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ESTERS OF DITHIOPHOSPHORIC ACIDS AND LUBRICATING OIL COMPOSITIONS CONTAINING SAME

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This invention relates to new compositions of matter and more particularly to a new class of chemical compounds which are useful in lubricating oil compositions, to lubricating oil compositions containing such compounds, and to methods for preparing such compounds. The lower molecular weight compounds are useful as multi-purpose lubricating oil additives and the higher molecular weight compounds are useful as synthetic lubricating oils.

The utilization of additives in lubricating oil compositions is well known. These additives are used to improve one or more characteristics of the lubricating oil compositions such as viscosity index, pour point, oxidation resistance, corrosion resistance, detergency, and the like, and are employed extensively in lubricating oil compositions for internal combusion engines such as automotive and aviation engines. Due to the increasing severity of engine operation, there is a continuing and critical need for new and improved additives which are capable of imparting improved characteristics to the lubricating oil compositions. Preferably, such new additives will improve more than one characteristic or property of the oil. In addition to the search for new and improved additives, considerable effort has been expended in the search for new and improved types of synthetic oils which may be used in such lubricating oil compositions. This has been necessary because it has been found that the quality of mineral oils, such as those derived from petroleum oils, is limited by the processing methods, such as solvent extraction, acid treatment, and the like, which are available.

A new class of chemical compounds has now been found which are useful in lubricating oil compositions, the lower molecular weight compounds being useful as multi-purpose lubricating oil additives and the higher molecular weight compounds being useful as synthetic lubricating oils. The lower molecular weight compounds are the products obtained by treating a compound selected from the group consisting of alkylene oxides and glycols and containing 2 to 18 carbon atoms with a dithiophosphate having the formula

$$[(RO)_2\overset{S}{\overset{\|}{P}}-S]_xY$$

where R is a hydrocarbon radical containing 3 to 20 carbon atoms; Y is selected from the group consisting of hydrogen and metals of Groups I and II of the periodic table, and x is the valence of Y. The R radicals in the formula may be different radicals. In the preferred embodiment of this portion of the invention, the alkylene oxides and glycols contain 3 to 6 carbon atoms and R is an alkyl radical containing 6 to 10 carbon atoms. Preferably 1 to 3 moles of the alkylene oxide or glycol are reacted with one mole of the dithiophosphate and the reaction is carried out at a temperature in the range of about 100 to 300° F. Preferably Y is an alkali metal, an alkaline earth metal or zinc. The above-mentioned compounds are useful as lubricating oil additives and may be used in synthetic lubricating oils as well as mineral oils in concentrations of about 0.1 to 10% and preferably 0.5 to 5% by weight based on the total composition. These relatively low molecular weight reaction products have been found to improve a number of properties of lubricating oil compositions. More specifically, it has been found that they are excellent sludge dispersants and sludge inhibitors; they stabilize other phosphorous sulfide-treated additives with respect to H_2S evolution; they function as emulsifying agents and are, therefore, useful in cutting oils; they have excellent extreme pressure properties and antiwear properties; they inhibit copper corrosion and reduce corrosion resulting from hydrogen halides and they are compatible wtih other conventional additives such as sulfonates, alkyl phenol sulfides, metal salts of alkyl phenol sulfides, phosphosulfurized metal salts of alkyl phenol sulfides and the like.

It has also been found that the above-described low molecular weight compounds may be treated with phosphorus pentasulfide (P_2S_5) and additional alkylene oxides or glycols to form higher molecular weight compounds which are useful as synthetic lubricating oils. Preferably, the low molecular weight compound, that is the reaction product of the dithiophosphate and the alkylene oxide or glycol, which is further reacted is a compound wherein Y is hydrogen. More specifically, it has been found that, by reacting one mole of the reaction product of the dithiophosphate and the alkylene oxide or glycol separately and in a sequence with at least the first member in a series consisting of (1) 0.25 mole of P_2S_5, (2) about 0.5 to 1.5 moles of an alkylene oxide or glycol, (3) about 0.125 mole of P_2S_5, and (4) about 0.25 to 0.75 mole of an alkylene oxide or glycol, a higher molecular weight compound is formed which is useful as a synthetic lubricating oil. These high molecular weight compounds have high viscosity indices, excellent extreme pressure properties and other properties which are advantageous for lubricating oils.

The dithiophosphates employed in the present invention have the general formula

$$[(RO)_2\overset{S}{\overset{\|}{P}}-S]_xY$$

where R is a hydrocarbon radical containing 3 to 20 carbon atoms; Y is selected from the group consisting of hydrogen and metals of Groups I and II of the periodic table, and x is the valence of Y. R may be an alkyl, aryl, alkaryl or aralkyl radical. Preferably R is an alkyl radical and preferably the alkyl radical contains 6 to 10 carbon atoms. When Y is a metal, it is preferably an alkali metal such as sodium or potassium; an alkaline earth metal such as calcium, barium or magnesium; or zinc. These metal dithiophosphates may be represented by the following formula

$$[(RO)_2\overset{S}{\overset{\|}{P}}-S]_xM$$

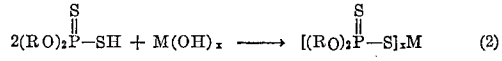
where M is a metal of Groups I and II of the periodic table and x is the valence of M.

