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POLYPHENYL ETHER COMPOSITIONS USEFUL AS FUNCTIONAL FLUIDS

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The invention relates to liquid fluids of high thermal stability and more particularly provides functional fluids comprising polyphenyl ethers and certain organometallic compounds as adjuvants therefor.

The polyphenyl ethers are known compounds which 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, heat-exchange media, as atomic reactor coolants, as diffusion pump fluids, as lubricants in motor operation generally, and particularly as jet engine lubricants.

With recent changes in the design of aircraft engines, there is a demand for lubricants which will perform satisfactorily under conditions far more rigorous than ever contemplated in the past. A particularly important requirement for lubricants intended for use in the newly designed engines is that their viscosity be unaffected by the high temperatures to which they are necessarily subjected.

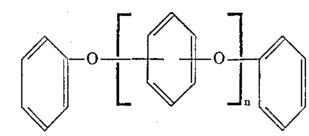
As is known in the art, petroleum lubricants generally comprise, in addition to the petroleum base stock, additives or adjuvants which impart specifically desired properties to the base stock, e.g., rust-inhibitors, antioxidants, extreme pressure-resisting agents, lubricity improvers, detersives, etc. The additives proposed heretofore have been designed to accommodate the requirements of petroleum base stocks for lubrication in conventional equipment such as internal combustion engines of the automotive type, diesel engines and the like. One feature in common with respect to these various applications was that the temperature of use was not excessive, i.e., it may vary from about 40° F. to 400° F. With the advent of extremely high speed aircraft of the jet type, it was found that neither the petroleum base stock nor the conventional additives used therewith were practical, because the lubricant and the additives had to be effective at temperatures which were above the decomposition points of the known additives, e.g., at temperatures which were generally within the range of 500° F. to 700° F. It was also found that when conventional additives were employed with functional fluids having higher thermal stability than that possessed by petroleum base stocks, the additives did not perform in a predictable manner, i.e., a material possessing antioxidant effect or an extreme pressure-resisting effect with the petroleum hydrocarbon lubricants generally did not possess such effects when used with the polyphenyl ether fluids.

Although the polypenyl 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 clog 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 necessary to inhibit oxidation phenomena which the higher temperatures favor.

Accordingly, an object of the present invention is the provision of improved polyphenyl ether fluid compositions. Another object of the invention is the provision of polyphenyl ether compositions having improved antioxidant properties. A most important object of the invention is the provision of polyphenyl ether compositions which possess an improved resistance to oxidation at temperatures of over 550° F.

These and other objects hereinafter disclosed are provided by the invention wherein there is employed a copper oxide as antioxidant for the polyphenyl ether liquid fluids. The presently useful copper oxides include cupric oxide (CuO), cuprous oxide (Cu_2O), and copper suboxide (Cu_4O). Cuprous oxide (Cu_2O) is preferred.

The polyphenyl ethers to which this invention pertains can be represented by the structure



where n is a whole number from 2 to 5. The preferred polyphenyl ethers are those having all their ether linkages in the meta position since the all-meta linked ethers are the best suited for many applications because of their wide liquid range and high degree of thermal stability. However, mixtures of the polyphenyl ethers, i.e., either isomeric mixtures or mixtures of homologous ethers, can also be used to obtain certain properties, e.g., lower solidification points. Examples of the polyphenyl ethers contemplated are the bis(phenoxyphenyl)ethers, e.g., bis(m-phenoxyphenyl)ether, the bis(phenoxyphenoxy)benzenes, e.g., m - bis(m - phenoxyphenoxy)benzene, m - bis(p-phenoxyphenoxy)benzene, o - bis(o - phenoxyphenoxy)benzene, the bis(phenoxyphenoxyphenyl)ethers, e.g., bis[m-(m - phenoxyphenoxy)phenyl]ether, bis[p - (p - phenoxyphenoxy)phenyl]ether, m-[(m - phenoxyphenoxy)(o-phenoxyphenyl)]ether and the bis(phenoxyphenoxyphenoxy) benzenes, e.g., m-bis[m - (m - phenoxyphenoxy)phenoxy] benzene, p-bis[p-(m-phenoxyphenoxy)phenoxy]benzene, or m-bis[m (p-phenoxyphenoxy)phenoxy]benzene. It is also contemplated that mixtures of the polyphenyl ethers can be used. For example, mixtures of polyphenyl ethers in which the non-terminal phenylene rings (i.e., those rings enclosed in the brackets in the above structural representation of the polyphenyl ethers contemplated) are linked through oxygen atoms in the meta and para positions, have been found to be particularly suitable as lubricants because such mixtures possess low solidification points and thus provide compositions having wider 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 where 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 about 10° F., whereas the three components solidify individually at temperatures above normal room temperatures.

The aforesaid polyphenyl ethers can be obtained by the Ullmann ether synthesis which broadly relates to ether forming reactions of e.g., alkali metal phenoxides such as sodium and potassium phenoxides 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 copper oxides are combined with the fluid polyphenyl ethers to the extent of 0.01% to 1.0% by weight, depending upon the nature of the oxide and of the ether fluid. The copper oxides have an antioxidant effect on the polyphenyl ethers, generally. The concentration of copper oxide at which the desired antioxidant effect is obtained is readily determined by use of conventional testing procedures known to those skilled in the art. The effectiveness of the present additives may not be the same over the entire range of concentration; for example, while it has been noted that in most cases the ability of the agent with respect to anti-wear and extreme pressure lubrication improves markedly as the concentration is increased, the reverse may be true insofar as antioxidant effect is concerned, lower amounts of the additive often resulting in a greater degree of stability to oxidation at the high temperatures than are attained by use of the greater amounts of the same additive.

