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LUBRICATING OIL

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5 Claims. (Cl. 252—48)

This invention relates to an improved lubricating oil adapted for use in internal combustion engines and particularly to a lubricating oil having one or more additives incorporated therein.

It is generally conceded that in the recent development of internal combustion engines, and particularly engines designed for heavy-duty service, the increase in operating temperatures, together with the reduction of clearances and the use of hard bearing alloys, such as copper-lead, cadmium-silver, etc., have set up such severe operating conditions as to necessitate an improvement in the highly solvent-refined mineral oils refined for use as crankcase lubricants. These rigorous operating conditions, which are most prevalent in Diesel and gasoline engines used in heavy duty bus and tractor service, have seriously accentuated such problems as corrosion, oxidation and resin formation in the solvent-refined mineral lubricating oils with the resultant deleterious effect on the efficiency of the engines. The nature and extent of these problems depend upon the conditions of operation of the particular engine type, the type and extent of refining of the base oil used, and numerous other factors.

The tendency of mineral lubricating oils to deposit gums, resins, soot and varnish-like materials about the valves, rings, pistons, cylinders and other engine parts can be largely overcome by the addition of certain types of additive ingredients which possess detergent properties when dissolved or dispersed in mineral lubricating oils. By detergent properties is meant not only that property which aids in dispersing, removing or purging foreign materials which accumulate on the surface of the engine parts, but also that property which prevents the accumulation or deposition of such materials, as distinguished from solvent action upon these accumulations or deposits.

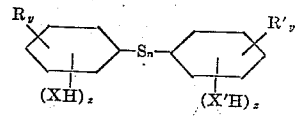
In addition thereto the added tendency of these oils to corrode the metal surfaces with which the lubricating oil comes in contact may be overcome or reduced by the addition of additive components which possess anti-oxidant or anti-corrosive properties when dissolved or dispersed in mineral lubricating oils. These anti-oxidant or anti-corrosive properties are meant to include all such properties which effect a reduction or elimination of weight loss of the lubricating metal surfaces, particularly bearing surfaces, which results from the corrosive action of the mineral lubricating oil.

It is the object of the present invention to provide a mineral oil composition which possesses the above-mentioned detergent and anti-oxidant or anti-corrosive properties by incorporating in a mineral lubricating oil a novel additive ingredient of multi-functional activity.

A further object of this invention is to provide a mineral oil composition possessing detergent properties and enhanced anti-oxidant or anti-corrosive properties by combining with the above-mentioned multi-functional additive an auxiliary additive ingredient and incorporating the combination in a mineral lubricating oil.

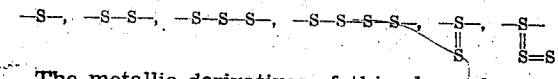
The invention is based upon the discovery of a novel class of multi-functional additives which may be broadly described as oil-soluble or oil-miscible metal derivatives of alkyl-substituted aryloxy or arylthio-oxy sulfides. It has been found that when small proportions of a compound within the scope of the above general class are blended with a mineral lubricating oil, a mineral oil composition is formed possessing excellent detergent and anti-oxidant or anti-corrosive properties.

Specifically, the compounds of the present invention may be described as oil-soluble or oil-miscible metal salts of the class of compounds having the structure:

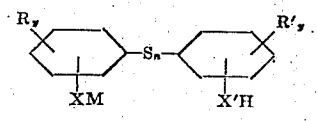


in which R and R' represent alkyl, aralkyl, cycloalkyl or naphthenyl radicals, the alkyl portion of which contains at least 5 carbon atoms. R' is preferably the same as R, but may also be a different radical, within the above group. X and X' represent either an oxygen or sulfur atom, and n, y, z are integers of 1 or more. n and y are usually 1, 2, 3 or 4, while z is usually 1, 2, or 3. Either or both of the aromatic nuclei diagrammatically shown may be substituted by a naphthyl, anthracyl or other condensed aromatic nuclei. The positions of the substituent in the formula are purely diagrammatic and may be connected to any position in the aromatic nuclei. The sulfide bond between the nuclei represented

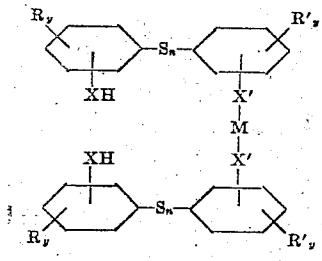
by S_n may be any one of the following structural groups.



