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MINERAL OIL COMPOSITION

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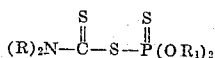
8 Claims. (Cl. 252-46.7)

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

In the development of petroleum base 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 as a result of the refining and they are more prone to form oil soluble acidic oxidation products which are corrosive. They are also generally less effective than the untreated oils in protecting the metal surfaces which they contact against rusting and corrosion due to oxygen and moisture.

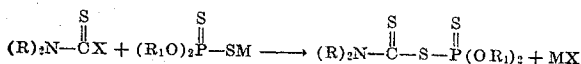
In accordance with the present invention a new class of compounds has been discovered which, when added to refined lubricating oils and other petroleum hydrocarbon oil products in small proportions, substantially reduce the tendency of such oils to corrode the metal surfaces, particularly the surfaces of copper-lead and cadmium-silver bearings which are employed in internal combustion engines, and they are likewise effective in inhibiting oxidation of hydrocarbon products generally.

The new class of materials which have been found to possess the antioxidant and stabilizing properties described above have the following general formula:



in which the R and R₁ groups represent hydrocarbon radicals each having in the range of 1 to 30 carbon atoms, preferably 1 to 15 carbon atoms. These hydrocarbon radicals may be open chain aliphatic radicals, which may be long or short, straight or branched, saturated or unsaturated, or they may be cycloaliphatic radicals or aromatic radicals such as aralkyl radicals, or alkaryl radicals. The R₁ radicals may be any one of the above general classes of hydrocarbon radicals; the R radicals are preferably selected from the group consisting of aliphatic and aralkyl radicals. It is particularly preferred that the R radicals be alkyl groups.

These compounds are conveniently prepared by mixing a salt of an organic-substituted dithio-phosphoric acid with a di-substituted thiocarbamyl halide whereby substantially equal molar quantities of the dithiophosphate and thiocarbamyl radicals combine in accordance with the following general reaction:



In the above formulas M represents a salt-forming atom or group, and X represents a halogen atom. The

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reaction is readily carried out by suspending a salt, e. g., a metal, ammonium or amine salt, of the thio acid of phosphorus in an inert medium such as petroleum ether or benzene, in which the reaction product is substantially completely soluble and in which the metallic halide by-product is substantially insoluble, and mixing therewith or adding the thiocarbamyl halide followed by refluxing and stirring. The reaction will proceed at substantially room temperature, but it is preferable to heat the mixture slightly, such as at reflux temperatures, in order to accelerate the reaction. The halide salt which separates from the liquid medium is then filtered off, and the solvent is removed by heating on a steam bath or under reduced pressure.

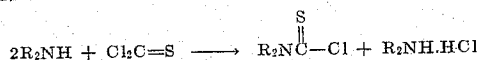
Specific compounds useful for the purposes of the present invention may be prepared by starting with materials having organic groups of a character falling within the scope of the compounds described above. For example, in preparing the organo-substituted thio acids of phosphorus, a large variety of alcohols and phenols may be employed as the original starting materials. Illustrative of such materials are the monohydric aliphatic alcohols such as ethyl alcohol, isopropyl alcohol, lauryl alcohol, stearyl alcohol, wax alcohols, and alcohols obtained by the oxidation of petroleum hydrocarbons. A group of alcohols of special interest are the "Oxo" alcohols, prepared by the reaction of carbon monoxide and hydrogen upon the olefins obtainable from petroleum products and hydrogenation of the resulting aldehydes. Such alcohols usually have a branched chain structure. Other alcohols which may be employed include unsaturated alcohols, such as oleyl alcohol and sulfurized alcohols, such as sulfurized oleyl alcohol, as well as substituted alcohols containing halogens or nitro groups. Likewise, cyclic alcohols, such as cyclohexyl alcohols, may be employed. An additional class of alcohols includes alcohols containing ether groups, illustrated by such compounds as ethylene glycol mono-n-butyl ether, diethylene glycol mono-2-ethylhexyl ether, dipropyleneglycol monomethyl ether, and tripropyleneglycol monoisopropyl ether. Many of these ether alcohols formed by the reaction of ethylene oxide or propylene oxide with aliphatic alcohols are known in the industry as "Dowanols," "Carbitols" or "Cellosolves." Among the phenols and naphthols which may likewise be employed in preparing organo-substituted acids of phosphorus are the simple phenols as well as alkylated phenols and analogous naphthols and their derivatives and phenol sulfides formed by reacting phenols with sulfur halides.

