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POLYPHENYL ETHER COMPOSITIONS CONTAINING AN ORGANOTIN THIOCYANATE

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This invention relates to liquid fluids of high thermal stability and more particularly provides lubricant compositions 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, as 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 and lubricity 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, deteratives, 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 compositions, e.g., at temperatures which were generally within the range of 500° F. to 700° F.

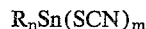
The polyphenyl ethers, like conventional petroleum lubricants, are somewhat deficient with respect to lubricity, anti-wear and extreme pressure-resisting properties, e.g., breakdown of lubricant film occurs under some conditions of use, particularly at the extreme pressures encountered in gear lubrication. 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.

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 lubricity. A further object is the provision of polyphenyl ether lubricants having improved anti-wear properties. Still a further object is the provision of polyphenyl ether compositions having improved extreme pressure-resisting properties. A most important object of the invention is the provision of polyphenyl ether lubricants which

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possess good anti-wear and extreme pressure-resisting properties at temperatures of over 550° F.

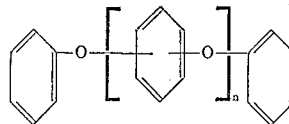
These and other objects hereinafter disclosed are provided by the invention wherein there is employed as additive for the polyphenyl ether lubricants an organotin thiocyanate of the formula



wherein R is a hydrocarbyl radical which is free of olefinic and acetylenic unsaturation and contains from 1 to 12 carbon atoms, n is 2 or 3, m is 1 or 2, and the sum of $m+n$ is 4. Examples of the presently useful thiocyanates of the above formula include the dihydrocarbyltin dithiocyanates, $R_2Sn(SCN)_2$, e.g., dimethyltin, diethyltin, diisopropyltin, dipentyltin, dihexyltin, ethyloctyltin, didecyltin, didodecyltin, diphenyltin, di- α -, m - or p -tolyltin, phenyl- m -xylyltin, bis(2-hexylphenyl)tin, dibenzyltin, dicyclohexyltin, bis(biphenyl)tin, di- α - or β -naphthyltin or ditetrahydronaphthyltin dithiocyanate.

Another class of presently useful compounds includes the trihydrocarbyltin thiocyanates, R_3SnSCN , e.g., triethyltin, tris(2-ethylhexyl)tin, tridecyltin, dimethyldodecyltin, tri- α - or m - or p -tolyltin, tri- α - or β -naphthyltin, tris(3-phenylpropyl)tin, tris(2-methylcyclopentyl)tin, or tribenzyltin thiocyanate.

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(phenoxyphenyl)ethers, 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, 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 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 positions, have been found to be particularly suitable as lubricants because such mixtures possess 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 temperature.

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 with aromatic halides such as bromobenzene in the presence of a copper catalyst such as metallic copper, copper hydroxides, or copper salts.

The organotin thiocyanate is combined with the fluid polyphenyl ethers to the extent of 0.5% to 10.0% by weight, depending upon the nature of the thiocyanate and of the ether fluid and upon the adjuvant effect desired. The organotin thiocyanates generally have a beneficial effect on the polyphenyl ether in that there is obtained increased lubricity and/or increased resistance to wear and extreme pressure.

This invention is further illustrated by, but not limited to, the following examples:

Example 1

In this example there was employed as lubricant base stock the following mixture of polyphenyl ethers:

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

The anti-wear and extreme pressure lubrication characteristics of triphenyltin thiocyanate in the above mixture of polyphenyl ethers were evaluated by means of the "Shell 4-Ball Extreme Pressure Tester," and the "Shell 4-Ball Wear Machine" measuring the scar diameter at 40 kg. in millimeters.

The Four-Ball Tester consists of four balls of stainless steel arranged in the form of an equilateral tetrahedron. The basic elements are three lower balls held immovably in a clamp to form a cradle in which a fourth or upper ball is caused to rotate about a vertical axis under prescribed conditions of load and speed. The contacting surfaces on the four-ball type apparatus are geometrically well-defined, thus providing obvious advantages in the study of wear and friction phenomena.

The points of contact are lubricated by the fluid under test, which is held in a cup surrounding the four-ball assembly. The circular scars worn in the surface of the three stationary balls were measured by means of a low power microscope. Using a 1.0 weight percent concentration of the triphenyltin thiocyanate with said polyphenyl ether, there was obtained a scar diameter of 2.29 mm. at 600° F. and 40 kg., as compared to 3.05 mm., the similarly obtained value for the mixture of ethers in the absence of an additive.

