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LUBRICANT COMPOSITIONS

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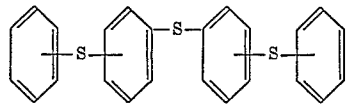
U.S. Cl. 252—48.2 8 Claims

ABSTRACT OF THE DISCLOSURE

A mixture of certain meta phenylene sulfides and oxysulfides in certain proportions useful as functional fluids such as lubricating oils and hydraulic fluids. The mixture may also contain certain polyphenyl ethers.

This invention relates to lubricant compositions comprising mixtures of aryl sulfides represented by the following formulae:

(a)



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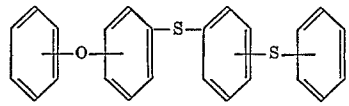

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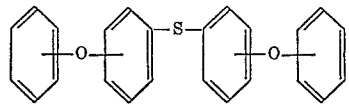


wherein the majority of the phenylene radicals of each compound are meta oriented.

In the past, hydrocarbon oils and later synthetic ester oils have been used as lubricants for various types of aircraft engines, including those engines known as turboprop engines. Preesnt design trends in aircraft engines, however, are to the pure jet type or turbofan. Aside from the mechanical differences in design between the turbofan and turboprop engines, there is a significant difference in the properties of the lubricants required for these engines, primarily because of increased operating temperatures. Furthermore, even within the area of turbofan engine design alone, there is a trend to increase the temperatures at which a lubricant must operate. As a result of these continually increasing operating temperatures, the synthetic ester oils have been found to be unsatisfactory as lubricants even though in some cases they are used simply because of the lack of any better lubricants.

Thus, the hydrocarbon oils are used for those applications where the maximum bulk oil temperature is in the range of about 200–275° F. and the ester oils for applications requiring bulk oil temperature of 275–400° F. Present temperature levels for turbofan lubricants are of the order of 400–450° F. (bulk oil temperature). However, it is evident that within the near future, temperatures of the order of 500° F or higher will be commonplace.

As the operating temperatures for lubricants have increased, it has become exceedingly difficult to find lubricants which properly function at these higher temperatures for any satisfactory lengths of time. Furthermore, it should always be realized that while the operating temperatures generally referred to are bulk oil temperatures, the actual temperatures at the points requiring lubrication exceed the bulk oil temperature and often times are one hundred to several hundred degrees higher.

In addition to the high temperature stability or durability problem, that is, the problem of finding a lubricant which will be thermally and oxidatively stable at temperatures as high as 500° F, the solution of this problem is further complicated by the fact that in order for a lubricant to be satisfactory for use in many aircraft engines, it must also be usable at temperatures as low as 20° F to 0° F. It is, therefore, evident that present trends require lubricants having not only an exceedingly wide liquid range but lubricants which are also thermally and oxidatively stable at quite high temperatures. Furthermore, present and future lubricants must, of course, possess at least adequate temperature viscosity properties and satisfactory lubricity, that is, the lubricants must not become too thin at the very high temperatures to which they are subjected nor must they become too thick at the lower temperatures and must at the same time be able to provide at least minimum lubricity over such range of temperatures. In general, such lubricants must also not be too volatile and even if somewhat volatile, must not, upon evaporation, leave any significant deposits to interfere with the proper operation of engine bearings. Other properties which must be possessed by satisfactory jet engine lubricants are low pour point, relatively high flash point and autogenous ignition temperatures and little or no corrosion towards metals.

Two of the most important properties for jet engine lubricants mentioned above are high temperature stability (thermal stability) and high temperature oxidative stability. High temperature and oxidative stability can be provided in at least two ways. Thus, a lubricant can be used which inherently possesses stability against degradation due to temperature and/or oxidation, or additives can be used which provide such stability. However, at temperatures much above 400° F., the stabilization of organic materials through the use of additives is exceedingly difficult, especially with present-day known additives. Above 400° F., for example, there is a drastic increase in the rate of oxidation and the ability of most compounds to prevent oxidation of organic materials rapidly decreases. In fact, many present-day additives which normally are considered to be oxidation stabilizers at lower temperatures reverse their roles at elevated temperatures and become pro-oxidants.

