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LUBRICATING COMPOSITIONS

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This invention relates to the stabilization of lubricating oils of the type known as crankcase oils; i. e. hydrocarbon oils of relatively low viscosity and pour point such as are used in the crankcases of internal combustion engines. More particularly, the invention relates to those classes of crankcase oils for truck, bus, aeroplane and marine gasoline and Diesel engines that are known as "heavy duty" oils which contain added chemicals that increase their effective service life under heavy operating conditions. A principal object of the invention resides in the provision of a crankcase lubricant of this type containing a class of compounds having both detergent and antioxidant properties, whereby the formation of hard sludge deposits is inhibited. A further object resides in the provision of an inhibitor of this class which is of the metal salt type, but which has little or none of the undesirable oxidizing action on hydrocarbon oils that is a characteristic of many metal salt additives.

In our copending application, Serial No. 401,960, filed July 11, 1941, we have demonstrated that the oil-soluble heavy metal salts of dithiophosphoric acid esters, when added to crankcase oils in concentrations of about 0.1% to 3%, are excellent detergents for the prevention of sludge deposits in the engine, and that these compounds also possess extremely important non-oxidizing or antioxidant properties when compared with other metal salt detergents. Our present invention relates to the specific class of oil-soluble heavy metal salts of dithiophosphoric acid esters in which at least one ester-forming radical is a higher branched-chain alkyl radical containing at least 6 carbon atoms.

We have found that the heavy metal salts of esters of dithiophosphoric acid containing at least one and preferably two branched-chain higher alkyl radicals are important addition agents for the stabilization of lubricating oils of the class referred to above. These compounds, by reason of the branched chain alkyl radicals which they contain, are quite soluble in lubricating oils. They possess surprisingly good stability against decomposition at the high temperatures encountered in heavy duty engine operation, and they are free from the tendency to cause foam in the oil during operation of the engine that is sometimes encountered when the higher straight-chain dialkyl dithiophosphates are used. Moreover, many of the compounds of our present invention can be prepared from branched-chain alcohols or alcohol mixtures that are considerably cheaper than the straight-chain alcohols described in our earlier application above referred to, and an important reduction in the cost of the lubricating oil additives is thereby obtained. Thus, for example, numerous branched-chain higher aliphatic alcohols and alcohol mixtures are obtainable as by-products in various chemical industries, and the use of dithiophosphates prepared from such by-product alcohols and alcohol mixtures constitutes one of the most important features of the invention.

Our invention in its broader aspects therefore consists in the addition to lubricating oils of the type of hydrocarbon crankcase oils of a heavy metal salt of a dithiophosphoric acid ester containing at least one branched-chain higher alkyl radical, either alone or in admixture with other ingredients, in amounts sufficient to exert sludge dispersing properties under heavy duty service conditions but without substantial increase in oxygen absorption and consequent sludge formation in the oil. The formation of sludge in crankcase oils is intimately related with the production of corrosive oxidation products of the type of organic acids, and accurate determination of these decomposition products is usually accomplished by measuring the naphtha-insoluble fraction of the oxidized oil. This feature of our invention can therefore be expressed by stating that the heavy metal salts in question do not increase the naphtha-insoluble value of the oil, and in fact these compounds usually bring about a marked reduction in this value.

It is an important advantage of our invention that a wide variety of branched-chain higher aliphatic alcohols may be used in preparing the reagents employed therein, either alone or in the form of higher alcohol mixtures, or as mixtures of branched chain higher aliphatic alcohols with ketones or with other ester-forming compounds such as higher or lower straight-chain alcohols, phenols and the like. Typical branched-chain higher alcohols that may be used in this manner are pentamethyl ethyl alcohol, pinacolyl alcohol ($(CH_3)_3C.CH(CH_3)OH$), 2-ethylhexyl alcohol, tetradecanol, undecanol, 5-ethylnonanol-2, and 3,9-diethyl tridecanol-6

$(C_4H_9CH(C_2H_5)C_2H_4CH(OH)C_2H_4CH(C_2H_5)_2)$

More important, however, are the mixtures of branched-chain alcohols obtained as by-products in the commercial hydrogenation of oxides of carbon and from other industrial sources such as the hydrogenation of higher aliphatic ketones in the presence of nickel catalysts. Thus, for example, the hydrogenation of carbon monoxide in the presence of promoted copper chromite catalysts produces methanol and ethanol as the principal products, but large quantities of by-products are obtained which consist of mixtures of numerous

branched-chain alcohols and ketones. Such mixtures are usually separated into fractions by distillation, and we have discovered that these fractions are especially well suited for use in the manufacture of lubricating oil additives by reaction with phosphorous pentasulfide for reasons that will be subsequently explained.

