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FUNCTIONAL FLUID COMPOSITIONS

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This 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, 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.

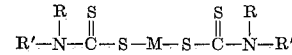
As is known in the art, petroleum lubricants generally comprise, in addition to the petroleum base stock, additives or adjuvants which impart specifically desired properties to the base stock, e.g., rust-inhibitors, antioxidants, extreme pressure-resisting agents, lubricity improvers, detersives, etc. 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 compositions, 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 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 chainge 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.

The polyphenyl ethers, like conventional petroleum lubricants, are also 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. 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.

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. Still another object of the invention is the provision of polyphenyl ether compositions having improved lubricity. A further object is the provision of polyphenyl ether compositions 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 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 as additive for the polyphenyl ether liquid fluids a heavy metal bis(N,N-diorganodithiocarbamate) of the formula

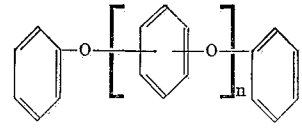


in which R and R′ individually are hydrocarbon radicals which are free of olefinic and acetylenic unsaturation and contain from 1 to 12 carbon atoms and together complete with the nitrogen to which they are attached, a saturated heterocyclic ring of from 5 to 6 members and from 4 to 10 carbon atoms, and M is a bivalent heavy metal ion.

Compounds of the above formula in which R and R′ are hydrocarbon are metal bis(N,N-dialkyldithiocarbamates), or bis(N,N-diaryldithiocarbamates), or bis[N,N-bis(aralkyl)dithiocarbamates], or bis[N,N-bis(alkaryl)dithiocarbamates], or bis(N,N-dicycloalkyldithiocarbamates), or bis(N-alkyl-N-aryldithiocarbamates), or bis(N-alkyl-N-aralkyldithiocarbamates), or bis(N-aryl-N-aralkyldithiocarbamates), or bis(N-alkaryl-N-cycloalkyldithithiocarbamates), etc.; i.e., the R and R′ of the above formula may be alkyl, aryl, aralkyl, alkaryl or cycloalkyl, and they may be the same or different. When taken together with the nitrogen atom to which they are attached, R and R′ complete a saturated heterocyclic nitrogen ring of from 5 to 6 members, e.g., the pyrrolidine, piperidine, morpholine, pyrazolidinedione, or thiomorpholine ring, etc.

The heavy metal ion may be, e.g., bivalent zinc, cadmium, mercury, indium, gallium, germanium, tin, lead, vanadium, chromium, molbydenum, tungsten, platinum, manganese, iron, cobalt, silver, nickel, etc. The bivalent heavy metal ions of Groups I–IV and VII–VIII are preferred.

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

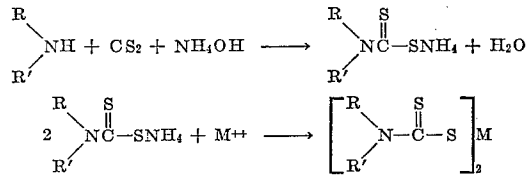


where *n* is a whole number from 2 to 5. The preferred polyphenyl ethers are those having all their ether linkages in the meta position since the all-meta linked ethers are the best suited for many applications because of their

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 posses 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, 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 presently useful metal diorganodithiocarbamates may be readily prepared, e.g., by reaction of a secondary amine with carbon disulfide and ammonium hydroxide or alkali metal hydroxide to obtain the ammonium or alkali metal salt and then reacting two moles of said salt with one mole of a metal salt, e.g., the acetate, thus:



where R and R′ individually denote a hydrocarbon radical which is free of olefinic and acetylenic unsaturation and taken and taken together complete, with the nitrogen to which they are attached, a heterocyclic ring of from 5 to 6 members, and M is a bivalent metal cation. Operating in this manner are obtained, e.g., the following presently useful compounds:

