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CRANKCASE LUBRICATING OIL COMPOSITION

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6 Claims. (Cl. 252—37)

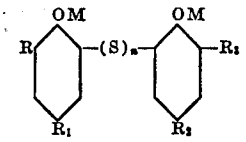
This invention relates to lubricating oils of the type used in the crankcases of internal combustion engines. More particularly, the invention relates to heavy duty oils for truck, bus, airplane and marine gasoline and Diesel engines which contain added chemicals that increase their effective service life under heavy operating conditions. A principal object of the invention resides in the provision of crankcase lubricants of this type containing additives having both detergent and anti-oxidant properties as well as anti-sludge properties so that the formation of hard sludge deposits is inhibited. A further object resides in the provision of lubricating oils containing inhibitors of the metal salt type which exhibit little or none of the undesirable oxidizing action on hydrocarbon oils that is a characteristic of many metal salt inhibitors.

It has previously been proposed to incorporate oil-soluble heavy metal salts of certain dithiophosphoric acid esters into crankcase oils in varying but relatively small amounts, the exact quantity depending upon the particular type of oil and the service for which it is intended. For the types of service referred to above the heavy metal salts of dithiophosphoric acid esters have been proposed for use in concentrations of about 0.1% to 3%, based on the weight of the oil, although in extreme cases such as in Diesel engines intended for tractors concentrations as high as 5–6% may be employed.

While the calcium, barium, aluminum, zinc and other heavy metal salts of dithiophosphoric acid esters possess good oxidation-inhibiting properties, and while many of these compounds are also good detergents, we have found that these compounds have a tendency to form oil-insoluble sludges in lubricating oils under the high temperature conditions of continuous operation. It is a further specific object of our present invention to overcome this serious operating disadvantage, and to provide lubricating oil compositions containing heavy metal salts of dithiophosphoric acid esters which are stable and will not form cloudy decomposition products when heated to high temperatures.

We have found that the metal salts, and particularly the calcium, barium, zinc, aluminum, tin and other divalent or polyvalent heavy metal salts of 2,4-dialkylphenol mono- and disulfides possess the property of solubilizing the heavy metal salts of dithiophosphoric acid esters and of stabilizing these esters against decomposition at elevated temperatures when incorporated therewith in a hydrocarbon lubricating oil composition. In addition to this important property, the heavy metal salts of 2,4-dialkylphenol sulfides are, in themselves, excellent anti-oxidants and corrosion inhibitors for hydrocarbon heavy duty lubricating oils, and they may therefore be added either in addition to the normal amount of dithiophosphoric acid ester salts ordinarily employed in the oil or to replace a part of these esters.

The metal salts of 2,4-dialkylphenol sulfides are compounds of the formula



in which R, R_1, R_2 and R_3 are alkyl radicals, n is 1 or 2, and each M may be a monovalent metal or the two M's may represent an atom of a divalent metal such as calcium, barium, zinc and the like or the corresponding portion of a polyvalent metal such as aluminum or chromium. The alkyl radicals R, R_1, R_2 and R_3 may be the same or different, but improved oil solubility and sludge-dispersing properties are obtained when one or more of these radicals contains from 5 to 21 carbon atoms. The best solubilizing and sludge dispersing properties are obtained when all the alkyl radicals contain from 5 to 21 carbon atoms, a typical class of excellent sludge dispersing and stabilizing agents for the heavy metal salts of dialkyl dithiophosphoric acid esters being the calcium, barium, zinc and tin salts of 2,4-diamylphenol monosulfide. These compounds are preferably prepared as described in our Patent No. 2,270,183, dated Jan. 13, 1942, and may be added to the lubricating oil in quantities of 0.1–3% or more, based on the weight of the oil.

In producing heat-stabilized hydrocarbon lubricating oil compositions containing heavy metal salts of diesters of dithiophosphoric acid, a quantity of dialylphenol sulfide salt is added which will stabilize the composition under the required conditions of service. The amounts mentioned above; namely, 0.1–3% or more on the basis of the oil, are usually sufficient to protect against the formation of sludge by an equal quantity of dithiophosphoric acid ester heavy metal salt, but when extreme temperature conditions are expected still larger amounts up to twice the weight of the dithiophosphoric acid ester salt may be employed. Usually, however, a satisfactory degree of stabilization is obtained when only rela-

tively minor quantities on the order of 20–70% of the weight of the dithiophosphoric acid ester heavy metal salt are employed. The exact ratio will therefore depend on the type of service and on the type of lubricating oil stock employed, since the dithiophosphoric acid ester salts exhibit a tendency to form sludges more readily in oil stocks from Naphthenic and Mid-Continent crudes than in paraffinic stocks from Pennsylvania crudes.

