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ADDITIVE FOR LUBRICANTS

Jesse S. Weissberg, Elizabeth, N. J., and John R. Jones, Seattle, Wash., assignors to Esso Research and Engineering Company, a corporation of Delaware

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23 Claims. (Cl. 252—42.7)

The present invention relates to new compositions of matter and methods for preparing same. More specifically, it concerns improved metal and sulfur-containing hydrocarbon substituted phenolic compounds particularly useful as lubricant additives.

It is well known in the art to employ metal alkyl phenates, metal alkyl thiophenates, metal alkyl phenol sulfides, their sulfurized and phosphosulfurized derivatives and the like as additives for improving various properties of lubricants. Such compounds, used alone as additives or in combination with other materials, improve the detergency of internal combustion engine lubricants thereby helping to maintain engine cleanliness.

It is a principal object of the present invention to provide a new and useful class of compounds of the above type. These compounds are oil-soluble and are effective additives for improving various properties of lubricants.

Briefly the compounds of the present invention are metal and sulfur-containing derivatives of phenolic-type compounds having the general formula

$$R_yR'_zArXH$$

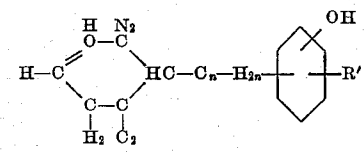
in which R is at least one cycloalkenyl radical attached through an alkylene radical having at least one carbon atom to an aromatic nucleus Ar. R' may be hydrogen or one or more alkyl groups attached to Ar. X is a nonmetal of group VI of the periodic table, and is preferably oxygen. The letter y is an integer in the range of 1 to 3, preferably 1; z is 0 to 2 but z is preferably 1. The sum of y and z should not exceed 4 for a benzene nucleus. Specifically R includes a cycloolefin radical of which the ring may contain 4 to 8 carbon atoms, although the cyclohexene ring is preferred from the standpoint of stability and ease of preparation. The cycloolefin may contain substituent groups such as alkyl groups and the like and, as previously mentioned, is attached through one or more carbon atoms to the aromatic nucleus.

When R' is an alkyl group, it may have in the range of 1 to 20 carbon atoms in normal or iso configuration and may comprise primary, secondary or tertiary groups. Preferably R' has in the range of 4 to 12 carbon atoms and includes specific alkyl radicals such as methyl, isopropyl, tert.-amyl, n-hexyl, tert.-octyl, isodecyl, n-dodecyl, C_{16}–C_{20} wax groups, and the like.

Ar is preferably a benzene nucleus, although it may consist of a plurality of rings such as biphenyl, or a condensed nucleus, exemplified by naphthalene, anthracene and the like.

It should be understood that the aromatic nucleus and/or the cycloolefin radical in the above general formula may have various other substituent atoms or groups such as carbonyl, alkoxyl, nitro, ester, keto, amino, aldehydo, chloromethyl, halogen atoms, etc.

A preferred embodiment of the phenolic-type compounds of the present invention may be represented diagrammatically as follows:



in which R' is an alkyl radical as defined above. In the alkylene chain connecting the cyclohexene radical and the benzene nucleus, n may be in the range of 1 to 10, preferably 2 to 4. Obviously the $—C_nH_{2n}—$ (alkylene) radical may be straight chain or branched. For example, one tertiary carbon atom containing two attached alkyl groups may connect the cycloalkenyl radical and aromatic nucleus. The olefinic double bond in the cyclohexene radical is shown in the 3 position with respect to the connecting carbon atoms, but it may be in the 1 or 2 positions. The hydroxyl, alkyl and cycloalkenylalkylene radicals may be attached in any convenient position on the benzene ring, but preferably the hydrocarbon groups are ortho-para with respect to the hydroxyl group.

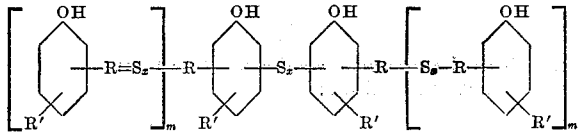
The substituted phenolic-type compounds may be prepared conveniently by alkylating a phenol, cresol, naphthol, or their thiophenol equivalents and other phenolic compounds with a cycloolefin containing an olefinic side chain. The alkylation may be carried out with the aid of conventional catalysts such as metal halides, sulfuric acid, phosphoric acid, etc. Specific alkenyl cycloalkenyl compounds include vinyl cyclohexene-3 (prepared by dimerizing butadiene-1,3); allyl cyclohexene-2; 3-pentencyclohexene-1; allyl cyclobutene-2; vinyl cycloheptene-3; 4-octen-cyclopentene-2, and the like. It is desired in this reaction that the olefinic side chain attach to the phenol leaving the naphthenic ring unsaturated. For this reason, it may be preferred to employ cycloalkenyl compounds containing alcohol, alkyl halide or other side chain substituent groups that will preferentially attach to the aromatic nucleus.

