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PHOSPHATE PARTIAL ESTER-ALDEHYDE-AMINE CONDENSATION PRODUCT AND LUBRICANT CONTAINING THE SAME

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4 Claims. (Cl. 260—461)

This invention relates to a new class of organic phosphorus compounds and to compositions containing them. More particularly it relates to condensation products obtained by reacting phosphate partial esters with both aldehydes and amines and to lubricating compositions containing these condensation products.

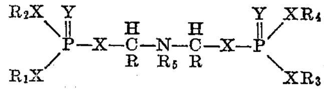
The condensation products of mono- and diaryl esters of phosphoric thioacids with aldehydes are disclosed and claimed in my copending application Serial No. 180,901, filed August 22, 1950.

It is old in the art to employ phosphate esters as addition agents in lubricating compositions to improve various characteristics of the lubricating compositions such as their resistance to oxidation, corrosiveness, detergency, oiliness, viscosity index and so forth. More recently, it has been found that phosphate esters containing sulfur in direct linkage with the phosphorus are particularly valuable modifying agents for lubricants, and a large number of such compounds have been used, chiefly as multifunctional additives for extreme pressure lubricants. For example, it is disclosed in U. S. 2,242,260, to Prutton, that extreme pressure agents are produced by reacting phosphorus pentasulfide with various organic compounds including stearic acid, lauryl alcohol, benzyl alcohol, naphthenic acid, butyl stearate, phenol and chlorophenol. Extreme pressure agents are also prepared by the method of U. S. 2,396,719, to Musselman et al., whereby phosphorus pentasulfide is reacted with an alcohol. The reaction product is preferably further reacted with a base such as ammonia, an amine or a metal oxide or hydroxide. U. S. 2,252,985, to Rutherford et al., discloses that the oxidation resistance of a lubricant is increased by the addition of alkaline earth metal salts of esters obtained by reacting aliphatic or aromatic alcohols or mercaptans with sulfur-containing acids of phosphorus. U. S. 2,470,405, to Leland, discloses that the load bearing quality of cutting oils is improved by the addition of esters having the formulas $P(XR)_3$ and $XP(XR)_3$, wherein X is either oxygen or sulfur, at least one R is hydrogen and the remaining R's are aliphatic or aromatic hydrocarbon radicals. U. S. 2,368,000, to Cook, discloses antifoaming agents prepared by reacting phosphorus pentasulfide with branched chain alcohols and neutralizing the product with heavy metal salts. U. S. 2,343,831, to Osborne, discloses dialkyl and diaryl dithiophosphate polysulfides as extreme pressure agents.

While compounds of the above type are very effective in improving a number of lubricant properties, they also possess certain disadvantages which are more or less serious depending upon the purpose for which the lubricant is to be employed. The esters themselves are highly acidic and corrosive, so that they must usually be employed in the form of their salts or other compounds. However, many of these compounds heretofore proposed hydrolyze or otherwise decompose at high temperatures, and the use of metal salts is undesirable in many cases, as for example where there are rigid restrictions upon the permissible amount of non-volatile ash remaining after combustion.

It is an object of the present invention to provide improved organic phosphorus compounds. A further object of this invention is to provide improved lubricants containing these compounds. Another object of the invention is to provide a novel class of multifunctional lubricant additives. Another object of the invention is to provide a class of compounds having the property of imparting improved lubricating characteristics to a lubricant composition without having undesirable or deleterious effects upon other properties of the lubricant composition.

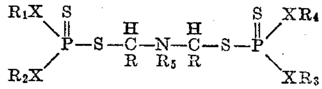
The novel compounds of my invention are the condensation products obtained by reacting partial esters and thio esters of phosphorus acids and thio acids of the types shown in the foregoing patents with aldehydes and primary amines. These compounds are preferably monomeric condensation products which are believed to have the following structure:



$$\begin{matrix}R_2X\\R_1X\end{matrix}\!\!>\overset{Y}{\overset{\|}{P}}-X-\underset{R}{\overset{H}{C}}-\underset{R_5}{N}-\underset{R}{\overset{H}{C}}-X-\overset{Y}{\overset{\|}{P}}\!<\!\!\begin{matrix}XR_4\\XR_3\end{matrix}$$