The dithiophosphates are prepared by methods well known to the art. More specifically, these dithiophosphates may be conveniently prepared in accordance with the following reaction:

$$4ROH + P_2S_5 \longrightarrow 2(RO)_2\overset{S}{\overset{\|}{P}}-SH + H_2S \qquad (1)$$

where R has the aforedescribed definition. The diester is the principal product. Small amounts of the mono- and tri-esters may also be formed. Mixtures of alcohols may be employed if desired. The above reaction may be carried out at a temperature in the range of about 150° to 300° F. for about 2 to 10 hours. To form dithiophosphates where Y is a metal, the dithiophosphate shown in Equation 1, which may also be termed a dithio-

phosphoric acid, is reacted with a basic reacting compound, such as the oxide or hydroxide, of a metal of Groups I and II of the periodic table. For example, the metal dithiophosphate may be prepared in accordance with the following reaction:



$$2(RO)_2\overset{S}{\overset{\|}{P}}-SH + M(OH)_x \longrightarrow [(RO)_2\overset{S}{\overset{\|}{P}}-S]_xM \qquad (2)$$

where M is a metal of Groups I and II of the periodic table. Specific compounds of the formula ROH which may be employed in these reactions include

Cyclohexanol
Isopropanol
2-ethylhexanol
Capryl alcohol
N-butanol
Oleyl alcohol
Stearyl alcohol
Methyl isobutyl carbinol

Especially preferred compounds of the formula ROH are Oxo alcohols which are derived from the well-known Oxo process. In the Oxo process, Oxo alcohols are synthesized from olefinic organic compounds and mixtures of CO and H_2 in the presence of a Group VIII metal catalyst, usually cobalt. The primary reaction product consists essentially of organic carbonyl compounds, mainly aldehydes having one more carbon atom per molecule than the olefinic feed material. This oxygenated product is then hydrogenated in a second catalytic stage to convert the aldehydes to the corresponding alcohols. Practically all types of organic compounds having an olefinic double bond, such as aliphatic olefins and diolefins, cycloolefins, aromatics with olefinic side chains, oxygenated organic compounds with olefinic double bonds, and the like, may be employed as starting materials. The metal catalyst may be present as a solid or in the form of a compound soluble in the olefinic feed stock. Suitable reaction conditions in the primary reaction include temperatures of about 150°–450° F., presures of 100 to 300 and higher atmospheres, H_2 to CO ratios of about 0.5–2:1, liquid feed rates of about 0.1 to 5.0 v./v./hr., and gas feed rates of about 1000 to 45,000 standard cubic feet of gas mixture per barrel of liquid olefin feed. Similar or higher temperatures and pressures, and hydrogenation catalysts such as nickel, copper, tungsten, oxides or sulfides of Group VI and Group VIII metals, etc., may be employed in the second stage for hydrogenation of the carbonyl compounds to alcohols. Specific Oxo alcohols prepared by the Oxo process include C_8 Oxo alcohol from butylene-propylene copolymer, C_9 Oxo alcohol from tripropylene and C_{13} Oxo alcohol from tetrapropylene.

Specific examples of the dithiophosphates which may be employed in this invention include zinc dihexyl dithiophosphate, zinc hexyl octyl dithiophosphate, barium isopropyl octyl dithiophosphate, sodium butyl tetradecyl dithiophosphate, dioctyl dithiophosphoric acid, calcium didodecyl dithiophosphate, potassium nonadecyl pentadecyl dithiophosphate, hexyl decyl dithiophosphoric acid, zinc isopropyl methylisobutylcarbinyl dithiophosphate, and magnesium cyclohexyl amyl dithiophosphate.

The alkylene oxides and glycols which are employed in the present invention are those containing 2 to 18 carbon atoms and preferably those containing 3 to 6 carbon atoms. The alkylene oxides may be represented by the general formula

$$C_mH_{2m}O$$

and the glycols may be represented by the general formula

$$C_mH_{2m+2}O_2$$

where m is an integer of 2 to 18. Specific examples of the alkylene oxides which may be employed include 1,2

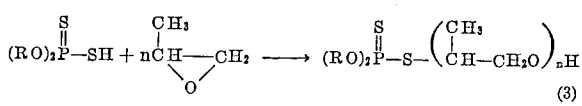
propylene oxide; 1,3 propylene oxide; 1,2-butylene oxide; ethylene oxide; 1,2-hexylene oxide; 2,3 amylene oxide; 1,2 decylene oxide; 2,3 octodecylene oxide and 2,3-octylene oxide. Specific examples of the glycols which may be employed include 1,2-propylene glycol; 1,3-propylene glycol; ethylene glycol; 1,2-butylene glycol; 2,3-butylene glycol; tetradecylene glycol; 1,2-amylene glycol; 3,4-hexylene glycol; 1,2 dodecylene glycol; 1,2 octylene glycol and 1,2 octodecylene glycol. Alkylene sulfides and thioglycols may be employed in the present invention in place of their oxygen derivatives, although the thio derivatives are less preferred due to their relatively strong and disagreeable odor.