The metallic derivatives of this class of compounds, in which the hydrogen of the hydroxyl (OH) or sulphydryl group (SH), illustrated above as XH and X'H respectively, is replaced by a metal, include any of the following metals or combinations thereof: sodium, potassium, calcium, barium, strontium, magnesium, aluminum, tin, iron, cobalt, nickel, copper, manganese and chromium. These derivatives also include the partial derivatives wherein the hydroxyl or sulphydryl groups are only partially converted into their metallic salts as follows:



(where M is a monovalent metal), and



(where M is a divalent metal).

As illustrative of the specific compounds whose oil-soluble metallic derivatives fall within the scope of the present invention, the following list of compounds is presented:

Di (pentadecylphenol) disulfide
Di (octylphenol) disulfide
Di (tridecylphenol) sulfide
Di (tridecylphenol) polysulfide
Di (octadecylphenol) trisulfide
Di (diamylphenol) disulfide
Di (dioctylphenol) sulfide
Octylphenol-amylphenol sulfide
Cetylnaphthol-isoamylphenol trisulfide
Di (o-phenylphenol) sulfide
Di (p-phenylphenol) disulfide
Di (p-phenylphenol) polysulfide
Di (o-benzylphenol) sulfide
Di (p-benzylphenol) disulfide
Di (amylresorcinol) sulfide
Di (octylpyrogallol) sulfide
Di (o-cyclohexylphenol) disulfide
Di (p-cyclohexylphenol) polysulfide
Di (o-cyclohexylphenol) sulfide
Di (naphthenylphenol) sulfide
Di (naphthenylphenol) disulfide
Di (pentadecyl-thiophenol) sulfide
Di (tridecyl-thiophenol) disulfide
Di (octyl-thiophenol) polysulfide
Di (o-cyclohexyl-thiophenol) disulfide
Di (p-benzyl-thiophenol) disulfide
Di (o-phenyl-thiophenol) disulfide
Di (naphthenyl-thiophenol) disulfide

The following examples illustrate suitable methods for preparing the above-described multi-functional additives:

Example I

34 grams of sulfur monochloride (0.25 mol) in a carbon disulfide solution were added to a carbon disulfide solution of 138 grams of tridecyl phenol (0.5 mol) with stirring. After the spontaneous evolution of hydrogen chloride had ceased, the reaction mixture was heated on a steam bath at 70–80° C. for two days to evaporate the solvent and residual hydrogen chloride. 152 grams of di (tridecylphenol) disulfide, which appeared as a dark oil, were obtained.

Example II

75.4 grams of di (tridecylphenol) disulfide were added to a solution of calcium ethylate made from 8.8 grams of calcium in 100 cc. absolute alcohol. The mixture was stirred for two hours at 75–80° C., then freed of solvent by heating at 80–85° C. in vacuo. The residual calcium salt was an oil-soluble dark, sticky mass, which gave the following analysis:

	Per cent
Ash	18.6
Sulfur	6.9
Free sulfur	0.86

Example III

To 700 grams of polymer phenol (hydroxyl No. 166), prepared by the alkylation of phenol with a mixture of olefins (bromine No. 129), with a boiling range of 350–450° F., which was separated from the raw polymer fraction from the catalytic polymerization of gasoline, was added an equal volume of carbon disulfide. A solution of 135 grams of sulfur monochloride in an equal volume of carbon disulfide was added portionwise to the solution of polymer phenol at room temperature while stirring. The resulting solution was maintained at room temperature until the spontaneous evolution of hydrogen chloride gas had ceased, then warmed gently on a steam bath to evaporate off the solvent, unreacted sulfur monochloride, and residual hydrogen chloride. The resulting di (polymer phenol) disulfide appeared as a dark residue and gave the following analysis:

	Per cent.
Total sulfur	8.13
Free sulfur	Trace

Example IV

In the preparation of a partially converted barium salt of di (polymer phenol) disulfide, 100 grams of di (polymer phenol) disulfide (approximately 0.135 mol), from Example III, were reacted with 11.5 grams of anhydrous barium hydroxide (approximately 0.0675 mol) in the presence of 200 cc. of toluene. The reaction mixture was stirred and heated to reflux under an automatic water separator for four hours, thereafter filtering through cloth and filter-cel. The filtrate then was freed of solvent by heating to 80–90° C. in vacuo. In the resulting salt it was found that only one-half of the phenolic groups was converted to the barium salt. It analyzed 7.62% sulfur and 7.0% barium.

