Patented Jan. 25, 1949

2,460,025

UNITED STATES PATENT OFFICE

2,460,025

LUBRICATING OIL COMPOSITION

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No Drawing. Application October 24, 1944, Serial No. 560,191

10 Claims. (Cl. 252—42.7)

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This invention relates to a method of preventing the deterioration of organic materials, and it relates more particularly to a new type of additive for improving the properties of mineral lubricating oils.

It is known that the addition of certain types of metal-containing organic compounds to lubricating oils improves various properties thereof, such as their oiliness characteristics and their detergent action in engines, particularly manifested in the maintenance of a clean engine during operation. Certain of these metal-containing compounds have the additional property of inhibiting the corrosion of alloy bearings, such as those of cadmium-silver and copper-lead, now so widely used in automotive engines, and among such compounds which have been found to be particularly useful are the metal salts of alkylated phenol sulfides in which the alkyl groups are of the comparatively short chain type, containing from 4 to 8 carbon atoms each. Representative compounds of this type are the alkaline earth metal salts of tert.-amyl phenol sulfide, tert.-octyl phenol sulfide, and di-tert.-amyl phenol sulfide.

Compounds of the above described type have been found to be somewhat limited in their usefulness perhaps because they have a limited solubility in many types of lubricating oils and have been found to be entirely satisfactory only when used with certain selected base stocks, such as a limited number of extracted Mid-Continent oils and certain types of extracted naphthenic stocks. These compounds are also often quite sensitive to water; that is, they are removed to some extent from a solution in oil by intimate contact with a small amount of water. In the case of the diamyl phenol sulfides there is occasionally some difficulty in converting all of the phenolic groups into the metal derivatives.

Related types of compounds of the class which has been described are the wax-alkylated phenol sulfide salts. These have been disclosed in the art as additives for lubricating oils, but it has been found that these compounds, although containing relatively large side chains, do not show as satisfactory detergent qualities as the shorter chain compounds described above, and they appear to be somewhat unsatisfactory from a solubility standpoint.

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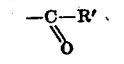
It has now been found, in accordance with the present invention, that metal salts of phenol sulfides which have highly branched long chain substituent aliphatic groups of 14 carbon atoms or more show unusually good detergent properties in lubricating oils which are used in both high and low temperature engine service. The preferred compounds are the salts of monosulfides disulfides, polysulfides, and mixed sulfides of alkylated phenols having long branched chain groups. These compounds have also been found to exhibit better oil solubility than the shorter chain compounds. Furthermore, they are less liable to separate from an oil solution in the presence of water, and they have been found to be effective in almost any type of reasonably well refined mineral oil. In view of these advantageous properties, the compounds of the present invention are distinctly superior not only to the shorter branched chain alkyl substituted phenol sulfide salts, but likewise superior to the straight chain wax-alkylated phenol sulfide salts. These superior properties will be exhibited in greater detail in specific examples which will be described below.

Defined more exactly, the new additives of the present invention are the compounds of the formula—

$$RAr(XM)S_x(MX)ArR$$

in which Ar represents an aromatic nucleus, R represents at least one branched chain aliphatic hydrocarbon radical containing at least 14 carbon atoms, X represents a nonmetallic element of group VI of the periodic table, M represents the hydrogen equivalent of a metal, S is sulfur, and x is an integer from 1 to 4. The aromatic nucleus may be a single benzene nucleus, a group of linked benzene nuclei as in biphenyl, or a condensed ring system, as in the naphthalene, anthracene and similar nuclei. The hydrocarbon radical R may be either saturated or unsaturated and preferably contains from 14 to 24 carbon atoms. The metals represented by M may be any of the metals, but those usually preferred are the divalent metals of group II of the periodic table, especially calcium, barium, strontium, magnesium or zinc; and in some cases other metals such as tin, nickel, aluminum, lithium, beryllium, and the like are desirable. The sulfur may be replaced by selenium or tellurium. It is to be

understood that the above formula includes compounds in which hydrogen atoms of the aromatic nuclei are substituted by various atoms or groups, such as halogen atoms, alkyl groups, aryl groups, aralkyl groups or any of the following typical groups: —OH, —SH, —OR′, —SR′, —NH_2, —SO_3M, —NO_2, —COOH, —COOR′, —COOM,



—CH_2OH, —CH_2SH, —CH_2SR', —SO_3H, —SO_3R', —CH_2NH_2, —CH_2NHR', —$CH_2NR'_2$, and the like, where R′ represents a hydrocarbon radical, e. g., an alkyl radical.