E. I. du Pont de Nemours & Co. sell the following fractions obtained from this source:

Fraction B–22—Approximate boiling range 130–150° C.
Fraction B–23—Approximate boiling range 150–160° C.
Fraction B–24—Approximate boiling range 160–200° C.
Fraction B–30—Approximate boiling range 200–300° C.

The composition of these various fractions is given by this manufacturer as follows:

Fraction B–22

Boiling range ——— Approximately 130–150° C.
Specific gravity at 15.6°/15.6° C ——— 0.8335–0.8375
Weight per U. S. gallon at 68° F ——— 6.94 lbs.
Saybolt viscosity at 100° F ——— About 30 seconds
Solubility in water at 20° C ——— About 0.6%
Solubility of water in B–22 at 20° C ——— Less than 3%
Solubility in H_2SO_4 ——— Not less than 70% in 85% H_2SO_4
Approximate composition:
Primary alcohols (principally 2 methyl pentanol-1, B. P. 148° C.) ——— 60–65%
Secondary alcohols (principally di-isopropyl carbinol, B. P. 139° C.) ——— 15–20%
Ketones (principally 2,4-dimethyl hexanone-3) ——— 18–20%
Esters—unidentified ——— 2%

Fraction B–23

Boiling range ——— Approximately 150–160° C.
Specific gravity at 15.6°/15.6° C ——— 0.8395–0.8435
Weight per U. S. gallon at 68° F ——— 6.99 lbs.
Saybolt viscosity at 100° F ——— About 31 seconds
Solubility in water ——— Less than 1.0%
Solubility in H_2SO_4 ——— Not less than 75% in 85% H_2SO_4
Approximate composition:
Primary alcohols (principally 2,4-dimethyl pentanol-1, B. P. 159° C.) ——— 43%
Secondary alcohols (principally 2,4-dimethyl hexanol-3, B. P. 158° C.) ——— 48%
Ketones—unidentified ——— 9%

Fraction B–24

Boiling range ——— Approximately 160–200° C.
Specific gravity at 15.6°/15.6° C ——— 0.8610–0.8660
Weight per U. S. gallon at 68° F ——— 7.17 lbs.
Saybolt viscosity at 100° F ——— About 32 seconds
Solubility in water ——— Less than 1.0%
Solubility in H_2SO_4 ——— Not less than 85% in 85% H_2SO_4
Approximate composition:
Primary alcohols;
4-methyl hexanol-1[1], B. P. about 165° C
2,4-dimethyl hexanol-1[1], B. P. about 178° C
4-methyl heptanol-1[1], B. P. about 185° C
——— 45%
Secondary alcohols—unidentified ——— 34%
Ketones—unidentified ——— 18%
Esters ——— 3%

[1] Tentative identification; probably other alcohols also present.

Fraction B–30

Boiling range ——— 200–300° C.
Specific gravity at 15.6°/15.6° C ——— 0.900–0.910
Weight per U. S. gallon at 68° F ——— 7.5–7.6 lbs.
Approximate composition:
Alcohols—primary and secondary ——— 68%
Ketones—unidentified ——— 12–17%
Miscellaneous (phenol bases, unsaturated alcohols, etc.) ——— 15–20%

It is a further specific object of the present invention to prepare dithiophosphates and their heavy metal salts from the above alcohol mixtures and mixtures of alcohols and ketones. These mixed dithiophosphates and their heavy metal salts we regard as new compositions of matter, and we have found that they possess surprisingly good properties when used as additives for lubricating oils of the type specified above.

