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COMPOUNDED HYDROCARBON OIL

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7 Claims. (Cl. 252—32.7)

This invention relates to lubricating oils and other products and to a new type of additive for improving the properties of such products as well as other organic materials. More particularly, the invention relates to the compounding of lubricating oils suitable for use as crankcase lubricants for internal combustion engines.

Because in recent years the requirements for lubricating oils for gasoline and Diesel engines have steadily been made more stringent, it has been proposed to add various ingredients to these oils to improve their behavior in such service. One property of these ingredients is to impart detergency to the oils, thus bringing about greater engine cleanliness and avoiding ring sticking, carbon formation, and varnish deposition. Certain of these ingredients also afford oxidation resistance properties to oils thereby tending to inhibit sludge formation and the development of corrosive ingredients in such oils. Corrosion preventing agents are particularly required when the oil is to come into contact at high temperatures with the newer type of alloys of silver and cadmium and of copper and lead, which are now widely used as bearing materials.

Various metal containing organic compounds, particularly the metallic salts of fatty acids, have been found to be quite effective as detergents, but these materials have the very great disadvantage of being corrosive to metal parts, particularly to the surfaces of alloy bearings. Also, certain metallic salts of inorganic acids having substituent oil-solubilizing organic groups have been found effective as detergents. Typical examples of these are cadmium, tin, and cobalt mahogany sulfonates. Such additives are not always satisfactory and often tend to increase the corrosiveness of oils in which they are used.

It is an object of the present invention to provide a new class of additives for lubricating oils which are not only not corrosive when blended with such oils but also have the property of inhibiting the normal corrosive tendency of the oils toward copper-lead and similar bearings. These new additives also improve engine cleanliness and reduce ring sticking, piston skirt varnish and sludge tendencies of oils used in automotive engines. They are also effective antioxidants for other types of organic compounds, as will be more fully set forth below.

The new class of additives for lubricating oils and other products which have been found to possess the valuable properties enumerated above comprises the polyvalent metal salts of sulfur containing substituted acids of phosphorus having an organic substituent therein. The acids of phosphorus from which these compounds are derived include especially the acids of trivalent and pentavalent phosphorus, particularly phosphorous acid, H_3PO_3, hypophosphorous acid, H_3PO_2, and orthophosphoric acid, H_3PO_4. These acids include particularly those in which an oil-solubilizing organic group is substituted for one or more of the hydrogen atoms of the acid. In the metallic salts derived from these acids one or more of the valence bonds of a given metallic atom may be joined to a single acid radical. Although sulfur is a preferred component of the salts used according to the present invention, the elements selenium and tellurium may be substituted for such sulfur to form compounds which are similarly effective. The organic substituent which is a necessary part of the structure of the preferred compounds should be one which imparts adequate oil solubility to the compounds, if they are to be incorporated in mineral lubricating oils.

Although salts derived from all of the sulfur containing acids of phosphorus are useful in accordance with the present invention, it has been found that an exceptionally valuable class of compounds includes the polyvalent metal salts of sulfur containing substituted acids of trivalent phosphorus having an organic substituent therein. These include particularly the salts of thiophosphorous acid. This preferred group of compounds may be defined more particularly by the general formula

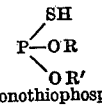
$$[(RX)_a(HY)_bPZ_c]_dM$$

where X, Y, and Z represent oxygen, sulfur, selenium, and tellurium, at least one atom of sulfur, selenium or tellurium being present, H and P represent hydrogen and phosphorus, respectively, R represents an organic group, a, b, c, and d represent small whole numbers, the total of a, b, and c being three, b being zero or one, and M represents a polyvalent metal, preferably an alkaline earth metal. Where more than one organic group R occurs in the compound, such groups may be alike or different. The organic groups may be alkyl, aryl, alkaryl, aralkyl, or heterocyclic groups, and they may include substituent groups or atoms, such as halogen atoms, hydroxyl groups, mercapto groups, amino groups, carboxyl groups and organic groups containing metals, as well as aryl and alkyl substituted derivatives of such groups.