The low molecular weight compounds of this invention which are useful as lubricating oil additives are the products obtained by reacting a dithiophosphate having the formula

$$[(RO)_2\overset{S}{\overset{\|}{P}}-S]_xY$$

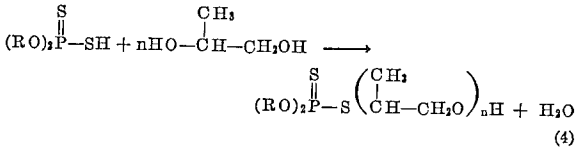
with an alkylene oxide or a glycol. Preferably 1 to 3 moles of the alkylene oxide or glycol are reacted with the dithiophosphate. The reaction may be carried out at a temperature ranging from room temperature (70° F.) to about 400° F. and preferably is carried out at a temperature in the range of about 100° to 300° F. The reaction proceeds slowly at temperatures below about 100° F., and at temperatures above about 400° F. the dithiophosphate may decompose. Atmospheric pressures may be employed, although elevated pressures such as up to 10 atmospheres may also be employed if desired. Elevated pressures are especially useful when employing ethylene oxide since at atmospheric conditions ethylene oxide is a gas. The reaction proceeds rapidly and will be substantially completed in about 0.5 to 5 hours. Generally a reaction time of 1 to 2 hours will be sufficient to assure completion of the reaction. The end of the reaction will be indicated when evolution of heat from the reaction mixture ceases. In carrying out the reaction, it is convenient to add the alkylene oxide or glycol to the dithiophosphate which has been preheated. Intimate mixing of the reactants by mechanical or other means will facilitate the reaction. It is often convenient to initially dissolve the dithiophosphate in an inert solvent such as a mineral lubricating oil and to carry out the reaction in this solvent medium.

Although the reaction products of this invention have not been positively identified at this time, it is believed that they have the following formulae and are formed in accordance with the following equations. For example, when the dithiophosphoric acid is reacted with n moles of propylene oxide, it is believed that the following product is produced:



$$(RO)_2\overset{S}{\overset{\|}{P}}-SH + nCH(CH_3)-CH_2 \longrightarrow (RO)_2\overset{S}{\overset{\|}{P}}-S-\left(CH(CH_3)-CH_2O\right)_nH \qquad (3)$$

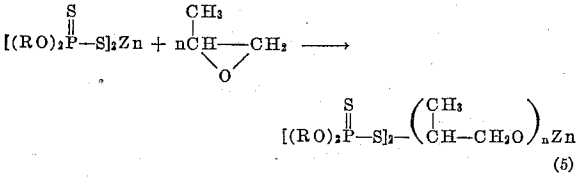
wherein n is preferably an integer of 1 to 3. In case glycols are employed, it is believed that the dithiophosphoric acid reacts with n moles of 1,2-propylene glycol, for example, as follows:



$$(RO)_2\overset{S}{\overset{\|}{P}}-SH + nHO-CH(CH_3)-CH_2OH \longrightarrow (RO)_2\overset{S}{\overset{\|}{P}}-S\left(CH(CH_3)-CH_2O\right)_nH + H_2O \qquad (4)$$

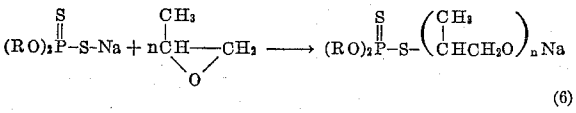
Thus it is believed that 1,2-propylene glycol is dehydrated in the reaction and forms a compound similar to that formed with propylene oxide. In the case where a metal dithiophosphate, for example such as zinc dithiophos-

phate, is reacted with n moles of propylene oxide, it is believed that the following reaction takes place:



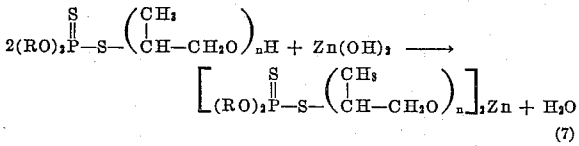
(5)

When a dithiophosphate of a monovalent metal, such as sodium, is reacted, for example, with propylene oxide, it is believed that the following reaction takes place:



(6)

The reaction product of a dithiophosphoric acid and an alkylene oxide or glycol may be reacted with a basic reacting compound of a metal to form the metal salt thereof. For example, where the reaction product of a dithiophosphoric acid and propylene oxide is reacted with zinc hydroxide, it is believed that the following reaction takes place:



(7)

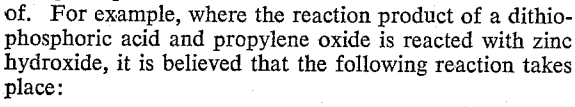
The reaction product of the dithiophosphates and the alkylene oxides or glycols may be further reacted with P_2S_5 and additional alkylene oxides or glycols to form high molecular weight compounds which are useful as synthetic lubricating oils. Preferably the dithiophosphate compounds employed to form lubricating oils are dithiophosphoric acids, that is where Y in the formula is hydrogen. If the low molecular weight reaction product of the dithiophosphate and the alkylene oxide or glycol is designated as Compound I, and P_2S_5 is designated as Compound II and the alkylene oxide or glycol is designated as Compound III, the reactions may be described as being carried out as follows: 1 mole of Compound I is reacted separately and in a sequence with at least the first member of a series consisting of (1) about 0.25 mole of Compound II, (2) about 0.5 to 1.5 moles of Compound III, (3) about 0.125 mole of Compound II, and (4) about 0.25 to 0.75 mole of Compound III. Thus four different compounds may be obtained by reacting the various compounds in accordance with the above-described procedure. More specifically, a first reaction is prepared by reacting 1 mole of the dithiophosphate-alkylene oxide or glycol reaction product with about 0.25 mole of P_2S_5; a second reaction product is obtained by reacting one mole of the first reaction product with about 1 to 3 moles of additional alkylene oxide or glycol; a third reaction product is obtained by reacting 1 mole of the second reaction product with about 0.25 mole of P_2S_5; and a fourth reaction product is obtained by reacting 1 mole of the third reaction product with about 1 to 3 moles of additional alkylene oxide or glycol. All of the four above-described products are useful as synthetic lubricating oils. The

reactions are carried out preferably at a temperature in the range of about 100° to 300° F. and each reaction will be substantially completed after a period of about 0.5 to 10 hours, generally after about 2 to 6 hours.

