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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.

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

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. 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 oil-soluble reaction products of organo-substituted dithiophosphoric acids and styrene oxide. Such products may be defined broadly by the formula:

\[
\text{RO} \quad \text{S} \quad \text{R}_{1} \quad \text{R}_{2} \\
\text{Si} \quad \text{O} \quad \text{OH} \\
\text{RO} \quad \text{R}_{3} \quad \text{R}_{4}
\]

where R is an aliphatic, cycloaliphatic or aliphatic- aromatic organic radical, preferably a hydrocarbon radical, and where one of the symbols R1, R2, R3, and R4 represents a phenyl radical and the others of the symbols R1, R2, R3, R4, and R5 represent hydrogen atoms. Two different R radicals may be present in the product. It is to be understood that the radicals represented by R in the above formula may also contain substituents such as halogen atoms or nitro groups. In general, the number of carbon atoms in the R radicals should be sufficient to form a product having good oil solubility. Oil solubilizing radicals of about 3 to 30 carbon atoms are preferred. When R is a cycloaliphatic hydrocarbon radical, it is preferred that it be an alkyl radical containing about 3 to 18 carbon atoms, particularly about 3 to 8 carbon atoms; when R is an aliphatic-aromatic hydrocarbon radical, it is preferred that it be an alkyl phenyl radical containing about 4 to 18 carbon atoms, particularly 6 to 12 carbon atoms, in the alkyl group; and when R is a cycloaliphatic hydrocarbon radical, it is preferred that it be an alkyl cyclohexyl radical containing about 1 to 4 carbon atoms in the alkyl group. The preferred compounds are those where R is an aliphatic radical of relatively short chain length, preferably as indicated above, an alkyl group containing about 3 to 8 carbon atoms.

The following typical examples are representative of the dithiophosphoric acids which may be reacted with styrene oxide in accordance with the present invention:

- Diisopropyl dithiophosphoric acid
- Di-n-butyl dithiophosphoric acid
- Di-n-propyl dithiophosphoric acid
- Di-tert-octyl dithiophosphoric acid
- Di-(ethylhexyl) dithiophosphoric acid
- Dinonyl dithiophosphoric acid
- Di-(Cs oxo) dithiophosphoric acid
- Di-ethyl dithiophosphoric acid
- Di-n-butyl dithiophosphoric acid
- Di-(n-propyl) dithiophosphoric acid
- Di-(n-butyl) dithiophosphoric acid
- Di-(2,4,6-trisubstituted) dithiophosphoric acid

The above listed dithiophosphoric acids may be prepared by reacting an alcohol or phenol with phosphorus pentasulfide in the presence of a suitable catalyst, and it is to be understood that the invention applies not only to simple acids but to mixtures of acids formed by reacting phosphorus pentasulfide with mixtures of alcohols, such, for example, as the mixtures of Cs to Cs aliphatic alcohols known as “Lori” alcohols, and the mixture of alcohols derived by the oxidation of paraffin wax. Included also are products derived from the mixture of branched chain aliphatic alcohols obtained in the “oxo” process.

The reaction between the dithiophosphoric acid and styrene oxide 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 styrene oxide 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 lubri-
cant 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 tested are illustrative only and are not to be construed as limiting the scope of the invention in any manner.

Example 1.—Diisopropyl dithiophosphoric acid-styrene oxide reaction product

A mixture of 120 g. (2 mols) of isopropanol and 111 g. (0.5 mol) of PaSs was heated at 95° C. for 45 minutes in a 1-L. 3-necked flask equipped with a stirrer, thermometer, reflux condenser and dropping funnel. 120 g. of styrene oxide (1 mol) was then added over a period of 1 hour, keeping the temperature under 50° C. by means of a cold water bath. The reaction mixture was then stirred at room temperature for 1 hour. A pale yellow liquid was obtained which upon analysis was found to contain 8.7% phosphorus and 16.6% sulfur.