The invention in its broader aspects is not limited by the type of dithiophosphoric acid ester with which the dialkylphenol sulfide metal salts are incorporated, since these sulfides will improve the heat stability and reduce the sludge forming tendencies of any heavy metal dithiophosphoric acid ester. Thus, for example, heavy metal salts of dialkyl dithiophosphoric acid esters in which each alcohol radical contains at least 5 carbon atoms and preferably 8 to 14 or more carbon atoms may be employed, including those compounds in which the alcohol radicals are either straight chain or branched chain primary or secondary alcohol radicals. Similarly, dithiophosphoric acid esters of cycloaliphatic alcohols may be employed, such as the heavy metal salts of dicyclohexyl dithiophosphate. Diaryl dithiophosphates may also be employed in the form of their heavy metal salts, and the oil solubilities of these classes of compounds are improved when the aryl groups contain aliphatic side chains as substituents. Typical compounds illustrative of these and other classes of dithiophosphoric acid esters that may be employed are the calcium, barium, zinc and tin salts of dicapryl dithiophosphate, di-n-octyl dithiophosphate, dilauryl dithiophosphate, di-octadecyl dithiophosphate, di(p-tert-amylphenyl) dithiophosphate, di(2,4-diamylphenyl dithiophosphate, di(dodecylphenyl) dithiophosphate, and esters of dithiophosphoric acid with at least one branched-chain higher alkyl radical such as those obtained by the reaction of P_2S_5 with mixtures of branched-chain alcohols obtained as by-products in the commercial hydrogenation of oxides of carbon such as the "B–22," "B–23," "B–24," and "B–30" fractions sold by E. I. du Pont de Nemours and Company and described in detail in our copending application Serial No. 421,650, filed December 4, 1941, the disclosure of which by reference is made a part hereof. Another class of compounds that can be stabilized by the addition of calcium, barium and other heavy metal salts of 2,4-dialkylphenol monosulfides are the heavy metal salts of complex dithiophosphoric acid esters in which a monocarboxylic acid is chemically combined with the dithiophosphoric acid radical by reacting phosphorous pentasulfide with a mixture containing a monohydric alcohol or monohydric phenol together with an aliphatic monocarboxylic acid. A large number of these complex dithiophosphates are described in detail as additives for hydrocarbon lubricating oils in our copending application Serial No. 452,888, filed July 30, 1942, and the addition of 2,4-dialkylphenol monosulfide salts to improve the heat stability in amounts of 0.5–1.5 parts by weight for each part of the complex dithiophosphoric acid esters is also described therein.

The invention will be further illustrated by the following specific examples. It should be understood, however, that although specific features of the invention may be described in detail in these examples, the invention in its broader aspects is not limited thereto.

Example 1

1.33% by weight of barium salts of dithiophosphoric acid esters were dissolved in "Havoline" oil of SAE 20 grade. The dithiophosphate composition consisted of a mixture of 1 part by weight of barium dilauryl dithiophosphate, 2.5 parts by weight of barium diamyl dithiophosphate and 2.5 parts by weight of "B–24" alcohol dithiophosphate. The resulting solution was separated into two parts, and 0.67% of barium 2,4-diamyl phenol monosulfide was added to the second part.

The two solutions were heated simultaneously for 1.5 hours in an oven maintained at 165° C. At the end of this heating period the second solution, containing the added barium dialkylphenol sulfide, was perfectly clear. The first solution showed a considerable separation of precipitate.

