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STABILIZED LUBRICATING COMPOSITIONS

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This invention relates to lubricating oil additives; to lubricating oil compositions containing the same; and particularly to those oils of the type known as crankcase oils. Although the improved lubricating oil compositions of the present invention are highly desirable for use in the crankcases of passenger automobiles, they are also especially valuable for heavy duty service in truck, bus, aeroplane, marine and diesel engines which operate for long periods of time at high temperatures.

The principal objects of the invention are to provide an improved lubricating oil of the heavy duty type which is heat stable, which is particularly resistant to sludge formation and oxidation, which is non-corrosive to alloy bearings and other metal parts under conditions of extreme service, and which is free from varnish formation and ring sticking tendencies.

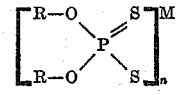
When conventional lubricating oils are subjected to high operating temperatures for extended periods of time, as are encountered in heavy duty service, they show a tendency to oxidize or decompose with the formation of complex and objectionable oxidation and decomposition products. Under the high temperature conditions obtaining in the engine, these decomposition products polymerize to form lacquer-like deposits on or between the moving parts of the engine causing them to stick or to wear rapidly. Even larger quantities of polymerization products remain dispersed in the partly oxidized crankcase oil and are rapidly precipitated to form a sludge when the engine cools or when fresh oil is added to the engine. These precipitated sludges become caked on the heated metal surfaces and cut down the effective life of the engine.

In United States patent applications, Serial No. 401,960, filed July 11, 1941, and Serial No. 415,411, filled Octoer 17, 1941, now abandoned, it is disclosed that hydrocarbon lubricating oil compositions having greatly improved detergent, anti-corrosive and anti-sludge forming properties may be prepared by the incorporation therein of minor amounts of various organic substituted dithiophosphates. While the lubricating oil compositions containing these organic substituted dithiophosphates are extremely resistant to sludge formation under conditions of heavy duty service, we have found that, when preparing these lubricating oil compositions from ordinary classes of lubricating oils which are not highly refined, a certain amount of sludge will form when the oil is subjected to high temperatures in heavy duty service for long periods of time in the presence of air or oxygen. With the more highly refined oils, however, such as those treated by the solvent refining process, the amount of sludge formed under such conditions is small. Since it is desirable, however, to use a lower cost oil in trucks, buses, diesel engines, etc., which operate almost continuously at high temperatures, a further improvement in the heat stability of lubricating oils refined by conventional methods is desirable.

We have found that these organic substituted dithiophosphates which are added to lubricating oils refined by

ordinary methods may be rendered more heat stable and more resistant to oxidation and decomposition and the lubricating oil compositions themselves may be made almost entirely resistant to sludge formation in heavy duty service for long periods of time at elevated temperatures by the incorporation therein of minor amounts of oil soluble reaction products of phosphorus sulfides and a member of the group consisting of either esters of tall oil fatty acids and alcohols or mixtures of such acids and alcohols, which reaction may be promoted by the presence of a free oxygen-containing gas.

The various dithiophosphates which we have found useful in improving lubricating oils and which may be employed to advantage with the oil-soluble reaction products of phosphorus sulfides are those having the general formula:



in which R is a member of the group consisting of aryl, alkyl, aralkyl, cycloalkyl, aryloxyalkyl, acylaryl and alkoxyaryl radicals; M is hydrogen or a salt-forming radical; and *n* is the valence of M. More specifically, compounds of this class include the dialkyl dithiophosphates such as dibutyl dithiophosphate, dihexyl dithiophosphate, di n-octyl dithiophosphate, dicapryl dithiophosphate, dilauryl dithiophosphate, dioctadecyl dithiophosphate, etc. We prefer to use those dialkyl dithiophosphates in which the alkyl group has from 5 to 30 carbon atoms since the longer alkyl chains tend to increase the solubility of the dithiophosphates in lubricating oils. The diaryl dithiophosphates and the diaryl dithiophosphates in which the aryl group bears an alkyl, alkoxy or cycloaliphatic group are also useful such as for example diphenyl dithiophosphate, di-(2,4-diamyl phenyl) dithiophosphate, dikeryl diphenyl dithiophosphate (a product obtained by treating chlorinated kerosene with a phenol in the presence of aluminum chloride and then reacting with P_2S_5) and the various di-(wax substituted diaryl) dithiophosphates as described in detail in application Serial No. 415,411, filed October 17, 1941, now abandoned. We also prefer the alkyl group in the alkaryl radical to have 5 to 50 carbon atoms so that the compounds are more easily oil-soluble. We may also employ the dicycloaliphatic dithiophosphates such as those prepared by reacting cyclopentanol, cyclohexanol, cycloheptanol, and methyl, ethyl, propyl and amyl substituted cyclopentanol, cyclohexanol and cycloheptanol, etc. with P_2S_5. The diaryloxyalkyl dithiophosphates such as di-(2,4-diamylphenoxyethyl) dithiophosphate, the diacylaryl dithiophosphates such as di-(lauroylphenyl) dithiophosphate and the dialkoxyaryl dithiophosphates may also be added to lubricating oils to improve the oxidation stability of the oil.

We prefer to employ these various organic substituted dithiophosphates in the form of their metal salts, preferably the alkaline earth metal salts. Among the various metal salts which may be employed are those of the salt-forming radicals nickel, aluminum, cadmium, tin, zinc, magnesium, calcium, strontium, barium and others.

The various organic substituted dithiophosphates described above are employed by us in our improved lubricating oil compositions, preferably in amounts ranging from 0.1 to 3% or more by weight and normally at a concentration of approximately 0.6%. Smaller amounts, 0.05 to 2.0% or more, of the heat stabilizer, that is, the oil soluble reaction products of phosphorus sulfides and

oxygen with the tall oil fatty acid-alcohol esters or mixtures may be employed with the dithiophosphates to enhance the heat stability thereof. The greater the tendency of the dithiophosphates to break down under high temperatures, or the higher its concentration in the oil composition, then, the more heat stabilizer should be employed. The amount of both of these substituents in the oil will also depend to some extent upon the purpose for which the oil is intended. For example, an oil intended for extremely heavy duty service should contain more of both the dithiophosphate and the phosphorus sulfide reaction product as compared with the amounts required by an oil intended for ordinary usage.

The general chemical reactions and the preparation and nature of the oil soluble reaction products of phosphorus sulfides such as those of phosphorus sesquisulfide, phosphorus pentasulfide, etc., involving the use of oxygen, are set forth in United States Patents 2,483,571, issued October 4, 1949, and 2,375,060, issued May 1, 1945, and reference thereto is incorporated herein.

The invention is particularly applicable to compositions comprising the organic substituted dithiophosphates, previously described, and to those reaction products of phosphorus sesquisulfide (P_4S_3) and the tall oil fatty acid-alcohol esters or mixtures.

As used herein, the term "tall oil fatty acids" is intended to refer to and include those fatty acids normally found in tall oil as well as those fatty acids having very similar properties, as required for the specific purposes herein referred to. For the purposes of this invention, these acids contain 16 to 18 carbon atoms and may contain one, two or more unsaturated bonds. Representative acids of this group would include oleic acid, linoleic acid, linolenic acid, the corresponding C_{16} unsaturated acids, stearic acid, palmitic acid, or mixtures of the same. For example, a mixture of fatty acids derived from a tall oil distillation process normally comprises approximately 40–60% oleic acid and approximately 60–40% linoleic acid with small quantities of other acids. Such a mixture has been found to be well suited for the application of the present inventive concept.

These tall oil fatty acids may be esterified with various alcohols prior to the reaction with phosphorus sulfide, in the presence of an oxygen containing gas, or they may merely form a mixture with these alcohols and then be reacted with the phosphorus sulfide in the presence of the oxygen containing gas.