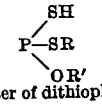
The group R in the compounds defined above should be an oil-solubilizing group when the com-

pound is to be dissolved in a mineral oil. Although alkyl radicals of 5 to 10 carbon atoms will often serve adequately as oil-solubilizing groups, more satisfactory products can be obtained if the alkyl group has from 12 to 20 or more carbon atoms, particularly if the additives are to be used in highly paraffinic base oils, since the latter generally do not possess as good solvent power as naphthenic base oils. Also, very desirable products can be prepared with alkylated phenols, such as isooctyl phenol, tert.-amyl phenol or octadecyl phenol, as starting materials.

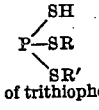
Typical acids from which these metal salts are derived are represented by the following formulas:



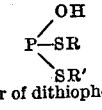
Di-ester of monothiophosphorous acid



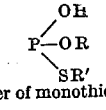
Monothio di-ester of dithiophosphorous acid



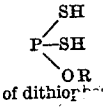
Dithio di-ester of trithiophosphorous acid



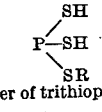
Dithio di-ester of dithiophosphorous acid



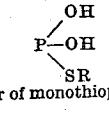
Monothio di-ester of monothiophosphorous acid



Mono-ester of dithiophosphorous acid



Monothio-ester of trithiophosphorous acid



Monothio-ester of monothiophosphorous acid

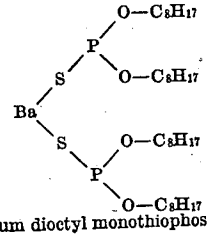
In the above formulas R and R' may be any organic group as defined in the preceding paragraph.

A subclass of compounds which are particularly suitable for the purposes of the invention and readily obtainable are the alkaline earth salts of acids of the formula

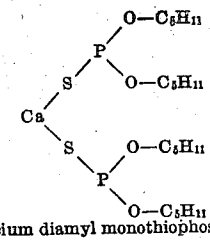
$$HSP(OR)_2$$

where R is an oil-solubilizing organic group.

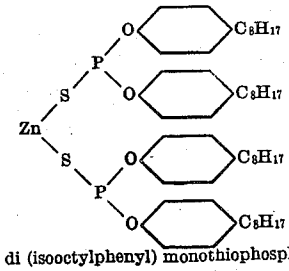
Typical examples of compounds which are particularly useful in lubricating oils are the following:



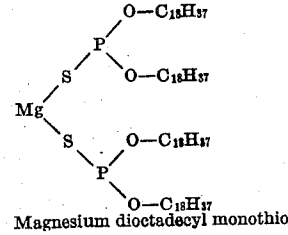
Barium dioctyl monothiophosphite



Calcium diamyl monothiophosphite



Zinc di (isooctylphenyl) monothiophosphite



Magnesium dioctadecyl monothiophosphite

Other typical examples of compounds illustrating the new group of lubricating oil additives as defined by the present invention include barium dicetyl dithiophosphite, zinc dicyclohexyl monothiophosphite, aluminum di(tert.-amyl phenyl) monothiophosphite, tin monolauryl dithiophosphite, cobalt naphthenyl monothiophosphite, nickel dioleyl dithiophosphite, calcium dioctyl trithiophosphite, magnesium di(isooctyl phenyl) monothiophosphite, barium di(isooctyl phenyl) monothiophosphite, calcium di(isooctyl phenyl) monothiophosphite, calcium hexadecyl phenyl monothiophosphite, barium octadecyl phenyl monothiophosphite, magnesium eicosyl phenyl monothiophosphite, and zinc tetracosyl phenyl monothiophosphite.