If desired, the phenol may first be alkylated with aliphatic alcohols, alkyl halides, alkyl phosphates, olefins and other alkylating agents in order to introduce one or more alkyl radicals on the aromatic nucleus. Olefinic materials such as petroleum refinery gases containing mixtures of olefins or individual olefins such as butene, amylene, di-isobutylene and the like may be used. If desired, the alkyl groups may be introduced after the cycloalkenyl radical has been attached to the phenol.

The sulfides of the phenolic-type compounds are formed by treatment with a halide of sulfur, such as sulfur monochloride or sulfur dichloride, at a temperature in the range of about 50° to 250° F. About 0.2 to 3 mols, preferably 0.5 to 1.0 mol, of sulfur halide may be used per mol of alkylated phenol. The reaction may be carried out in a suitable organic solvent, such as a light hydrocarbon or chlorinated hydrocarbon (hexane, ethylene dichloride, and the like).

The formation of sulfides of alkyl phenols by the above reaction is well known. In such sulfides, one or more sulfur atoms interconnect two aromatic nuclei. The sulfides of the present invention, however, are quite different in configuration to the conventionally produced sulfides. For example, the sulfides of the present invention are oil soluble materials having much higher molecular weights than conventional alkyl phenol sulfides, even though the starting materials have substantially the same molecular weights.

It is postulated that the sulfides of the present invention contain sulfur interconnecting two naphthene radicals as well as connecting two aromatic radicals. It is possible that at least a substantial portion of the sulfide may comprise complex molecules having a structure as follows:



in which x may be a small integer such as in the range of 1.0 to 4, and in which m is 0 or an integer, at least one m being one or more. R in the formula is the cycloalkenyl-alkylene radical as defined above. This structure is indicated by the high molecular weights of the products as well as by the sulfur contents thereof. It is also possible that some other polymerization or condensation reactions may take place during the sulfurization step. It is not desired to be bound by any theoretical structure of the products since the postulates are tentative and since it has not been possible to determine exact structures because of the complexity of the product.

The sulfides prepared by the above procedure may be used per se to stabilize mineral lubricating oils, synthetic oils, etc. However, in a preferred embodiment of the invention, their metal derivatives are prepared. The metals are substituted for the hydrogen in the —XH or —OH groups of the above formulas forming salt of the compounds having detergency, antioxidant and the like properties. Suitable metals are calcium, barium, strontium, magnesium, zinc, tin, lead, aluminum, cobalt, nickel and the like. Preferred metals are divalent metals of group II of the periodic table.

The metal salts may be formed by adding a metal, metallic oxide, hydroxide, sulfide, alkoxide, hydride, or carbide to a mineral oil solution or other solution of the above sulfide at an elevated temperature such as 170°–400° F. Thus, barium salts of the phenol sulfide are prepared by reacting the sulfide with barium hydroxide, preferably as a hydrate, $Ba(OH)_2.8H_2O$. Calcium methylate or other calcium alcoholate may be used to prepare calcium salts. A heavy metal salt can be prepared from an alkali metal salt by double decomposition. Other well known procedures may be used to form the metal derivatives.

The salt may be prepared by treating the phenol sulfide with just sufficient metal or basic reacting metal compound to completely neutralize the OH or SH radicals. Basic metal salts, having advantages for certain uses, may be prepared by adding a metallic oxide or hydroxide to a solution of the phenolic sulfide in a quantity greater than that required to form the normal salt. Mixed metal salts may be formed by treating the sulfide with two or more metallic compounds.

If desired, further improvements in antioxidant and corrosion inhibition properties may be obtained by reacting the metal salts of the phenol sulfide with sulfur or both sulfur and phosphorus in order to introduce additional sulfur as well as phosphorus into the molecule. Sulfurizing agents for this purpose include elemental sulfur, mixtures of elemental sulfur and phosphorus, sulfides of phosphorus, such as P_2S_5, P_4S_3, P_4S_7, etc. This reaction may be carried out at a temperature in the range of about 200–450° F. for a time sufficient to complete the reaction. About 2 to 25% by weight of sulfurizing agent may be used.