wherein X is oxygen or sulfur, Y is either oxygen or sulfur or is absent, R_5 is an organic radical and R, R_1, R_2, R_3 and R_4 represent hydrogen or organic radicals which may be the same or different, at least one organic radical being attached to each phosphorus atom through an oxygen or a sulfur atom. The organic radicals may be aliphatic groups, including open chain and cyclic, saturated and unsaturated aliphatic groups, aromatic groups, or substituted aliphatic or aromatic groups. Sufficient alkyl carbon atoms are contained in these organic groups to impart oil-solubility to the molecule. These organic groups may also contain any of the inorganic substitutents commonly employed in lubricant additives, such as halogen atoms, hydroxyl groups, carboxyl groups, nitro groups, amino groups, mercaptan groups and so forth.

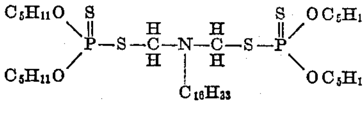
My preferred compounds for use as lubricant additives may be represented by the following formula



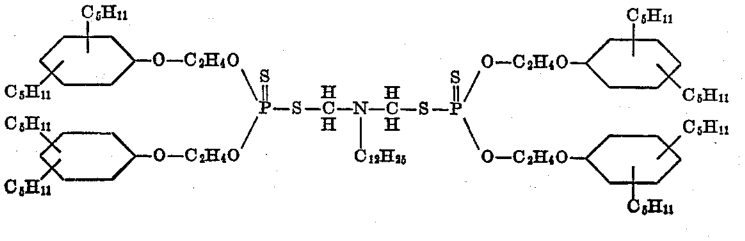
$$\begin{matrix}R_1X\\R_2X\end{matrix}\!\!>\overset{S}{\overset{\|}{P}}-S-\underset{R}{\overset{H}{C}}-\underset{R_5}{N}-\underset{R}{\overset{H}{C}}-S-\overset{S}{\overset{\|}{P}}\!<\!\!\begin{matrix}XR_4\\XR_3\end{matrix}$$

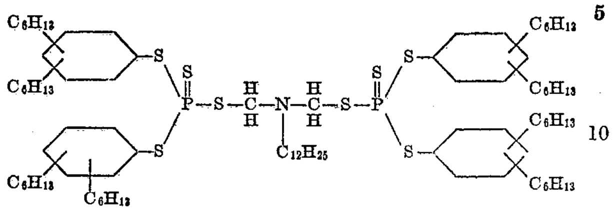
wherein X is oxygen or sulfur, R is hydrogen or an organic group and R_1, R_2, R_3 and R_4 and R_5 are organic groups as described above.

As specific examples of such compounds which are particularly suitable for use as lubricant additives are the following:



$$\begin{matrix}C_5H_{11}O\\C_5H_{11}O\end{matrix}\!\!>\overset{S}{\overset{\|}{P}}-S-\underset{H}{\overset{H}{C}}-\underset{C_{16}H_{33}}{N}-\underset{H}{\overset{H}{C}}-S-\overset{S}{\overset{\|}{P}}\!<\!\!\begin{matrix}OC_5H_{11}\\OC_5H_{11}\end{matrix}$$



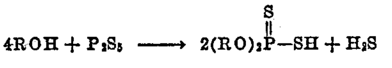


Addition agents of the above type have important advantages over the known types of phosphate ester additives, particularly in that they possess increased chemical stability and decreased acidity and corrosiveness and do not add to the non-volatile ash content of the lubricant. They are antioxidant and corrosion-inhibiting both when used alone and with other more corrosive additives.

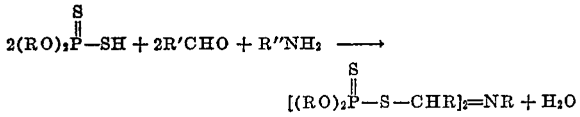
The amount of these phosphorus compounds which may be added to lubricating oils may be varied depending upon the effect desired and upon the characteristics of the base oil. In general, small proportions, for example from 0.1% to 10%, and preferably from about 0.5% to about 2%, are employed. However either greater or less amounts may be used if desired.