These compounds have been found to impart excellent detergent and anti-oxidant or anti-corrosive properties to a mineral lubricating oil when they are blended therewith in proportions ranging from 0.1–5.0% by weight. These proportions vary with the particular type of mineral oil used and the purpose for which it is intended. However, the proportions preferred herein are between 0.25 and 2.0% by weight.

An additional feature of the present invention is the combination of the foregoing multi-functional additives with an auxiliary additive in-

gredient to further enhance the anti-oxidant or anti-corrosive properties of the mineral oil composition with which the additives are used. In certain Diesel and gasoline engines, which are designed for special heavy duty service, a higher degree of anti-oxidant or anti-corrosive properties is desired, and for this purpose an anti-oxidant or anti-corrosive improving additive is added with the compounds aforementioned. The class of compounds which may be used to impart the additional anti-corrosive property may be any one of the generally accepted sulfurized anti-corrosives. Among the particularly effective sulfurized anti-corrosive compounds found suitable for purposes of the invention are the sulfurized esters of oleic acid, such as sulfurized ethyl oleate, sulfurized high boiling gasoline polymers, such as the sulfurized clay tower polymers, sulfurized fatty oils, such as sulfurized sperm oil, sulfurized wax compounds, such as sulphurized paraffin wax, sulfurized resin derivatives, such as sulfurized abietene, sulfurized tall oil, and sulfurized terpene hydrocarbons, such as the sulfurized terpinolenes and isomers thereof, which are disclosed and claimed in the copending application of Knowles et al., Serial No. 391,468 filed May 2, 1941. The amount of sulfurized compound added to the mineral lubricating oil in combination with the multi-functional additive is usually within the proportion range of 0.5 to 5.0% by weight and preferably between 1.0 and 3.0%, depending upon the type of lubricating oil used.

These sulfurized auxiliary additives may be prepared in accordance with the copending applications of Edwin C. Knowles and Frederick C. McCoy, Serial Nos. 358,876, 358,877 and 358,878, respectively, all filed September 28, 1940, wherein a light-colored sulfurized material is prepared by the direct action of sulfur to the unsaturated material at approximately 300° F. in the presence of water and under pressure of hydrogen sulfide. This pressure, which is at least 50 pounds per square inch, is maintained until all the free sulfur has entered into combination and lasts usually from one-half to three hours. The sulfurized products formed by this process are directly soluble in a mineral oil and possess the added advantage in that the reaction product is a light-colored compound as against the usual dark-colored sulfurized compounds.

As illustrative of the anti-corrosive properties of a lubricating oil containing either or both of the aforementioned class of compounds, the results of the following empirical tests are presented. A copper-lead bearing specimen, incased in a special non-wear bushing and rotatably mounted on a stainless steel shaft, was immersed in a glass pot of the oil to be tested. The tested oil was heated to a controlled temperature of either 250° F. or 350° F. and continuously circulated between the bearing specimen and the shaft for periods of time varying from two to ten hours. The bearing specimen was weighed before the test and at two-hour intervals and the loss in weight recorded in milligrams. The reference oil which was used throughout this test was a solvent-refined dewaxed Mid-Continent lubricating oil distillate of an SAE 30 grade.

To this reference oil were added varying proportions of the additives of the present invention, taken individually and in combination, and the results compared. The metal derivatives tested, unless otherwise noted, are the normal salts, e. g. containing no free hydroxyl groups. The results of two runs at 250° F. and 350° F., respectively, are presented:

Bearing corrosion—Copper lead (10 hours)

Oil tested	Loss of weight in mg.	
	250° F.	350° F.
Reference oil	38, 39	133, 185
Reference oil+0.5% barium di (tridecyl phenolate) disulfide	1, 1	67, 71
Reference oil+0.5% barium di (polymer-phenolate) disulfide	0, 0	
Reference oil+0.5% calcium di (tridecyl phenolate) disulfide	2, 3	
Reference oil+3.0% sulfurized sperm oil	18, 19	14, 6
Reference oil+0.5% barium di (tridecyl phenolate) disulfide+3.0% sulfurized sperm oil	2, 3	14, 20
Reference oil+0.5% barium di (polymer-phenolate) disulfide+3.0% sulfurized sperm oil	0, 0	29, 16
Reference oil+0.5% barium di (polymer-phenolate) disulfide+1.0% sulfurized terpinolene	0, 1	0, 5
Reference oil+0.5% barium di (polymer-phenolate) disulfide+2.0% sulfurized ethyl oleate	0, 1	26, 13
Reference oil+0.5% barium di (polymer-phenolate) disulfide+3.0% sulfurized clay tower polymers	0, 0	0, 1

The results obtained by this test indicate the exceptional non-corrosive characteristics of the combination of barium di (polymer-phenolate) disulfide with sulfurized terpinolene and sulfurized clay tower polymers in a solvent refined lubricating oil at both temperatures of 250 and 350° F.

