

UNITED STATES PATENT OFFICE

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LUBRICATING COMPOSITION

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This invention relates to the production of improvement agents for lubricating oils, and relates more particularly to the production of mineral oil solutions of heavy metal salts of esters of dithiophosphoric acid which are suitable for use as antioxidant and detergent agents in the improvement of lubricating oils.

In lubricating internal combustion engines, and particularly when severe operating conditions are encountered, ordinary mineral oils have proved inadequate for use due to the deposition of "varnish" or "sludge" on cylinder walls, pistons, and rings. Formation of these deposits is due primarily to oxidation and polymerization of the lubricating oils, as well as to like effects from products of fuel combustion which find their way by leakage into the engine. The sludge and varnish depositions are undesirable because they contribute to ring sticking, piston and cylinder wear, and corrosion of the bearing surfaces.

Lubricating oils, and particularly those lubricating oils adapted for use under severe operating conditions, are compounded with various agents, each of which counteracts one or more of the aforementioned undesirable effects. Several addition agents have been suggested for use as detergents and antioxidants for lubricating oils, all of which agents have desirable characteristics concerning the prevention of sludge and varnish formation in internal combustion engines.

Addition agents having particularly desirable detergent and antioxidant qualities are the heavy metal salts of esters of dithiophosphoric acid, which are formed by reacting alkyl or alkaryl compounds with phosphorus pentasulfide and neutralizing the acids so produced with oxides or hydroxides containing various heavy metals such as calcium, barium, zinc, tin, and the like. The dithiophosphoric acid ester neutralization has ordinarily been carried out in the presence of volatile solvents such as the lower alcohols (methanol, butanol, and the like), or in solvent mixtures comprising small amounts of these lower alcohols together with greater amounts of indifferent volatile hydrocarbon solvents such as toluol, and the like. For economic practicability, it has heretofore been essential to recover the solvent materials, usually by evaporation under reduced pressure at elevated temperature.

I have found that the neutralization of these

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dithiophosphoric acid esters may advantageously be carried out in a mineral oil solution and/or dispersion in the presence of an amount of water small enough as to render its subsequent removal unnecessary. Thus the primary object of this invention resides in the provision of a method of producing heavy metal salts of esters of dithiophosphoric acid in mineral oil solution and/or dispersion whereby solvent recovery may be dispensed with, resulting in the elimination of a troublesome and expensive operational procedure.

A further object of the invention is the prevention of decomposition of these improvement agents for lubricating oils by the elimination of the relatively high temperatures which have previously been necessary for effecting removal of solvent material therefrom.

In its broader aspects the method of my invention consists in the addition of an ester of dithiophosphoric acid to a dispersion in mineral oil of an oxide or hydroxide of a heavy metal in the presence of a small amount of water. Neutralization of the acid material is carried out at temperatures between the freezing and boiling points of water, the particular temperature being based in part on convenience, but in particular according to the viscosity of the acid ester being treated. Thus, for example, an alkyl or dialkyl dithiophosphoric acid, having a relatively low viscosity, may readily be subjected to neutralization treatment at temperatures of 20° C., or lower if desired. On the other hand, alkaryl and dialkaryl dithiophosphoric acids are, in many instances, very viscous or even semi-solid substances at ordinary temperatures and may most conveniently be subjected to neutralization treatment at relatively elevated temperatures, as for example temperatures of from about 50° C. to about 90° C. The amount of water employed is such that it can be tolerated by the mineral oil solution of the neutral salt and may range from about 0.1% to about 5.0%, depending on the hydrophobic characteristics of the particular salt employed.

In my copending application, Serial No. 643,749 filed concurrently herewith and now abandoned, I have described a variation of the present method and wherein a small amount of volatile organic solvent is employed in the stead of the water of the present invention.

The dithiophosphoric acid esters suitable for

use in the present invention include monoalkyl, dialkyl, monoalkaryl, and dialkaryl esters of dithiophosphoric acid which may be produced from primary alcohols such as 2-methyl pentanol-1, 2,4-dimethyl pentanol-1, 4-methyl hexanol-1, 4-methyl heptanol-1, and the like, and secondary alcohols such as di-isopropyl carbinol, and the like. Alkaryl compounds which are especially suitable for producing these dithiophosphoric acid esters include mono- and di-alkyl phenols, including tri-isobutyl phenol, di-octyl phenol, dodecyl phenol, and the like compounds.