While the compounds of my invention are preferably the monomeric condensation products as shown in the formula, a certain amount of more or less polymeric product is also formed in the condensation reaction, and such compounds are also included within the purview of this invention, since it is conceived that useful resins and high molecular weight products having pour point-reducing and other valuable properties may be obtained by this reaction.

The esters used in preparing the condensation products of my invention may be one or more of the following types: mono-esters of phosphorous and phosphoric acid, di-esters of phosphorous and phosphoric acids, mono-thio esters of phosphorous and phosphoric acids, di-thio esters of phosphorous and phosphoric acids, mono- and di-esters of tri-thio phosphorous acids, mono- and di-thio esters of tri-thio phosphorous acids, mono- and di-esters of tetra-thio phosphoric acid, and mono- and di-thio esters of tetra-thio phosphoric acids. Esters of the above types may be obtained by any of the familiar esterification reactions between an aliphatic or aromatic alcohol or mercaptan and an oxygen and/or sulfur-containing phosphorus acid, such as phosphorous acid, phosphoric acid, thio phosphorous acid, thio phosphoric acid, phosphorus pentoxide, or a phosphorus sulfide such as phosphorus pentasulfide, phosphorus trisulfide or phosphorus heptasulfide, or by other ester-forming reactions such as the reaction between a halogenated hydrocarbon and a phosphorus acid salt such as disodium hydrogen phosphate. Esters suitable for preparing the preferred compounds of our invention may be readily obtained by reacting an alcohol or a mercaptan with phosphorus pentasulfide. The reaction of an alcohol with phosphorus pentasulfide and the condensation of the ester obtained with an aldehyde and a primary amine take place according to the following equations:



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



$$2(RO)_2\overset{S}{\overset{\|}{P}}{-}SH + 2R'CHO + R''NH_2 \longrightarrow [(RO)_2\overset{S}{\overset{\|}{P}}{-}S{-}CHR]_2{=}NR + H_2O$$

wherein R and R'' are organic groups and R' is an organic group or hydrogen.

The alcohols employed in the above reaction may be aliphatic alcohols, including straight or branched chain or cyclic alcohols, preferably those containing from about 4 to about 20 carbon atoms in the molecule, aromatic alcohols, preferably alkylated aromatic alcohols, or heterocyclic alcohols and such alcohols containing substituent groups in so far as these do not interfere to any appreciable extent with the esterification or condensation reaction. Suitable alcohols which may be mentioned include amyl alcohol, octyl alcohol, cetyl alcohol, lauryl alcohol, stearyl alcohol, benzyl alcohol, phenyl ethyl alcohol, diamyl phenoxy ethanol, cyclohexanol, methyl cyclohexanol, terpineol, cardanol, phenol, naphthol, cresol, xylenol, chlorophenol, octyl phenol, diamyl phenol and hydroquinone. The corresponding mercaptans and thio phenols may be used in place of these alcohols. Instead of a single alcohol or mercaptan, mixtures of two or more different alcohols or mercaptans or mixtures of both alcohols and mercaptans may be employed in the esterification reaction in order to obtain mixed esters.

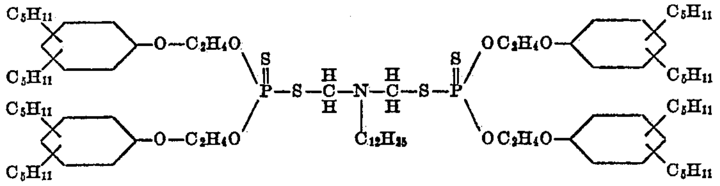
The aldehydes and amines employed in the condensation reaction may likewise be aliphatic, aromatic or heterocyclic in character and may contain substituent groups such as those mentioned above in so far as these do not interfere with the condensation reaction. Suitable aldehydes which may be mentioned include formaldehyde, acetaldehyde, trichloroacetaldehyde, butyraldehyde, benzaldehyde, salicylaldehyde and furfural. Examples of suitable amines are monoamyl amine, monobutylamine, monocyclohexyl amine, monocetyl amine and monolauryl amine. The amines may be employed as such or in the form of their salts, such as an amine hydrochloride.