Another class of mixed higher branched-chain alcohols that we have found suitable for use in the preparation of dithiophosphate heavy metal salt additives for crankcase lubricants are those obtained by the reduction of the corresponding higher aliphatic ketones with hydrogen. Thus, for example, mixtures of beta, gamma-unsaturated ketones obtained by the rearrangement of alpha, beta-unsaturated ketones produced by the condensation of ketones of lower molecular weight may be employed. Typical alcohols that can be produced cheaply by the method are 4-methyl hexanol-2, 5-methyl hexanol-3, 4-methyl heptanol-2 and 5-methyl heptanol-3. We have found, however, that the higher aliphatic ketones of the type found in the duPont alcohols are frequently advantageous in lubricating oils, for they appear to act as solubilizing agents for dithiophosphate heavy metal salts prepared from the corresponding alcohols and prevent the deposition of sludges at low temperatures, and the hydrogenation of the ketones present in these alcohol mixtures is not recommended.

The dithiophosphates of the above-described classes are preferably prepared by reacting the corresponding alcohols or alcohol mixtures with phosphorous pentasulfide, preferably in the ratio of about 4 moles of the alcohol for each mole of P_2S_5. The reaction is carried out by heating the reagents at 90–100° C. or higher with stirring, in the presence or absence of a solvent, until the evolution of hydrogen sulfide is practically complete. The heavy metal salts are then produced from the free dithiophosphoric acid esters so obtained by dissolving the acid esters in a low-boiling mixture of polar and non-polar solvents, such as a mixture of ethyl alcohol and benzene, toluol or other low-boiling hydrocarbon, introducing the theoretical quantity of a reactive heavy metal oxide such as barium oxide, calcium oxide and the like and agitating the mixture until a solution of the heavy metal salt is obtained. Alternatively, the alkali metal salts of the free dithiophosphoric acid esters may be formed by neutralizing with sodium carbonate or sodium hydroxide and these products may be converted to the corresponding heavy metal dithiophosphates by double decomposition with an aqueous solution of a heavy metal salt. The alkaline earth metal salts, and particularly the barium and calcium salts of the branched-chain alkyl dithiophosphoric acid esters are the preferred compounds for use in practicing the present invention, but any other heavy metal salt may be prepared in this manner and used such as the zinc, aluminum or tin salts.

Another important feature of the invention resides in the introduction of additional heat stabilizers or anti-sludging agents into crankcase lubricants containing heavy metal salts of branched chain alkyl dithiophosphates. We have found that such compounds as the heavy metal salts of diamyl phenol monosulfide described in our Patent No. 2,249,626 and oil-soluble organic sulfonates and their heavy metal salts such as calcium petroleum sulfonate or calcium didecyl sulfosuccinate described in our copending application, Serial No. 419,016, filed November 13, 1941, will cooperate effectively with the dithiophosphates referred to above to improve the heat stability of the oil. Thus, for example, two samples of conventionally refined Mid-Continent base lubricating oil of 10–W grade containing 1% by weight of barium dialkyl dithiophosphates, the alkyl groups being those of branched chain alcohols obtained from "B–24" alcohol, were heated at 330° F. in an open glass beaker for 24 hours. One sample of the oil also contained 0.45% of calcium petroleum sulfonate. This sample was clear after the heating period, while a small amount of sediment was found in the cooled sample to which no calcium petroleum sulfonate was added.

The invention will be illustrated in greater detail by the following specific examples, which describe the results obtained with representative embodiments thereof. It should be understood, however, that although these examples may illustrate in detail some of the more specific features of the invention they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

400 parts by weight of 2-ethylhexanol-1 were mixed with 190 parts of powdered phosphorous pentasulfide and the mixture was heated with stirring at 80–90° C. for 2.5 to 3 hours until the evolution of hydrogen sulfide was substantially complete. The resulting dioctyl dithiophosphoric acid was a brownish yellow liquid. 300 parts by weight of the liquid were dissolved in a mixture of 120 parts of ethanol and 240 parts of benzene and an excess of powdered barium oxide was introduced. A total of 71 parts by weight of 92% BaO was added, this being an excess of 8 parts over the amount theoretically necessary to form a neutral barium salt.