Although again the high molecular weight reaction products have not been positively identified at this time it is believed that they have the following formulae and are formed in accordance with the following reactions. When the reaction product of the dithiophosphate and the alkylene oxide or glycol is reacted with P_2S_5, it is believed that the following reaction occurs:

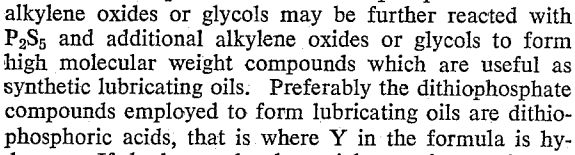
(8)

The reaction product of Equation 8 may then be further reacted with, for example, additional propylene oxide in accordance with the following postulated equation:



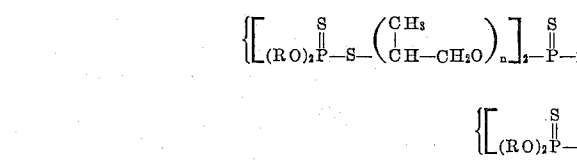
(9)

Then the reaction product of Equation 9 may be further reacted with additional P_2S_5 in accordance with the following postulated equation:



(10)

Then the reaction product of Equation 10 may be further reacted with additional propylene oxide in accordance with the following postulated equation:



(11)

The following examples are intended to set forth the invention in greater detail but it will be understood that it is not intended that the invention be limited in any way to these examples.

EXAMPLE I.—PREPARATION OF REACTION PRODUCTS

A. *Preparation of zinc di-C_6–C_8 alkyl dithiophosphate—Propylene oxide reaction product—Product A*

A commercially available additive concentrate consisting of about 57.5% by weight of a zinc di-C_6–C_8 alkyl dithiophosphate in a diluent mineral oil was reacted with propylene oxide to form an additive in accordance with this invention. The untreated commercial additive concentrate will be referred to hereinafter as Product A–U, the U referring to the fact that it was untreated. The additive of the present invention, Product A, was prepared as follows:

386.0 grams of Product A–U were placed into a three-neck, round bottom flask to which were attached a water cooled condenser, an air driven stirrer, a dropping funnel, and a thermometer. The flask and contents were heated

to a temperature of 190° F. 100 cc. (82 g.) of previously chilled propylene oxide was added in 5 cc. portions by means of the dropping funnel. Heat was given off during the addition of the propylene oxide. The temperature of the reaction mixture was maintained at 180° F. by means of an ice bath. After all of the propylene oxide was added, the reaction mixture was heated at 250° F. and nitrogen blown for 2 hours. Prior to the propylene oxide treatment, Product A–U had a phosphorus content of 4.70%, sulfur content of 10.33%, neutralization number of 82.6 and saponification number of 89.4; after propylene oxide treatment, the product had a phosphorus content of 4.15%, sulfur content of 8.67%, neutralization number of 50.7 and saponification number of 65.3.

B. *Preparation of barium di-C_6–C_8 alkyl dithiophosphate—Propylene oxide reaction product—Product B*

A commercially available additive concentrate, hereinafter termed Product B–U, consisting of (1) about 85% by weight of an oil solution containing as the active ingredient about 46% by weight of barium di-C_6–C_8 alkyl dithiophosphate and (2) about 15% by weight of an oil solution containing as the active ingredient about 40% by weight of barium sulfonate was treated with propylene oxide in accordance with the present invention as follows to form a Product B:

351.0 grams of Product B–U were treated with 100 cc. of propylene oxide in a similar manner as described in the procedure for the propylene oxide treatment of Product A–U.

Anaylsis of Product B–U:

Ba, percent	6.79
P, percent	2.61
Neut. No.	0.41
Sap. No.	10.36

Analysis of Product B:

Ba, percent	6.57
P, percent	2.71
Neut. No.	0.10
Sap. No.	13.26

C. *Preparation of di C_8 Oxo dithiophosphoric acid—Propylene oxide reaction product—Product C*

Initially a C_8 Oxo alcohol was treated with P_2S_5 to form a di C_8 Oxo dithiophosphoric acid (Product C–U) as follows:

A mixture of 1500 grams of C_8 Oxo alcohol and 700 grams of powdered P_2S_5 was placed in a glass reaction vessel and agitated at 180±10° F. for a period of 6 hours. The reaction mixture was cooled and filtered through a sintered glass funnel to remove unreacted P_2S_5. The P_2S_5-treated C_8 Oxo alcohol was a liquid having the following analysis:

Neut. No.	158
Sap. No.	169.5
S, percent	18.3
P, percent	8.96

Product C–U was then treated with propylene oxide to form Product C as follows:

1200 grams of Product C–U were treated with 300 cc. of propylene oxide in a similar manner as described in the procedure for the preparation of Product A. Reaction Product C–U had a neutralization number of 13.9, a saponification number of 174.6, phosphorus content of 8.28% and sulfur content of 15.8%.