The condensation reaction is carried out by reacting a phosphate partial ester of the type described above with an aldehyde and a primary amine, preferably in an alcohol solution which is slightly acid with hydrochloric acid. The molar ratio of phosphate ester:amine:aldehyde employed in the reaction may range from about 2:1:2 to about 2:3:4. It is preferably about 2:1:2.

The following detailed procedure illustrates a method which may be used for preparing the compounds of my invention.

EXAMPLE

Preparation of a condensation product of diamyl phenoxy ethanol-P₂S₅ reaction product with formaldehyde and monolauryl amine, having the probable formula:



A diamyl phenoxy ethanol-P₂S₅ reaction product was prepared by adding 222 g. of P₂S₅ to a solution of 1112 g. of diamyl phenoxy ethanol in 2 l. of toluene with stirring, and refluxing the reaction mixture for 45 minutes. The solution was then filtered through asbestos and the solvent distilled from the filtrate. 1200 g. of reaction product was obtained, analyzing 8.69% sulfur and 4.20% phosphorus, as compared with theoretical values of 9.78% and 4.74%, respectively. 440 g. of this product was added to a solution of 115 g. of monolauryl amine in the form of hydrochloride in 500 cc. of absolute alcohol which had been made slightly acid with hydrochloric acid. 55 grams of an aqueous solution containing 37% of formaldehyde by weight was next added and the reaction mixture heated with stirring for 2 hours and then poured into a separatory funnel. The lower layer separating out in the separatory funnel was dissolved in ether, washed 3 times with water, and dried over $CaCl_2$. The ether solution was finally filtered and the ether removed by stripping. 372.5 g. of product was obtained which analyzed 3.91% phosphorus, 8.16% sulfur and 0.829% nitrogen, as compared with theoretical values of 4.08%, 8.43% and 0.927%, respectively.

The value of this compound as a lubricant additive has been demonstrated by means of a special test which is designed to show the corrosiveness and oxidation stability of a lubricating oil under the bearing lubrication conditions existing in an internal combustion engine. In this test a lubricating oil at an elevated temperature is continuously circulated and recirculated over a bearing specimen in the presence of air and of catalytic metal surfaces, and the corrosiveness of the oil determined by measuring the loss in weight of the bearing at two hour intervals up to ten hours. The test apparatus comprises a stainless steel motor-driven spinner enclosing a copper-lead bearing specimen and a stationary stainless steel shaft connected to a base plate assembly. Copper baffles are also attached to the base plate assembly for the purpose of imparting turbulence to the oil and to act as oxidation catalysts. The bearing specimen is connected to the spinner by means of a special non-wearing bushing, so that the entire weight loss of the bearing is attributable to the corrosive action of the oil. The spinner enclosing the bearing specimen is immersed in the test oil maintained at 350° F. in a glass vessel and is rotated at a speed of 3000 revolutions per minute about the stainless steel stationary shaft. The oil is forced through the bearing clearance by capillary attraction and centrifugal force and is sprayed into the air through holes near the periphery of the rotating spinner.

The above test was also carried out with the addition of lead peroxide to the test oil, in order to simulate the conditions prevailing in the crank-case of an engine when gasoline containing high concentrations of tetraethyl lead is used. According to this modification of the test, one gram of powdered lead peroxide (PbO_2) is thoroughly mixed into a 125 cc. sample of the test oil before the beginning of the test and an additional gram of lead peroxide in a 5 cc. portion of the test oil is added at each two hour interval during the test.

The following table shows results obtained in the above described tests with a solvent-refined, dewaxed, Mid-Continent lubricating oil of S. A. E. 30 grade containing 1.0% of the phosphate ester-aldehyde-amine condensation product described.

Corrosion test results

Hours of test	Weight loss in mg.		
	Base oil	Base oil +1.0% additive	Base oil +1.0% additive +PbO_2
2	8-23	4-2	0-0
4	30-45	6-5	0-0
6	58-65	10-5	1-0
8	82-84	22-10	1-0
10	96-102	52-32	2-1

The above table shows the substantial improvement in the corrosiveness of a mineral lubricating oil obtained by the addition of a small amount of a phosphorus compound of my invention.