Another lubricating problem associated with present-day design and design trends in jet engines is that the increased thrust needed to obtain high speeds and altitudes results in further increases in not only operating temperatures but also higher bearing pressures.

A further problem in obtaining a lubricant which has good temperature properties is that those materials having a low crystallizing point also have a high evaporation rate at the temperatures of the order of 400° F.–500° F.

In summary, as discussed above, a satisfactory jet engine lubricant must possess a wide variety of properties. Furthermore, all of these properties are not only difficult to obtain in the same fluid, but some of them tend to be mutually exclusive.

It is, therefore, an object of this invention to provide novel functional fluid compositions having high temperature thermal and oxidative stability. It is a further object of this invention to provide novel compositions which also have wide liquid ranges without attendant high evaporation rates, which, therefore, makes them especially attractive for use as jet engine lubricants.

It is also an object of this invention to provide novel synthetic lubricant compositions which possess outstanding lubricating ability in addition to other very desirable properties. It is a further object of this invention to provide novel functional fluid compositions which are useful as electronic coolants, coolants and insulators for electric

power devices, e.g., transformers, atomic reactor coolants, diffusion pump fluids, damping fluids, bases for greases, force transmission fluids (hydraulic fluids) and as filter mediums for air conditioning systems. Other objects will become apparent to those skilled in the art from the following detailed description of this invention.

It has now been found that compositions comprising aryl sulfides represented by the above Formulae *a*, *b* and *c* have properties which make them well suited for the uses disclosed above and particularly those applications such as jet engine lubricants requiring thermal and oxidative stability and wide liquid range.

The individual compounds of the compositions of this invention are miscible with each other and therefore compositions of this invention can be prepared which vary from each other in specific properties such as viscosity and pour point. Thus, compositions of this invention can be prepared for any of the various uses mentioned above and, by varying the proportions of each component, an optimum combination of properties for each different use can be achieved.

It is to be understood that as used herein, the term "majority" is intended to mean above about 80% of the total number of linkages possible in the mixture and the term "minor amount" is intended to mean up to about 20% of the total number of linkages possible in the mixture. Thus, mixtures of compounds represented by the above Formulae *a*, *b* and *c* can contain minor amounts of ortho and para linkages. Those mixtures of compounds containing all meta linkages are preferred because of their lower crystallizing points. Accordingly, preferred compositions of this invention comprise mixtures of (1) bis(m-phenylmercaptophenyl) sulfide, (2) 3-phenoxy-3'-phenylmercaptodiphenyl sulfide and (3) bis(m-phenoxyphenyl) sulfide.

Compositions of this invention, particularly useful as jet engine lubricants, are prepared by combining the components designated (1), (2) and (3) above in the weight percent ranges of from about 1% to about 40% of (1), from about 40% to about 80% of (2) and from about 1% to about 40% of (3). More particularly, compositions comprising components (1), (2) and (3) in the weight percent range of from about 10% to about 30% of (1), from about 40% to about 80% of (2) and from about 10% to about 30% of (3) are preferred.

Compositions of this invention can be produced by blending the individual components together with adequate mixing to produce a homogeneous mixture or they can be prepared by reacting chlorophenyl phenyl sulfide and chlorophenyl phenyl ether wherein the majority of the halogen atoms are in the meta-position with sodium sulfide in mol ratios of about 1–2:1–2:1.5–2, respectively, as exemplified in Example 1 below wherein parts are parts by weight.