D. *Preparation of zinc di C_8 Oxo dithiophosphate—Propylene oxide reaction product—Product D*

Initially a zinc di C_8 Oxo dithiophosphate (Product D–U) was prepared as follows:

145 grams of Product C–U and 20 grams of powdered zinc oxide were charged to a reaction vessel and stirred for 2 hours at 250° F. The reaction product was filtered hot through a sintered glass funnel.

Product D–U was then treated with propylene oxide to form Product D as follows:

160 grams of Product D–U were treated with 100 cc. of propylene oxide in a similar manner as described in the procedure for the propylene oxide treatment of Product A–U.

E. *Preparation of di C_8 Oxo dithiophosphoric acid—Propylene oxide reaction product—Product E*

A reaction product of di C_8 Oxo dithiophosphoric acid and propylene oxide, Product E, was prepared as follows:

1815 grams of Product C–U were treated with 400 cc. of propylene oxide as directed in the procedure for the preparation of Product A. Product E had a neutralization number of 14, a saponification number of 175, and analyzed 15.8% sulfur and 8.28% phosphorus. Product E, which was a liquid, had an SSU viscosity at 210° F. of 45.5 and a viscosity index of 66.

F. *Preparation of di C_8 Oxo dithiophosphoric acid—Propylene oxide—P_2S_5 reaction product—Product F*

Product E was then treated with phosphorus pentasulfide, P_2S_5, as follows to form a Product F:

465 grams of Product E and 100 grams of powdered P_2S_5 were charged to a reaction vessel and agitated at 250° F. for 6 hours. The reaction mixture was filtered hot through a sintered glass funnel.

G. *Preparation of di C_8 Oxxo dithiophosphoric acid—Propylene oxide—P_2S_5—Propylene oxide reaction product—Product G*

Product F was further treated with additional propylene oxide to form a Product G as follows:

486 grams of Product F were treated with 50 cc. of propylene oxide in accordance with the instructions as given for the procedure of the preparation of Product A. Product G had a neutralization number of 34, a saponification number of 249, and analyzed 18.20% sulfur and 9.47% phosphorus. Product G, which was a liquid, had an SSU viscosity at 100° F. of 831.5, an SSU viscosity at 210° F. of 83.3, and a viscosity index of 103.

H. *Preparation of di-isopropyl dithiophosphoric acid—Propylene oxide reaction product—Product H*

275 grams of isopropyl alcohol and 80 grams of powdered P_2S_5 were charged to a flask and stirred for 2 hours at 180° F. To the reaction product 90 cc. of propylene oxide were added. Procedure for the propylene oxide addition is described in the preparation of Product A. The reaction Product H was filtered hot.

Analysis of P_2S_5-treated isopropyl alcohol:

Neut. No.	251
Sap. No.	284.6

Analysis of Product H:

Neut. No.	35.9
Sap. No.	221.5

I. *Preparation of zinc di-C_6–C_8 alkyl dithiophosphate—1,2-propylene glycol reaction product—Product I*

354 grams of Product A–U were placed into a three-neck, round bottoms flask to which were attached an air-driven stirrer, a dropping funnel and a thermometer. The flask and contents were heated to a temperature of 225° F. 40 cc. of chilled 1,2-propylene glycol were added in 5 cc. portions. Some heat was given off during the course of the addition. The reaction mixture was heated for 2 hours at 250° F.

EXAMPLE II.—CARBON BLACK DISPERSANCY TEST

Product A, Product A–U, Product B, and Product B–U were each dissolved in a mineral lubricating oil

which consisted of a solvent-extracted mineral oil (a blend of Mid-Continent neutral and bright stock) of SAE–10 grade to form the following compositions:

Composition I consisted of 3.0 wt. percent of Product A and 97.0% by weight of the aforementioned mineral lubricating oil.

Composition II consisted of 3.0 wt. percent of Product A–U and 97.0% of the mineral lubricating oil.

Composition III consisted of 2.5% by weight of Product B and 97.5% by weight of the mineral lubricating oil.

Composition IV consisted of 2.5% by weight of Product B–U and 97.5% by weight of the mineral lubricating oil.

These compositions were then evaluated in a Carbon Black Dispersancy Test which was carried out by adding 6 grams of carbon black with thorough mixing to 294 grams of each oil composition. The resultant blends were maintained at 200° F. for 48 hours in a 500 cc. graduate. Thereafter 150 gram portions of the oil blends were decanted from the graduates and filtered through weighed sintered glass funnels and the weight of carbon black determined. This test is an indication of the ability of an additive to disperse materials such as engine sludge in lubricating oil compositions. The following results were obtained in this test:

TABLE I.—RESULTS OF CARBON BLACK DISPERSANCY TEST

Composition	Additive Product	Grams of Suspended Carbon Black per 150 Grams of Blend
Mineral Lubricating Oil Alone	None	0.03
I	A	1.15
II	A–U	0.25
III	B	0.95
IV	B–U	0.59

It will be noted that Product A dispersed more than four times as much carbon black as the untreated product, Product A–U. Also, it will be noted that Product B dispersed nearly twice as much carbon black as the untreated parent product, Product B–U. Thus the low molecular weight reaction products of this invention are shown to be excellent dispersants for such materials as carbon black in lubricating oil compositions.