Among the alcohols suitable for use with the above mentioned acids, either for esterification purposes or merely to form mixtures therewith, are the aliphatic monohydroxy alcohols such as octadecanol, oleyl alcohol, butanol, lauryl alcohol, tridecyl alcohol, cetyl alcohol, octyl alcohol, isopropanol, etc.; the polyhydroxy alcohols such as ethylene glycol, propylene glycol; the alcohols containing aromatic or cycloaliphatic substituents such as octylphenoxyethanol, dihydroabietyl alcohol; the sterols such as B-sitosterol; etc.

The preparation of the oil soluble phosphorus sulfide reaction products of these esters or mixtures will be further described in greater detail by the following specific examples. It should be understood, however, that, although these examples may set forth in particular detail some of the more specific features of the invention, such is not to be construed as limitative thereof.

EXAMPLE 1

Materials used:	Grams
Octadecyl ester of "Acintol FA #1"	529
Butanol	100
Sodium hydroxide (in 25 ml. of water)	16
Zinc chloride (in 25 ml. of water)	28
Phosphorus sesquisulfide	40
Zinc oxide	11
Barium hydroxide octahydrate	159

The preparation of the octadecyl ester of "Acintol FA #1" was as follows: ("Acintol FA #1" is a mixture of tall oil fatty acids having from about 40 to about 60% oleic acid and from about 60 to about 40% linoleic acid and small percentages, approximately 3–5%, of other fatty acids).

Materials used:		
Octadecanol	grams (1 mole)	268
"Acintol FA #1"	do	298
Toluene	grams	500
Para toluene sulfonic acid	do	4

The above materials were refluxed for three hours while removing the water which formed with a water trap. In this manner, 18 ml. or 1 mole of water was removed. After washing with water, then with sodium carbonate, and again with water, the volatile materials were removed under vacuum at 100° C. to give 529 grams of the desired ester.

The ester, butanol, and sodium hydroxide solution were refluxed for 1½–2 hours. The zinc chloride solution was then added to the mixture and refluxed for an additional ½ hour. After removing the water and butanol under vacuum at 100° C. the phosphorus sesquisulfide was added. After heating this reaction mixture to 130° C., a stream of air was blown into the reaction mixture. An exothermic reaction developed and white fumes were evolved. The reaction temperature was controlled by the rate of addition of air. After about one hour, the white fumes ceased, the exothermic reaction diminished, and air was passed through the mixture for an additional ½ hour, while holding the temperature at 130–140° C. At this point, the zinc oxide and 10 ml. of water were added and the mixture heated for about ¾ of an hour at 90–100° C. The barium octahydrate was then added and the reaction gradually heated to 120° C., followed by blowing with air at this temperature to remove the water. After the removal of water was complete, 55 grams of "Hy-flo" were added and the product filtered through a pre-coated, steam-jacketed vacuum filter. The resulting amber, oil-soluble liquid was the P_4S_3-oxygen-octadecyl ester of tall oil fatty acids reaction product and had the following analysis:

	Percent
Barium	9.42
Zinc	2.72
Phosphorus	2.65
Sulfur	1.63

EXAMPLE 2

Materials used:	Grams
Isopropyl ester of "Acintol FA #1" (prepared in same general manner as the ester used in Example 1 from isopropyl alcohol and "Acintol FA #1")	444
Butanol	100
Sodium hydroxide (in 15 ml. of water)	13
Zinc chloride (in 25 ml. of water)	23
Phosphorus sesquisulfide	33
Zinc oxide	9
Barium hydroxide octahydrate	132

The above materials were reacted in the same general manner as set forth in Example 1.

