

## UNITED STATES PATENT OFFICE

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## CORROSION PREVENTING AGENT

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The present invention relates to the improvement of hydrocarbon products derived from petroleum sources and more particularly to the preparation of improved mineral lubricating oil compositions by the incorporation therein of a new class of additives which impart improved properties to such hydrocarbon products.

In the development of petroleum lubricating oils the trend has been to use more and more efficient refining methods in order to reduce the tendency of the oils to form carbon and deposits of solid matter or sludge. While such highly refined oils possess many advantages, their resistance to oxidation, particularly under conditions of severe service, is generally decreased and they are more prone to form soluble acidic oxidation products which are corrosive. They are generally less effective than the untreated oils in protecting the metal surfaces which they contact against rusting and corrosion due to oxygen and moisture. Although generally superior to lightly refined oils they may deposit films of "varnish" on hot metal surfaces, such as the pistons of internal combustion engines, under very severe engine operating conditions.

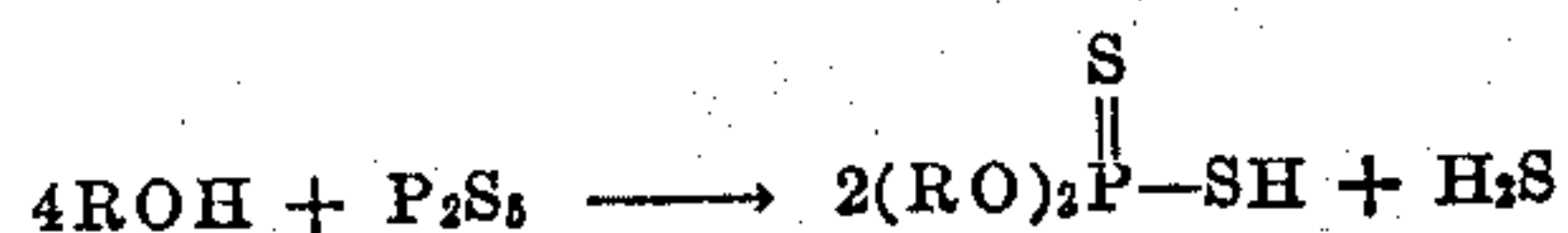
In accordance with the present invention a new class of compounds has been discovered which when added to refined lubricating oils in small proportions substantially reduce the tendency of such oils to corrode metal surfaces, and which are particularly effective in inhibiting the corrosion of copper-lead and cadmium-silver bearings. These substances are also effective in dispersing sludge and in maintaining a clean engine condition. They are likewise effective in inhibiting oxidation of other petroleum hydrocarbon products, as will be more fully explained hereinafter.

The new class of materials which have been found to possess the stabilizing and detergent qualities described above may be considered as metal salts of hydrocarbon-substituted acids of phosphorus in which a portion of the hydrocarbon groups contain a sulfurized olefinic linkage. The products are formed by first reacting a mixture of a sulfurized unsaturated monohydric aliphatic alcohol and an unsulfurized saturated monohydric alcohol with phosphorus pentasulfide ( $P_2S_5$ ) or phosphorus heptasulfide ( $P_4S_7$ ) to form an acidic product, and then neutralizing this product with a metallic base of a metal of groups I to III of the periodic system. Products prepared from the mixture of sulfurized and unsulfurized alcohols have been found to be more

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uniformly soluble in mineral oils than the corresponding products prepared from sulfurized alcohols only. Difficulties in preparing soluble products from sulfurized alcohols are believed to be due to the building up of large molecules by cross-linking by the sulfur atoms between the double bonds of different molecules: but when a portion of the molecule contains a saturated hydrocarbon group, this cross-linking is eliminated or reduced to a marked degree. The product formed when the mixture of sulfurized and unsulfurized alcohols is reacted with a sulfide of phosphorus is undoubtedly a mixture of various types of molecules and the exact constitution of the same is not known.

It is well known that organo-substituted dithiophosphoric acids may be formed by reacting four mols of an aliphatic alcohol with one mol of phosphorus pentasulfide in accordance with the equation—



In preparing the additives of the present invention the alcohols and phosphorus pentasulfide are reacted in the same proportions, that is, four mols of total alcohol are reacted with one mol of phosphorus pentasulfide. When phosphorus heptasulfide is employed, twice the above amount of alcohols will be employed. In this case the product will normally consist of mixtures of dithiophosphoric acid and monothiophosphorous acid.