Copper bis(N,N-dibutyldithiocarbamate), green black needles, M.P. 67–71° C.
Cobalt bis(N,N-dibutyldithiocarbamate), deep green plates, M.P. 127–131° C.
Nickel bis(N,N-dibutyldithiocarbamate), olive drab plates, M.P. 82–84° C.
Copper bis(N,N-diphenyldithiocarbamate), brown powder, M.P. 300–304° C.
Cobalt bis(N,N-diphenyldithiocarbamate), green powder, M.P. over 340° C.
Nickel bis(N,N-diphenyldithiocarbamate), pea-green powder, M.P. 290–315° C.
Copper bis(morpholinodithiocarbamate), dark brown powder, M.P. 310° C.
Cobalt bis(morpholinodithiocarbamate), green powder, M.P. 290° C.
Nickel bis(morpholinodithiocarbamate), pea-green powder, M.P. 345° C.
Copper bis(piperidinodithiocarbamate), dark brown powder, M.P. 210° C.
Cobalt bis(piperidinodithiocarbamate), green powder, M.P. 250–252° C.
Nickel bis(piperidinodithiocarbamate), pea-green powder, M.P. 289–295° C.
Manganous bis(piperidinodithiocarbamate), M.P. 162–190° C.

Other presently useful diorganodithiocarbamates are, e.g.,

Zinc bis(N,N-dioctyldithiocarbamate),
Tin bis(N,N-dibenzyldithiocarbamate),
Nickel bis(N,N-didodecyldithiocarbamate),
Iron bis(N,N-di-4-tolyldithiocarbamate),
Cobalt bis(N,N-dicyclopentyldithiocarbamate),
Copper bis[N,N-bis(2-phenylethyl)dithiocarbamate],
Cadmium bis(N-ethyl-N-phenyldithiocarbamate),
Silver bis(N-cyclohexyl-N-phenyldithiocarbamate),
Nickel bis(N,N-di-α-naphthyldithiocarbamate),
Tungsten bis(N,N-dimethyldithiocarbamate),
Indium bis(N,N-dixylyldithiocarbamate),
Mercury bis[N,N-bis(4-isopropylphenyl)dithiocarbamate],
Gallium bis[N-hexy-N-(2-methylcyclopentyl)dithiocarbamate],
Molybdenum bis(N-benzyl-N-phenyldithiocarbamate),
Manganese bis(N,N-dipentyldithiocarbamate),
Germanium bis(N,N-difluorenyldithiocarbamate),
Chromium bis(N,N-dihexyldithiocarbamate),
Platinum bis(N,N-diisopropyldithiocarbamate),
Nickel bis(N,N-diacenaphthenyldithiocarbamate),
Copper bis[N,N-bis(tetrahydronaphthyldithiocarbamate),
Cobalt bis(N,N-dipyrrolidinodithiocarbamate),
Indium bis(N,N-dithiomorpholinodithiocarbamate),
Nickel bis[N,N-bis(3,5-dioxopyrazolidino)dithocarbamate],
Cadmium bis(N,N-dimorpholinodithiocarbamate,
Copper bis(N-phenyl-N-piperidinodithiocarbamate).

The metal diorganodithiocarbamates are combined with the fluid polyphenyl ethers to the extent of 0.5% to 5.0% by weight, depending upon the nature of the dithiocarbamate and of the ether fluid and upon the adjuvant effect desired. The heavy metal diorganodithiocarbamates generally have a beneficial effect on the polyphenyl ether in that there is obtained improvement in stability to oxidation and/or increased lubricity and/or increased resistance to wear and extreme pressure. All of these benefits do not necessarily result from the use of one additive, although a number of these compounds do confer a plurality of such effects when employed with the ethers within the above-stated range of concentration. Whether or not a desired adjuvant 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 is also not 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 not limited to, the following examples:

Example 1

The antioxidant effect of some metal bis(N,N-diphenyldithiocarbamates) on a polyphenyl ether fluid was determined by bubbling air through a 20 milliliter sample at 600° F. for 48 hours and then 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 the presence of metals also has 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, steel, 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. Using weighed pieces of metal, the anti-corrosive effect of the additive could also be obtained.