The mixture was heated with stirring to 40–50° C. and stirred at these temperatures for about 40 minutes, after which the solution of barium dioctyl dithiophosphate was filtered off. Upon evaporation of the solvent the salt was obtained as a yellow, low-melting solid, soluble in hot, 10–W grade lubricating oil to the extent of about 50%. By adding barium diamylphenol monosulfide it was possible to prevent separation of the dithiophosphate from a 50% solution at low temperatures.

The efficiency of the heavy metal salts of branched-chain dialkyl dithiophosphates described in this and subsequent examples as detergents and antioxidants for crankcase lubricants was determined by the Catalytic Indiana test. The apparatus for this test consists of a constant temperature bath maintained at 341° F. in which a number of large glass test tubes are immersed. 300 cc. samples of the oil under test are poured into these tubes and air at the rate of 10 liters per hour is bubbled through the oil. In order to reproduce the conditions existing in the crankcase of an engine weighed strips of copper-lead alloy are suspended in the oil samples. As metallic surfaces, particularly copper, greatly accelerate the rate of oxidation and decomposition of the oil in the absence of oxygen this is an important factor in the test. Bearing corrosion rates are determined by again weighing the strips after 70 hours immersion, which was the test period employed in evaluating the products of the present invention.

The detergent properties of additives present in the oil under test are determined by an inspection of the deposit left on the walls of the tube after it has been drained and rinsed once with solvent naphtha.

A Mid-Continent, solvent-refined lubricating oil containing 0.12% by weight of barium di-(ethylhexyl) dithiophosphate and 0.6% of barium diamylphenol monosulfide was tested in comparison with another sample of the same oil containing no additive. The copper-lead bearing strip in the oil containing the dithiophosphate lost 4 milligrams by corrosion, while the corrosion loss caused by the untreated oil was 328 milligrams. The tube containing the treated oil was almost completely clean after a solvent naphtha rinse, whereas the tube that contained the untreated oil was completely coated on its inner surface with a hard, adherent, naphtha-insoluble film.

Example 2

80 parts by weight of tetradecanol of the formula

$$C_4H_9.CH.(C_2H_5).C_2H_4.\underset{\underset{OH}{|}}{CH}.CH_2.CH(CH_3)_2$$

were mixed with 21 parts of powdered P_2S_5 and the mixture was reacted at 95° C. for 2 hours. 60 parts of the product were dissolved in a mixture of 20 parts ethanol and 40 parts toluol and neutralized by the addition of 9.6 parts of 92% barium oxide, following the procedure outlined in Example 1. Part of the solvent was evaporated and 68 parts of 10–W grade lubricating oil were added, after which evaporation of the volatile solvent was completed by heating under a partial vacuum. There was thus produced a 50% solution of the barium di-tetradecyl dithiophosphate in lubricating oil.

A sample of the lubricating oil described in Example 1 containing 0.38% of this product showed zero bearing loss in the Catalytic Indiana test. The tube containing the oil was relatively clean after a single rinse with solvent naphtha, and the small amount of deposit was soft and easily removed with a brush.

Example 3

120 parts by weight of undecanol of the formula

$$C_4H_9.CH(C_2H_5).C_2H_4.\underset{\underset{OH}{|}}{CH}.CH_3$$

and 39 parts of P_2S_5 were reacted as in Example 1. 50 parts by weight of the resulting di-undecyl dithiophosphoric acid were dissolved in a mixture of polar and non-polar solvents as before, neutralized by the addition of 7.6 parts of 100% BaO, and the solvents evaporated. The product, a yellow solid of low melting point, was easily soluble in lubricating oils.

0.3% of the barium di-undecyl dithiophosphate was dissolved in a sample of the oil described in Example 1, which was then subjected

to the Catalytic Indiana test. The bearing actually gained 14 milligrams in the test and the tube contained no naphtha-insoluble deposit.

Example 4

60 parts by weight of "B–22" alcohol and 31 parts of finely ground phosphorous pentasulfide were mixed and heated with stirring at 85–95° C. for 2 hours, after which time the evolution of hydrogen sulfide was practically complete. The resulting crude dialkyl dithiophosphoric acid had a neutralization number corresponding to a monobasic acid having a molecular weight of 377.