The two types of alcohols, that is, the sulfurized and unsulfurized alcohols, are chosen so that the total number of carbon atoms in the two types will be not less than 16 carbon atoms, while each alcohol may vary in chain length from 1 or 2 to about 20 carbon atoms. The unsaturated alcohol cannot have less than 2 carbon atoms. While it is preferable to employ equimolar mixtures of the two alcohols, the ratio of the sulfurized to the unsulfurized alcohol may vary from about 2:1 to about 1:2. Examples of suitable unsaturated alcohols which may be sulfurized and employed in accordance with the present invention include allyl alcohol, methallyl alcohol, crotonyl alcohol, hexenyl alcohol, octenyl alcohol, nonenyl alcohol, citronellol, undecenyl alcohol, oleyl alcohol, and the like, and the reaction products of butadiene monoxide with saturated alcohols. The diolefin alcohols are also suitable. The unsulfurized saturated aliphatic alcohols which are employed in admixture with the



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sulfurized alcohols include methyl alcohol, ethyl alcohol, isopropyl alcohol, n-octyl alcohol, tert.-octyl alcohol, n-decyl alcohol, stearyl alcohol, and the like.

The alcohol mixture and sulfide of phosphorus are preferably reacted together in the presence of an inert solvent, such as benzene, chloroform, ethylene dichloride, dioxane, or the like, and the temperature of the reaction should be from about 50 to 150° C. It is generally convenient to employ a solvent having a boiling point within this range and to conduct the reaction at the refluxing temperature of the solvent. The reaction is conducted until no more hydrogen sulfide is evolved.

The acidic material produced by the above described reaction is neutralized with a metallic base. The preferred metals are those of group II of the periodic table, especially magnesium, zinc, and the alkaline earth metals. However, it is possible to prepare useful compounds from the alkali, metals, aluminum, and other metals of groups I and III. In preparing the salts the oxides, hydroxides, and alcoholates of the metals are convenient neutralizing materials.

The quantity of the additives of the present invention which is most advantageously blended in mineral lubricating oils or other petroleum hydrocarbon products will depend upon the property of the additive which it is most desired to exploit. When employed for detergent and sludge dispersing properties, the quantity most suitable will generally vary from 1 to 5% by weight. For merely inhibiting bearing corrosion and generally when employed as an antioxidant the quantity most desired will be from 0.05 to 2%, although quantities as great as 5% may on occasion be used. For commercial purposes, it is convenient to prepare concentrated oil solutions in which the amount of additive in the composition ranges from 25 to 50% by weight and to transport and store them in such form. In preparing a lubricating oil composition for use as a crankcase lubricant, the concentrate will be prepared from a lubricating oil base and will be blended with additional quantities of the base oil as and when required.

The preparation and testing of examples of the compounds of the present invention are illustrated by the examples to be described in detail below, but such examples are not to be construed as limiting the scope of the invention in any manner.

*Example 1.—Calcium decanol-sulfurized oleyl dithiophosphate*

(a) Sulfurized oleyl alcohol is prepared by heating 6200 g. (23.2 mols) of commercial oleyl alcohol to 138° C. and adding 726 g. (22.8 mols) of sulfur with stirring. The temperature was raised to 170° C. and heating and stirring were continued at this temperature for three hours. The sulfurized product contained 10.15% sulfur.

(b) A three-way reaction flask equipped with a stirrer and a return condenser was charged with 60 g. (0.2 mol) of sulfurized oleyl alcohol prepared as described in (a), 31.6 g. (0.2 mol) of n-decanol, 22 g. (0.1 mol) of  $P_2S_5$ , and 30 cc. of dioxane. The mixture was then refluxed until no more hydrogen sulfide was given off, and the solvent removed by distillation.

(c) The product obtained in (b) was dissolved in 150 cc. of solvent naphtha. 150 cc. of water was added and the mixture was treated with a slight excess of hydrated lime and stirred

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until the aqueous mixture became permanently basic to litmus. The aqueous layer was then removed by means of a separatory funnel and the naphtha layer dried over calcium chloride and filtered. The filtrate was evaporated to dryness at 100° C. and 2 mm. pressure. The residue consisted of 110 g. of a soft, light colored resin which proved to be readily soluble in mineral lubricating oil. The product contained 2.84% calcium, 14.30% sulfur, and 5.48% phosphorus.