The product which was obtained was the P_4S_3-oxygen-isopropyl ester of tall oil fatty acid reaction product and had the following analysis:

	Percent
Barium	6.4
Zinc	1.71
Phosphorus	2.1
Sulfur	1.9

EXAMPLE 3

Materials used:	Grams
Ethylene glycol diester of "Acintol FA #1" (prepared from ethylene glycol and "Acintol FA #1" in the same general manner as the ester prepared for Example 1)	534
Butanol	135
Sodium hydroxide (in 25 ml. of water)	16
Zinc chloride (in 35 ml. of water)	28
Phosphorus sesquisulfide	40
Zinc oxide	11
Barium hydroxide octahydrate	160

The above materials were reacted together in the same general manner as in Example 1. The clear amber oil-soluble liquid was the P_4S_3-oxygen-ethylene glycol ester of tall oil fatty acids reaction product and had the following analysis:

	Percent
Barium	6.2
Zinc	1.9
Phosphorus	1.8
Sulfur	1.6

EXAMPLE 4

Materials used:	Grams
Lauryl oleate (prepared from lauryl alcohol and oleic acid in the same general manner as the ester prepared for Example 1)	430
Butanol	100
Sodium hydroxide (in 20 ml. of water)	13
Zinc chloride (in 30 ml. of water)	23
Phosphorus sesquisulfide	33
Zinc oxide	9
Barium hydroxide octahydrate	132

The above materials were reacted in the same general manner as in Example 1. The resulting oil soluble amber liquid was the P_4S_3-oxygen-lauryl oleate reaction product and had the following analysis:

	Percent
Barium	9.14
Zinc	2.45
Phosphorus	2.53
Sulfur	1.48

EXAMPLE 5

Materials used:	Grams
Oleyl stearate (prepared from oleyl alcohol and stearic acid in the same general manner as the ester prepared for Example 1)	497
Butanol	75
Sodium hydroxide (in 15 ml. of water)	12
Zinc chloride (in 25 ml. of water)	21
Phosphorus sesquisulfide	30
SAE #10 oil	497
Zinc oxide	8
Barium hydroxide octahydrate	124

The above materials were reacted together in the same general manner as in Example 1 with the exception that the oil was added at the same time as the zinc oxide. The resulting dark amber oil-soluble liquid was the P_4S_3-oxygen-oleyl stearate reaction product and had the following analysis:

	Percent
Barium	4.7
Zinc	1.1
Phosphorus	1.2
Sulfur	0.8

EXAMPLE 6

Materials used:	
Octadecanol	grams (1 mole) 268
Oleic acid	do 282
Butanol	grams 100
Sodium hydroxide (in 20 ml. water)	do 17
Zinc chloride (in 35 ml. of water)	do 29
Phosphorus sesquisulfide	do 41
Zinc oxide	do 11
Barium hydroxide octahydrate	do 550
SAE #10 oil	do 550

The octadecanol, oleic acid, butanol and sodium hydroxide solution were refluxed for about one hour. The zinc chloride solution was then added and the reaction mixture heated to reflux for an additional ½ hour. The water and butanol were removed by heating to 110–120° C. under vacuum. The phosphorus sequisulfide was then added and after heating the reaction mixture to 125–135° C., a stream of air was blown into the reaction. The exotherm which developed was maintained at 130–140° C. by regulating the rate of addition of the air. At the conclusion of the exotherm, air blowing was continued for an additional ½ hour while maintaining the temperature at 130–140° C. The oil, zinc oxide, and 11 ml. of water were added to this mixture, which was then heated to 100° C. for about one hour. The barium hydroxide octahydrate was then added and the temperature slowly raised to 120° C. The reaction was maintained at 120° C. while air was blown through the reaction mixture to remove the water. After the removal of water was complete, 75 grams of "Hy-flo" were added and the reaction mixture filtered through a steam-heated, precoated vacuum filter. The resulting dark amber oil-soluble liquid was the P_4S_3-oxygen reaction product of an octadecanol-oleic acid mixture and had the following analysis:

	Percent
Barium	4.97
Zinc	1.88
Phosphorus	1.5
Sulfur	0.9

EXAMPLE 7

Materials used:	Grams
Octadecanol	260
"Acintol FA #1"	286
Butanol	100
Sodium hydroxide (in 20 ml. of water)	17
Zinc chloride (in 35 ml. of water)	29
Phosphorus sequisulfide	41
SAE #10 oil	546
Zinc oxide	11
Barium hydroxide octahydrate	164

The above materials were reacted together in the same general manner as in Example 6. The resulting dark brown oil-soluble liquid was the P_4S_3-oxygen reaction product of an octadecanol-tall oil fatty acid mixture and had the following analysis:

	Percent
Barium	5.4
Zinc	1.7
Phosphorus	1.5
Sulfur	1.1

EXAMPLE 8

Materials used:	Grams
Tridecyl alcohol	190
Oleic acid	282
Butanol	100
Sodium hydroxide (in 20 ml. of water)	14
Zinc chloride (in 40 ml. of water)	25
Phosphorus sesquisulfide	35
Zinc oxide	9
Barium hydroxide octahydrate	142

The above materials were reacted together in the same

general manner as in Example 6 with the exception that no oil was used. The resulting amber oil-soluble liquid was the P_4S_3-oxygen reaction product of tridecyl alcohol-oleic acid mixture and had the following analysis:

	Percent
Barium	9.6
Zinc	3.8
Phosphorus	2.9
Sulfur	1.0

The excellent compatibility and solubility of these oil soluble reaction products of phosphorus sulfides in hydrocarbon lubricating oil compositions containing the dithiophosphates leads to another important advantage, namely, the ease with which these compounds are blended with the oil compositions. This step is further simplified by our practice of very simply dissolving them in the lubricating oils up to the extent of 50% or higher concentrations for storage and shipping purposes. In this way the blender of the ultimate composition need only pour the additive composition into the stock lubricating oil with suitable stirring in order to obtain the desired lubricant.

The invention will be further described in more specific detail by reference to and discussion of the following results obtained from heat stability tests which were run on various oil compositions selected to best illustrate the inventive concept.

These tests consisted of the following procedure: a 200 gram sample of the selected oil composition was placed in a 400 ml. short form, Pyrex beaker and set in a partially ventilated oven which was maintained at 250° F.; the test sample was observed at regular intervals during a 125 hour period. After 125 hours, the sample was removed from the oven and allowed to stand and cool for 24 hours. The sample was then observed for hazing, precipitation and/or gelling. Precipitating and/or gelling were considered as failures; a small amount of precipitation or sedimentation, however, could be tolerated; hazing, although not a crucial factor, was an indication of heat instability.

The following results were noted on blends using a solvent refined Mid-Continent base oil, S. A. E. 10:

Table 1

Percent Zinc dihexyl-dithio-phosphate	Percent neutralized P_4S_3-oxygen reaction product of Octadecanol-Tall oil Fatty acid Ester	Hours	Appearance of blend
----------	(Control)	125	Clear, some darkening, slight sediment.
0.6	do	125	Opaque, black.
0.6	0.05	120	Clear, slight sediment.
0.6	0.10	120	Do.
0.6	1.00	125	Clear, no precipitate.

Table 2

Percent Zinc dihexyl-dithio-phosphate	Percent neutralized P_4S_3-oxygen reaction product of Octadecanol-Tall oil Fatty acid mixture	Hours	Appearance of blend
----------	(Control)	125	Clear, some darkening, slight sediment.
0.6	do	125	Opaque, black.
0.6	0.05	144	Clear, some darkening, slight precipitate.
0.6	0.10	144	Do.

From a consideration of Table 1, it will be realized that the oil composition, without any zinc dihexyldithiophosphate inhibitor and without any P_4S_3-oxygen reaction product of octadecanol-fatty acid ester remained clear, although there was some darkening accompanied by the formation of a slight sediment. The addition of 0.6% zinc dihexyldithiophosphate, alone, when tested, as above, rendered the oil blend opaque and black as an indication of the relative heat instability thereof. However, it is to be noted that the addition of as little as 0.05% of the heat stabilizer stabilized the blend sufficiently so that it did not become opaque or black upon exposure to high temperatures for the test period and was classified as clear and merely containing a small precipitate.

