United States Patent Office 3,226,325 Patented Dec. 28, 1965

3,226,325

LUBRICANT COMPOSITION CONTAINING A HALOPHENOL

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. 277,025
7 Claims. (Cl. 252—54)

This invention relates to liquid fluids of high thermal stability, and more particularly, provides functional fluids comprising polyphenyl ethers and certain halogenated aromatic hydroxy 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.

Although the polyphenyl ethers possess extremely good thermal stability, at temperatures of, say, over 550° F., they tend to deteriorate, not because of a decomposition reaction, but because at the higher temperatures they become quite readily oxidizable. The lubricity of the polyphenyl ethers is thereby impaired, since the oxidation products do not possess lubricating properties; moreover, the change in viscosity which is a consequence of the oxidation not only makes for inefficiency, but also may result in clogging up the moving parts of the mechanism which the lubricant was originally intended to protect. Hence, when the polyphenyl ethers are to be used at the higher temperatures under conditions requiring exposure to air, it is important to inhibit oxidation phenomena which the higher temperatures favor.

The polyphenyl ethers, like conventional petroleum lubricants, are also somewhat deficient with respect to lubricity, anti-wear and extreme pressure-resisting properties. Breakdown of lubricant film occurs under some conditions of use, particularly at the extreme pressures encountered in gear lubrication. Here again, conventional lubricity, anti-wear and extreme pressure-resisting (E.P.) additives are generally ineffective with the polyphenyl ethers and do not withstand the very high temperatures at which the high thermal stability of the ethers could make them of most use.

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 and oxidation resistance.

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 halogenated aromatic hydroxy compound have improved lubricity properties and ability to resist oxidation degradation at high temperatures.

The beneficial effects of the present additives on the oxidation resistance of the polyphenyl ethers is surprising. Unhalogenated phenols have not been observed to exert such a protective effect. The particularly beneficial effect of an iodophenol as employed herein on the lubricity properties of the polyphenyl ether base fluid is also unexpected. With the present base fluid, a greater improvement in both wear and extreme pressure characteristics has been found with iodine as the halogen substituent than with chlorine. Using an iodinated compound, moreover, a reduction in wear is produced throughout a wide temperature range, extending to the high temperatures at which the polyphenyl ether base fluids are especially useful. Use of an iodophenol as provided herein in compounding polyphenyl ether base lubricants is particularly valuable since, unlike some lubricity-improving additives, it does not have a harmful effect on the oxidation resistance of the fluid, but rather enhances it.

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 stated benzene rings in chains as ether linkages. One or more of the stated 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 and tolyl. 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 of 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 alkyl polyphenyl ethers suitable for base fluids are 3-ring polyphenyl ethers like 1-(p-methylphenoxy)-4-phenoxybenzene and 2,4-diphenoxy-1-methyl-

benzene, 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 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, biphenylyl ether, dibiphenylyloxybenzene, bis(biphenylyloxyphenyl) ether, and the like.

A preferred class of the polyphenyl ethers comprises those consisting of benzene rings joined in a chain by oxygen atoms as ether linkages between each ring.

Examples of the polyphenyl ethers contemplated in this class are the bis(phenoxyphenyl) ethers (4 benzene rings joined in a chain by 4 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, 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 5 ring polyphenyl ethers 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 is liquid at room temperature (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, by the Ullmann ether synthesis, by a procedure involving reaction of alkali metal phenoxides such as sodium and potassium phenoxides with aromatic halides such as bromobenzene in the presence of a catalyst such as metallic copper, copper hydroxides or copper salts.

Referring to the additives combined with the above-described polyphenyl ether base fluids in accordance with this invention, these are composed of an aromatic hydrocarbon nucleus having as aromatic ring carbon atom substituents at least one hydroxyl group and more than one halogen atom. The halogen has an atomic weight of below 130, and may be fluorine, chlorine, bromine or iodine, with iodine preferred. The aromatic nucleus may be monocyclic or may be polycyclic, including chain and fused polycyclic nuclei.

Thus, exemplary of the presently useful iodine-substituted aromatic hydroxy compounds are for example diiodophenol, triiodophenol, tetraiodophenol, pentaiodophenol, triiodo-α-naphthol, triiodo-β-naphthol, tetraiodo-α-naphthol, tetraiodo-β-naphthol, hexaiodonaphthol, triiodophenylphenol, tetraiododiphenol, triiodohydroquinone, tetraiodohydroquinone, pentaiodophenanthrol, and additionally, halogenated hydroxy aromatic compounds wherein the halogen substituents are inclusive not only of iodine but also of other lower molecular weight halogens including for example chlorodiiodophenol, bromodiiodophenol, chlorotriiodophenol, dichlorotriiodophenol, fluorodiiodophenol, chlorotriiodonaphthol, pentachlorophenyltetraiodophenol and so forth. Further examplary of the additives of this invention are fluorine-, chlorine- and bromine-substituted aromatic hydroxy compounds such as trichlorophenol, dichlorophenol, tetrachlorophenol, pentachlorophenol, bromodichlorophenol, dibromochlorophenol, tribromophenol, trifluorophenol, chlorodifluorophenol, dichlorofluorophenol, dichlorodifluorophenol, trichloronaphthol, tribromonaphthol, hexachlorobiphenol, hexachlorophenylphenol, dichlorotrifluorophenylphenol, tribromophenylphenol, trichlorohydroquinone and so forth.