The above defined compounds are generally prepared by first alkylating a phenol, then converting the alkylated phenol to a sulfide by means of a sulfur halide, and finally producing a metal salt by reacting the alkylated phenol sulfide with a metallic base, or by other methods such as double decomposition. As starting materials, various phenols may be used, such as phenol, cresols, xylenols, phenyl phenol, petroleum phenols, resorcinol, alpha and beta naphthols, and the like.

It should be understood that throughout the specification and in the claims the terms "sulfide" and "disulfide" are used in a generic sense and include not only the more or less pure sulfide or disulfide but also small amounts of polysulfides or mixtures of mono-, di-, or polysulfides as well as polymers of the phenol sulfides. When preparing alkyl phenol sulfides on a commercial scale, using technical grades of sulfur chlorides, ratios of 1.5 or so mols of sulfur halide to 2 mols of alkylated phenol will often be found desirable. In such a case, although the product obtained when using sulfur dichloride will be expected to be essentially an alkyl phenol monosulfide, and when using sulfur monochloride an alkyl phenol disulfide, some quantities of polysulfides and of polymeric materials will also be formed.

As has been stated above, the phenol sulfide salt of the present invention should contain on each nucleus at least one highly branched chain aliphatic hydrocarbon group having at least 14 carbon atoms, the group being either saturated or unsaturated. The invention includes compounds with two or more such substituent groups on each nucleus, but it is often preferable to have present only one such substituent group on each nucleus.

To prepare the alkylated phenols to be used in the present invention the most satisfactory alkylating agents are olefin polymers such as those of ethylene, propene, butene, isobutene, amylenes and the like, the molecular weight of the polymers being so chosen as to furnish alkyl groups having preferably an average of 14 or more carbon atoms. Cracked petroleum fractions constitute a very convenient source of olefinic material. Thus, a C_3 cut or C_4 cut may be used and suitably treated to effect the proper degree of polymerization, using such catalysts as clay, $AlCl_3$, BF_3, H_2SO_4, $ClSO_3H$, FSO_3H, $BF_3.H_2O$, etc. Olefin polymers that occur as by-products in various refinery processes may also be employed, such as the bottoms from polymer gasoline manufacture.

One of the more preferable materials for alkylating the phenols is a butene polymer or copolymer known as naphtha rerun tower bottoms, occurring as a by-product in the manufacture of secondary butyl alcohol from a C_4 cut obtained from refinery cracking operations. This

C_4 cut contains n-butane, isobutane, butene-1, butene-2, isobutene, butadiene and traces of other olefinic or cyclic materials as well as of C_3 and C_5 hydrocarbons. The typical C_4 cut will contain about 45%–50% of total unsaturates, including about 16% of isobutene and about 1% of butadiene, although the composition will vary from time to time. The C_4 cut is treated with sulfuric acid, which converts the isobutene to dimer and trimer, these polymers having other commercial uses, and converts the n-butene to secondary butyl sulfate and secondary butyl hydrogen sulfate which are later hydrolyzed to form sec.-butyl alcohol. During this step some of the butene is converted to polymeric material which is recovered as naphtha rerun tower bottoms. This material is not entirely butene polymers, but is undoubtedly a complex product in which not only butene polymers but also copolymers with isobutene, butadiene, diisobutene, and triisobutene are present.

To prepare the preferred alkyl phenols which are to be converted to the products of the present invention, that portion of the naphtha rerun tower bottoms boiling between about 400° F. and 600° F. is normally employed as alkylating material. This will give phenols having branched alkyl chains with an average of about 15 to 20 carbon atoms. In some cases a wider cut or a lower boiling cut may be employed, e. g., one boiling from 300°–350° F. to 500°–600° F., in which case C_{12} to C_{16} alkylated phenols will also be included. Use of a cut having an end point above 600° F. will cause the introduction of longer alkyl chains, e. g., C_{20}—C_{24}. It should be pointed out that under the conditions outlined above it appears to be necessary that small quantities of a diolefin be present in the feed stock for the treatment with sulfuric acid, in order that any appreciable amount of material boiling above 400° F. may be obtained from the naphtha rerun tower bottoms.

Although a preferred source of alkylating materials has been described above, it should be understood that many other materials of a similar type may be used. The most suitable, however, are the polymers of normal butenes, or co-polymers of isobutylene and normal butenes and/or diolefins such as butadiene, isoprene, etc.