In the standard Almen test for measuring the extreme pressure properties of lubricating compositions, a blend of 1.0% of this condensation product with the same base oil as described above, had an Almen value of 18 pounds, as compared with 9 pounds for the base oil alone.

According to the particular compound of this class selected, improvements in anticorrosiveness and extreme pressure properties as well as other properties such as detergency and so forth which are exhibited by the phosphate esters generally, may be obtained in varying degrees.

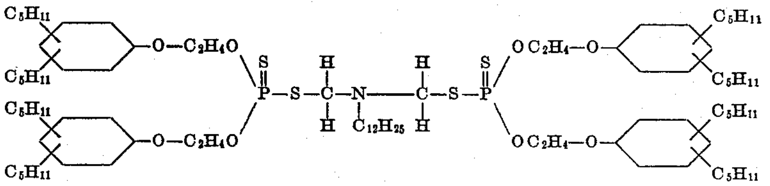
Although a Mid-Continent paraffinic base lubricating oil was used in the example, the use of my compounds as lubricant additives is not limited to any particular base stock, since these compounds may be employed in mineral lubricating oil bases of a wide variety obtained from various types of crudes or synthetic oils by any of the conventional refining methods and also in other oleaginous materials such as animal or vegetable oils. Other compounding ingredients may also be present in the lubricant composition such as pour point depressors, oiliness agents, corrosion inhibitors, antioxidants, extreme pressure agents, viscosity index improving agents and thickeneing agents such as soaps either in minor amounts or in grease-forming proportions.

The use of my novel compounds is furthermore not limited to their use as lubricant additives, since it is to be expected from a consideration of their properties that they will find a number of other uses such as, for example, as antioxidants and corrosion inhibitors in various types of industrial oils and in gasoline, as modifying agents in plastics and so forth.

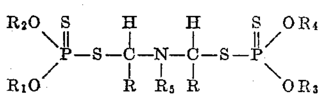
Obviously many modifications and variations of the invention as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A compound having the formula



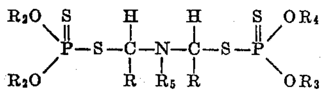
2. A compound having the formula



$$\underset{R_1O}{\overset{R_2O}{}}\!>\overset{S}{\overset{\|}{P}}-S-\underset{R}{\overset{H}{C}}-\underset{R_5}{N}-\underset{R}{\overset{H}{C}}-S-\overset{S}{\overset{\|}{P}}<\!\underset{OR_3}{\overset{OR_4}{}}$$

wherein R is selected from the group consisting of hydrogen and aliphatic hydrocarbon groups, R_1, R_2, R_3 and R_4 are selected from the group consisting of C_4–C_{20} aliphatic hydrocarbon groups, alkylated phenyl groups and alkoxyaralkyl groups, and R_5 is an aliphatic hydrocarbon group.

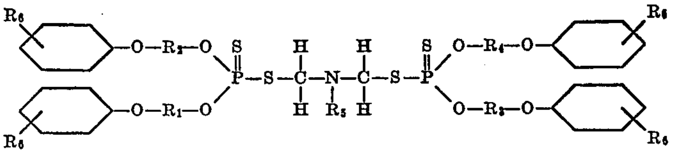
3. A compound having the formula



$$\underset{R_2O}{\overset{R_2O}{}}\!>\overset{S}{\overset{\|}{P}}-S-\underset{R}{\overset{H}{C}}-\underset{R_5}{N}-\underset{R}{\overset{H}{C}}-S-\overset{S}{\overset{\|}{P}}<\!\underset{OR_3}{\overset{OR_4}{}}$$

wherein R is selected from the group consisting of hydrogen and aliphatic hydrocarbon groups, R_1, R_2, R_3 and R_4 are alkoxyaralkyl groups and R_5 is an aliphatic hydrocarbon group.

4. A compound having the formula



wherein R_1, R_2, R_3 and R_4 are low molecular weight alkylene groups, R_5 is an alkyl group containing about 5 to 16 carbon atoms, and R_6 represents one or more alkyl groups.

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