Example 2

Dilauryltin dithiocyanate was added to the mixture of polyphenyl ethers described in Example 1 in a quantity to give a 4% by weight concentration of the dithiocyanate. The resulting mixture was evaluated in a Shell Four-Ball Wear Test apparatus which had been modified to detect metal-to-metal contact electrically. The test procedure involved increasing the loading on the Shell Four-Ball apparatus until a greater than 50% metal-to-metal contact was established. Operating in this manner, it was determined that the mixture of polyphenyl ethers, alone, supported a load of only up to 4 kg., whereas that which contained the 4% concentration of dilauryltin dithiocyan-

ate supported a load of 8 kg. under the same testing conditions.

The organotin thiocyanates possess adjuvant 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 Examples 1 and 2, the polyphenyl ether component may be any one polyphenyl ether having from 4 to 7 benzene rings. For example, the triphenyltin thiocyanate of Example 1 or the dilauryltin dithiocyanate of Example 2 is a very good anti-wear and extreme pressure-resisting additive 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 organotin thiocyanates with respect to improved lubricity and film strength under conditions of high pressure at high temperature, mixtures having varying proportions of the ethers are advantageously modified.

It is evident from the data presented above that addition of the present thiocyanates to the polyphenyl ethers results in one or more beneficial effects, i.e., there is brought about increased resistance to wear and/or improvement in stability at operating conditions involving high pressure and temperature.

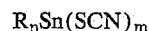
Since the quantity of the organotin thiocyanate which is employed with the polyphenyl ether fluid will vary with adjuvant effect sought, with the nature of the polyphenyl ether and the nature of the individual adjuvant, it is evident that no rigid limits of adjuvant content can be set forth. Generally, polyphenyl ether compositions comprising from 0.10% to 10% by weight of the present additive demonstrate adjuvant 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 organotin thiocyanate to be used can best be expressed simply as an adjuvant amount. Variations or modifications 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 thiocyanates hereinbefore defined and the polyphenyl ether fluid consists of polyphenyl ethers having from 4 to 7 benzene rings.

Although the organotin thiocyanates confer a variety of beneficial properties to the polyphenyl ether fluids, they may be used 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 we claim is:

1. A lubricant composition comprising a major amount of a polyphenyl ether having from 4 to 7 benzene rings and from 3 to 6 oxygen atoms and from 0.10% to 10% by weight, of the ether, of a compound of the formula



wherein R is a hydrocarbyl radical free of olefinic and acetylenic unsaturation and containing from 1 to 12 carbon atoms, n is a number of 2 to 3, m is a number of 1 to 2 and $m+n$ equals 4.

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2. The lubricant composition of claim 1, further characterized in that n is 3 and m is 1.

3. The lubricant composition of claim 1, further characterized in that n is 2 and m is 2.

4. A lubricant composition comprising a major amount of a polyphenyl ether having from 4 to 7 benzene rings and from 3 to 6 oxygen atoms and from 0.10% to 10% by weight, of the ether, of triaryltin thiocyanate having from 6 to 12 carbon atoms in each aryl radical.

5. The composition defined in claim 4 further limited in that the triaryltin thiocyanate is triphenyltin thiocyanate.

6. A lubricant composition comprising a major amount of a polyphenyl ether having from 4 to 7 benzene rings and from 3 to 6 oxygen atoms and from 0.10% to 10% by weight, of the ether, of a dialkyltin dithiocyanate having from 1 to 12 carbon atoms in each alkyl radical.

7. The composition defined in claim 6 further limited in

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that the dialkyltin dithiocyanate is dilauryltin dithiocyanate.

References Cited by the Examiner

UNITED STATES PATENTS

2,181,913	12/1939	Rosen	252—400 X
2,181,914	12/1939	Rosen	252—400 X
2,181,915	12/1939	Rosen	252—400 X
2,199,944	5/1940	Van Peski et al.	252—46.4
2,318,629	5/1943	Pruyton	252—46.4
3,006,852	10/1961	Barnum et al.	252—52

FOREIGN PATENTS

851,651 10/1960 Great Britain.

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