EXAMPLE 1

Into a suitable reaction vessel there were charged a mixture of 90 parts of m-chlorophenyl phenyl ether, 79.4 parts of m-chlorophenyl phenyl sulfide, 61.4 parts of 61% sodium sulfide hydrate and 260 parts of N-methylpyrrolidone. The resulting mixture was heated to 210° C, water and low boilers being collected as the temperature rose. The reaction mixture was held at 210–215° C. for 16 hours, the solvent was then distilled and water was added. The organic layer was separated, washed with water and distilled, yielding 100 parts of product which boiled at 200–250° C. (0.1 mm.). The product was a mixture comprised by weight of 28% bis(m-phenylmercaptophenyl) sulfide, 50% of 3-phenoxy-3'-phenylmercaptodiphenyl sulfide and 22% of bis(m-phenoxyphenyl) sulfide.

The individual components of the compositions of this invention can be prepared by reacting an alkali metal salt of a thiophenol or phenol with a suitable halide in a suitable carboxamide solvent such as N,N'-dimethylacetamide or N-methyl-2-pyrrolidone at temperatures of the order of 100° C.–250° C. but preferably 160° C.–230° C. The individual components of the compositions of this invention can also be prepared by the Ullman synthesis by reacting an alkali metal phenate or thiophenate and a suitable halide in the presence of copper at temperatures in the order of 180° C. to 260° C.

The preparation of the individual components of the compositions of this invention is illustrated by the following non-limiting examples.

EXAMPLE 2

Preparation of bis(m-phenylmercaptophenyl) sulfide

Into a suitable reaction vessel fitted with agitation means, means for measuring reaction mass temperatures and vapor temperatures, heating means, reactant and product inlets and outlets and also fitted with a reflux condenser, there were charged a mixture of 44 grams of thiophenol and 26 grams of 86% potassium hydroxide in 150 ml. of dimethylacetamide. The mixture was heated to obtain the potassium salt of thiophenol and to drive off water of reaction. The mixture was cooled to about 120° C. and 59.2 grams of bis(m-bromophenyl) sulfide were charged and the resulting mixture heated at 165° C–170° C. for about 14 hours. The reaction mass was then allowed to cool to room temperature and then washed with 200 ml. of 12.5% sodium hydroxide. The organic layer was separated, diluted with benzene, then washed with water and dried under vacuum. The residue solidified and was crystallized from an isopropanol benzene mixture to give bis(m-phenylmercaptophenyl) sulfide.

EXAMPLE 3

Preparation of 3-phenoxy-3'-phenylmercaptodiphenyl sulfide

Into a suitable reaction vessel there were charged 14 ml. of water and 70 grams of 85% potassium hydroxide and the resulting mixture was heated to 110° C., after which there was added 125 grams of phenol. Then, 15 ml. of toluene was added and the water removed by azeotropic distillation until a pot temperature of 265° C. was reached. The reaction mass was then cooled to 240° C. and 2 grams of cupric chloride were added. The reaction mass was then heated slightly as 329 grams of m-(m-phenylmercaptophenylmercapto)phenyl chloride was slowly added. The reaction mass was then heated at 255° C.–260° C. for about 6 hours and quenched. An aqueous layer was then separated, extracted with toluene and the extract combined with the organic layer. The organic material was extracted with water, filtered, and the toluene stripped to give 233 grams of 3-phenoxy-3'-phenylmercaptodiphenyl sulfide, which had a boiling range of 236° C.–240° C. at 0.1 mm. of mercury.

EXAMPLE 4

Preparation of bis(m-phenoxyphenyl) sulfide

Following the procedure set forth in Example 1, 163.5 parts of m-chlorophenyl phenyl ether was reacted with 61.4 parts of 61% sodium sulfide hydrate in 260 parts of N-methylpyrrolidone to produce bis(m-phenoxyphenyl) sulfide.

The following example is included to demonstrate the manner of preparing a composition of the invention comprising a mixture of compounds containing a majority of meta linkages.