*Example 2.—Barium decanol-sulfurized oleyl dithiophosphate*

276 g. (0.5 mol) of the product obtained in Example 1 (b) was dissolved in a mixture of 275 cc. of methanol and 50 cc. of ethyl ether. To this was added 80 g. (0.25 mol) of barium hydrate,  $Ba(OH)_2 \cdot 8H_2O$ , dissolved in 200 cc. of methanol. The mixture was stirred for one-half hour and filtered to remove a trace of undissolved material. On evaporation of the filtrate, 265 g. of a light colored residue was obtained. This was purified by dissolving in benzol, filtering and removing the solvent at 100° C. and 2 mm. pressure. 245 g. of a light colored resin was obtained, which was readily soluble in oil, and which was found to contain 10.56% barium, 14.21% sulfur, and 5.42% phosphorus.

*Example 3.—Bearing corrosion test*

Blends containing 0.5% and 1.0%, respectively, of each of the products of Examples 1 and 2 in a paraffinic type mineral lubricating oil of SAE 20 grade and a sample of the unblended base oil were submitted to a corrosion test designed to measure the effectiveness of the product in inhibiting the corrosiveness of a typical mineral lubricating oil towards the surfaces of copper-lead bearings. The test was conducted as follows: 500 cc. of the oil was placed in a glass oxidation tube (13 inches long and 2 5/8 inches in diameter) fitted at the bottom with a 1/4 inch 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 sufficient 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 4-hour period the bearings were removed, washed with naphtha and weighed to determine the amount of loss by corrosion. The bearings were then repolished (to increase the severity of the test), reweighed, and then subjected to the test for additional 4-hour periods in like manner. The results are given in the following table as "corrosion life," which indicates the number of hours required for the bearings to lose 100 mg. in weight, determined by interpolation of the data obtained in the various periods.

Oil or Oil Blend	Bearing Corrosion Life (Hrs.)
Base oil	4
Base oil + 0.5% Ca salt (Example 1)	28
Base oil + 1.0% Ca salt (Example 1)	36
Base oil + 0.5% Ba salt (Example 2)	30
Base oil + 1.0% Ba salt (Example 2)	40



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**Example 4.—Carbon black dispersion test**

A carbon black dispersion test was carried out as described in U. S. Patent 2,390,342, to measure the comparative effectiveness of the additives of the present invention as agents for dispersing sludge in lubricating oil. In this test 6% by weight of activated carbon was added to the oil blend containing the additive and thoroughly dispersed in the oil by stirring with an "egg beater" type mixer for 15 minutes while the temperature of the oil was maintained at 250° F. 250 cc. of the blend was then placed in a 250 cc. graduated cylinder and allowed to settle for 24 hours while the temperature was maintained at 200° F. If an additive is not a dispersing agent, the carbon black settles rapidly at this point leaving clear oil at the top in an hour or two. A very effective disperser will maintain the carbon black in suspension so that no change in the opaque slurry is apparent even after a 24-hour period. With all but the most potent dispersing agents stratification occurs with a black layer at the bottom (high concentration of carbon black) and a blue opaque layer at the top (reduced carbon black concentration). Cases of this type, known as "blue line" separations, are only detectable in reflected light. The base oil used for this test was a paraffinic oil of SAE 20 grade. The results of the test when applied to blends containing the products of Examples 1 and 2 are shown in the following table, in which the results are shown as the volume of dispersed carbon black remaining after the settling period.

Oil or Oil Blend	Cc. Dispersed Carbon Black
Base oil.....	163
Base oil + 1% product of Example 1.....	250
Base oil + 1% product of Example 2.....	250

The above results show that in the cases of the blends with the additive a perfect dispersion of the carbon black was maintained throughout the period of the test.

The products of the present invention may be employed not only in ordinary hydrocarbon lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, phosphites, thiophosphates, and thiophosphites, metal xanthates and thioxanthates, metal thiocarbamates, and the like. Other types of additives, such as phenols and phenol sulfides, may also be present.

The lubricating oil base stock 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 by solvent extraction with solvents such as phenol, sulfur dioxide, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils resembling petroleum oils, prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen

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or by the hydrogenation of coal or its products.

For the best results the base stock chosen should normally be an oil which with the new additive 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, no strict rule can be laid down for the choice of the base stock. The additives are normally sufficiently soluble in the base stock, but in some cases auxiliary solvent agents may be used. The lubricating oils will usually range from about 40 to 150 seconds (Saybolt) viscosity at 210° F. The viscosity index may range from 0 to 100 or even higher.

Other agents than those which have been mentioned may be present in the oil composition, such as dyes, pour point depressants, heat thickened fatty oils, sulfurized fatty oils, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, and the like.

Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having preferably 8-20 carbon atoms, e. g., octyl alcohol, lauryl alcohol, stearyl alcohol, and the like.