The invention is further illustrated by, but no limited to, the following examples:

Example 1

In this example, there was employed a mixture of polyphenyl ethers consisting by weight of

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

The rate of oxidation of the above mixture, in the presence or absence of cuprous oxide or cupric oxide was determined by means of an oxygen absorption test using a Dornte-type apparatus [J. Inst. Petrol., 41, 283 (1955)] equipped with an electrically heated deepwell unit in which the sample was heated by immersion of the test cell. Oxygen was passed, at a rate of 12 liters/hour into the test sample maintained at 600° F. and consisting of either 50 g. of said mixture of ethers or the same quantity of said mixture plus 0.2 percent by weight of one of said oxides. The mixture of polyphenyl ethers, in the absence of any additive, was found to oxidize at the rate of 70 ml. of O_2/hour. In the presence of the cupric oxide the rate was reduced to 38 ml. of O_2/hour and in the presence of the cuprous oxide the oxidation rate was only 18 ml. of O_2/hour. That the decreased rate of oxidation is not due to the presence of metal was determined by operating in the presence of the same quantity of minutely suspended copper, zinc or silver. At the end of 4 hours at the 600° F. temperature and the same rate of oxygen introduction, the following results were noted:

Additive:	Ml. of O_2 consumed
None	350
Zinc	312
Silver	302
Copper	225
Cuprous oxide	72

At the end of ca. 5.5 hours, the sample which contained the cuprous oxide had consumed only ca. 105 ml. of oxygen whereas that which contained the copper had consumed 350 ml. of oxygen. Observation of the "control," i.e., the sample of ether mixture which contained no additive, was discontinued at the end of about 5 hours at which point ca. 500 ml. of oxygen had been consumed.

Example 2

The antioxidant effect of cuprous oxide on a polyphenyl ether fluid was determined by bubbling air through a 20 milliliter sample of the mixture of ethers described in Example 1, in the presence or absence of 0.2% weight of the oxide at 600° F. for 24 hrs. at 1 liter/hr., and determining the viscosity (at 100° F.) and percent loss in weight of the treated sample. The percent change in viscosity (before and after oxidation) was taken as an index of antioxidant activity. Since some metals had been found to have an effect on the oxidation of polyphenyl ether fluids at high temperatures, the testing was also conducted in the presence of metals. In order to determine metal effect, one set of duplicate samples of ether fluid

plus additive contained copper, iron, aluminum and silver wires, whereas another duplicate set contained only the ether fluid and additive. Duplicate sets of no-additive controls were also employed, one set of only the ether fluid and another set in which the metal wires were immersed in the ether fluids. The following results were obtained:

Additive	Viscosity Increase, Percent	
	No Wires	With Wires
None	54.0	39.0
Cuprous oxide	18.9	19.0

The copper oxides possess antioxidant effect for the polyphenyl ether functional fluids, generally. Thus, instead of the mixture of 65% by weight of m-bis(m-phenoxyphenoxy)benzene, 30% by weight of m-[(m-phenoxyphenoxy)(p-phenoxyphenoxy)]benzene and 5% by weight of m-bis(p-phenoxyphenoxy)benzene which is used in the above examples, the polyphenyl ether component may be any one polyphenyl ether having from 4 to 7 benzene rings. For example, cuprous or cupric oxide is a very good antioxidant for any one of the three ethers of the polyphenyl ether mixture of Example 1, as well as for such other polyphenyl ethers as p-bis-[p-(m-phenoxyphenoxy)phenoxy]benzene, or m-[(m-phenoxyphenoxy)(o-phenoxyphenoxy)]benzene, or m-bis[m-(p-phenoxyphenoxy)phenoxy]benzene, or mixtures thereof in any proportion. Lubricant mixtures of ethers are generally so constituted as to give simultaneously an optimum of thermal stability and lubricity at the temperatures to which they will be exposed in operation; but since the polyphenyl ethers, generally, are benefited by the copper oxides with respect to increasing stability to oxygen at high temperatures, mixtures having varying proportions of the ethers are advantageously modified.

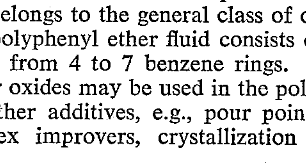
Since the quantity of the copper oxide which is employed with the polyphenyl ether fluid will vary with the nature of the polyphenyl ether and the nature of the copper oxide, it is evident that no rigid limits of antioxidant content can be set forth. Generally, polyphenyl ether compositions comprising from 0.01% to 1.0% by weight of the present additive demonstrate antioxidant effect. Determination of the optimum quantities is readily conducted by routine procedures, as will be apparent to those skilled in the art. Hence, the amount of the copper oxide to be used can best be expressed simply as an antioxidant amount. Variations or modification of the compounds and quantities employed in the examples can be made to accommodate different requirements, so long as the additive belongs to the general class of oxides of copper and the polyphenyl ether fluid consists of polyphenyl ethers having from 4 to 7 benzene rings.

The copper oxides may be used in the polyphenyl ether fluids with other additives, e.g., pour point depressants, viscosity index improvers, crystallization suppressants, dyes, etc.

Other modes of applying the principles of this invention may be employed instead of those specifically set forth above, changes being made as regards the details herein disclosed, provided the elements set forth in any of the following claims, or equivalents thereof may be employed.

What I claim is:

1. A functional fluid composition consisting essentially of a polyphenyl ether of the formula



wherein n is a whole number of 2 to 5 and from 0.01% to 1.0% by weight of a copper compound selected from the class consisting of cupric oxide and cuprous oxide.

2. The composition defined in claim **1**, further limited in that the copper compound is cupric oxide.

3. The composition defined in claim **1**, further limited in that the copper compound is cuprous oxide.

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