EXAMPLE 5

Following the procedure set forth in Example 1, a mixture of 397.3 parts of m-chlorodiphenyl sulfide, 452.4 parts of an isomeric mixture of chlorodiphenyl ether containing about 80% by weight, of the all meta isomer, the remainder being the ortho and para isomers, 309 parts of 61% sodium sulfide hydrate and 1250 ml. of N-methylpyrrolidone was reacted to produce, upon fractionation, a main fraction containing, by weight, about

22% bis(m-phenoxyphenyl) sulfide, 2.05% 3-phenoxy-4'-phenoxy diphenyl sulfide, 45% m-phenoxyphenyl-m-phenylmercaptophenyl sulfide, 1.6% m-phenylmercaptophenyl-p-phenoxyphenyl sulfide, 28.25% bis(m-phenylmercapto) sulfide and about 1.1% of higher boiling materials.

The individual compounds represented by the above formulas have many properties needed for a jet engine lubricant. On the other hand, each has some deficiency which can be cured by combining them to form compositions of this invention.

Some of the properties often measured in determining the suitability of a fluid as a jet engine lubricant and the method used for such determination include the following:

Property	Method
Viscosity	ASTM D-445-61.
Pour point	ASTM D-97.
Evaporation loss	ASTM D-972 (modified as to temperature).
Oxidation and corrosion (O and C)	Federal Test Method Standard 791, Method 5208.4 (modified as to temperature).

In addition, the solution point of the composition of this invention was also measured. Because the compositions of the instant invention are mixtures having wide melting points ranges, solution points were determined.

Solution points were determined by placing a test composition in a jacketed tube provided with an agitator and, with the agitator running, circulating throuugh the jacket, a cooling solution held a temperature of 16–23° F. This temperature range was considered high enough to prevent a glass from forming and low enough to speed up potential crystallization. After a test composition had been agitated for about a day, seeds of one of the components were added. Those mixtures which did not crystallize after one week were warmed to room temperature to make the fluids pourable and were transferred to small bottles with lids. The bottles were then placed in cold storage at 0° F. and −30° F. In either case, upon the inducement of crystallization, the container was heated gradually with agitation and the temperature noted at which the last crystal dissolved. Using the aforedescribed tests and procedures, properties of various compounds utilized herein were determined and such properties are set forth in Table I, below.

TABLE I

Property	Bis(m-phenylmercaptophenyl) sulfide	3-phenoxy-3'-phenylmercapto diphenyl sulfide	Bis(m-phenoxyphenyl) sulfide
Viscosity cs.:			
210° F	6.19	6.24	6.03
100° F	60.37	62.5	62.23
Melting point, ° C	56	−4	27–29
Evaporation loss 6½ hrs. at 500° F., percent	8	16.4	32.4
Lubricity, shell 4-ball wear at 15 minutes, 400° F., 1,200 r.p.m. steel on steel:			
40 kg. load	1.39	1.14	.930
50 kg. load	1.35	.86	.967

There are obviously many criteria by which particular compositions can be judged in terms of whether they are improved as compared to the components of such compositions. Furthermore, different criteria will be used as between different specific applications. For example, it can be said that all jet engine lubricants should have good high temperature stability yet a specific application of a jet engine lubricant may also require a solution point of at most 50° F., whereas a different application may specify an evaporation loss no greater than 25%; another application may require fairly high extreme pressure lubricating ability and a still different application may emphasize viscosity characteristics. Also, many applications will require a combination of properties. Of course, in all such different applications, the unemphasized properties will still have to meet some minimum standard. As a result of the situation just described, it is often difficult and sometimes impossible to provide lubricant compositions with all the properties envisioned by an engine manufacturer. The compositions finally selected for a given application are, therefore, often a compromise with respect to some properties.

The present invention provides compositions which have at least one improved property as compared to some property of the individual components of such compositions which makes such compositions better suited for various applications, and particularly as jet engine lubricants.

Some properties of a typical composition of this invention are listed below in Table II. A mixture produced according to Example 1 above was used and the various properties were determined as described above.