EXAMPLE III.—ACETONE-INSOLUBLE SLUDGE DISPERSANCY TEST

Composition I containing 3.0% by weight of Product A and Composition II containing 3.0% by weight of Product A–U were evaluated in an Acetone-Insoluble Sludge Dispersancy Test. In this test, 6 grams of acetone-insoluble sludge obtained from automotive engines were added to 294 grams of each of the two compositions with thorough mixing and the resultant blends were stored at 200° F. for 48 hours in a 500 cc. graduate. Then 150 grams of each oil blend were decanted and filtered through a sintered glass funnel and the amount of acetone-insoluble sludge collected on each filter was determined. The following results were obtained in this test:

TABLE II.—RESULTS OF ACETONE-INSOLUBLE SLUDGE DISPERSANCY TEST

Composition	Additive Product	Grams of Suspended Carbon Black per 150 Grams of Blend
Mineral Lubricating Oil Alone	None	0.19
I	A	0.50
II	A–U	0.34

It will be noted from the results of these tests that Product A prepared in accordance with this invention suspended almost 50% more sludge than did the untreated additive product, Product A–U. This test is another indication of the excellent sludge dispersancy properties of the products of this invention.

EXAMPLE IV.—SLUDGE FORMATION INHIBITOR TEST

In this example, Product A and Product A–U were evaluated as sludge formation inhibitors. These additives were dissolved in a filtered used drain oil obtained from a laboratory engine test in which a high-deposit-forming fuel and an SAE–10 grade lubricating oil were used. Since filtered used drain oil continues to form sludge upon standing, this test is an indication of the effectiveness of an additive to inhibit sludge formation. Two blends were prepared—one containing 3.0% by weight of Product A and 97.0% by weight of the filtered used drain oil and the other blend consisting of 3.0 wt. percent of Product A–U and 97.0% by weight of the filtered used drain oil. The blends were stored for one week at 200° F., after which each blend was filtered and the quantity of deposits on each filter was determined by weighing. The following results were obtained in this particular test:

TABLE III.—RESULTS OF SLUDGE FORMATION INHIBITOR TEST

Additive Product	Grams Sludge Formed per 330 Grams of Used Oil
None	0.38
A	0.29
A–U	0.34

This test shows that Product A is a sludge inhibitor and is superior to the untreated compound, Product A–U.

The superior load-carrying properties of the products of this invention are shown by Examples V, VI, and VII.

EXAMPLE V.—SAE TEST

Product A, Product A–U, Product C, and Product C–U were evaluated in this particular test. Separate blends were prepared, each containing 0.7% by weight of the particular additive in a lubricating oil base stock composition which consisted of 95% by weight of an SAE–10 grade mineral oil and 5.0% by weight of a commercial detergent-inhibitor additive. The following four separate compositions were prepared: Composition V contained 0.7% by weight of Product A; Composition VI contained 0.7% by weight of Product A–U; Composition VII contained 0.7% by weight of Product C, and Composition VIII contained 0.7% by weight of Product C–U.

The SAE Test is carried out as described in J.I.P. vol. 32 (1936). The following results were obtained in this test:

TABLE IV.—RESULTS OF SAE TEST

Composition	Additive Product	Scale Reading, Pounds
V	A	95
VI	A–U	60
VII	C	95
VIII	C–U	90

It will be noted that the additive of this invention Product C is superior to the untreated additive Product C–U in the SAE Test. Also it will be noted that the other additive of this invention, Product A, which was evaluated in this test, was substantially superior to the untreated Product A–U.

EXAMPLE VI.—ALMEN MACHINE TEST

Composition VII and Composition VIII described in Example V were evaluated in the Almen Machine Test as described in J.I.P. vol. 32 (1936). The following results were obtained in the Almen Test:

TABLE V.—RESULTS OF ALMEN TEST

Composition	Additive Product	Weights Carried
VII	C	7
VIII	C-U	5

It will be noted that the additive of this invention Product C was superior in this test to the untreated additive Product C–U.

EXAMPLE VII.—TIMKEN TEST

Composition V and Composition VI were evaluated in the Timken Test as described in J.I.P. vol. 32 (1936). The results of the Timken Test were as follows:

TABLE VI.—RESULTS OF TIMKEN TEST

Composition	Additive Product	Load Carried, Pounds
V	A	10
VI	A-U	8

It will be noted that the additive of this invention Product A was superior in this test to the untreated additive Product A–U.

Other tests were conducted to evaluate further the low molecular weight reaction products of this invention. In these tests it was shown that the alkylene oxide- or glycol-treated dithiophosphates showed several advantages over the untreated additive products for use as motor oil additives. These advantages were: (1) less corrosive to copper; (2) improved color; (3) improved water sensitivity characteristics in oil blends containing conventional additives; (4) increased resistance to hydrogen bromide corrosion. All of the products tested met the conventional motor oil inspection requirements for flash, fire, compatibility, and hydrogen sulfide odor.

When the additives of the present invention, that is the low molecular weight reaction products of dithiophosphates and alkylene oxides or glycols, are employed as lubricating oil additives, they are preferably added to the lubricating oil compositions in proportions of about 0.1% to about 10.0% and preferably 0.5 to about 5.0%, based on the total composition. The proportions giving the best results will vary somewhat according to the nature of the additive and the specific purpose which the lubricant is to serve in a given case. For commercial purposes, it is convenient to prepare concentrated oil solutions in which the amount of additive in the composition ranges from 25% to 50% by weight, and to transport and store them in such form. In preparing a lubricating oil composition for use as a crankcase lubricant, the additive concentrate is merely blended with the base oil in the required amount.