Each of the dithiocarbamates shown below was tested for use as antioxidant at the indicated concentration, for 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 following results were obtained:

Metal bis(N,N-diphenyldithiocarbamate)	Con'cn, wt. Percent	Viscosity Increase, Percent	
		No Wires	With Wires
None	----------	108.57	70.15
Nickel	1.0	53.26	50.86
Copper	0.5	29.42	28.31
Cobalt	0.5	11.66	13.62

Example 2

Employing the testing procedure of Example 1, except that air-flow was conducted for only 24 hours, antioxidant activity was determined for the dithiocarbamates shown below. The percent increases in viscosity in the absence or presence of the copper, aluminum, and steel wires, using the mixture of polyphenyl ethers described in Example 1 at the indicated concentration of the dithiocarbamate were found to be as follows:

Additive	Con'cn, wt. Percent	Viscosity Increase, Percent	
		No Wires	With Wires
None	----------	60.15	44.03
Cu bis(N,N-dibutyldithiocarbamate)	1.0	25.1	25.9
Co bis(N,N-dibutyldithiocarbamate)	1.0	19.4	18.8
Ni bis(N,N-dibutyldithiocarbamate)	1.0	----------	27.0
Co bis(piperidinodithiocarbamate)	0.5	22.44	22.44
Cu bis(piperidinodithiocarbamate)	0.5	22.11	26.46
Co bis(morpholinodithiocarbamate)	0.5	19.84	21.69

Example 3

In this example, nickel bis(N,N-di-n-butyldithiocarbamate) was tested at a 1.0 percent by weight concentration as an intioxidant for a mixture of polyphenyl ethers consisting about 90 percent by weight of ethers containing 5 benzene rings and 4 oxygen atoms, with the balance being ethers containing 4 benzene rings and 3 oxygen atoms. Testing was conducted at 600° F., as in Example 1, except that there were used only copper, aluminum and iron wires. There was thus obtained a viscosity increase of only 0.16% for the test specimen containing the dithiocarbamate as compared to 26.9%, the viscosity increase of the polyphenyl ether mixture, alone.

Example 4

The anti-wear and extreme pressure lubrication characteristics of copper bis(N,N-dibutyldithiocarbamate) in polyphenyl ether fluids 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 4-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 4-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 immersion in the fluid under test, which is held in a cup surrounding the 4-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 copper bis(N,N-dibutyldithiocarbamate) with the polyphenyl ether mixture of Example 2, there was obtained a scar diameter of 0.99 mm. at 167° F. and 40 kg., as compared to 1.82 mm., the similarly obtained value for the mixture of ethers in the absence of an additive.

The weld point of the balls was determined by having them immersed in the test lubricant [the polyphenyl ether of Example 1 containing 1.0 weight percent of copper bis(N,N-dibutyldithiocarbamate)] and gradually increasing the load on the balls by increments of 10 kg. until the balls were welded together in a one minute test period. A value of 310 kg. was obtained as against 150 kg. for the mixture of ethers, alone.

The polyphenyl ether fluid containing copper N,N-dibutyldithiocarbamate as additive was also submitted to the Falex antiweld test [see, e.g., the articles by V. A. Ryan in "Lubrication Engineering," September 1946, and by S. Kyropoulos in "Refiner Natural Gasoline Mfr.," 18, 32–24 (1939)]. In this procedure, there was employed a Faville-Le Vally Falex lubricant testing machine with heating element, 4,500 lb. pressure gage indicating bearing loads, calibrated, circular, toother loader capable of providing wear estimates, and torque indicating gage. The machine is essentially a device in which a pin is rotated between two V-shaped bearing blocks which are immersed in an oil cup containing 55 ml. of the lubricant which is to be tested. The bearing blocks are inserted in self-aligning recesses in the short lever arms, or jaws, of the loading-applying mechanism. Pressure is applied through the loading mechanism which fits loosely over the bifurcated ends of the long lever arms. The ratchet wheel is turned up by hand until the loading mechanism takes hold, which is indicated by registration of applied load on its attached gage. Additional load is applied by engaging the load applying arm with the ratchet wheel. The eccentric motion of the load applying arm increases the application of load, one tooth at a time. The entire mechanism is free to swing about its axis, this tendency to turn being resisted by the syphon operated gage which registers torque in pound-inches. In the present test, the machine was operated at 290 r.p.m.

The Falex test value for the mixture of polyphenyl ethers of Example 1 containing 1.0 percent by weight of copper bis(N,N-dibutyldithiocarbamate) was 2250, whereas that for said ether mixture alone was 500.