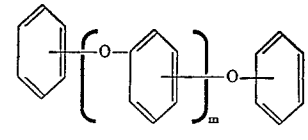
TABLE II

Property:	Result
Viscosity, cs.:	
210° F.	6.1
100° F.	5.9
Solution point, ° C.	28
Pour point, ° F.	5
Evaporation loss (6½ hrs. at 500° F.; 760 mm.) percent	16.9
Lubricity, shell 4-ball wear @ 15 minutes, 400° F., 1,200 r.p.m., steel on steel:	
40 kg. load	.913
50 kg. load	.992
O and C test 500° F.:	
Viscosity change, 100° F. percent	2.2
Copper corrosion, mg./cm.²	−1.94

From the foregoing, it is evident that the present invention provides those working in the art with novel compositions suitable for many uses and particularly useful as jet engine lubricants. In addition, it is evident that the compositions of this invention possess unique properties as well as unique combinations of properties.

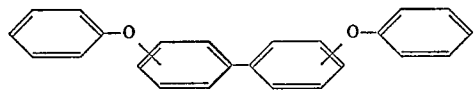
Although the compositions described above are generally quite suitable for most applications, it may also be desirable to add small amounts of various other functional addition agents such as viscosity index improvers, e.g., a polymerized methacrylate ester, an alkylated polystyrene, or the polyether condensation products of ethylene oxide or propylene oxide, or both, with a glycol such as ethylene glycol, propylene glycol, butanediol, etc., or with an aliphatic alcohol such as butanol, octanol, decanol, tridecanol, etc., pour point depressants, oxidation inhibiting agents, anti-wear and lubricity agents, antifoaming agents such as the silicone polymers, and the like.

While this invention has been described with respect to certain embodiments, it is to be understood that it is not so limited in that variations and modifications thereof obvious to those skilled in the art may be employed without departing from the spirit and scope of this invention. Thus, for example, the compositions of this invention, in addition to the compounds represented by Formulae (*a*), (*b*) and (*c*) above, can contain from about 25% to about 75, by weight, of four- and five-ring polyphenyl ethers which can be represented by the formula

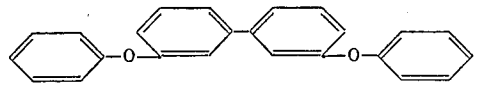


where *m* is 2 or 3, such as bis (m-phenoxyphenyl) ether, m-phenoxyphenyl p-phenoxyphenyl ether, m-bis(m-phenoxyphenoxy)benzene, m - [(m - phenoxyphenoxy)(p-phenoxyphenoxy)]benzene, p-[(p-phenoxy-phenoxy)(m-

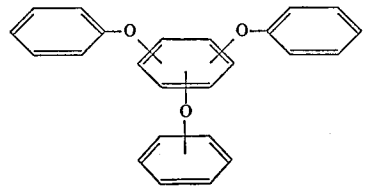
phenoxyphenoxy)]benzene, p-bis(m-phenoxyphenoxy) benzene, m-(p-phenoxyphenoxy)benzene and o-bis(m-phenoxyphenoxy)benzene, by the formula



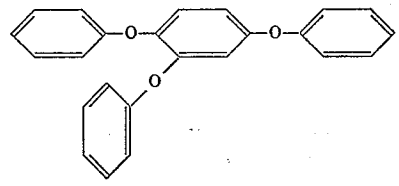
such as 3,3'-bisphenoxy biphenyl



and by the structure



such as 1,2,4-triphenoxybenzene



and mixtures and combinations of (*a*) through (*c*).