Although preference has been expressed for the metal salts of thiophosphorous acids, the invention is not limited to such compounds, but includes also polyvalent metal salts, especially the alkaline earth metal salts, of other sulfur containing acids of phosphorus, or acids of phosphorus containing selenium or tellurium in place of sulfur, particularly the sulfur containing phosphoric acids. Examples of compounds of this type which are effective as lubricating oil additives and which do not exhibit the corrosive effects found in other metal containing organic compounds are barium dioctyl dithiophosphate, calcium dioctyl dithiophosphate, magnesium monolauryl monothiophosphate, zinc dioctadecyl trithiophosphate, tin dicetyl dithiophosphate, nickel cyclohexyl monothiophosphate, tin di(tert.-butyl phenyl) trithiophosphate, aluminum dicresyl dithiophosphate, calcium di(tert.-amyl phenyl) dithiophosphate, barium di(isooctyl phenyl) dithiophosphate, magnesium di(dodecyl phenyl) dithiophosphate, zinc di(hexadecyl phenyl) dithiophosphate, calcium di(eicosyl phenyl) dithiophosphate, barium di(tetracosyl phenyl) dithiophosphate, calcium dilauryl dithiophosphate, barium dioleyl dithiophosphate, magnesium dicetyl dithiophosphate, and zinc dioctadecyl dithiophosphate.

Generally, the additives of the present invention are most advantageously blended with lubricating oil base stocks in concentrations greater than approximately 0.02%, preferably greater than approximately 0.05%, and the amount may be as high as 2% or even 5% or higher, if desired. The exact amount to be used depends to a certain extent on the particular compounds used, the character of the mineral oil base and the operating conditions of the engine in which the lubricant is to be employed.

The following examples illustrate methods of preparing the preferred compounds of the present invention and typical tests which have been applied to demonstrate their usefulness in lubricating oils. These examples are given as illustrations only and are not to be considered as limiting the scope of the invention in any way.

EXAMPLE 1

Preparation of barium dioctyl dithiophosphate

Dioctyl dithiophosphoric acid was first prepared by heating a mixture of 520 parts by weight of 2-ethyl hexanol and 222 parts by weight of powdered phosphorus pentasulfide to about 80° C. with agitation for 3–4 hours, agitating for a further period of about 16 hours at 40–60° C. with a slow stream of air passing through the flask, and filtering to remove unreacted phosphorus pentasulfide. The crude product was neutralized with alcoholic sodium hydroxide and the alcohol and water of reaction were stripped off under vacuum leaving a straw colored clear viscous oil. 75 parts by weight of this sodium salt of dioctyl dithiophosphoric acid were dissolved in 120 parts by weight of absolute alcohol, and 36 parts by weight of barium bromide ($BaBr_2.2H_2O$) were added along with about 80 parts by weight of additional alcohol. It was found that the barium bromide was not very soluble in the alcohol, but by agitating the mixture substantially all of the barium bromide was made to react. The alcoholic solution was evaporated and the residue taken up with ethyl ether. The ether solution was filtered and then evaporated, leaving 63 parts by weight of straw colored semi-fluid material which was found to consist chiefly of the barium salt of dioctyl dithiophosphoric acid.

EXAMPLE 2

Preparation of barium dioctyl monothiophosphite

The sodium salt of dioctyl monothiophosphorous acid was first prepared by heating a mixture of 520 parts by weight of octyl alcohol (2-ethyl hexanol) and 158 parts by weight of phosphorus trisulfide to 80–90° C. until no more H_2S was given off, diluting the product with ether, neutralizing with alcoholic sodium hydroxide and stripping off the solvent under vacuum. 113 parts by weight of this sodium salt were dissolved in methyl alcohol and added to 62 parts by weight of barium bromide ($BaBr_2.2H_2O$) in about 80 parts by weight of methyl alcohol. The mixture was agitated for one hour after which naphtha was added and the mixture washed with water to remove NaBr, excess $BaBr_2$ and most of the alcohol. The naphtha layer was evaporated, leaving a clear dark colored oil, found to be principally barium dioctyl monothiophosphite.

