

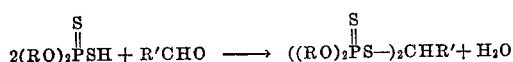
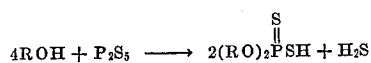
[illegible]
$$\begin{array}{c}
 \text{C}_6\text{H}_{11} \\
 \diagup \quad \diagdown \\
 \text{C}_6\text{H}_{11} \\
 \diagup \quad \diagdown \\
 \text{C}_6\text{H}_{11} \\
 \diagup \quad \diagdown \\
 \text{C}_6\text{H}_{11}
 \end{array}
 \begin{array}{c}
 \text{O} \\
 | \\
 \text{C}_2\text{H}_4 \\
 | \\
 \text{O}
 \end{array}
 \begin{array}{c}
 \text{S} \\
 || \\
 \text{P} \\
 | \\
 \text{S}
 \end{array}
 \begin{array}{c}
 \text{H} \\
 | \\
 \text{C} \\
 | \\
 \text{H}
 \end{array}
 \begin{array}{c}
 \text{S} \\
 || \\
 \text{P} \\
 | \\
 \text{S}
 \end{array}
 \begin{array}{c}
 \text{O} \\
 | \\
 \text{C}_2\text{H}_4 \\
 | \\
 \text{O}
 \end{array}
 \begin{array}{c}
 \text{C}_6\text{H}_{11} \\
 \diagup \quad \diagdown \\
 \text{C}_6\text{H}_{11} \\
 \diagup \quad \diagdown \\
 \text{C}_6\text{H}_{11} \\
 \diagup \quad \diagdown \\
 \text{C}_6\text{H}_{11}
 \end{array}$$

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 products may be formed when monoesters are present in the reaction mixture, 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 condensation reaction.

These 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 acids, 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 di-sodium hydrogen phosphate. Esters suitable for preparing the preferred compounds of my 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 take place according to the following equations:



wherein R is an organic group 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 al-

cohols and mercaptans may be employed in the esterification reaction in order to obtain mixed esters.

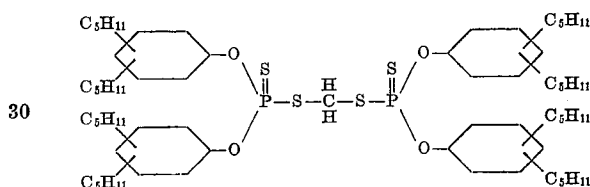
The aldehydes employed in the condensation reaction may likewise be aliphatic, aromatic or heterocyclic in character and may contain substituent groups such as those mentioned above in so far as these do not interfere with the condensation reaction. Suitable aldehydes which may be mentioned include formaldehyde, acetaldehyde, trichloroacetaldehyde, butyraldehyde, benzaldehyde, salicylaldehyde and furfural.

The condensation reaction is carried out by reacting a phosphate partial ester of the type described above, or a salt of the ester such as the sodium salt, with an aldehyde, preferably in an alcohol solution in the presence of hydrochloric acid. The molar ratio of phosphate ester: aldehyde employed in the reaction may range from about 2:1 to about 2:6. It is preferably about 2:1.

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

EXAMPLE

Preparation of a condensation product between diamyl phenol-P₂S₅ reaction product and formaldehyde, having the formula



A diamyl phenol-P₂S₅ reaction product was prepared by adding 96 g. of P₂S₅ slowly to a solution of 500 g. of diamyl phenol in 250 cc. of xylene, refluxing the reaction mixture for 3 hours and permitting it to stand until the reaction was complete. The solution was finally filtered and the solvent removed by stripping. 587 g. of reaction product was obtained having a neutralization number of 82.3. 560 g. of this product was dissolved in 860 cc. of absolute alcohol and 100 g. of aqueous formaldehyde (37% by weight) and 50 cc. of concentrated HCl added. Gaseous HCl was passed in and the reaction mixture refluxed for 3 hours. It was then cooled and shaken with 1 liter of water in a separatory funnel. After separation of the water layer the product remaining was dissolved in ether, the ether solution washed repeatedly with water and an aqueous salt solution until the washings were neutral to litmus and the ether finally removed by steam stripping. 544 g. of product was obtained having a specific gravity of 0.991 and a neutralization number of 23.8.

The value of this compound as a lubricant additive has been demonstrated by means of a special test which was 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 a sample of the test oil maintained at 350° F. in a glass vessel and is rotated at a speed of 3000 revolutions per minute about the stain-

5

less 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 following table shows results obtained by carrying out this test with a solvent-refined, dewaxed, Mid-Continent lubricating oil of S. A. E. 30 grade containing 1.0% of the phosphate ester-aldehyde condensation product described.

Corrosion test results

Hours of test	Weight loss in mg.	
	Base oil	Base oil +1.0% additive
2	8-23	0-1
4	30-45	0-1
6	58-65	0-3
8	82-84	11-12
10	96-102	22-17

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 13 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 thickening 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

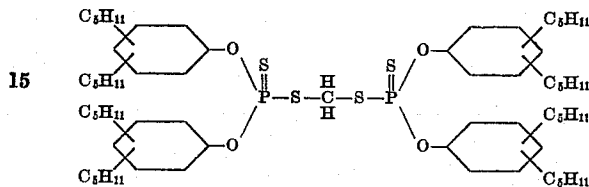
6

they will find a number of other uses such as, for example, 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. The condensation product resulting from the reaction of a phosphoric acid partial ester with an aldehyde, said phosphoric acid partial ester being selected from the group consisting of mono- and diaryl esters of phosphoric thioacids.

3. Claim 2 wherein the phosphoric acid partial ester is a diaryldithiophosphoric acid diester.

4. The condensation product according to claim 2 in which said phosphoric acid partial ester is reacted; with an aldehyde in a molar ratio of from about 2:1 to about 2:6 in the presence of an acid catalyst.

5. The condensation product according to claim 2 wherein the aldehyde is formaldehyde.

6. The condensation product of an O,O-dialkylphenyl diester of dithiophosphoric acid and a low molecular weight aliphatic aldehyde.

7. The condensation product according to claim 6, wherein the aldehyde is formaldehyde.

8. The condensation product of a diamylphenol-P₂S₅ reaction product and formaldehyde.

References Cited in the file of this patent

UNITED STATES PATENTS

2,266,514	Romieux	Dec. 16, 1941
2,343,831	Osborne	Mar. 7, 1944
2,382,622	Ton Toy	Aug. 14, 1945
2,436,141	Goebel	Feb. 17, 1948
2,443,264	Mikeska	June 15, 1948
2,531,129	Hook	Nov. 21, 1950
2,565,920	Hook	Aug. 28, 1951
2,586,655	Hook	Feb. 19, 1952
2,589,675	Cook	Mar. 18, 1952