I have found that the neutralization of esters of dithiophosphoric acid may be carried out in a manner which eliminates the necessity for removal of solvent material, and results in a neutral solution of the salt in mineral oil by the inclusion in the neutralizing medium of an amount of water not substantially greater than 5% based on the volume of the salt-oil solution. This amount of water may be added to the oil and is ultimately found in solution without having caused the formation of separate water and oil layers or emulsion characteristics.

In carrying out the method of the invention the dithiophosphoric acid ester is added with vigorous agitation to a suspension in mineral oil, containing from 0.1% to 5.0% of water, of an oxide or hydroxide such as lime, zinc oxide, or the like. The oil suspension containing the neutralizing agent may be preheated, if desired, to from about 50° C. to about 70° C. before addition of the acid ester, and the neutralization reaction, being of an exothermic nature, is controlled by cooling to a temperature not exceeding about 90° C. during the addition of the acid ester. I have found that optimum results are obtained when the quantity of acid ester employed is substantially equal to, but not greater than, the quantity of oil dispersion. The neutralizing agent employed may range from about 1 to about 3 times the theoretical quantity as calculated from the equivalent weight of the acid ester. Very satisfactory results have been obtained by the preparation of a neutral solution, of 50% dilution, of the heavy metal salts of esters of dithiophosphoric acid in mineral oil containing up to about 2% water after filtration of the solution to remove excess neutralizing agent and oil-insoluble salts formed during the neutralization reaction.

Ordinarily the mineral oil solutions of heavy metal salts of dithiophosphoric acid esters obtained by the method of my invention are clear liquids, indicating that the water present is held in solution by the particular acid ester salt which has been produced. The degree of solubility imparted to the water depends largely upon the heavy metal present. Thus, for example, calcium imparts a higher degree of solubility to the water than does barium or zinc. This becomes apparent by the appearance of a slight turbidity of the oil-salt solution when, in the presence of barium or zinc, the water present is in substantial excess of about 0.3-0.7%, while in the presence of calcium, water may be present in the solution to an amount not substantially in excess of 2-3%, all amounts being based on relative volumes of materials. The turbidity of the oil-salt solution may be dispelled or minimized by the addition thereto of a small amount of CaSO_4 which effectively removes a portion of the water upon filtration, although this treatment is not necessary except to improve the appearance of the product inasmuch as the turbidity contributes no deleterious effect to the

antioxidant and detergent qualities of the products.

The invention will be illustrated in greater detail by the following examples showing specific embodiments thereof. The examples, however, are intended for purposes of illustration only, the limitations of the invention being defined by the appended claims.

Example 1

An alkyl ester of dithiophosphoric acid was prepared employing a mixture of branched-chain alcohols and ketones produced by E. I. du Pont de Nemours & Company and comprising a fraction obtained by the hydrogenation of carbon monoxide in the presence of promoted copper chromite catalysts having an approximate boiling range of 160° to 200° C. This fraction, known as B-24, contains about 45% primary alcohols, 34% secondary alcohols, 18% ketones, and 3% esters. The acid ester was prepared by charging to a 30-gallon glass-lined kettle 115 pounds B-24 mixture and 60 pounds P_2S_5 . This mixture was heated at 90° C. for 2 hours. The acid ester was added gradually, with constant agitation, to a mixture of 125 pounds of lubricating oil of S. A. E. 10 grade, containing 23 pounds ZnO and 1.5 pounds water, the mixture having previously been heated to 65°-75° C. The reaction mixture was tested for free H_2S with lead acetate paper, and more ZnO was added until the reaction mixture was neutral. The product was a clear solution while hot but which, however, exhibited a tendency to become turbid on cooling, due to the presence of small droplets of water. The addition of a small amount of CaSO_4 to remove a portion of the water resulted in a clear, stable oil solution of the zinc salt of the dithiophosphoric acid ester.