The acids of phosphorus which may be employed in preparing the reaction products of the present invention may be organic-substituted thiophosphorous acids, thiophosphoric acids, thiophosphonic acids, and thiophosphinic acids, but the thiophosphoric acids are preferred. These organo-substituted thiophosphorus and thiophosphoric acids may be readily prepared by methods known to the art. These include reacting alcohols, mercaptans, phenols, or thiophenols with sulfides of phosphorus, e. g., P₂S₅, P₄S₇, P₂S₃ and the like. The salts are readily prepared by reaction with metal hydroxides, ammonium hydroxides, amines and the like.

Specific dithiophosphoric acids, whose salts may be used in the above reaction, include methylethyl dithiophosphoric acid, diisobutyl dithiophosphoric acid, dicyclohexyl dithiophosphoric acid, di(methylcyclohexyl) dithiophosphoric acid, di(di-isobutylphenol) dithiophosphoric acid, didecyl dithiophosphoric acid, and the like.

The di-organo thiocarbamyl halides used in the practice of the present invention are readily prepared by means

known to the art such as reacting an amine with thiophosgene in accordance with the following equation:



The hydrogen radicals in the thiocarbamyl halide are, as mentioned above, alkyl or aralkyl radicals which may be of the type mentioned heretofore in connection with the dithiophosphate salts. Specific thiocarbamyl compounds include dimethylthiocarbamyl chloride, methylisopropylthiocarbamyl chloride, diisopropylthiocarbamyl chloride, di-n-butylthiocarbamyl chloride, di-n-dodecylthiocarbamyl chloride, dioctadecylthiocarbamyl chloride, phenylethylthiocarbamyl chloride and the like.

It is to be understood that not only single compounds such as metallic salts of single acids of phosphorus and single thiocarbamyl halides may be employed in the preparation of the products, but mixtures of salts of mixed acids of phosphorus, as well as mixtures of thiocarbamyl halides may be employed in the preparation thereof. The products of the reactions involving such mixtures will necessarily be mixtures of various products, but these mixed products will fall within the general scope of the above definition.

For general antioxidant purposes, and particularly when the additives are to be employed in mineral lubricating oils, the amount of additive, based on the total composition, will generally range from about 0.02 to about 5% by weight, preferably about 0.1 to 3% by weight. The preparation and testing of additives 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 I.—Diethylthiocarbamyl chloride-potassium diisopropyl dithiophosphate reaction product

A mixture of 18.1 g. (0.12 mol) of diethylthiocarbamyl chloride, 30.2 g. (0.12 mol) of potassium diisopropyl dithiophosphate, and 300 ml. of petroleum ether was refluxed (48° C.) with stirring for 8 hours, during which time the white reaction mixture turned light yellow. The white crystalline precipitate of potassium chloride was removed by filtration, followed by evaporation of the petroleum ether on the steam bath. 39.0 g. of a clear yellow liquid was obtained which analyzed 8.6% P, 29.1% S, and 4.1% N.

Example II.—Diethylthiocarbamyl chloride-potassium di(methylcyclohexyl) dithiophosphate reaction product

This preparation was carried out as described in Example I using 18.1 g. (0.12 mol) of di-ethylthiocarbamyl chloride and 43.2 g. (0.12 mol) of potassium di(methylcyclohexyl) dithiophosphate. A clear yellow liquid was obtained which analyzed 6.0% P, 21.0% S, and 2.6% N.