In another aspect of the present invention, the alkylated phenols and thiophenols may be reacted with a metal or metallic compound by the procedure described above to form metal phenates or metal thiophenates. The basic metal compounds may also be formed. Sulfur-containing derivatives are then formed by reacting the metal phenate with sulfur, sulfides of phosphorus or other sulfurizing agent. The procedure described in the preceding paragraph may be used. The resulting compounds are somewhat different in structure, chemical characteristics and the like to the sulfurized metal alkyl phenol sulfides described above.

Generally, the additives of the present invention are most advantageously blended with lubricating oil base stocks in concentrations between the approximate limits of 0.01% and 10.0% and preferably from 0.1% to 2.0% by weight, although larger amounts may be used for some purposes. The exact amount of addition agent required for maximum improvement depends to a certain extent on the particular products used, the nature of the lubricating oil base stock and the general operating conditions of the engine in which the lubricant is to be employed. This same general range of concentration will also be effective when the additives are to be used in greases and in extreme pressure lubricants, although in the latter instance greater amounts, up to 20%, may also be employed.

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 addition agent.

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. 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 coal 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.

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 aviation engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 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, organo metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agent, resins, rubber, olefin polymers, voltolized fats or fatty oils, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Specific examples of such other agents include phenyl alpha-naphthylamine, voltolized sperm oil, 2,6-di-tert.-butyl-4-methyl phenol, sulfurized sperm oil, p-tert.-amyl phenol sulfide, dibenzyl disulfide, polyisobutylene, sulfurized wax olefins, tricresyl phosphate, diamyl trisulfide, and the condensation product of phenol with a sulfur chloride-di-isobutylene reaction product. Solvents and assisting agents, such as esters, ketones, alcohols, amines, nitriles, aldehydes, halogenated or nitrated compounds, and the like, may also be employed.

In addition to being employed in crankcase lubricants,

the additives of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, heat transfer media, general machinery oils, steam cylinder oils, cutting oils, insulating oils, process oils, rust preventive compositions, hydraulic oils and greases. Also their use in motor fuels, diesel fuels and kerosene is contemplated. A particular application in this regard is their use in motor fuels containing tetraethyl lead or other anti-knock agents. In such, the additives of the present invention serve not only as antioxidants for the fuel but also as stabilizers for the antiknock agent itself. These additives exhibit anti-oxidant properties and are believed also to possess ability to modify surface activity. Hence 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. In general, they may be used in any organic materials subject to deterioration by atmospheric oxygen.

In the following examples are described various preparations of products in accordance with this invention and the results obtained on testing the same in various lubricating oil blends. It is to be understood that these examples, given for illustrative purposes, are not to be construed as limiting the scope of the invention in any way other than as indicated in the claims below.

Example 1.—Preparation of cyclohexenylethylene-tert. octyl phenol

412 g. (2 mols) of tert.-octyl phenol were melted in a reactor and 6 g. of gaseous BF_3 catalyst were bubbled into the liquid. 270 g. (2.5 mols) of vinyl cyclohexene-3 were then added slowly to the mixture which was at a temperature of 158° F. There was a slight rise in temperature during addition. The mixture was heated to 194° F. and then the temperature began to rise of its own accord to about 248° F. A heavy liquid formed. The material was cooled to 194° F., digested for two hours and then fractionated at a reduced pressure of 20 mm. mercury. The major portion of the distillate boiled between 374°–446° F. at 20 mm. mercury and consisted chiefly of cyclohexenylethylene-tert.-octyl phenol. This fraction was designated as Product A and was liquid at room temperature.

Example 2.—Sulfurization of various phenols

Product B.—316 g. (1 mol) of Product A (Example 1) were dissolved in an equal amount of hexane solvent. The mixture was treated with 89 g. (0.87 mol) of commercial sulfur dichloride at a temperature of 86° F. After digesting for 30 minutes, the hexane was stripped from the sulfurized material. The chlorine free sulfurized material was a free flowing liquid at room temperature. It dissolved in 345 g. of a mid-continent lubricant base stock having an S. S. U. viscosity, at 100° F. of about 150 to form an oil concentrate containing about 50 weight % of the sulfurized material. The sulfide of cyclohexenylethylene-tert.-octyl phenol was readily soluble in the lubricant base stock, and the oil concentrate had good viscosity characteristics. The concentrate analyzed 2.97% by weight sulfur. The molecular weight of the sulfide was determined to be about 1220 showing an average of 2.3 atoms of sulfur per molecule and 3.6 alkylated phenol radicals per molecule. It is therefore indicated that the sulfide is a mixture of several compounds and includes at least some compounds containing sulfur interconnecting cyclohexene radicals as well as interconnecting benzene radicals. The product may also contain polymers or other condensation products; the structures are not known with certainty.