Example 2

A sample of Diesel lubricating oil of SAE 30 grade containing 1.25% of its weight of a mixture of 3 parts by weight of barium di-(dodecylphenyl) dithiophosphate and 1 part of barium 2,4-diamylphenol monosulfide was subjected to a high temperature Lauson engine test for 25 hours. In this test the engine coolant was maintained at 400° F. and the oil at 225° F. during the entire period with the engine operating at 1860 R. P. M. under two-thirds load. At the end of the test both piston rings were free and their grooves were clean, the oil ring was free and its groove and the oil control groove were clean. The upper and lower copper-lead bearings lost 5 and 2 mg., respectively. The oil inspection data were as follows:

	Naphtha insoluble	Conradson carbon	Neut. No.	Vis. @ 100° F.
Fresh oil	Nil	0.34	−0.17	496
Used oil	0.01	0.55	0.30	629

It is evident from these figures that the oil remained stable under the high operating temperature, and the clean condition of the engine after the test showed that substantially no sludge was deposited.

Example 3

2.44 parts by weight of commercial powdered phosphorous pentasulfide were mixed with 1020 parts of a mixture of cycloparaffinic alcohols of 15–18 carbon atoms obtained by polymerizing a mixture of the corresponding ketones in the presence of an alkaline catalyst, fractionating to separate the unpolymerized material and reducing the polymers with hydrogen. The mixture was heated at 90–105° C. for about 2–3 hours until the evolution of hydrogen sulfide was substantially complete after which the resulting dithiophosphoric acid diester was dissolved in a mixture of 360 parts of ethanol and 720 parts of benzene.

One half of the solution was neutralized by the addition of 60 parts of calcium oxide, this being a slight excess over the amount theoretically required to form a neutral calcium salt. The mixture was stirred at 40–50° C. for about 30 minutes after which the solution of the calcium salt was filtered off. The solvent was then evaporated to obtain the salt in solid form.

The remaining portion of the solution was reacted with an excess of zinc oxide by the same procedure to form the zinc salt.

Equal quantities by weight of the above de-

scribed calcium and zinc salts were dissolved in lubricating oil of SAE 30 grade and barium di-(2,4-diamylphenol) monosulfide was added in amounts such that a mixture of 3 parts by weight of the mixed dicycloalkyl dithiophosphate salts and 1 part by weight of the diamylphenol monosulfide salt was suspended in the oil as a 50% solution.

2.5% by weight of this 50% solution were dissolved in Diesel oil of SAE 30 grade which was then tested for 25 hours in the Lauson engine under the operating conditions described in Example 2. After the test both compression rings were clean and free, the oil ring was free and very clean, and the weight loss of the bearings (copper-lead alloy) was only 1 mg. for the upper bearing and 2 mg. for the lower. The oil inspection data were as follows:

	Naphtha insoluble	Conradson carbon	Neut. No.	Vis. @ 100° F.
Fresh oil	Nil	0.24	0.01	505
Used oil	0.01	0.39	0.17	746

Example 4

A dialkyl dithiophosphoric acid ester was prepared by reacting P_2S_5 with a mixture of equal parts by weight of octadecanol and wool-grease by the method described in Example 3 and was transformed into its calcium salt. A mixture of 2 parts by weight of this salt and 1 part of barium di(2,4-diamylphenol) monosulfide was dissolved in lubricating oil to a 50% solution.

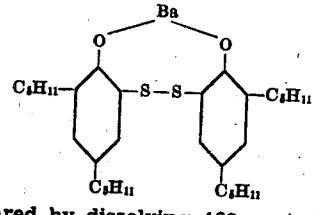
2.5% of the additive solution was added to a SAE 30 lubricating oil prepared from Mid-Continent (Smackover field) stock and the oil was then subjected to a 120 hour test in the Lauson engine operating at 1860 R. P. M. under two-thirds load. The coolant temperature was 345° F. and the oil temperature 225° F. The bearing metal was copper-lead alloy.

After 63 hours the losses in weight of the upper and lower bearings were 9 and 4 mg. respectively, and after 120 hours they were 15 and 10 mg. At the end of the test the piston color was good and both piston rings were in excellent condition. The oil ring was very clean and contained no carbon and the ports were free. The oil inspection data was as follows:

	Naphtha insoluble	Conradson carbon	Neut. No.	Vis. @ 100° F.
Fresh oil	Nil	0.38	−0.06	316
Used oil	0.06	1.09	0.60	568

Example 5

Barium di-(2,4-diamylphenol) disulfide of the formula:



was prepared by dissolving 468 parts by weight (2 mols) of 2,4-diamylphenol in 180 parts of petroleum naphtha and adding a solution of 135 parts of sulfur monochloride in 65 parts of petroleum naphtha with vigorous stirring. The temperature was maintained at about 20–30° C. until all the sulfur monochloride was added and the mixture was then heated under reflux for 45 minutes or until all the hydrogen chloride had been liberated. 245 parts of ethyl alcohol were then added and about 350 parts of $Ba(OH)_2 \cdot 8H_2O$ were stirred in, this being an excess over the amount necessary to form the barium salt. The mixture was heated with stirring until the salt formation was complete, boiled until the last traces of water were expelled, and filtered and the solvent evaporated from the filtrate.