The metal bis(diorganodithiocarbamates) 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, 2 and 4, the polyphenyl ether component may be any one polyphenyl ether having from 4 to 7 benzene rings. For example, the copper bis(N,N-diphenyldithiocarbamate) of Example 1 or the cobalt bis(N,N-dimorpholinodithiocarbamate) of Example 2 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 present metal bis(N,N-diorganodithiocarbamates) with respect to increasing stability to oxygen and/or film strength under conditions of high pressure at high temperatures, mixtures having varying proportions of the ethers are advantageously modified.

It is evident from the data presented above that addition of the present dithiocarbamates to the polyphenyl ethers results in one or more beneficial effects, i.e., there is brought about increased resistance to oxygen and/or improvement in stability at operating conditions involving high pressure and temperature. At the same time, there may be generally decreased attack to metal so that anticorrosive effect is often demonstrated.

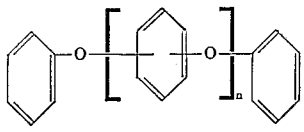
Since the quantity of the metal bis(N,N-diorganodithiocarbamate) which is employed with the polyphenyl ether fluid will vary with adjuvant effect sought, with the nature of the polyphenyl ether and the nature of the individual adjuvant, it is evident that no rigid limits of adjuvant content can be set forth. For many purposes, particularly for antioxidant and anti-corrosive effects, very low quantities, say, quantities of as low as 0.01% by weight based on the weight of the polyphenyl ether fluid, are satisfactory. For other purposes, e.g., extreme pressure-resisting effect, higher concentrations will be more advantageous. Generally, polyphenyl ether compositions comprising from 0.01% to 10% by weight of the present additive demonstrate adjuvant effect. At concentrations of up to 10%, optimum improvement of the polyphenyl ethers is obtained with respect to antioxidant and lubricity and solubility of the additive in the polyphenyl ethers is generally realized. 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 dithiocarbamate 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 organometallic compounds hereinbefore defined and the polyphenyl ether fluid consists of polyphenyl ethers having from 4 to 7 benzene rings.

Although the metal bis(N,N-diorganodithiocarbamates) 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.

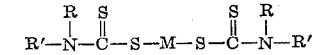
Other modes of applying the principles of this invention may be employed instead of those specifically set forth above, changes being made as regards the details herein disclosed, provided the elements set forth in any of the following claims, or equivalents thereof may be employed.

What we claim is:

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



wherein *n* is a whole number of from 2 to 5 and from 0.01% to 10%, by weight of the ether, of a dithiocarbamate of the formula



in which R and R′ individually are hydrocarbon radicals which are free of olefinic and acetylenic unsaturation and contain from 1 to 12 carbon atoms and together complete, with the nitrogen to which they are attached, a saturated heterocyclic ring of from 5 to 6 members in the ring and a total of from 4 to 10 carbon atoms, and M is a bivalent heavy metal ion.

2. The composition defined in claim **1**, further limited in that the dithiocarbamate is cobalt bis(N,N-diphenyldithiocarbamate).

3. The composition defined in claim **1**, further limited in that the dithiocarbamate is copper bis(N,N-diphenyldithiocarbamate).

4. The composition defined in claim **1**, further limited in that the dithiocarbamate is nickel bis(N,N-diphenyldithiocarbamate).

5. The composition defined in claim **1**, further limited in that the dithiocarbamate is copper bis(N,N-dibutyldithiocarbamate).

6. The composition defined in claim **1**, further limited in that the dithiocarbamate is cobalt bis(N,N-dibutyldithiocarbamate).

7. The composition defined in claim **1**, further limited in that the dithiocarbamate is cobalt bis(piperidinodithiocarbamate).

8. The composition defined in claim **1**, further limited in that the dithiocarbamate is cobalt bis(morpholinodithiocarbamate).

9. The composition defined in claim **1**, further limited in that the dithiocarbamate is copper bis(piperidinodithiocarbamate).

10. The composition defined in claim **1**, further limited in that the dithiocarbamate is nickel bis(N,N-dibutyldithiocarbamate).

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