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CORROSION PREVENTING AGENT

John P. McDermott, Springfield, N. J., assignor to Esso Research and Engineering Company, a corporation of Delaware

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5 Claims. (Cl. 252—46.6)

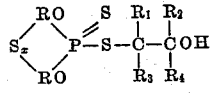
The present invention relates to the improvement of hydrocarbon products derived from petroleum sources and more particularly to the preparation of improved mineral lubricating oil compositions by the incorporation therein of a new class of additives which impart improved properties to such hydrocarbon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

This application is a continuation-in-part of patent application Serial No. 192,617, filed on October 27, 1950, now abandoned.

In the development of petroleum lurbicating 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 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.

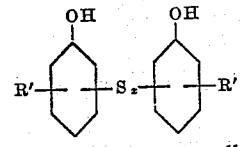
In accordance with the present invention a new class of products has been discovered which when added to refined lubricating oils in small proportions substantially reduce the tendency of such oils to corrode metal surfaces, and which are particularly effective in inhibiting the corrosion of copper-lead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

The new class of materials which have been found to possess the antioxidant and stabilizing qualities described above are the condensation products of epoxides with the reaction products of phenol sulfides and phosphorus pentasulfide. It is believed that the condensation product formed in accordance with this invention is predominantly a compound of the formula:



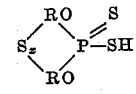
where R is an aromatic or aliphatic-aromatic hydrocarbon radical, x is an integer of 1 to 2; and where one of the symbols R_1, R_2, R_3 and R_4 represent a hydrogen atom, an aliphatic hydrocarbon radical containing 1 to 4 carbon atoms or a phenyl radical and the others of the symbols R_1, R_2, R_3, and R_4 represent hydrogen atoms. Preferably one of the symbols R_1, R_2, R_3 and R_4 represents an aliphatic hydrocarbon radical containing 1 to 4 carbon atoms or a phenyl group and the others represent hydrogen atoms.

The phenol sulfides which may be reacted with phosphorus pentasulfide in accordance with this invention have the general formula:



where R' is a hydrogen atom or an alkyl radical. The preferred phenol sulfides are alkyl phenol sulfides containing 4 to 24 or more carbon atoms in each alkyl group. Particularly preferred alkyl phenol sulfides contain 6 to 12 carbon atoms in the alkyl group attached to each of the two benzoid nuclei. The symbol x is an integer of 1 to 2. It is preferred that R' contain at least 4 carbon atoms to provide a final additive product which has good oil solubility. The preparation of these phenol sulfides is well known in the art and is described in detail for example in U. S. 2,518,379 (column 4, lines 8–53). Specific examples of these phenol sulfides include tert. octyl phenol sulfide, nonyl phenol sulfide, amyl phenol sulfide, cetyl phenol sulfide, etc. These are prepared preferably by reacting sulfur chloride with the particular alkyl phenol.

The reaction between the phenol sulfide and phosphorus pentasulfide is carried out using approximately the same reaction conditions which are well known in the art for preparing dithiophosphoric acids from alcohols and phosphorus pentasulfide. However, in the present reaction about 2 moles of phenol sulfide are reacted with one mole of P_2S_5 to form a product believed to be predominantly



(Dithiophosphoric acid)

This reaction is carried out at a temperature of about 125° to 175° C., preferably about 140° to 160° C. by stirring the reactants together until the P_2S_5 has been consumed. This can be noted visually. The reaction time required will generally be in the range of about 0.5 to 5 hours, usually about 1 to 2 hours. After the reaction is completed the reaction product is preferably blown with nitrogen or other inert gas to remove hydrogen sulfide therefrom. If desired, the reaction may be carried out in a solvent such as a mineral oil, e. g., a mineral lubricating oil.

The epoxides which are condensed with the phenol sulfide-P_2S_5 reaction products in accordance with this invention include especially the well-known alkylene oxides having 2 to 6 and preferably 3 to 4 carbon atoms per molecule, such as ethylene oxide, propylene oxide, the butylene and isobutylene oxides, and butadiene monoxide. Styrene oxide may also be employed and is particularly preferred since it forms compounds of this invention which are especially potent antioxidants and corrosion inhibitors. Propylene oxide is also a preferred epoxide since it is readily available at low cost.

The reaction between the dithiophosphoric acid (the phenol sulfide-P_2S_5 reaction product) and the epoxide is a spontaneous exothermic reaction which takes place immediately upon contact of the reactants at normal room temperatures, and may be conveniently conducted by adding about one mole of the epoxide slowly to one mole of the dithiophosphoric acid while rapidly stirring the reaction mixture and controlling the temperature by means of a water or ice bath. Generally temperatures in the range of about 20° to 100° C. may be employed. No catalyst is required, and the time required for the completion of the reaction is not greater than two hours

and is usually much less. Reaction times of about 0.2 to 2 hours may generally be employed. Solvents are not normally required, but in some cases it may be convenient to conduct the reaction in the presence of well known inert solvents such as ethylene dichloride, benzene, xylene, or a mineral oil.

The amount of the additives of the present invention which is to be employed in mineral lubricating oil compositions or other petroleum hydrocarbon compositions (which generally will contain a major proportion of the petroleum hydrocarbon oil) will normally range from about 0.02% to 5%, more generally from about 0.1 to about 2% by weight, based on the total composition, and the particular amount in individual cases will be selected in accordance with the requirements of the case and in view of the properties of the base stock employed. 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 additive concentrate is merely blended with the base oil in the required amount.

The preparation and testing of the additives of the present invention are illustrated in the examples described below, but it is to be understood that the additives prepared and their application in various tests are illustrative only and are not to be construed as limiting the scope of the invention in any manner.