The methods of alkylation useful for the preparation of the alkylated phenols will generally vary with the particular material being used. Most of the unsaturated materials will react quite readily with the phenols in the presence of hydrogen chloride and a Friedel-Crafts catalyst, such as aluminum chloride. Other suitable catalysts include hydrogen fluoride and boron trifluoride, sulfuric acid, ferric chloride, zinc chloride, bismuth trichloride, antimony trichloride, stannic chloride, clay, etc. In the case of the more saturated hydrocarbons it is desirable to halogenate the same and then to condense with the phenol in the presence of a Friedel-Crafts catalyst. In some cases it may be desirable to halogenate the olefin polymer itself to facilitate alkylation of the phenol.

When alkylating phenol with the cut from the naphtha rerun tower bottoms described above, and when employing aluminum chloride as the alkylation catalyst, good results have been obtained by using the following procedure: (1) Add the phenol to the butene polymer and saturate the mixture with hydrogen chloride; (2) add the aluminum chloride catalyst to the agitated mixture at 80°–120° F.; (3) react for about 2 hours at

120° F.; (4) remove the catalyst and unreacted phenol by water washing; and (5) distill the product with the aid of steam to a 400° F. end point, taking overhead unreacted polymers and lower phenols. Yields with the aluminum chloride catalyst in such a process are about 55%–60%, based on the phenol used (amount of catalyst used=4.2% $AlCl_3$+7% HCl, based on the amount of olefin in the reaction). Yields of the order of 70% may be obtained if boron trifluoride is employed as the catalyst (4.2% of catalyst, based on the olefin used). Additional catalyst increases the yields somewhat.

When employing aluminum chloride catalyst as in the procedure outlined above it may be found preferable in some cases to saturate the olefin polymer with HCl and then add this to an agitated mixture of the aluminum chloride and phenol. Also, instead of removing the alkylation catalyst by water washing, a dry method may be employed involving percolation of the alkylated phenol through clay, or the addition of clay to the crude alkylated phenol followed by heating and filtering.

Although the yields described above are obtainable when equal molecular proportions of olefin and phenol are reacted, and these proportions are generally preferred, the percentage conversion of the phenol to alkylated phenol can be increased by using higher olefin/phenol ratios, while the percentage conversion of olefin can be increased by employing lower olefin/phenol ratios. Further utilization of the olefinic material can often be effected by recovering unreacted olefin from the reaction mixture and recycling it with fresh phenol and catalyst.

In the alkylation of phenols by the use of alkylating agents and catalysts of the types described above temperatures of 50°–250° F. may be used, although temperatures within the range of 120°–150° F. appear to be the most desirable. A reaction time of 2–3 hours is generally adequate.

For converting the alkyl phenols to phenol sulfides the conventional processes are used; that is, the alkylated phenols are reacted with sulfur monochloride or dichloride or mixtures of these in a ratio of 2 mols of phenol to 1–2 mols of sulfur halide in the presence of a suitable solvent such as ethylene dichloride, chloroform, benzene, petroleum naphtha, or the like. To prepare the metal salts, the alkyl phenol sulfides are preferably dissolved in mineral oil and neutralized with a metal oxide or hydroxide, e. g.,

$$Ba(OH)_2.8H_2O$$

using a defoaming aid and plasticizer, such as stearyl alcohol. The metal salts may also be prepared by other methods such as by double decomposition, from the sodium salt of the alkyl phenol sulfide and a heavy metal chloride in a suitable medium.

When the additives of the present invention are used in lubricating oils, they are most advantageously blended with the base stocks in concentrations between the approximate limits of 0.02% and 5.0%, and preferably from 0.1% to 2.0%, although larger amounts may be employed. The exact amount to be used depends to some extent on the particular compounds used, the characteristics of the mineral oil base, and the operating conditions of the engine in which the lubricant is to be employed. The additives are useful not only in lubricating oils but in organic materials generally for the purpose of inhibiting deterioration in the presence of oxygen, as will be explained more fully hereinafter. The quantity to be used in various materials will vary according to the nature of the material and its tendency to oxidize.

It is often convenient to prepare concentrates of the additives in oil, containing, say, 25 to 75% of effective addition agent, the concentrate later being added to a suitable lubricating oil base stock to give a finished blend containing the desired percentage of additive. Thus, when using a 40% concentrate, 2.5% of this material may be blended with a suitable base stock to give a finished oil containing 1% of effective additive.

Below are given several examples of the preparation of the alkylated phenol sulfide salts of the present invention and of tests of the usefulness of these salts when blended in lubricating oils.