In order to illustrate the aforementioned detergent properties of the additives of the present invention, a test was devised which simulated as closely as possible the actual operating conditions of an internal combustion engine. This test was conducted on a single cylinder standard Lauson engine and the results obtained evaluated by visual inspection according to a classification of bad, fair and good. A heavy varnish deposit was obtained upon the piston of the Lauson engine by utilizing a solvent-refined, dewaxed Mid-Continent lubricating oil of an SAE 10 grade and running the engine at 1800 R. P. M. with a jacket temperature of 212° F., a crankcase temperature of 300° F., and with a crankcase ventilation of 0.4 cubic feet of air per minute for twenty-four hours. Then without cleaning the piston, the oil was changed to the compounded oil containing the proposed additives and the engine operated at 1800 R. P. M., with a jacket temperature of 315° F., a crankcase temperature of 200° F., and with no crankcase ventilation for twenty-four hours. At the end of the twenty-four hour period, the engine was dismantled, the condition of the piston noted and the oil classified.

The following results were obtained with a solvent-refined, dewaxed Mid-Continent lubricating oil of SAE 30 grade as a reference oil together with this reference oil compounded with the proposed additives:

Lauson detergency test

Oil tested	Rating
Reference oil	Bad
Reference oil+3.0% sulfurized sperm oil	Fair
Reference oil+3.0% sulfurized sperm oil+0.5% barium di (tridecyl phenolate) disulfide.	Fair

The effect of the proposed additives in reducing oil ring sludge is shown by the results of a so-called oil ring sludge test. In this test a CFR

(Cooperative Fuel Research) Diesel engine was operated for thirty-six hours at 1200 R. P. M., with a jacket temperature of 210° F. and a rich fuel mixture fed at the rate of 20 cc. per minute to aggravate sludge formation. The runs from the test were first made by using a reference oil, such as a solvent-refined, dewaxed Mid-Continent lubricating oil SAE 30 grade, and then, upon the same reference oil, compounded with varying proportions of the proposed additives. At the completion of each run the oil rings were taken out and weighed, and the results of the test tabulated as the percentage improvement of the compounded oils over the reference oil as follows:

Oil ring sludging test

Reference oil 3.0% sulfurized sperm oil	4% less oil ring sludge than reference oil.
Reference oil 3.0% sulfurized sperm oil, 0.5% barium di (tridecyl phenolate) disulfide	19% less oil ring sludge than reference oil.

As a final test to indicate the effectiveness of the compounded oils proposed by the present invention under actual operating conditions, a special test was devised which is a modification of the test described in a Diesel Lubricant Test Manual, Laboratory Test No. 1, put out by the Caterpillar Tractor Company. This test was carried out in a single cylinder Diesel engine operating at 900 R. P. M. with a water jacket temperature of 175° F., and run continuously for periods of 120 and 240 hours, or until rings are stuck, as indicated by the increase in blowby. The crankcase oil was drained every 60 hours and fresh oil added thereto. At the end of the 120 and 240 hour runs the engine was thoroughly examined and any carbonaceous deposits, lacquer formation, or corrosion characteristics noted. In the present instance the reference oil used was a solvent-refined, dewaxed Mid-Continent lubricating oil of SAE 30 grade.