The halogenated aromatic hydroxy compound 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, whereas lowering the concentration sometimes enhances antioxidant effects. For purposes of supplying additive concentrates, adapted for convenient formulation of finished lubricant compositions, useful compositions may comprise up to about a 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 halogenated aromatic hydroxy compound, 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 haloalkanoic compounds 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 example, 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 Study of Lubrication in Using the 4-Ball Type Machine," by R. G. Larsen, Lubrication Engineering, 1, 35–43, 59 (Aug. 1945).

For determination of the extreme pressure properties in the 4-Ball E.P. 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 temperature for which wear scar diameters worn in the surface of the three lower stationary balls are reported.

For determination of the antioxidant affect of the presently employed additives, air is bubbled through duplicate samples at 600° F. for 24 hours at a rate of 1 liter per hour of air, in the presence and absence of Fe, Cu, Al and Ag wires. The percent change in viscosity (at 100° F.) from before to after oxidation is an index of anti-oxidant activity.

Example 1

A lubricant composition is prepared by combining pentachlorophenol with a polyphenyl ether of the following composition, by weight: 65% m-bis(m-phenoxyphenoxy)benzene, 30% m - [(m - phenoxyphenoxy)(p-phenoxyphenoxy)]benzene, 5% m - bis(p - phenoxyphenoxy)benzene, in a proportion of 1 gram (g.) of the phenol to 100 g. of the base fluid.

A portion of the base fluid used to provide the above-described composition 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 140 kg.

Employing the lubricant composition described above, consisting of 1% of pentachlorophenol combined with the same polyphenyl ether, the weld point is 190 kg.

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

	Wear Scar Diameter, mm.	
	167° F.	400° F.
With additive	1.58	1.18
Without additive	1.75	2.12

Example 2

A lubricant composition is prepared by combining 2,4,6-triiodophenol with a polyphenyl ether base fluid of the composition stated in Example 1, in a concentration of 1.0 g. per 100 g. of base fluid. The solution of the additive in the polyphenyl ether is subjected to test of its extreme pressure and wear properties as compared to the untreated base fluid, with the following results:

	Weld Point, kg.	Wear Scar Diameter, mm.		
		167° F.	400° F.	600° F.
With Additive	230	1.76	2.15	1.91
Without Additive	160	1.79	3.30	2.93

Example 3

This example provides an illustration of the improved oxidation stability of compositions of this invention as compared to the base fluid in the absence of additive.

The additive-containing lubricant composition described in Example 1, containing 1% pentachlorophenol, is subjected to the above described oxidation test, conducted with and without the presence of wires of Fe, Ag, Cu and Al. Whereas the polyphenyl ether base fluid without additives suffers a 60% increase in viscosity in the absence of the wires, and 45% in their presence, the composition including the chlorophenol undergoes only about a 25% viscosity increase in the same length of time, and the presence or absence of the metals does not affect its oxidation stability.

Example 4

This example provides another illustration of the improved oxidation stability of compositions of this invention as compared to the base fluid in the absence of additive.

The additive-containing lubricant composition described in Example 2, containing 1% triiodophenol, is subjected to the above described oxidation test, conducted with and without the presence of wires of Fe, Ag, Cu and Al. Whereas the polyphenyl ether base fluid without additives is found to undergo a 57% increase in viscosity in the absence of the wires, and 37% in their presence, the composition including the iodophenol undergoes only about a 34% viscosity increase in the same length of time in the presence of the metals and about 38% in their absence.

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 lubricant composition comprising a major amount of a polyphenyl ether base fluid and a halogenated compound composed of an aromatic hydrocarbon nucleus having as aromatic ring carbon atom substituents at least one hydroxyl group and more than one halogen atom, in an amount sufficient to improve lubricity properties and high temperature oxidative degradation resistance of the said base fluid.

2. The composition of claim 1 wherein said halogenated compound is a polyhalophenol.

3. The composition of claim 1 wherein said halogenated compound is an iodine-substituted aromatic hydroxy compound.

4. The composition of claim 3 wherein said halogenated compound is a polyiodophenol.

5. The composition of claim 4 wherein said halogenated compound is triiodophenol.

6. The composition of claim 2 wherein said halogenated compound is a polychlorophenol.

7. The composition of claim 6 wherein said halogenated compound is pentachlorophenol.

References Cited by the Examiner

UNITED STATES PATENTS

2,161,560	6/1939	Crossby	252—54
2,180,008	11/1939	Lincoln et al.	252—54
2,213,532	9/1940	Prutton et al.	252—54
2,250,384	7/1941	Lincoln et al.	252—54
2,469,469	5/1949	Kluge et al.	252—54
3,080,321	3/1963	Blake et al.	252—52 X

FOREIGN PATENTS

851,651	10/1960	Great Britain.

DANIEL E. WYMAN, *Primary Examiner.*