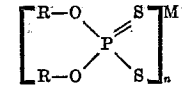
Similar results are to be noted from a consideration of Table 2, wherein again a small amount (0.05%) of a heat stabilizer comprising a phosphorus sulfide reaction product of a mixture of octadecanol and tall oil fatty acids was sufficient to overcome the heat instability of the zinc dihexyldithiophosphate. Increased amounts of the heat stabilizer correspondingly improved the appearance of the oil blend and its heat stability.

From the foregoing, it will be seen that we have provided a lubricating oil composition comprising an organic substituted dithiophosphate and a heat stabilizer consisting of an oil soluble reaction product of phosphorus sulfide, and various esters or acid-alcohol mixtures, which composition is heat stable, is particularly resistant to sludge formation and oxidation, is non-corrosive to alloy bearings and other metal parts under conditions of extreme service, and is free of varnish formation and ring sticking tendencies.

Although we have described but a few specific preparations of such reaction products of phosphorus sulfides and have referred briefly to the results of specific tests of such compounds in lubricating oil compositions containing dithiophosphates, we consider the same not to be limited thereto. It is understood that suitable changes, variations and modifications may be made without departing from the spirit and scope of the invention.

What we claim is:

1. A hydrocarbon mineral lubricating oil composition comprising a hydrocarbon mineral lubricating oil and, as an antioxidant and anticorrosive agent having a tendency toward heat instability and the formation of sludge upon continued heating thereof at high temperatures, 0.1–3.0% by weight of a dithiophosphate having the formula:



in which R is an alkyl radical containing from 5 to 30 carbon atoms; M is a polyvalent metal from the group consisting of nickel, aluminum, cadmium, tin, zinc, magnesium, calcium, strontium and barium; and n is the valence of M said oil also containing as a heat stabilizer for said dithiophosphate 0.05–2% by weight of an oil soluble, neutralized reaction product of a phosphorus sulfide and a member of the group consisting of tall oil fatty acids—alcohol esters and tall oil fatty acid—alcohol mixtures.

2. The composition as defined in claim 1, wherein the tall oil fatty acids comprise unsaturated monocarboxylic acids having 16 to 18 carbon atoms.

3. The composition as defined in claim 1, wherein the tall oil fatty acids comprise 40–60% oleic acid and 60–40% linoleic acid.

4. The composition as defined in claim 1, wherein the tall oil fatty acid comprises oleic acid.

5. The composition as defined in claim 1, wherein the tall oil fatty acid comprises linoleic acid.

6. The composition as defined in claim 1, wherein the alcohol is octadecanol.

7. The composition as defined in claim 1, wherein the alcohol is ethylene glycol.

8. The composition as defined in claim 1, wherein the phosphorus sulfide is phosphorus sesquisulfide.

9. The composition as defined in claim 1, wherein the dithiophosphate is a polyvalent metal salt of dihexyldithiophosphate.

10. The composition as defined in claim 1, wherein

the dithiophosphate is a polyvalent metal salt of dilauryldithiophosphate.

11. The composition as defined in claim 1, wherein the dithiophosphate is a polyvalent metal salt of dicapryldithiophosphate.

12. The composition as defined in claim 1, wherein the polyvalent metal is zinc.

13. The composition as defined in claim 1, wherein the polyvalent metal is barium.

14. The composition as defined in claim 1 wherein the antioxidant and anticorrosive agent is zinc dihexyldithiophosphate and the heat stabilizer is a neutralized P_4S_3-oxygen reaction product of octadecanol-tall oil fatty acid ester.

15. The composition as defined in claim 1, wherein the antioxidant and anticorrosive agent is zinc dihexyldithiophosphate and the heat stabilizer is a neutralized P_4S_3-oxygen reaction product of octadecanol-tall oil fatty acid mixture.

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