Example 2.—Di-(methylene cyclohexyl) dithiophosphoric acid-styrene oxide reaction product

A mixture of 228 g. (2 mols) of methylene cyclohexanol and 111 g. (0.5 mol) of PaSs was heated at 105° C. for 1 hour. The product, di-(methylene cyclohexyl) dithiophosphoric acid, was then filtered to remove a small amount of unreacted PaSs, after which the filtrate was blown with nitrogen for 20 minutes on the steam bath.

With rapid stirring, 120 g. (1 mol) of styrene oxide was added dropwise over a period of about one hour keeping the temperature under 50° C. by means of a cold water bath. The reaction mixture was then stirred at room temperature for 1 hour followed by nitrogen blowing for 30 minutes. A viscous dark liquid was obtained which analyzed 5.4% phosphorus and 12.2% sulfur.

Example 3.—Di-(nonylphenol) dithiophosphoric acid-styrene oxide reaction product

A mixture of 440 g. (2 mols) of nonylphenol and 111 g. (0.5 mol) of PaSs was heated at 150° C. for 1.5 hours. After it was prepared, the viscous product was dissolved in an equal volume of carbon tetrachloride and filtered, followed by nitrogen blowing for 20 minutes.

With rapid stirring, 120 g. (1 mol) of styrene oxide was added dropwise over a period of about one hour keeping the temperature under 50° C. by means of a cold water bath. The reaction mixture was then stirred at room temperature for 1 hour followed by nitrogen blowing on the steam bath for 45 minutes (the carbon tetrachloride solvent was removed by this blowing step). The viscous amber colored liquid analyzed 4.5% phosphorus and 9.75% sulfur.

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.

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 stainless steel tube (13 inches long and 2.5 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 heat-
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 petroleum hydrocarbon product containing dissolved therein a corrosion inhibiting amount of an oil-soluble compound of the formula—

\[
\begin{align*}
\text{RO} & \quad \text{S} \quad \text{R}_1 \quad \text{R}_2 \\
\text{RO} & \quad \text{S} \quad \text{O} \quad \text{OH}
\end{align*}
\]

where R is an organic radical selected from the group consisting of aliphatic, cycloaliphatic and aliphatic-aromatic organic radicals; and where one of the symbols R1, R2, R3, and R4 represents a phenyl radical and the others of the symbols R1, R2, R3 and R4 represent hydrogen atoms.

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

3. A composition according to claim 1 in which R represents a hydrocarbon radical.

4. A composition according to claim 1 in which R is an alkyl group containing 3 to 8 carbon atoms.

5. A composition according to claim 1 in which R represents a methyl-cyclohexyl radical.

6. A composition according to claim 1 in which R represents an isopropyl radical.

7. A composition according to claim 1 in which R represents a nonyl phenyl radical.

8. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and in the range of about 0.02 to 5% by weight, based on the total composition, of an oil-soluble compound of the formula—

\[
\begin{align*}
\text{RO} & \quad \text{S} \quad \text{R}_1 \quad \text{R}_2 \\
\text{RO} & \quad \text{S} \quad \text{O} \quad \text{OH}
\end{align*}
\]

where R is an organic radical selected from the group consisting of aliphatic, cycloaliphatic and aliphatic-aromatic organic radicals; and where one of the symbols R1, R2, R3, and R4 represents a phenyl radical and the others of the symbols R1, R2, R3 and R4 represent hydrogen atoms.

9. A composition consisting essentially of a mineral lubricating oil and about 25 to 50% by weight of an oil-soluble compound of the formula—

\[
\begin{align*}
\text{RO} & \quad \text{S} \quad \text{R}_1 \quad \text{R}_2 \\
\text{RO} & \quad \text{S} \quad \text{O} \quad \text{OH}
\end{align*}
\]

where R is an organic radical selected from the group consisting of aliphatic, cycloaliphatic and aliphatic-aromatic organic radicals; and where one of the symbols R1, R2, R3, and R4 represents a phenyl radical and the others of the symbols R1, R2, R3 and R4 represent hydrogen atoms.

References Cited in the file of this patent

UNITED STATES PATENTS

2,531,129 Hook et al. ------------ Nov. 21, 1950