65 parts by weight of the product were dissolved in a mixture of 25 parts ethanol and 30 parts toluene and 15 parts by weight of powdered BaO were added. The mixture was stirred with gentle heating to dissolve the barium salt, filtered, and the solvent was evaporated. The product was a light yellow crystalline solid melting below 150° C., soluble in lubricating oils with difficulty but easily solubilized therein by the addition of small quantities of barium diamylphenol monosulfide.

A lubricating oil of the type described in Example 1 containing 0.4% of the product formed almost no naphtha-insoluble deposit when subjected to the Catalytic Indiana test. The copper-lead bearing strip showed a gain in the test of 30 milligrams.

Example 5

60 parts by weight of "B–23" alcohol and 23 parts of phosphorous pentasulfide were reacted for 2 hours at 90–95° C. as in Example 1. The resulting crude dialkyl dithiophosphoric acid ester had a neutralization number corresponding to a monobasic acid having a molecular weight of 391. 77 parts by weight of this product and 17 parts of BaO were stirred with gentle heating (40–50° C.) in a mixture of 25 parts of ethanol and 50 parts toluene, the resulting solution was filtered and the solvent evaporated. The product was an amorphous yellow solid of low melting point that was soluble in lubricating oil of 10–W grade to the extent of about 50% by weight.

A sample of the lubricating oil of Example 1 containing 0.4% of this product showed excellent results when subjected to the Catalytic Indiana test. The tube contained almost no naphtha-insoluble deposit and the bearing loss was 2 milligrams.

Example 6

136 parts by weight of "B–24" alcohol was mixed with 72 parts of finely ground phosphorous pentasulfide and the mixture was stirred and heated at 90–105° C. for 2–3 hours until evolution of hydrogen sulfide was substantially complete. The unreacted P_2S_5 was allowed to settle and the supernatant liquid was decanted. The product consisted principally of mixed branched-chain dialkyl dithiophosphoric acids together with smaller quantities of thioketones and possibly some thioesters.

100 parts by weight of the product were dissolved in a mixture of 50 parts of toluene and 25 parts of ethanol and 20 parts of powdered barium oxide were added with stirring. The agitation was continued at 40–50° C. for 0.5–1 hour, or until all the free acid was neutralized. An additional 50 parts of toluene were then added and the solution was filtered and the solvent evaporated, the last traces being taken off under reduced pressure. The residue was a yellowish-brown liquid, readily soluble both in gasoline and lubricating oil of 10–W grade but practically insoluble in water.

In producing heavy metal salts of mixed dithiophosphoric acid esters on a large scale it is preferable to blend the product with an equal quantity of lubricating oil during evaporation of the solvent so that a 50% blend in lubricating oil is obtained. Such a blend is very convenient for handling and storing the product, and it can be readily mixed with any desired quantity of lubricating oil to produce a concentration of 0.1–3% of the heavy metal dithiophosphate in the oil.

0.4% of the product were added to a solvent-extracted Pennsylvania oil of 10–W grade, which was then subjected to the Catalytic Indiana test in comparison with an untreated sample of the same oil. The bearing metal immersed in the treated sample gained 10 milligrams while the metal in the untreated sample lost 215, and there was practically no naphtha-insoluble deposit on the walls of the tube containing the treated sample.

The "B–24" dithiophosphate barium salt was also tested in lubricating oil by the Underwood test. This test consists in heating 1500 cc. samples of the oil to 325° F. and continuously spraying a portion of the heated oil against a 2" x 10" freshly sanded copper strip and two freshly sanded bearings for five hours while permitting free circulation of air through the apparatus. 0.116% of iron naphthenate, equivalent to 0.01% of Fe_2O_3, was added to the oil before testing in order to reproduce the conditions present in an engine as a result of acid corrosion of the metal by acidic oxidation products in the oil. The results are given in the following table.

Oil	A.P.I. gravity used oil	Bearing loss, mg.		Naphtha insol., percent	Neut. No.
		Cu-Pb	Ag-Cd		
Control (A. P. I. gravity 31.1°)	21.4	71	885	0.3	9.41
+0.4% barium di-"B–24" dithiophosphate	30.0	2	18	0	0.61

What we claim is:

1. A lubricating composition comprising a hydrocarbon lubricating oil having dispersed therein a heavy metal salt of the reaction product of phosphorous pentasulfide with a mixture of higher branched-chain aliphatic alcohols containing at least 6 carbon atoms.