EXAMPLE 3

Preparation of calcium dioctyl monothiophosphite

83 parts by weight of dioctyl monothiophosphorous acid $(C_8H_{17}O)_2P—SH$ were added to 10 parts by weight of sodium hydroxide in absolute methyl alcohol. To this solution was added 18 parts by weight of calcium chloride in methyl alcohol. The resulting product was filtered and the alcohol evaporated off. Naphtha was added and the undissolved material filtered off. The naphtha was then evaporated from the solution, leaving a somewhat fluid liquid which was readily soluble in lubricating oil. This product was found to be mainly calcium dioctyl monothiophosphite.

EXAMPLE 4

Preparation of calcium diamyl monothiophosphite

352 parts by weight of amyl alcohol were added to 158 parts by weight of phosphorus trisulfide and 100 parts of calcium carbonate in a reaction vessel provided with stirrer and reflux condenser. The mixture was stirred for about 16 hours without external heating. During this time the temperature rose to about 50° C. An additional quantity of amyl alcohol (176 parts) was added, then the temperature was gradually raised to 100° C. and the mixture was allowed to stand on the steam bath overnight. The product was then filtered and the filtrate heated to 100° C. under 5 mm. vacuum to remove unreacted alcohol. The resulting calcium diamyl monothiophosphite was a clear but rather dark colored fluid oil.

EXAMPLE 5

Preparation of calcium dioctyl dithiophosphate

440 parts by weight of phosphorus pentasulfide, 1170 parts by weight of octyl alcohol and 250 parts by weight of sodium carbonate were heated gradually to 70° C. with agitation and maintained at this temperature for about four hours. The product was filtered and the filtrate heated to 100°–110° C. with about 168 parts by weight of sodium carbonate until no more CO_2 was evolved. After filtering, the filtrate was diluted with about 400 parts by weight of absolute ethyl alcohol and 360 parts by weight of calcium nitrate in about 800 parts by weight of ethyl alcohol. The resulting precipitated sodium nitrate was filtered off, the ethyl alcohol removed under vacuum and the residue diluted with about 1100 parts by weight of petroleum ether and again filtered to remove unreacted calcium nitrate and additional sodium nitrate. The filtrate was shaken overnight with mercury to remove free sulfur and the mercury sulfide filtered off. The naphtha was stripped off and the residue was heated to 135–140° C. for about one-half hour at 3–4 mm. pressure to remove unreacted octyl alcohol. The product consisted of calicum dioctyl dithiophosphate.

EXAMPLE 6

Preparation of zinc di(isooctyl phenyl) monothiophosphite

412 parts of isooctyl phenol are added to 760 parts of a refined paraffinic lubricating oil having a Saybolt viscosity of 52 seconds at 210° F. and the mixture is heated to 100° C. While the mixture is stirred, 87 parts of phosphorus trisulfide (P_4S_7) are added slowly. The temperature is then raised to 150–160° C. slowly and 41 parts of zinc oxide are added. After an additional hour of heating and stirring at 160° C., the product is filtered, yielding a 40% concentrate of zinc di(isoctyl phenyl) monothiophosphite in mineral oil.

EXAMPLE 7

Preparation of magnesium dioctadecyl monothiophosphite

1080 parts of commercial stearyl alcohol are added to 1850 parts of a refined mineral lubricating oil of S. A. E. 20 grade and the mixture is heated to 100° C. To the mixture there are added slowly with stirring 174 parts of phosphorus trisulfide (P_4S_7), and the temperature is gradually raised to 160° C. After all of the phosphorus sulfide has reacted, the temperature is held at 160° C. while 40 parts of magnesium oxide are aded. Stirring is continued for an additional 4 hours at 160° C. and the product is filtered, yielding a 40% concentrate of magnesium dioctadecyl monothiophosphite in mineral lubricating oil.