The low molecular weight 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 alcoholates, metal alkyl phenol sulfides, metal organo phosphates, phosphites, thiophosphates, and thiophosphites, metal xanthates and thioxanthates, metal thiocarbamates, and the like. Other types of additives, such as alkyl phenols and phenol sulfides, may also be present.

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 by solvent extraction with solvents such as phenol, sulfur dioxide, 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.

Other lubricating oil base stocks which may be used include synthetic lubricating oils having a viscosity of at least 30 SSU at 100° F. such as esters of monobasic acids (e.g. ester of C_8 Oxo alcohol with C_8 Oxo acid, ester of C_{13} Oxo alcohol with octanoic acid, etc.), esters of dibasic acids (e.g. di-2-ethyl hexyl sebacate, di-nonyl adipate, etc.), esters of glycols (e.g. C_{13} Oxo acid diester of tetraethylene glycol, etc.), complex esters (e.g. the complex ester formed by reacting one mode of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, complex ester formed by reacting one mole of tetraethylene glycol with two moles of sebacic acid and two moles of 2-ethyl hexanol, complex ester formed by reacting together one mole of azelaic acid, one mole of tetraethylene glycol, one mole of C_8 Oxo alcohol, and one mole of C_8 Oxo acid), esters of phosphoric acid (e.g. the ester formed by contacting three moles of the mono methyl ether of ethylene glycol with one mole of phosphorus oxychloride, etc.), halocarbon oils (e.g. the polymer of chlorotrifluoroethylene containing twelve recurring units of chlorotrifluoroethylene), alkyl silicates (e.g. methyl polysiloxanes, ethyl polysiloxanes, methyl-phenyl polysiloxanes, ethyl-phenyl polysiloxanes, etc.), sulfite esters (e.g. ester formed by reacting one mole of sulfur oxychloride with two moles of the methyl ether of ethylene glycol, etc.), carbonates (e.g. the carbonate formed by reacting C_8 Oxo alcohol with ethyl carbonate to form a half ester and reacting this half ester with tetraethylene glycol), mercaptals (e.g. the mercaptal formed by reacting 2-ethyl hexyl mercaptan with formaldehyde), formals (e.g. the formal formed by reacting C_{13} Oxo alcohol with formaldehyde), polyglycol type synthetic oils (e.g. the compound formed by condensing butyl alcohol with fourteen units of propylene oxide, etc.), or mixtures of any of the above in any proportions. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or volatilized products may be employed in admixtures with mineral oils. Also mixtures of any of the above-mentioned oils in any proportions may be used.

For the best results the base stock chosen should normally be an oil which with 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, no strict rule can be laid down for the choice of the base stock. The additives are normally sufficiently soluble in the base stock, but in some cases auxiliary solvent agents may be used. The lubricating oils will usually range from about 40 to 150 seconds (Saybolt) viscosity at 210° F. The viscosity index may range from 0 to 100 or even higher.

Other agents than those which have been mentioned may be present in the oil composition, such as dyes, pour point depressants, heat thickened fatty oils, sulfurized fatty oils, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, olefin polymers, and the like. Assisting agents which are particularly desirable as plasticizers and defoamers and which may be included in the composition are the higher alcohols having

preferably 8 to 20 carbon atoms, e.g. octyl alcohol, lauryl alcohol, stearyl alcohol, and the like.

In addition to being employed in lubricants, the additives of the present invention may also be used in other mineral oil products such as motor fuels, hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils, transformer oils, industrial oils, process oils and the like, and generally as useful additives in mineral and synthetic oil products. They may also be used in gear lubricants, greases and other products containing mineral or synthetic oils as ingredients.

The higher molecular weight reaction products, that is the reaction products of dithiophosphates and alkylene oxides or glycols which are further treated with P_2S_5 and additional alkylene oxides or glycols, may be employed as lubricating oils in lubricating oil compositions. Generally, when they are used as the sole lubricating oil base stock in lubricating oil compositions, they will be em-employed in major proportions, such as in the range of about 55 to 95% by weight based on the total composition. However, if desired, the higher molecular weight reaction products of this invention may be employed together with mineral oils and/or other synthetic lubricating oils of the type previously described, in which event the high molecular weight products of this invention may be present in minor proportions such as in the range of about 5 to 45% by weight based on the total composition. In general, therefore, the higher molecular weight reaction products of this invention which are useful as synthetic lubricating oils may be employed in the lubricating oil compositions from concentrations as little as about 1% or less to concentrations of about 99% or more by weight based on the total composition.

The high molecular weight reaction products of this invention may be employed in lubricating oil compositions which contain the low molecular reaction products of this invention and conventional additives such as those previously disclosed. In addition to being used in lubricants, the high molecular weight reaction products of the present invention may be used in other mineral and synthetic oil products such as hydraulic fluids, industrial oils, greases, and the like. The high and low molecular weight products of this invention are also useful as flotation agents for ores, soil-conditioning agents and insecticides.

What is claimed is:

1. The product obtained by reacting one mole of a compound having the formula

$$(RO)_2\overset{\overset{S}{\|}}{P}SH$$

where R is a hydrocarbon radical containing 3 to 20 carbon atoms with 1 to 3 moles of a compound selected from the group consisting of alkylene oxides and glycols and containing 2 to 18 carbon atoms, and reacting four moles of the resultant compound with about one mole of P_2S_5, the reactions being carried out at a temperature in the range of about 100° to 300° F.