2. A crankcase lubricant comprising a hydrocarbon lubricating oil having dispersed therein a composition operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil at elevated temperatures, said composition comprising as its essential ingredient the phosphorous pentasulfide reaction product of a mixture consisting predominantly of higher branched-chain aliphatic alcohols of at least 6 carbon atoms, said reaction products being in the form of their heavy metal salts.

3. A crankcase lubricant comprising a hydrocarbon lubricating oil having dispersed therein a composition operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil at elevated temperatures, said composition comprising as its essential ingredient the phosphorous pentasulfide reaction product of a fraction of a byproduct obtained in the catalytic hydrogenation of oxides of carbon and consisting predominantly of branched-

chain aliphatic alcohols within the range of 6 to 8 carbon atoms, said phosphorous pentasulfide reaction products being in the form of their heavy metal salts.

4. A crankcase lubricant comprising a hydrocarbon lubricating oil having dispersed therein a composition operative to assist in preventing the deposition of hard deposits due to sludge formation in the oil at elevated temperatures, said composition comprising as its essential ingredient a phosphorous pentasulfide reaction product of a fraction of a byproduct obtained in the catalytic hydrogenation of oxides of carbon, said fraction having an approximate boiling range of 160–200° C. and containing about 45% of a mixture of primary alcohols chiefly 4-methylhexanol-1, 2,4-dimethylhexanol-1, and 4-methylheptanol-1 and about 34% of secondary alcohols and 18% of ketones boiling within the range specified above, said phosphorous pentasulfide reaction products being in the form of their heavy metal salts.

5. A method of preparing an improvement agent for lubricant oils which comprises the steps of heating phosphorous pentasulfide with a mixture of branched-chain higher aliphatic alcohols until the evolution of hydrogen sulfide is substantially complete and neutralizing the reaction product with a reactive heavy metal oxide to form a heavy metal salt thereof.

6. A method of preparing an improvement agent for lubricant oils which comprises the steps of heating phosphorous pentasulfide with a fraction of a byproduct obtained in the catalytic hydrogenation of oxides of carbon and consisting predominantly of branched-chain aliphatic alcohols within the range of 6 to 8 carbon atoms until the evolution of hydrogen sulfide is substantially complete and neutralizing the reaction product with a reactive heavy metal oxide to form a heavy metal salt thereof.

7. A method of preparing an improvement agent for lubricant oils which comprises the steps of mixing phosphorous pentasulfide with a fraction of a byproduct obtained in the catalytic hydrogenation of oxides of carbon, said fraction having an approximate boiling range of 160–200° C. and containing about 45% of a mixture of primary alcohols chiefly 4-methylhexanol-1, 2,4-dimethylhexanol-1 and 4-methylheptanol-1 and about 34% of secondary alcohols and 18% of ketones boiling within the range specified above, heating the mixture until the evolution of hydrogen sulfide is substantially complete and neutralizing the reaction product with a reactive heavy metal oxide to form a heavy metal salt thereof.

8. In the production of a heavy metal salt of an ester of dithiophosphoric acid suitable for use as an improvement agent for lubricant oils, the steps which consist in dissolving a diester of dithiophosphoric acid in a low-boiling mixture of polar and non-polar solvents, adding a heavy metal oxide and agitating the mixture until a solution of the heavy metal salt is obtained.

9. In the production of a heavy metal salt of an ester of dithiophosphoric acid suitable for use as an improvement agent for lubricant oils, the steps which consist in dissolving a dialkyl dithiophosphoric acid ester in a mixture of a low-boiling alcohol and a low-boiling hydrocarbon, adding a heavy metal oxide and agitating the mixture until a solution of the heavy metal salt is obtained.

10. The method of obtaining a solution of a heavy metal salt of a dialkyl ester of dithiophosphoric acid in lubricating oil which comprises the steps of dissolving a dialkyl dithiophosphoric acid ester in a low-boiling mixture of polar and non-polar solvents, adding a heavy metal oxide, agitating until a solution of the heavy metal salt is obtained, adding an excess of hydrocarbon lubricating oil, and heating to drive off the low-boiling solvents.

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