Example 1

Approximately 3600 grams of naphtha rerun tower bottoms was distilled to 400° F. under atmospheric pressure, leaving about 1720 grams of material of higher boiling point. This latter material was then distilled with fire and steam to 400° F., taking overhead about 1635 grams of product boiling in the range of 400–600° F. A mixture of 672 grams of the butene polymer thus obtained and 282 grams of phenol was placed in a 2-liter, 3-neck flask equipped with a stirrer, dropping funnel and thermometer and immersed in an ice-water bath to provide cooling. Over a period of 1½ hours 297 grams of 95% H_2SO_4 was added dropwise to the stirred mixture, the temperature being maintained at 45–55° F. Stirring was continued for an additional 2¼ hours, the temperature being allowed to rise to 65° F. for the first hour and finally to 88° F. The mixture was then allowed to stand overnight, after which it was again stirred. 712 grams of this product was mixed with 700 cc. of water and placed in a 2-liter copper-lined steel bomb where it was heated with shaking for about 3 hours at 100–170° C. in order to effect hydrolysis of sulfonic acid groups present in the alkylated product. The mixture was removed from the bomb, the aqueous layer removed and the phenolic layer washed with water, then with 5% sodium carbonate and again with water. Final traces of water were removed by blowing with nitrogen at 220° F., and the product was then distilled with fire and steam to 350° F. end point, giving 124 grams of distillate and 300 grams of bottoms. The latter was filtered through Celite (acid-treated kieselguhr), giving 239 grams of finished alkylated phenols. Analysis of the final product showed it to contain alkyl side chains of 16 to 20 carbon atoms with an average length of 19 carbon atoms.

Analysis

Carbon	per cent	82.94
Hydrogen	do	13.36
Acetyl value	mg. KOH/g. acetylated products	138.5

Example 2

(*a*) A solution of 100 grams of the alkylated phenol of Example 1 in 234 grams of chloroform was placed in a reaction flask equipped with stirrer and reflux condenser. Over a 35 minute period 24.3 grams SCl_2 was added dropwise to the mixture, the temperature being maintained at 26–29° C. After an additional 30 minutes of stirring the mixture was heated at reflux temperature for 2 hours. The chloroform was then removed by evaporation at a maximum temperature

of about 200° F. The residue, weighing 108.5 grams, was a tough gummy material, soluble in mineral lubricating oil. This alkylated phenol sulfide contained 7.45% sulfur.

(*b*) The same procedure was followed as in (*a*) except that 31.8 grams of S_2Cl_2 was substituted for the 24.3 grams of SCl_2. The product, after removal of the solvent, was a tough gummy material which became brittle on cooling. It contained 12.95% sulfur and was soluble in mineral lubricating oil.

(*c*) The alkyl phenol sulfides were converted to metal salts in the following manner: 76 grams of the alkyl phenol sulfide from (*a*), 80 grams of the disulfide from (*b*), and 42 grams of commercial stearyl alcohol were dissolved in 210 grams of refined mineral lubricating oil of 52 seconds viscosity (Saybolt—210° F.) with heating and stirring. While the temperature was held at 105° C., there was added gradually over a 1 hour period 83 grams of $Ba(OH)_2.8H_2O$, nitrogen being blown through the mixture at the same time to facilitate water removal. After all of the barium hydroxide had been added the temperature was raised to 130–140° C. for 15 minutes, stirring and nitrogen blowing being continued. The mixture was then filtered with the aid of celite. The filtered product, obtained in a 403 gram yield, was essentially a 40% concentrate of barium salts of the mixed monosulfide and disulfides of C_{16}–C_{20} branched chain alkyl phenols, the other components of the concentrate being 50% mineral oil and 10% stearyl alcohol. Analysis of the concentrate showed it to contain 3.64% sulfur and 6.12% barium.

Example 3

The alkylating material used in this example was similar to that employed in Example 1, namely butene polymers of 400–600° F. boiling range obtained from naphtha rerun tower bottoms. This material was used to alkylate phenol in several batches, using aluminum chloride and hydrogen chloride as catalysts. Essentially the same procedure was employed in each alkylation, although the proportions of reactants and catalyst and time of reaction were varied to a slight extent to study the effect of these variables on the yield of alkylated phenol. The amounts used in each batch are shown in the following table:

Batch	Grams Butene Polymer	Grams Phenol	Grams $AlCl_3$
a	450	190	13
b	1,120	474	160
c	582	146	50
d	672	170	57
e	1,568	658	222

In batches *a*, *b* and *e*, 240 parts of butene polymer were employed for each 100 parts of phenol. In batches *c* and *d* the proportion was 400 parts of polymer for 100 parts of phenol. The procedure employed in each case was essentially as follows:

The phenol and the butene polymer were added to a reaction flask and the mixture was saturated with dry HCl, the temperature being maintained at about 85°–100° F. The $AlCl_3$ catalyst was added gradually over a period of 1 to 2 hours, the mixture being stirred and kept at an average temperature of 90° F. (85° F. minimum, 98° F. maximum). A total reaction time of 18 hours was employed for batches *a* and *b*, 6 hours for batch *c*, 45 hours for batch *d*, and 25 hours for batch *e*.