Example 2

170 pounds of di-octyl phenol and 33 pounds of P_2S_5 were charged to a 30-gallon glass-lined kettle and heated at approximately 140° C. for 3.5 hours. The acid ester so produced was added to a dispersion in 175 pounds of lubricating oil of S. A. E. 10 grade of 25 pounds lime and 2 pounds water. Over a period of 35 minutes 202 pounds of the acid were added to the oil dispersion, the temperature being held at 85°-90° C. The final slurry was alkaline to phenolphthalein in alcohol. 33 pounds of lubricating oil of S. A. E. 10 grade were added to bring the oil-to-acid ratio to 1.03:1, and the batch was heated to 110° C. and filtered through a preheated filter press coated with Hyflo. The color of the acid-oil concentrate was satisfactory, and the product was approximately neutral, and remained clear on cooling.

Example 3

133 pounds tri-isobutyl phenol was charged to a 30-gallon glass-lined kettle and heated with 31 pounds P_2S_5 at 140°-145° C. with agitation for a total reaction time of 4.5 hours. A slurry containing 135 pounds of lubricating oil of S. A. E. 10 grade, 30 pounds hydrated lime, and 2 pounds water was made up at 70° C. The acid, heated to 90°-100° C., was run into the oil-lime slurry through a cheesecloth bag which removed excess P_2S_5 . The reaction was exothermic and was maintained at 70°-80° C. by means of cooling water and regulation of the acid flow. The neutralization was complete with the addition of the last of the

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acid. The product, after filtering, was a clear solution.

In subjecting the addition agents of the preceding examples to motor tests, the oil solutions of the dithiophosphoric acid ester salts were added, in amounts of approximately 2%, to a commercial lubricating oil. The addition agent-containing lubrication oil was tested by continuous runs of 25 hours duration in a Lauson engine, wherein the engine jacket was maintained at a temperature of about 400° F., and the sump at about 225° F.; engine speed was 1850 R. P. M. Test results are given in the following table:

Compound (Example No.)	Ring Condition	Ring Belt Rating ¹	Over-all Rating ²	Ring-Slot Condition	Bearing Corrosion, mg./Bearing ³
1.-----	Top ring stuck, others free.-----	3.1	3.4	Clean.-----	10.0
2.-----	All rings free.-----	3.9	4.2	do.-----	5.0
3.-----	do.-----	4.1	4.4	do.-----	2.0

NOTE

¹ Ring belt rating represents the average values regarding visual appearance of the rings, grooves, and lands; ratings are: 4.0-5 excellent, 3.8-3.9 good, 3.5-3.7 fair, 0-3.5 poor.

² Over-all rating is computed similarly to ring belt rating, but includes all cylinder, piston, and bearing appearances.

³ Bearing corrosion up to 10 mg./bearing is permissible.

These tests results compare very favorably with test results of addition agents produced by previously known methods surpassing, in most cases, previously obtained results. I attribute the improved quality of these addition agents to the elimination of the relatively severe temperatures ordinarily employed in the removal of solvent from the dithiophosphoric acid ester salts, thereby minimizing the decomposition of the dithiophosphoric acid esters.

It will be readily apparent from the foregoing description that the method of my invention provides several distinct advantages, of economic importance, over prior methods of producing dithiophosphoric acid esters suitable for use as lubricating oil improvement agents, by the provision of a method whereby the dithiophosphoric acid ester salts may be prepared in a mineral oil solution and/or dispersion, and wherein the removal of solvent material is rendered unnecessary.

I claim:

1. Process for preparing a solution in lubricating oil of a heavy metal salt of an oil-soluble di-

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ester of dithiophosphoric acid which comprises the steps of adding an oil-soluble diester of dithiophosphoric acid to a dispersion in mineral oil of a divalent metal base selected from the group consisting of the oxides and hydroxides of calcium and zinc, said dispersion containing from about 0.1% to about 5.0% of water, reacting the acid and alkaline materials at a temperature within the range of from about 20° C. to about 90° C., and removing the oil-insoluble reaction salts by filtration.

2. Process for preparing a solution in lubricating oil of a heavy metal salt of an oil-soluble di-

ester of dithiophosphoric acid which comprises the steps of adding an oil-soluble diester of dithiophosphoric acid to a dispersion in mineral oil of a divalent metal base selected from the group consisting of the oxides and hydroxides of calcium and zinc, said dispersion containing from about 0.1% to about 2.0% of water, reacting the acid and alkaline materials at temperatures within the range of from about 20° C. to about 90° C., and removing the oil-insoluble reaction salts by filtration.

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The following references are of record in the file of this patent:

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