Example 1.—Tert.-octylphenyl sulfide dithiophosphoric acid-butadiene monoxide reaction product

A mixture of 460 g. (0.5 mol) of a 50% oil solution of tert.-octylphenol sulfide (containing an average of about 1.5 atoms of S for each pair of benzene rings) and 55.5 g. (0.25 mol) of P_2S_5 was heated at 145° C. for 1 hour with rapid stirring, followed by filtration and a 20-minute nitrogen blowing period on the steam bath. The product was predominantly tert.-octylphenol sulfide dithiophosphoric acid.

The product was transferred to a 4-necked 2-liter flask equipped with a stirrer, thermometer, dropping funnel, and reflux condenser. 35.0 g. (0.5 mol) of butadiene monoxide was added dropwise over a period of 45 minutes, maintaining the temperature below 45° C. by means of an ice bath. After stirring for an additional hour at this temperature, the product was blown with nitrogen on the steam bath for 25 minutes. A clear, dark red, viscous liquid was obtained which analyzed 2.6% phosphorus and 9.4% sulfur.

Example 2.—Tert.-octylphenyl sulfide dithiophosphoric acid-styrene oxide reaction product

The tert.-octylphenol sulfide dithiophosphoric acid was prepared as described in Example 1.

At a temperature of 45° C., 60 g. (0.5 mol) of styrene oxide was added to the thiophosphoric acid over a period of about 45 minutes with rapid stirring. After stirring for an additional hour at this temperature, the product was placed on the steam bath and blown with nitrogen for 25 minutes. A clear, dark red, viscous liquid was obtained which analyzed 2.6% phosphorus and 8.8% sulfur.

Example 3.—Nonylphenol sulfide dithiophosphoric acid-propylene oxide reaction product

A mixture of 495 g. (0.5 mol) of a 50% oil solution of nonylphenol sulfide (containing an average of about 1.8 atoms of S for each pair of benzene rings) and 55.5 g. (0.25 mol) of P_2S_5 was heated at 150° C. for 1 hour with rapid stirring. The product was then filtered and blown with nitrogen on the steam bath for 20 minutes.

With rapid stirring, 30 g. (0.5 mol) of propylene oxide was added dropwise over a period of about 30 minutes, maintaining the temperature below 30° C. by means of an ice bath. After stirring for an additional hour at room temperature, the product was blown with nitrogen for about 25 minutes on the steam bath. A clear, dark red, viscous liquid was obtained which analyzed 2.1% P and 9.0% S.

Example 4.—S. O. D. corrosion test

Blends were prepared containing 0.25% by weight of each of the products of Examples 1 to 3 in a paraffinic mineral lubricating oil of SAE 20 grade. Where the product was obtained in the form of a mineral oil solution a quantity of the product was employed which was equivalent to 0.25% of the active compound.

These blends and a sample of the unblended base oil were submitted to a corrosion test, known as the S. O. D. corrosion test, designed to measure the effectiveness of the product in inhibiting the corrosiveness of a typical mineral lubricating oil toward the surfaces of copper-lead bearings. The test was conducted as follows: 500 cc. of the oils was placed in a glass oxidation tube (13 inches long and 2⅝ inches in diameter) fitted at the bottom with a ¼ 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	9
Base oil + 0.25% product of Example 1	44
Base oil + 0.25% product of Example 2	56
Base oil + 0.25% product of Example 3	30

Example 5.—Lauson engine test

A blend containing 1% by weight of the active ingredient of the product of Example 2 in a solvent extracted Mid-continent oil of SAE 10 grade and a sample of the unblended base oil were employed as the crankcase lubricant in tests with a Lauson engine operating at 295° F. jacket temperature and 300° F. oil temperature, 1800 R. P. M. speed, and 1.5 indicated kilowatt load, the tests being conducted for 25 hours each. The loss in weight of the copper-lead bearing was determined. The results of these observations are as follows:

Lubricant	Bearing Weight Loss (mg./bearing)
Base Oil	74
Base oil + 1% product of Example 2	18

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 oxanthates 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 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.

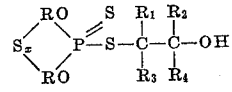
Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having preferably 8–20 carbon atoms, e. g., octyl alcohol, lauryl alcohol, stearyl alcohol, and the like.

In addition to being employed in lubricants, the additives of the present invention may also be used in other petroleum 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 mineral oil containing dissolved therein a corrosion inhibiting amount of an oil-soluble compound of the formula



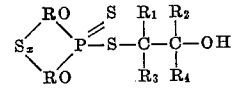
wherein R is an aromatic radical having one alkyl group containing 4 to 24 carbon atoms; wherein x is an integer of from 1 to 2; wherein one of the symbols R_1, R_2, R_3 and R_4 represents a radical selected from the group consisting of a hydrogen atom, an aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, and a phenyl radical; and wherein the others of said symbols are hydrogen atoms.

2. The composition of claim 1 wherein said alkyl group contains from 6 to 12 carbon atoms.

3. The composition of claim 1 wherein one of said symbols is a phenyl radical.

4. The composition of claim 1 wherein said oil-soluble compounds is present in an amount in the range of 0.02 to 5.0 wt. percent.

5. A mineral lubricating oil having a viscosity in the range of 40 to 150 seconds (Saybolt) at 210° F. containing dissolved therein a corrosion inhibiting amount of an oil-soluble compound of the formula



wherein R is an aromatic radical having one alkyl group containing 4 to 24 carbon atoms; wherein x is an integer of from 1 to 2; wherein one of the symbols R_1, R_2, R_3 and R_4 represents a radical selected from the group consisting of a hydrogen atom, an aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms, and a phenyl radical; and wherein the others of said symbols are hydrogen atoms.

No references cited.