To stop the reaction, 200–300 cc. of isopropyl alcohol was added to the reaction mixture, followed by 350–400 cc. of water. The mixture was then washed four times with water and finally distilled with fire and steam to 400° F. end point. The desired alkylated phenol was obtained as the bottoms from this distillation. The products of the five batches were mixed together to obtain a supply of alkylated phenols for subsequent conversion to phenol sulfides.

Analysis of the composite mixture

Carbon ---------- per cent--	83.53
Hydrogen ---------- do----	12.02
Acetyl No ------ mg. KOH/gram acetylated product--	140.6

Example 4

(*a*) A solution of 1100 grams of the mixed alkylated phenols of Example 3 in 2570 grams of chloroform was placed in a reaction flask. Then, while the temperature was maintained at 25°–32° C., 350 grams of sulfur monochloride (S_2Cl_2) was slowly added with stirring over a period of 1½ hours. After an additional half hour of stirring the mixture was heated under reflux for three hours. The chloroform was then stripped off, leaving as a residue the desired alkylated phenol disulfide, containing 13.44% sulfur.

(*b*) Employing the same procedure as in (*a*), the corresponding alkylated phenol monosulfide was prepared by reaction of 268 grams of sulfur dichloride (SCl_2) with 1100 grams of alkylated phenols from Example 3, dissolved in 2570 grams of chloroform. The product obtained after evaporation of the solvent contained 6.46% sulfur.

(*c*) 800 grams of the alkylated phenol disulfide of (*a*), 760 grams of the alkylated phenol monosulfide of (*b*), and 252 grams of commercial stearyl alcohol were dissolved in 2268 grams of a refined mineral lubricating oil of 52 seconds Saybolt viscosity (210° F.). Over a 3 hour period 900 grams of barium hydroxide octahydrate ($Ba(OH)_2.8H_2O$) was added gradually, the mixture being stirred and its temperature maintained in the range 110°–130° C. During this period a stream of nitrogen was blown through the reaction mixture to facilitate removal of water. Following the barium hydroxide addition the temperature was raised to 140° C. for 15 minutes and the product then was filtered, using celite as a filter aid. There was obtained 4070 grams of filtered product, this being an additive concentrate containing 54% mineral oil, 6% stearyl alcohol and 40% barium salt of C_{16}–C_{20} branched chain alkylated phenol monosulfide-disulfide. This concentrate was found to contain 7.2% barium and 3.6% sulfur.

Example 5

(*a*) Employing essentially the procedure outlined in Example 3, a large batch of alkylated phenol was prepared in a glass lined reactor, starting with 24.6 kilograms of butene polymers, 10.4 kilograms of phenol, and 1 kilogram of $AlCl_3$. The butene polymer-phenol mixture was saturated with HCl and the $AlCl_3$ was added over a 3 hour period, a reaction temperature of 115°–120° F. being employed. After a total of 6 hours reaction time, 2 gallons of 99% isopropyl alcohol was added followed by 5 gallons of water to remove the catalyst. The alkylated phenols were then washed with water and distilled as in Example 3. A composite of this batch of alkylated phenols and of a similar batch prepared from the same quantities of reactants and catalyst but

at a slightly higher temperature (120°–150° F.) had the following analysis:

Carbon	per cent	83.17
Hydrogen	do	12.06
Acetyl No	mg. KOH/gram acetylated product	135.0

(b) Portions of the above alkylated phenol composite were separately converted to monosulfides and disulfides by the procedures outlined in Examples 4 (*a*) and 4 (*b*). Then 2.7 kilograms of the monosulfide, 2.9 kilograms of the disulfide, and 0.9 kilogram of commercial stearyl alcohol were dissolved in 8.1 kilograms of refined S. A. E. 20 grade mineral lubricating oil at 100° C. The temperature was raised to 135° C.; then over a 3-hour period 3 kilograms of $Ba(OH)_2.8H_2O$ was added gradually with stirring, the temperature being maintained at 135°–150° C. and nitrogen being blown through the mixture to facilitate the removal of water. Heating was continued at 150° C. for 15 minutes after the barium hydroxide had been added. The mixture was then filtered with the use of celite filter aid, yielding 12.8 kilograms of an oil concentrate of the desired additive material, barium salts of C_{16}–C_{20} branched chain alkyl phenol sulfide-disulfides. The concentrate contained 6.9% barium and 3.9% sulfur.