In addition to being employed in lubricants, the additives of the present invention may also be used in other mineral oil products such as motor fuels, heating oils, hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils, transformer oils, industrial oils, process oils, and the like, and generally as antioxidants in mineral oil products. They may also be used in gear lubricants, greases and other products containing mineral oils as ingredients.

What is claimed is:

1. A composition consisting essentially of a petroleum hydrocarbon product to which has been added at least an oxidation inhibiting amount of a soluble metal salt of an acidic product obtained by reacting a mixture of a sulfurized unsaturated monohydric aliphatic alcohol having 2 to 20 carbon atoms per molecule and a saturated monohydric aliphatic alcohol having 1 to 20 carbon atoms per molecule, the total number of carbon atoms in the said mixture of alcohols being not less than 16, and the molar ratio of the sulfurized alcohol to the unsulfurized alcohol being from 2:1 to 1:2, with a sulfide of phosphorus of the class consisting of phosphorus pentasulfide and phosphorus heptasulfide, in such a molar ratio that two molecules of alcohol are present for each atom of phosphorus, the reaction between the alcohols and the sulfide of phosphorus being conducted at a temperature of 50-150° C., and the metal of the metal salt being chosen from metals of groups I to III of the periodic table.

2. A composition according to claim 1 in which the petroleum hydrocarbon product is a mineral lubricating oil fraction.

3. A composition according to claim 1 in which the ratio of the sulfurized alcohol to the unsulfurized alcohol is approximately 1:1.

4. A composition according to claim 1 in which the sulfide of phosphorus is phosphorus pentasulfide.

5. A composition according to claim 1 in which the sulfide of phosphorus is phosphorus pentasulfide and in which the sulfurized alcohol is sulfurized oleyl alcohol.

6. A composition consisting essentially of a mineral lubricating oil to which has been added



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at least an oxidation inhibiting amount of a metal salt of an acidic product obtained by reacting a mixture of substantially equimolar quantities of sulfurized oleyl alcohol and n-decanol with phosphorus pentasulfide in the ratio of about four mols of total alcohols for each mol of phosphorus pentasulfide, the reaction between the alcohols and phosphorus pentasulfide being conducted at a temperature of 50-150° C., and the metal of the metal salt being selected from groups I to III of the periodic system.

7. A composition according to claim 6 in which the metal of the metal salt is calcium.

8. A composition according to claim 6 in which the metal of the metal salt is barium.

9. A composition consisting essentially of a mineral lubricating oil and an additive as defined in claim 1, the amount of said additive in composition being 25 to 50% by weight.

10. A composition consisting essentially of a mineral lubricating oil and an additive as defined in claim 7, the amount of said additive in the composition being 25 to 50% by weight.

11. A composition consisting essentially of a mineral lubricating oil and an additive as defined in claim 8, the amount of said additive in the composition being 25 to 50% by weight.

12. As a new composition of matter a metal salt of an acidic product obtained by reacting a mixture of a sulfurized unsaturated monohydric aliphatic alcohol having 2 to 20 carbon atoms per molecule and a saturated monohydric aliphatic alcohol having 1 to 20 carbon atoms per molecule, the total number of carbon atoms in the said mixture of alcohols being not less than 16, and the molar ratio of the sulfurized alcohol to the unsulfurized alcohol being from 2:1 to 1:2, with a sulfide of phosphorus of the class consisting of phosphorus pentasulfide and phosphorus heptasulfide, in such a molar ratio that two molecules

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of alcohol are present for each atom of phosphorus, the reaction between the alcohols and the sulfides of phosphorus being conducted at a temperature of 50-150° C., and the metal of the metal salt being chosen from metals of groups I to III of the periodic table.

13. A composition according to claim 12 in which the ratio of the sulfurized alcohol to the unsulfurized alcohol is approximately 1:1.

14. A composition according to claim 12 in which the sulfide of phosphorus is phosphorus pentasulfide.

15. A composition according to claim 12 in which the sulfurized alcohol is sulfurized oleyl alcohol, and in which the sulfide of phosphorus is phosphorus pentasulfide.

16. As a new composition of matter a metal salt of an acidic product obtained by reacting a mixture of substantially equimolar quantities of sulfurized oleyl alcohol and n-decanol with phosphorus pentasulfide in the ratio of about four mols of total alcohols for each mol of phosphorus pentasulfide, the reaction between the alcohols and phosphorus pentasulfide being conducted at a temperature of 50-150° C., and the metal of the metal salt being selected from groups I to III of the periodic system.

17. A composition according to claim 16 in which the metal of the metal salt is calcium.

18. A composition according to claim 16 in which the metal of the metal salt is barium.

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