Engine part	Reference oil	Reference oil+0.5% barium di (polymerphenolate) disulfide
Copper-lead bearing weight loss:		
120 hours	0.000 grams	0.019 grams. No visible wear or corrosion.
240 hours	0.027 grams	0.024 grams. No visible wear or corrosion.
Piston crown:		
120 hours	Normal	Normal.
240 hours	do	Very light carbon.
Piston rings:		
120 hours	Nos. 3 and 4 slight lacquer. Nos. 5 and 6 sludge deposit with No. 5 sticking and No. 6 slight sticking.	Nos. 1, 2 and 3 clean. Nos. 4, 5 and 6 slight trace of lacquer. No ring sticking.
240 hours	Nos. 1, 2 and 3 clean, but No. 1 ring 90% stuck in ring groove. Nos. 4, 5 and 6 show lacquer on top of ring and signs of sticking.	Nos. 1, 2, 3 and 6 clean. Nos. 4 and 5 slight lacquer on top of rings. No ring sticking.
Ring grooves:		
120 hours	All clean	No. 1 trace of varnish. Nos. 2, 3 and 4 trace to slight varnish. Nos. 5 and 6 light brown varnish.
240 hours	No. 1 hard carbon build-up. Nos. 2, 4, 5 and 6 black lacquer. No. 3 trace of lacquer.	Same as 120 hours.
Piston skirt:		
120 hours	1" ring of heavy brown varnish and other spotted areas. 4" dark brown varnish formation extending along axis of piston.	Clean except for 3" light brown varnish formation extending along axis of piston.
240 hours	2" ring of brown varnish around piston and 3" black-brown varnish formation along axis of piston.	2¼" light varnish formation extending along axis of piston.
Under piston deposit:		
120 hours		Slight trace.
240 hours	Black, granular deposit	Trace.
Oil filter:		
120 hours	Light coating of lint sludge	Fine lint sludge covering entire screen, mesh visible.
240 hours	Surface covered with lint sludge, no mesh visible	Same as 120 hours.

The multi-functional additives of the present invention may further be used in combination with other additive ingredients, such as pour point depressors, oiliness agents, extreme pressure, addition agents, blooming agents, viscosity index improving agents, color stabilizers, etc., without departing from the spirit of the invention.

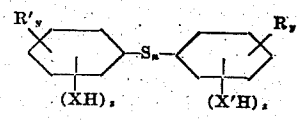
Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

What we claim is:

1. A Diesel lubricant comprising a mineral lubricating oil having incorporated therein 0.25 to 2.0% by weight of an oil-soluble metal salt of an alkyl phenol sulfide and 1.0 to 3.0% by weight of a sulfurized high boiling gasoline polymer.

2. A lubricating composition comprising a mineral lubricating oil having incorporated therein the combination of 0.1–5.0% by weight of an oil-soluble metal derivative of an alkyl substituted aryloxy sulfide and 0.5–5.0% by weight of a sulfurized hydrocarbon possessing anti-corrosive properties.

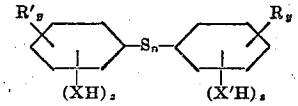
3. A lubricating composition comprising a mineral lubricating oil and the combination of 0.1–5.0% by weight of an oil-soluble metal derivative of a compound of the formula



in which R and R' are radicals selected from the group consisting of alkyl, aralkyl, cycloalkyl and naphthenyl, the alkyl portion of which contains at least 8 carbon atoms, X and X' are elements from the group consisting of oxygen and sulfur, *n*, *y*, *z* are integers of at least 1, and in which the aromatic nuclei are selected from the group consisting of phenyl, naphthyl, anthracyl and other condensed nuclei, and 0.5–5.0% by weight of a sulfurized hydrocarbon possessing anti-corrosive properties.

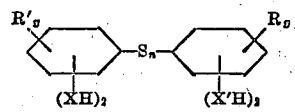
4. An improved lubricating oil comprising a mineral lubricating oil and the combination of

0.1–5.0% by weight of an oil-soluble metal derivative of a compound of the formula:



in which R and R′ are radicals selected from the group consisting of alkyl, aralkyl, cycloalkyl and naphthenyl radicals, tne alkyl portion of which contains at least 5 carbon atoms; X and X′ are elements from the group consisting of oxygen and sulfur; *n*, *y* and *z* are integers of at least 1, and 0.5–5.0% by weight of a sulfurized hydrocarbon possessing anti-corrosive properties.

5. An improved lubricating oil comprising a mineral lubricating oil having incorporated therein 0.1-5.0% by weight of an oil-soluble metal derivative of a compound of the formula



in which R and R′ are radicals selected from the group consisting of alkyl, aralkyl, cycloalkyl and naphthenyl radicals, the alkyl portion of which contains at least 5 carbon atoms; X and X′ are elements from the group consisting of oxygen and sulfur; *n*, *y* and *z* are integers of at least 1, and 0.5–5.0% by weight of a sulfurized high-boiling gasoline polymer.

JOHN ROBERT MORRIS.
RUSH F. McCLEARY.