2. The product obtained by reacting one mole of the product of claim **1** with 1 to 3 moles of a compound selected from the group consisting of alkylene oxides and glycols and containing 2 to 18 carbon atoms, the reaction being carried out at a temperature in the range of about 100° to 300° F.

3. The product obtained by reacting 4 moles of the product of claim **2** with about one mole of P_2S_5, the reaction being carried out at a temperature in the range of about 100° to 300° F.

4. The product obtained by reacting one mole of the product of claim **3** with 1 to 3 moles of a compound selected from the group consisting of alkylene oxides and glycols and containing 2 to 18 carbon atoms, the reaction being carried out at a temperature in the range of about 100° to 300° F.

5. A lubricating oil composition comprising a major proportion of the product of claim **1**.

6. A method for preparing compounds useful as lubricating oil components which comprises reacting separately and in a sequence one mole of a Compound I with at least the first member of a series consisting of (1) about 0.25 mole of a Compound II, (2) about 0.5 to 1.5 moles of a Compound III, (3) about 0.125 mole of Compound II and (4) about 0.25 to 0.75 mole of Compound III at a temperature in the range of about 100° to 300° F.; wherein Compound I is the reaction product of a dithiophosphoric acid of the formula

$$(RO)_2\overset{\overset{S}{\|}}{P}SH$$

with 1 to 3 moles of Compound III,where R is a hydrocarbon radical containing 3 to 20 carbon atoms; Compound II is P_2S_5; and Compound III is selected from the group consisting of alkylene oxides and glycols and contains 2 to 18 carbon atoms.

7. The product obtained by reacting separately and in a sequence one mole of a Compound I with at least the first member of a series consisting of (1) about 0.25 mole of a Compound II, (2) about 0.5 to 1.5 moles of a Compound III; (3) about 0.125 mole of Compound II and (4) about 0.25 to 0.75 mole of Compound III at a temperature in the range of about 100° to 300° F.; wherein Compound I is the reaction product of a dithiophosphoric acid of the formula

$$(RO)_2\overset{\overset{S}{\|}}{P}SH$$

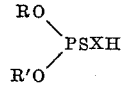
with 1 to 3 moles of Compound III, where R is a hydrocarbon radical containing 3 to 20 carbon atoms; Compound II is P_2S_5; and Compound III is selected from the group consisting of alkylene oxides and glycols and contains 2 to 18 carbon atoms.

8. A lubricating composition consisting essentially of a mineral lubricating oil and from 1 to 10% by weight of a phosphorous- and sulfur-containing material prepared by the process which comprises the reaction of a metal salt, wherein the metal is selected from the class consisting of alkali and alkaline earth metals and zinc, of a phosphorodithioic acid having the structure

$$(RO)_2PSSH$$

wherein R is a hydrocarbon radical containing from 3 to 20 carbon atoms, with at least a substantially equivalent amount of an alkylene oxide containing from 2 to 18 carbon atoms at a temperature within the range of 100–300° F.

9. The process of preparing phosphorus- and sulfur-containing compositions which comprises the reaction of a metal salt of a phosphorothioic acid having the structure



where R and R′ are organic radicals selected from the class consisting of alkyl, cycloalkyl, aryl, aralkyl, alkaryl, and alkenyl, and where X is sulfur, with at least a substantially equivalent amount of an organic compound selected from the class consisting of epoxy alkanes and thioepoxy lower alkanes, the metal of said metal salt being selected from the class consisting of sodium, lithium, potassium, calcium, barium, strontium, magnesium, cadmium and zinc.

10. The process of claim **9** characterized further in that R and R′ of the phosphorothioic acid are saturated hydrocarbon radicals.

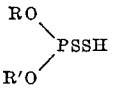
11. The process of claim **9** characterized further in that the phosphorothioic acid is a phosphorodithioic acid.

12. The process of claim **9** characterized further in that R and R′ of the phosphorothioic acid are alkyl radicals.

13. The process of claim 9 characterized further in that the second-named reactant is an epoxy alkane.

14. The process of claim 9 characterized further in that the metal salt is a salt of a polyvalent metal.

15. The process of preparing phosphorus- and sulfur-containing compositions which comprises the reaction of a metal salt of a phosphorodithioic acid having the structure



where R and R' are alkyl radicals with at least a substantially equivalent amount of an epoxy alkane, the metal of the said metal salt being selected from the class consisting of sodium, lithium, potassium, calcium, barium, strontium, magnesium, cadmium and zinc.

16. The process of claim 15 characterized further in that the epoxy alkane is propylene oxide.

17. The process of claim 9 characterized further in that the metal salt is a zinc salt.

18. The product obtained by the process of claim 9.

19. The product obtained by the process of claim 15.

20. The process of preparing phosphorus- and sulfur-containing compositions which comprises the reaction of a metal salt of a phosphorus thioic acid in which the organic radicals are hydrocarbon radicals, said phosphorus thioic acid being a phosphorodithioic acid, with at least a substantially equivalent amount of an organic

compound selected from the class consisting of epoxy alkanes and thioepoxy lower alkanes, the metal of said metal salt being selected from the class consisting of sodium, lithium, potassium, calcium, barium, strontium, magnesium, cadmium and zinc.

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