Example 6

Branched chain C_{16}–C_{20} alkyl phenol was prepared in the following manner, using boron fluoride catalyst. 1340 grams of BF_3 was injected into 13.2 kilograms of phenol which was placed in a glass lined reactor. During a two-hour period 31.4 kilograms of butene polymers of 400°–600° F. boiling range (obtained from naphtha rerun tower bottoms as in previous examples) was added. After the first 15 minutes the temperature had risen from 80° F. to 95° F. The temperature was allowed to rise to 115° F. and held at this point during the addition of the remaining butene polymer. It was then allowed to rise to 120° F. for an additional 4 hour period, the total reaction time being 6 hours.

The reaction mixture was then washed 5 times with hot water (170°–185° F.), 12 liters of water being used each time. The crude product was then steam distilled up to 400° F. bottoms temperature, the desired alkylated phenols being obtained in 30.7 kilogram yield as the bottoms from this distillation. Analysis of the distillate and of the water from the above washing step indicated that 77% of the phenol and 76% of the butene polymer had reacted.

Employing the procedure described in Example 2, 3 kilograms of the above alkylated phenol was dissolved in 7 kilograms of chloroform and converted to alkyl phenol monosulfides by reaction with 729 grams of sulfur dichloride. Similarly, another 3 kilogram portion of the alkylated phenols was converted to alkyl phenol disulfides by reaction with 954 grams of S_2Cl_2. 760 grams of the alkyl phenol monosulfide, 780 grams of the disulfide and 270 grams of commercial stearyl alcohol were dissolved in 2430 grams of refined S. A. E. 20 grade mineral lubricating oil heated to 125° C. Over a period of 2 hours 692 grams of $Ba(OH)_2.8H_2O$ was added gradually, the mixture being agitated and blown with nitrogen to facilitate removal of water. Following the addition of the barium hydroxide, heating was continued for 30 minutes at 140° C. and the product was then filtered, giving an oil concentrate of the desired additive, barium salts of C_{16}–C_{20} alkylated phenol sulfides. The concentrate contained 5.82% barium and 3.41% sulfur.

Example 7

The effectiveness of the products prepared as described in the foregoing examples in inhibiting the corrosion of a typical lubricating oil toward the surfaces of copper-lead bearings was determined by a test which will be described below. The base oil used was a well refined solvent extracted paraffinic lubricating oil of S. A. E. 20 grade. A blank sample of this oil and samples of the oil containing small quantities of the various additives, were submitted to the following corrosion test:

500 cc. of the oil was placed in a glass oxidation tube (13" long and 2⅝" diameter) fitted at the bottom with a ¼" bore air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was maintained at 325° F. during the test. Two quarter sections of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attached to opposite sides of a stainless steel rod which was then immersed in the test oil and rotated at 600 R. P. M., thus providing efficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. At the end of each four-hour period the bearings were removed, washed with naphtha, and weighed to determine the amount of loss by corrosion. They were then repolished (to increase the severity of the test), reweighed, and placed in the oil for another four-hour period. The cumulative weight losses of all the bearings used in a given test at the end of the various four-hour periods are given in the following table. The additive is designated by the number of the example in the present specification in which the additive is described. It will readily be noted that the additives of the present invention are very effective inhibitors of bearing corrosion.

Oil	Cumulative Bearing Weight Loss (mg. per 25 sq. cm. surface)					
	4 Hrs.	8 Hrs.	12 Hrs.	16 Hrs.	20 Hrs.	24 Hrs.
Base Oil	5	181	------	------	------	------
Base Oil+0.625% of Concentrate of Example 2c	1	3	8	13	32	56
Base Oil+0.625% of Concentrate of Example 4c	1	4	9	10	92	158
Base Oil+0.625% of Concentrate of Example 5b	0	5	11	24	59	158

Example 8

In the following engine performance tests, samples of unblended base oil and of blends containing this oil with various alkylated phenol sulfide salts were tested in a single cylinder Caterpillar Diesel engine, each run being made for 60 hours at 850 R. P. M., with 18.7 brake horse power output, and oil temperature of 200° F., and atmospheric temperature of 140° F. At the end of each test individual parts of the engine were inspected and given demerit ratings based on their condition. An overall demerit rating was then calculated, the individual demerit ratings being weighted according to the relative importance of the various engine parts. It should be noted that the lower the demerit rating the better the engine condition, and hence the better the oil performed in the engine. The results of

these engine tests are shown in the following table:

Oil	Engine Demerits				
	Overall	Ring Zone	Piston Skirt Varnish	Ring Grooves and Sides	
				#1 and 2 Rings	#4 and 5 Rings
Base Oil A	1.24	1.69	1.00	8.50	11.50
Base Oil A+1% Barium Wax Phenol Sulfide-Disulfide [1]+0.25% Stearyl Alcohol	1.48	1.82	1.12	14.00	10.00
Base Oil A+1% Barium tert.-Octyl Phenol Sulfide-Disulfide+0.25% Stearyl Alcohol	0.83	0.79	0.12	6.00	2.50
Base Oil B+1% Barium tert.-Octyl Phenol Sulfide-Disulfide+0.25% Stearyl Alcohol	0.99	1.14	0.38	6.50	8.50
Base Oil B+1% Barium C_{16}-C_{20} Branched Chain Alkyl Phenol Sulfide-Disulfide (2.5% Concentrate of Example 2c)+0.25% Stearyl Alcohol	0.73	0.59	0	5.00	2.50

Base Oil A—Conventionally refined coastal oil of 55 seconds Saybolt Viscosity (210° F.).
Base Oil B—Refined solvent extracted paraffinic oil of S. A. E. 20 grade.
[1] Wax phenol prepared by alkylating phenol with chlorinated paraffin wax. Phenol sulfide-disulfide salts prepared in essentially the same manner as for additives of the present invention.

It will be seen that the C_{16}–C_{20} branched chain alkyl phenol sulfide salt was more satisfactory than the C_8 alkyl phenol sulfide salt. By comparison, a C_{16}–C_{20} straight chain alkyl phenol sulfide salt (wax phenol) was not satisfactory, the blend being even worse than the base oil.

EXAMPLE 9

Another similar series of engine performance tests was carried out in a single cylinder caterpillar Diesel engine, each run being made for 126 hours at 1,000 R. P. M., with 19.8 brake horse power output, an oil temperature of 150° F., and jacket temperature of 180° F.

The results of the tests are shown in the following table, in which the data have the same meaning as in the preceding example.

Oil	Engine Demerits				
	Over all	Ring Zone	Skirt Varnish	Ring Grooves and Sides	
				#1 and 2 Rings	#4 and 5 Rings
Base Oil [1]+1% Barium tert.-Octyl Phenol Sulfide-Disulfide [2]+0.25% Stearyl Alcohol	0.83	0.78	0	6.50	4.50
Base Oil+1% Barium salts of Kero phenol [3] Sulfide-Disulfide+0.25% Stearyl Alcohol	1.11	1.41	0.31	9.00	9.50
Base Oil+1% Barium C_{16}-C_{20} Branched Chain Alkyl Phenol Sulfide-Disulfide+0.25% Stearyl Alcohol (2.5% Concentrate of Example 4c)	0.70	0.48	0	3.75	2.50
Base Oil+1% Barium C_{16}-C_{20} Branched Chain Alkyl Phenol Sulfide-Disulfide+0.25% Stearyl Alcohol (2.5% Concentrate of Example 5b)	0.71	0.42	0	3.50	1.00

[1] Base Oil—S. A. E. 30 grade extracted Mid-Continent lubricating oil.
[2] Tert.-octyl phenol prepared by alkylating phenol with diisobutylene. Barium salts of the phenol sulfide disulfide prepared in essentially the same manner as for additives of the present invention.
[3] Kero phenols prepared by alkylation of phenol with chlorinated kerosene. Phenol sulfide-disulfide salts prepared in essentially the same manner as for additives of the present invention.

EXAMPLE 10

Another series of engine performance tests was carried out under the conditions described in Example 9, except that a four-ring piston was used in each case instead of a six-ring piston.

The results from these tests are shown in the following table, the data having the same significance as in the preceding examples.

Oil	Engine Demerits		
	Overall	Ring Zone	Skirt Varnish
Base Oil [1]	2.24	2.32	0.21
Base Oil+1% Barium tert.-Octyl Phenol Sulfide-Disulfide+0.25% Stearyl Alcohol	1.36	1.16	0
Base Oil+1% Barium C_{16}-C_{20} Branched Chain Alkyl Phenol Sulfide-Disulfide+0.25% Stearyl Alcohol	0.71	0.32	0

[1] Refined solvent extracted paraffinic oil of S. A. E. 30 grade. The base oil employed in the blends was the same type of oil made in the same way from the same crude source but was of S. A. E. 20 grade.