Example III.—Di-n-butylthiocarbamyl chloride-potassium di-(tert.-octylphenol) dithiophosphate reaction product

This preparation was carried out as described in Example I using 24.8 g. (0.12 mol) of di-n-butylthiocarbamyl chloride and 65.3 g. (0.12 mol) of potassium di(tert.-octylphenol) dithiophosphate. A viscous yellow oil was obtained which analyzed 3.3% P, 8.6% S, and 2.0% N.

Example IV.—Di-isobutylthiocarbamyl chloride-potassium diisopropyl dithiophosphate reaction product

This preparation was carried out as described in Example I using 24.8 g. (0.12 mol) of di-isobutylthiocarbamyl chloride and 30.2 g. (0.12 mol) of potassium di-isopropyl dithiophosphate. A brownish yellow liquid was obtained which analyzed 7.0% P, 28.0% S and 3.7% N.

Example V.—Laboratory bearing corrosion test

Blends containing 0.25% each of the products of Examples I through IV in a paraffinic type mineral lubricating oil of SAE-20 grade and a sample of the unblended base oil were submitted to a laboratory test designed to

measure the effectiveness of the products 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 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 the 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 a 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. The bearings were then repolished (to increase the severity of the test), reweighed, and then subjected to the test for additional four-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.

Additive in SAE-20 grade oil:	Bearing corrosion life (hours)
None	8
Product I—0.25%	40
Product II—0.25%	24
Product III—0.25%	18
Product IV—0.25%	44

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 alcohulates, metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, amines and amine derivatives, reaction products of metal phenates and sulfur, reaction products of metal phenates and phosphorus sulfides, metal phenol sulfonates, and the like. Thus the additives of the present invention may be used in lubricating oils containing such other addition agents as barium tert.-octylphenol sulfide, calcium tert.-amylphenol sulfide, nickel oleate, barium octadecylate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert.-amylphenol sulfide, calcium petroleum sulfonate, zinc methylcyclohexyl thiophosphate, calcium dichlorostearate, etc. Other types of additives, such as phenols and phenol sulfides, may be employed.

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, dichlorodiethyl 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 coal tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable

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or fish oils or their hydrogenated or volatilized products may be employed in admixture with mineral oils.

For the best results the base stock chosen should normally be an oil which without 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 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 engine and 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 material 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 agents, resins, rubber, olefin polymers, volatilized 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 as plasticizers and defoamers are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms, e. g., lauryl alcohol, stearyl alcohol, wax oxidation alcohols, and the like.

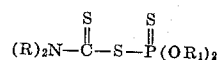
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In addition to being employed in crankcase lubricants the additives of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, general machinery oils, process oils, rust preventive compositions and greases.

The additives of the present invention may be employed as antioxidants or stabilizing agents not only in mineral lubricating oils, but also in petroleum hydrocarbon oil products, generally, where improved resistance to oxidation is desired. Thus the products may be added to motor oils, diesel fuels, kerosene, hydrocarbon polymer oils, and the like.

What is claimed is:

1. A mineral lubricating oil having incorporated therein an oxidation inhibiting amount of a compound having the formula



wherein R is an aliphatic hydrocarbon radical, R₁ is a hydrocarbon radical, and R and R₁ each contain in the range of 1 to 15 carbon atoms.

2. A composition according to claim 1 in which R is an alkyl group having in the range of 1 to 15 carbon atoms.

3. A composition according to claim 2 in which R is an ethyl radical.

4. A composition according to claim 3 in which R₁ is an isopropyl radical.

5. A composition according to claim 3 in which R₁ is a methylcyclohexyl radical.

6. A composition according to claim 2 in which R is a butyl radical.

7. A composition according to claim 6 in which R₁ is a tert.-octyl phenol radical.

8. A composition according to claim 6 in which R₁ is an isopropyl radical.

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