Product C.—A portion of tert.-octylphenol was treated with sulfur dichloride under conditions similar to those used in preparing Product B. A 50% concentrate of the resulting sulfide in lubricant base oil analyzed about 5.5 weight % sulfur. The tert.-octylphenol sulfide had an average molecular weight of 461 and contained about one sulfur atom interconnecting two alkyl phenol radicals.

Product D.—A portion of di-tert.-octylphenol (containing two alkyl radicals per phenol radical) was treated with sulfur dichloride under the conditions similar to these employed in preparing Product B. A 50% concentration of the sulfide in oil was also prepared which analyzed about 2.4% by weight of sulfur. The average molecular weight of the di-tert.-octylphenol sulfide was 690 and contained about one sulfur atom interconnecting two alkyl phenol radicals.

It is interesting to observe from these preparations that the alkyl phenol of the present invention, although having substantially the same molecular weight as the di-tert.-octylphenol, produced a sulfide having almost twice the molecular weight of the sulfide derived from the latter compound.

Example 3.—Preparation of barium salts of the sulfides

Product E.—400 g. of Product B (50% concentrate) was blended with 200 g. of the same lubricant base stock used to prepare this concentrate. The mixture was heated to 250° F., and 300 g. of barium hydroxide pentahydrate were added slowly and the mixture was digested for one hour. The material was heated to 300° F. and filtered through a diatomaceous filter aid. The filtered product consisted of about 35% by weight of the barium salt of Product B in oil. The oil concentrate analyzed 3.66% by weight barium and 1.54% by weight sulfur. The concentrate was found to be substantially non-corrosive to copper and to have only a trace sensitivity to water. The barium salt was readily soluble in the lubricant base stock in high concentrations.

Product F.—This product was prepared by treating Product C with barium hydrate using the above procedure for making Product E. The resulting oil concentrate containing about 35% by weight of barium tert.-octyl phenol sulfide analyzed about 3.6% by weight sulfur and 9.0% by weight barium.

Product G.—Product D was treated with barium hydrate by the procedure used in making Product E. The resulting oil concentrate containing about 35% by weight of barium di-tert.-octylphenol sulfide analyzed about 1.5 weight % sulfur and 7.6 weight % barium.

Example 4.—Laboratory bearing corrosion test

Blends were prepared containing 0.25 weight % of the active ingredient of each of Product E, F and G in an S. A. E. grade 20 lubricant base oil. These blends and a sample of the base oil were submitted to a laboratory test designed to measure the antioxidant characteristics of the additives by determining the effectiveness of the additives in inhibiting the corrosiveness of a typical mineral lubricant towards the surfaces of copper-lead bearings. The test was conducted substantially in accordance with that described in Example 12 of U. S. 2,529,303, issued in the name of John P. McDermott on November 7, 1950. The results are given in the following table as "corrosion life" which indicates the number of hours required for the bearings to lose 150 milligrams in weight, determined by interpolating the data obtained in various 4-hour periods. The table also presents comparative analytical data on the oil concentrates containing the products.

Product	Analysis of 35% Oil Concentrates, Weight Percent		Bearing Corrosion Life of Oil Containing 0.25 wt. percent Active Ingredient, Hours
	Sulfur	Barium	
None [1]	0	0	17
E	1.5	3.7	32
F	3.6	9.0	20
G	1.5	7.6	20

[1] Base oil only.

It is observed that the compound of the present invention (Product E), although having a considerably lower barium content than the prior art products, is markedly superior to the latter products in antioxidant properties as measured by the bearing corrosion test.

What is claimed is:

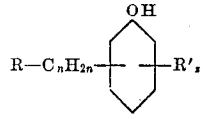
1. The process of producing sulfur-containing phenolic-type compounds which comprises the step of reacting a sulfur halide with a compound having the general formula

$$R_yR_zArOH$$

wherein R is a cycloalkenyl radical containing 4 to 8 carbon atoms in the ring attached through an alkylene radical having in the range of 1 to 10 carbon atoms to an aromatic nucleus Ar, R′ is an alkyl radical attached to said nucleus and having in the range of 1 to 20 carbon atoms, y is an integer from 1 to 3, z is an integer from 0 to 2 and the sum of y and z is no more than 4, said reaction being carried out at a temperature in the range of about 50° to 250° F., whereby a product containing added sulfur is formed.