The products of the present invention may be employed not only as the sole additives in hydrocarbon lubricating oils but also in conjunction with other detergent type additives such as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal phenol sulfonates, other metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, reaction products of metal phenates or metal phenol sulfides and sulfur, reaction products of metal phenates or metal phenol sulfides and phosphorus sulfides, and the like. Thus, the new additives of this invention may be used in lubricating oils containing such addition agents as nickel oleate, barium octadecylate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum napthenate, calcium cetyl phosphate, barium di-tert.-amyl phenol sulfide, calcium petroleum sulfonate, zinc methyl cyclohexyl thiophosphate, calcuim dichlorostearate, etc.

The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils, or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloro ethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of

olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed, either alone or in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additives present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel service, particularly with high speed Diesel engines, and in gasoline engine service, oils of higher viscosity index are often required, for example up to 75 or 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organometallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, defoaming or antifoaming agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like, may also be employed.

Assisting agents which are particularly desirable are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol ($C_8H_{17}OH$), lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol ($C_{16}H_{33}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol, ($C_{18}H_{37}OH$), and the like; the corresponding olefinic alcohols, such as oleyl alcohol; cyclic alcohols, such as napthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes, the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc.

In addition to being employed in crankcase lubricants and in extreme pressure lubricants, the additives of the present invention may also be used in various industrial and process oils such as spindle oils, textile oils, metal cutting oils, engine flushing oils, turbine oils, insulatng and transformer oils, steam cylinder oils, slushing compositions, and greases. Also their use in motor fuels, Diesel fuels and kerosene is contemplated. Since these additives exhibit antioxidant properties and are believed also to possess ability to modify surface activity, they may be employed in asphalts, road oils, waxes, fatty oils of animal or vegetable origin, soaps, and plastics. Similarly, they may be used in natural and synthetic rubber compounding both as vulcanization assistants and as antioxidants, and generally they may be used in any organic materials subject to deterioration by atmospheric oxygen.

The present invention is not to be considered as limited by any of the examples described herein, which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

We claim:

1. A hydrocarbon material susceptible to deterioration by oxidation containing dissolved therein a small quantity, sufficient to stabilize said material against such oxidation, of a compound of the formula

$$RAr(XM)S_x(MX)ArR$$

in which Ar is an aromatic hydrocarbon nucleus, R is a branched chain aliphatic hydrocarbon radical containing 14 to 24 carbon atoms, X is a nonmetallic element of group VI of the periodic table, M is the hydrogen equivalent of a metal, S is sulfur, and x is an integer from 1 to 4.

2. A mineral lubricating oil containing dissolved therein a small quantity, sufficient to stabilize said oil against deterioration by oxidation, of a compound of the formula

$$RAr(XM)S_x(MX)ArR$$

in which Ar is an aromatic hydrocarbon nucleus, R is a branched chain aliphatic hydrocarbon radical containing 14 to 24 carbon atoms, X is a nonmetallic element of group VI of the periodic table, M is the hydrogen equivalent of a metal, S is sulfur, and x is an integer from 1 to 4.

3. A mineral lubricating oil containing dissolved therein a small quantity, sufficient to stabilize said oil against deterioration by oxidation, of a metal salt of an alkylated phenol sulfide in which at least one branched chain alkyl group containing 14 to 24 carbon atoms is attached to each benzene nucleus.

4. A composition according to claim 4 in which the alkyl group contains from 16 to 20 carbon atoms.

5. A composition according to claim 4 in which the metal of the metal salt is a divalent metal of group II of the periodic table.

6. A mineral lubricating oil additive concentrate containing 25–75% of a metal salt of an alkylated phenol sulfide in which at least one branched chain alkyl group containing 14 to 24 carbon atoms is attached to each benzene nucleus.

7. A mineral lubricating oil additive concentrate containing about 40% of barium salts of alkylated phenol sulfides in which at least one branched chain containing 16 to 20 carbon atoms is attached to each benzene nucleus, about 10% of stearyl alcohol, and about 50% of mineral lubricating oil.

8. As a new composition of matter a compound of the formula

$$RAr(XM)S_x(MX)ArR$$

in which Ar is an aromatic hydrocarbon nucleus, R is a branched chain aliphatic hydrocarbon radical containing from 14 to 24 carbon atoms, X is a nonmetallic element of group VI of the periodic table, M is the hydrogen equivalent of a metal, S is sulfur, and x is an integer from 1 to 4.

9. As a new composition of matter a metal salt of an alkylated phenol sulfide in which at least one branched chain alkyl group containing from 14 to 24 carbon atoms is attached to each benzene nucleus.

10. A composition according to claim 9 in which the metal of the metal salt is a divalent metal of group II of the periodic table.

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Certificate of Correction

Patent No. 2,460,025 January 25, 1949

JOHN G. McNAB ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 14, lines 64 and 67, for the claim reference numeral "4" read *3*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of March, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

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