described in Example 1, containing 1% 3-(benzylideneamino)rhodanine, is subjected to the above-described oxidation test, conducted in the presence of wires of Fe, Ag, Cu and Al. Whereas the polyphenyl ether base fluid without additives suffers a 70% increase in viscosity in 48 hours under these conditions, the composition including the aminorhodanine derivative undergoes only a 60% viscosity increase in the same length of time. By contrast, the same base fluid combined with 1 g./100 g. of 3-aminorhodanine exhibits a 100% increase in viscosity under the stated conditions, and the oxidized material contains solid deposits, whereas the oxidized composition containing the Schiff base is clear after the test, as is the case with the base fluid itself.

While the invention has been described with reference to specific preferred embodiments thereof, it is to be appreciated that modifications and variations can be made without departing from the scope of the invention, which is limited only as defined in the appended claims.

What is claimed is:

1. A functional fluid consisting essentially of a base fluid consisting of a polyphenyl ether having from 3 to 7 benzene rings and from 1 to 6 oxygen atoms joining the said benzene rings in chains as ether linkages, and a lubricity-improving amount of a 3-aminorhodanine Schiff base prepared by the condensation of a hydrocarbyl compound taken from the group consisting of hydrocarbyl mono and dicarboxaldehydes with a rhodanine compound taken from the group consisting of 3-aminorhodanine and 5-hydrocarbyl-3-aminorhodanines, wherein the hydrocarbon radicals in the said Schiff base are taken from the group consisting of aromatic and satu-

rated aliphatic hydrocarbon radicals and contain up to 14 carbon atoms.

2. The composition of claim 1 in which said Schiff base is a 3-(arylmethyleneamino)rhodanine.

3. A functional fluid composition consisting essentially of a polyphenyl ether base fluid consisting of from 3 to 7 benzene rings joined in a chain by oxygen atoms as ether linkages between each ring, and a lubricity-improving amount of 3-(benzylideneamino)rhodanine.

References Cited by the Examiner

UNITED STATES PATENTS

2,796,401	6/1957	Kluge et al.	252—47.5
2,796,403	6/1957	Watson et al.	252—47.5
2,796,404	6/1957	Levin	252—47.5

DANIEL E. WYMAN, *Primary Examiner.*

J. R. McBRIDE, L. G. XIARHOS, *Assistant Examiners.*