A mixture of 1 part by weight of the above salt and 3 parts of calcium di-(triisobutylphenyl) dithiophosphate was dissolved in lubricating oil to a 50% solution and 2.5% of this solution was added to a hydrocarbon Diesel lubricant of SAE 30 grade. The lubricant was then subjected to a 24-hour high temperature test in a Lauson engine having copper-lead bearings and operating under the conditions described in Example 2. After 24 hours the upper and lower bearing losses were 4 and 8 milligrams, respectively, the oil ring was free, its groove was clean and the oil slots and drain holes were clean. The oil inspection data were as follows:

	Naphtha insoluble	Conradson carbon	Neut. No.	Vis. @ 100° F.
Fresh oil	Nil	0.65	−0.23	476
Used oil	0.20	1.53	0.53	739

Example 6

A Mid-Continent, solvent-refined lubricating oil containing 0.12% by weight of barium di-(ethylhexyl) dithiophosphate and 0.6% of barium 2,4-diamylphenol monosulfide was tested in comparison with another sample of the same oil containing no additive 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 presence 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 is the test period normally used.

The bearing strip in the oil containing the dithiophosphate-sulfide mixture 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, whereas the tube that contained the untreated oil was completely coated on its inner surface with a hard, adherent, naphtha-insoluble film.

This application is a continuation-in-part of our copending applications Serial Nos. 401,960, filed July 11, 1941 and 421,650, filed December 4, 1941.

What we claim is:

1. A lubricating composition comprising a hydrocarbon lubricating oil having dissolved therein 0.1% to 6% by weight of a heavy metal salt of a dithiophosphoric acid ester and a metal salt of a dialkylphenol sulfide in amounts of 20–200% of

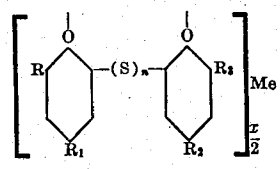
the weight of said dithiophosphoric acid ester salt.

2. A lubricating composition comprising a hydrocarbon lubricating oil having dissolved therein 0.1% to 6% by weight of a heavy metal salt of a dithiophosphoric acid ester and a heavy metal salt of a dialkylphenol sulfide in amounts of 20–200% of the weight of said dithiophosphoric acid ester salt.

3. A lubricating composition comprising a hydrocarbon lubricating oil having dissolved therein 0.1% to 6% by weight of a heavy metal salt of a dithiophosphoric acid ester and a heavy metal salt of a 2,4-dialkylphenol sulfide in amounts of 20–200% of the weight of said dithiophosphoric acid ester salt.

4. A lubricating composition comprising a hydrocarbon lubricating oil having dissolved therein 0.1% to 6% by weight of a heavy metal salt of a dithiophosphoric acid ester and a heavy metal salt of a 2,4-diamylphenol sulfide in amounts of 20–200% of the weight of said dithiophosphoric acid ester salt.

5. A lubricating composition comprising a hydrocarbon lubricating oil containing 0.1% to 3% by weight of a heavy metal salt of a dithiophosphoric acid ester and 0.1% to 3% by weight of a heavy metal dialkylphenol sulfide of formula



wherein R, R_1, R_2 and R_3 are alkyl radicals at least one of which contains 5–21 carbon atoms, n is an integer not greater than 2, Me is a polyvalent metal and x is the valence of Me.

6. A lubricating composition comprising a hydrocarbon lubricating oil having dissolved therein 0.1% to 3% by weight of a heavy metal salt of a diester of dithiophosphoric acid formed by reacting P_2S_5 with a mixture of equal parts by weight of octadecanol and wool-grease, together with a heavy metal salt of a dialkyl phenol sulfide in amounts of 20–200% of the weight of said dithiophosphoric acid ester salt.

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