EXAMPLE 8

Bearing corrosion tests

Samples of a base oil consisting of a conventionally refined Coastal naphthenic base mineral lubricating oil of 55 Saybolt seconds viscosity at 210° F., as well as samples of this oil blended with various additives of the present invention, prepared as described in the preceding examples, were subjected to the standard Underwood bearing corrosion test, which was conducted as follows:

The polished bearings of the Underwood machine were thoroughly abraded with emery cloth to expose a fresh metal surface so that corrosion would proceed uniformly, and then accurately weighed. The apparatus was filled with 1500 cc. of the lubricant under test and the pump and heater started. The oil pressure was regulated to 10 pounds per square inch by means of by-pass valves and maintained at this pressure throughout the test. As soon as the oil attained the desired test temperature the heater and pump were turned off just long enough to put the already prepared and weighed bearings in place. Two copper-lead and two cadmium-silver bearing halves were used simultaneously in each test. At the end of the test period the bearings were removed, cleaned with naphtha, dried and weighed. The weight loss was taken as a measure of the corrosiveness of the oil.

In Table I are shown the results of tests with the various oil blends, as indicated. For comparison a test was also made of the same base oil blended with nickel oleate, a typical metallic soap detergent-type additive.

Table I

Oil blend	Hours run	Oil temp., ° F.	Bearing weight losses, grams/50 sq. cm. area	
			Cu-Pb	Cd-Ag
Base oil	5	325	0.017	0.000
Base oil+0.5% nickel oleate	5	325	0.337	1.753
Base oil+0.2% barium dioctyl dithiophosphate	5	325	[1] +0.007	0.005
Base oil+0.5% barium dioctyl monothiophosphite	5	325	0.006	0.002
Base oil+0.5% calcium dioctyl monothiophosphite	5	325	0.017	0.007
Base oil	20	275	0.003	0.001
Base oil+1.0% calcium dioctyl monothiophosphite	20	275	[1] +0.011	0.002
Base oil	60	210	0.006	0.002
Base oil+0.5% nickel oleate	27	210	1.007	0.482
Base oil+1.0% calcium dioctyl dithiophosphate	60	210	0.011	[1] +0.005

[1] Indicates that bearings gained in weight.

It will be seen from the results of these tests that the metal thiophosphate and thiophosphite salts of the present invention do not increase the corrosiveness of the base oil toward alloy metal bearings and in practically all instances serve to inhibit the slight corrosiveness of the base oil.

EXAMPLE 9

Normal temperature Caterpillar Diesel engine tests

In the following tests the base oil was the same as that used in Example 8. This was blended with calcium dioctyl monothiophosphite and with calcium dioctyl dithiophosphate, and samples of these blends, as well as a sample of the unblended base oil, were tested in a single cylinder Caterpillar Diesel engine equipped with Babbitt bearings and operated at 16.7 B. H. P. output, 850 R. P. M., 140° F. oil temperature and 70° F. atmospheric temperature. After each run the engine parts were inspected and given demerit ratings based on their condition. The individual ratings were weighted according to their relative importance and an overall demerit rating calculated from them. It should be noted that the lower the demerit rating, the better the engine condition and, hence, the better the performance of the oil in the engine. The results of these engine tests are shown in Table II.

Table II

Oil blend	Hours	Engine demerits			
		Overall	Ring zone	Piston skirts	Oil filter
Base oil	[1] 60	1.01	1.25	1.0	1
	110	1.45	1.86	1.5	2
	242	1.96	2.58	2.0	4
Base oil+1.0% calcium dioctyl monothiophosphite	[1] 60	0.52	0.37	0.25	0.06
	112	0.71	0.63	0.5	0.12
	250	1.09	1.48	1.3	0.50
Base oil+1.0% calcium dioctyl dithiophosphate	60	0.95	1.02	0.12	0.75

[1] 60-hour demerit ratings were calculated by plotting 110 and 250 hour data and interpolating.

It can be seen from the above results that, although the calcium dioctyl dithiophosphate showed certain positive improvements over the unblended oil tested, the blend containing calcium dioctyl monothiophosphite showed a very distinct superiority over the thiophosphate blend. After 112 hours of operation with the thiophosphite blend the engine condition was found to be much better than after only 60 hours with the thiophosphate blend. Also, after 250 hours with the thiophosphite blend the cleanliness of engine parts was much better than with the base oil alone after only 110 hours of operation.