Thus, it is contemplated that mixtures of the polyphenyl ethers described above (*c*) can be utilized to provide the compositions of this invention. For example, mixtures of polyphenyl ethers in which the non-terminal phenylene rings are linked through oxygen atoms in the meta and/or para positions, have been found to be particularly suitable. An example of such preferred polyphenyl ether compositions are those containing, in percent by weight, from about 0 to 6% of o-bis(m-phenoxyphenoxy)benzene (1), about 40 to 85% of m-bis(m-phenoxyphenoxy)benzene (2), about 0 to 40% of m-[(m-phenoxyphenoxy)(p-phenoxyphenoxy)]benzene (3), about 0 to 12% of p-bis(m-phenoxyphenoxy)benzene (4), about 0 to 10% of p-[(p-phenoxyphenoxy)(m-phenoxyphenoxy)]benzene (5), and about 0 to 6% of m-bis(p-phenoxyphenoxy)benzene (6). Typical compositions of such preferred compositions are listed below. The number in parentheses refers to the compound mentioned above having the same number thereafter.

TYPICAL COMPOSITIONS

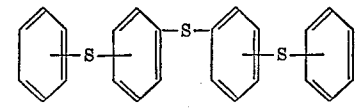
Component	Compositions, percent by weight of components			
	A	B	C	D
(1)	0	6	5	4.5
(2)	63	82	80	43.5
(3)	31	0	4	40
(4)	0	12	11	4
(5)	0	0	0	8
(6)	6	0	0	0

Particularly useful compositions can be made by adding to compositions of this invention a mixture of polyphenyl ethers consisting, by weight, of about 65% m-bis(m-phenoxyphenoxy)benzene, about 30% m-[(m-phenoxyphenoxy)(p-phenoxyphenoxy)]benzene and about 5% m-bis(p-phenoxyphenoxy)benzene.

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

1. A composition comprising a mixture of aryl sulfides represented by the formulae:

(a)



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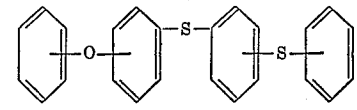

and

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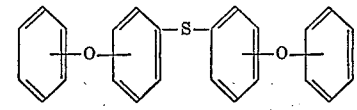


wherein the majority of the phenylene radicals of each sulfide are meta oriented, and the weight percent ranges of (a), (b) and (c) are about 10–30:40–80:10–30, respectively.

2. A composition of claim **1** wherein (a) is bis(m-phenylmercaptophenyl) sulfide.

3. A composition of claim **1** wherein (b) is 3-phenoxy-3'-phenylmercaptodiphenyl sulfide.

4. A composition of claim **1** wherein (c) is bis(m-phenoxyphenyl) sulfide.

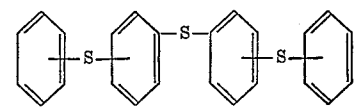
5. A composition of claim **1** wherein (a) is bis(m-phenylmercaptophenyl) sulfide, (b) is 3-phenoxy-3'-phenylmercaptodiphenyl sulfide and (c) is bis(m-phenoxyphenyl) sulfide.

6. A composition of claim **5** wherein the weight percent range of (a), (b) and (c) are 25–35:45–55:15–25 respectively.

7. A composition comprising:

(A) a mixture of aryl sulfides represented by the formulae

(a)



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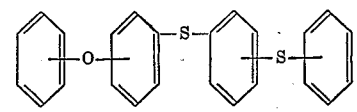
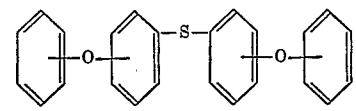


and

(c)



wherein the majority of the phenylene radicals of each sulfide are meta oriented, and the weight percent ranges of (a), (b) and (c) are about 10–30:40–80:10–30, respectively; and

(B) polyphenyl ethers selected from the group consisting of four- and five-ring polyphenyl ethers and mixtures thereof, wherein B comprises from about 25% to about 75%, by weight, of the total composition.

8. A composition of claim **7** wherein B is a mixture consisting of, by weight, about 65% m-bis(m-phenoxy-

phenoxy)benzene, about 30% m-[(m-phenoxyphenoxy)(p-phenoxyphenoxy)]benzene and about 5% m-bis(p-phenoxyphenoxy)benzene.

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U.S. Cl. X.R.

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