2. A process as in claim 1 wherein said product is reacted with a basic reacting compound of a divalent metal of group II of the periodic table to form the metal salt derivative thereof.

3. The process of producing sulfide derivatives of alkylated phenols which comprises the steps of reacting a sulfur chloride with a compound having the general formula



wherein R is a cyclohexenyl radical, R′ is an alkyl radical having in the range of 1 to 20 carbon atoms, n is an integer from 1 to 10, and z is 0 to 1, said reaction being carried out at a temperature in the range of 50° to 250° F. whereby a sulfide derivative of said compound is formed.

4. A process as in claim 3 wherein the range of 0. 2 to 3 mols of sulfur chloride are used for each mol of said compound.

5. A process as in claim 4 wherein said sulfide derivative is treated with at least sufficient basic reacting compound of a divalent metal of group II of the periodic table to neutralize same.

6. A process as in claim 5 wherein said neutralization is carried out in a mineral lubricating oil.

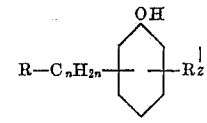
7. As a new composition of matter, the product obtained by reacting a sulfur halide with a compound having the general formula

$$R_yR_zArOH$$

wherein R is a cycloalkenyl radical containing 4 to 8 carbon atoms in the ring attached through an alkylene radical having in the range of 1 to 10 carbon atoms to an aromatic nucleus Ar, R′ is an alkyl radical attached to said nucleus and having in the range of 1 to 20 carbon atoms, y is an integer from 1 to 3, z is an integer from 0 to 2 and the sum of y and z is no more than 4, said reaction being carried out at a temperature in the range of about 50° to 250° F. whereby a product containing added sulfur is formed.

8. A metal salt of the product defined by claim 7, said metal being a divalent metal of group II of the periodic table.

9. As a new composition of matter, the product obtained by reacting a sulfur chloride with a compound having the formula



wherein R is a cyclohexenyl radical, R′ is an alkyl radical having in the range of 1 to 20 carbon atoms, n is an integer from 1 to 10, and z is 0 to 1, said reaction being carried out at a temperature in the range of 50° to 250° F. whereby a sulfide derivative of said compound is formed.

10. A composition as in claim 9 wherein n is in the range of 2 to 4 and z is 1.

11. A composition as in claim 10 wherein n is 2.

12. A divalent metal salt of the product defined by claim 9, said metal being a divalent metal of group II of the periodic table.

13. A lubricant composition comprising a major preparation of a lubricating oil and in the range of 0.01 to 10% by weight of the product defined by claim 7.

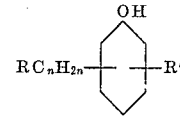
14. A lubricant composition comprising a major preparation of a lubricating oil and in the range of 0.01 to 10% by weight of the product defined by claim 8.

15. A lubricant composition comprising a major proportion of a lubricating oil and in the range of 0.01 to 10% by weight of the product defined by claim 9.

16. A lubricant composition comprising a major proportion of a lubricating oil and in the range of 0.01 to 10% by weight of the product defined by claim 12.

17. A lubricant composition comprising a major proportion of a lubricating oil and in the range of 0.01 to 10% by weight of the product defined by claim 19.

18. As a new composition of matter, the product obtained by reacting a sulfur chloride with a compound having the formula



wherein R is a cyclohexenyl radical, R′ is a tert. octyl radical, and n is an integer from 1 to 10, said reaction being carried out at a temperature in the range of 50° to 250° F. whereby a sulfide derivative of said compound is formed.

19. The barium salt of the product defined by claim 18.

20. As a new composition of matter, the product obtained by reacting cyclohexenylethylene-tert. octyl phenol with a sulfur chloride, the reaction being carried out at a temperature in the range of 50° to 250° F., whereby a sulfide derivative of said phenol is formed.

21. The barium salt of the product defined by claim 20.

22. A lubricant composition comprising a major proportion of a mineral lubricating oil and in the range of about 0.01 to 10% by weight of the product defined by claim 21.

23. An additive concentrate consisting essentially of a mineral lubricating oil and in the range of about 25 to 75% by weight of the product defined by claim 21.

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