EXAMPLE 10

High temperature Caterpillar Diesel engine tests

In this series of tests the same base oil was used as in Example 9, the tests being carried out in a high temperature single cylinder Caterpillar Diesel engine fitted with copper-lead bearings and operated at 16.7 B. H. P. output, 850 R. P. M., 195° F. oil temperature, and 140° F. atmospheric temperature. The engine parts were inspected and given ratings as in Example 9. The results are shown in Table III, which includes also the copper-lead bearing weight losses.

Table III

Oil blend	Hours	Engine demerits				Cu-Pb bearing weight loss grams
		Overall	Ring zone	Piston skirts	Oil filter	
Base oil	60	1.48	2.64	1.0	0.75	0.037
Base oil+1.0% calcium dioctyl dithiophosphate	60	0.88	1.09	0.0	1.5	0.000

The lubricating oil base stocks 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, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloro ethyl ether, propane, nitrobenzene, crotonaldehyde, 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 coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed, either alone or in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additives 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 or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel service, particularly with high speed Diesel engines, and in gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 or 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used, such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like, may also be employed.

Assisting agents which are particularly desirable are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol, $C_8H_{17}OH$, lauryl alcohol, $C_{12}H_{25}OH$, cetyl alcohol, $C_{16}H_{33}OH$, stearyl alcohol, sometimes referred to as octadecyl alcohol, $C_{18}H_{37}OH$, and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols, such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes, the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc.

In addition to being employed in crankcase lubricants and in extreme pressure lubricants, the additives of the present invention may also be used in spindle oils, textile oils, metal cutting oils, engine flushing oils, turbine oils, insulating and transformer oils, steam cylinder oils, slushing compositions, and greases. Also their use in motor fuels, Diesel fuels and kerosene is contemplated. Since these additives exhibit antioxidant properties and are believed also to possess ability to modify surface activity, they may be employed in asphalts, road oils, waxes, fatty oils of animal or vegetable origin, soaps, and plastics. Similarly, they may be used in natural and synthetic rubber compounding both as vulcanization assistants and as antioxidants, and generally they may be used in any organic materials subject to deterioration by atmospheric oxygen.

The present invention is not to be considered as limited by any of the examples described herein which are given by way of illustration only, but it is to be limited solely by the terms of the appended claims.

We claim:

1. An improved lubricant which comprises an oil base and a small quantity, sufficient to substantially inhibit deterioration of the oil during use, of a compound of the formula

$$[(RX)_a(HY)_bPZ_c]_dM$$

in which R is an organic group, X, Y, and Z are elements of the group consisting of oxygen, sulfur, selenium, and tellurium, at least one atom being a member of the class consisting of sulfur, selenium, and tellurium, H is hydrogen, P is phosphorus, M is a polyvalent metal, a, c, and d are small whole numbers, b is zero or one, and $a+b+c=3$.

2. A lubricant for internal combustion engines which comprises a mineral oil base and a small

quantity, sufficient to substantially inhibit deterioration of the oil during use, of a polyvalent metal salt of a sulfur containing substituted acid of trivalent phosphorus having an organic substituent therein.

3. A lubricant for internal combustion engines which comprises a mineral oil base and a small quantity, sufficient to substantially inhibit deterioration of the oil during use, of an alkaline earth salt of an acid of the formula

$$HSP(OR)_2$$

where R is an oil-solubilizing organic group.

4. A lubricant according to claim 3 in which R in the formula represents an alkyl group having at least five carbon atoms.

5. A lubricant for internal combustion engines which comprises a mineral oil base and about 0.2% to about 5.0% of zinc di(isooctyl phenyl) monothiophosphite.

6. A lubricant for internal combustion engines which comprises a mineral oil base and about 0.2% to about 5.0% of calcium dioctyl monothiophosphite.

7. A lubricant for internal combustion engines which comprises a mineral oil base and about 0.2% to about 5.0% of magnesium dioctadecyl monothiophosphite.

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