

1

3,418,240

LUBRICANTS CONTAINING A TRIORGANOSILYL PHOSPHONATE AS AN EXTREME PRESSURE AGENT

Herbert Myers, Barrington, and William F. Olszewski, Cherry Hill, N.J., assignors to Mobil Oil Corporation, a corporation of New York

No Drawing. Filed June 15, 1966, Ser. No. 557,612
10 Claims. (Cl. 252—46.7)

ABSTRACT OF THE DISCLOSURE

Lubricant compositions and other industrial fluids have improved extreme pressure properties by the presence of a bis(triorganosilyl)phosphonate. These phosphonates are produced by the reaction of at least two moles of triorganosilyl halide with a dialkylphosphonate.

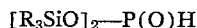
This invention relates to phosphorus-containing additives for organic media, and in particular it relates to phosphorus additives for lubricant compositions.

The increasing demands on today's lubricants stem from the more arduous conditions necessary to operate modern equipment being lubricated than in the past. For example, oil lubricants used in today's automotive and aircraft engines in gear and transmission systems, and in other such equipment often require reinforcement of the lubricant to resist the ever-increasing pressures under which the equipment operates. It is therefore necessary to increase the extreme pressure properties of the lubricant so that as it moves between the moving metal parts, the lubricant film may withstand the pressure without being disrupted. This requirement is ordinarily fulfilled by adding to the lubricant composition an additive which may help to prevent undue metal-to-metal contact.

Many of these additives are organophosphorus compounds. The solubility of the additive in the organic medium and the percent of phosphorus atoms in the additive molecule influence the effectiveness of additive performance in extreme pressure conditions. Thus an additive that contains a high percent of phosphorus atoms and substantial oil solubility possesses the most desirable characteristics.

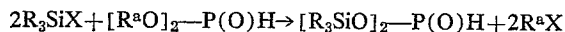
It is an object of this invention to provide novel organic compositions. Another object is to provide effective extreme pressure additives for lubricating compositions. A further object is to provide a method for preparing phosphorus-containing additives for lubricant compositions used under extreme pressure conditions.

It has now been discovered that organic compositions may be given improved extreme pressure properties by the addition thereto of an effective amount of a bis(triorganosilyl)phosphonate having the structure:



wherein R is alkyl, cycloalkyl, aralkyl, alkylene, aryl or alkaryl; or said radicals containing other functional groups in which atoms of oxygen, nitrogen, sulfur and halogen may be present, such as hydroxy, amino, sulfhydryl and chloro groups. The number of carbon atoms in the alkyl groups including those wherein the alkyl group is a substituent of an aryl group may range from 1 to about 20 carbon atoms, and preferably 1 to about 10 carbon atoms. These compounds have been found to provide excellent pressure resisting properties to many different types of lubricating oils and other organic medium.

The preparation of the (triorganosilyl)phosphonates of this invention is carried out by the following reaction:

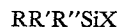


2

where R is defined above, R^a is an alkyl radical containing from about 1 to 10 carbon atoms, preferably 1 to 5, and X is a halogen radical, preferably chlorine or bromine. The reaction to form the products of this invention may be performed by simply heating the two reactants together at a temperature ranging from about 85° to about 200° C. In this reaction the organic group, R^a, of the phosphonate reactant forms a halide byproduct. The byproduct may be distilled from the reaction mixture as the reaction proceeds.

The preferred mole ratio of the triorganosilane reactant to the phosphonate reactant is 2:1. When low molecular weight silanes are used, i.e., R contains 1 to 10 carbon atoms, the ratio may be slightly higher to compensate for any reactant lost by volatilization. However, a ratio in the range of from about 2 to 4:1 is usually satisfactory in this invention.

The monohalosilane reactant may either have identical organo groups or mixed organo groups. The formula for the reactant is



wherein each of the R's have the definition as expressed above for R and X is a halogen radical. The R's may thus be methyl, ethyl, propyl, i-propyl, butyl, i-butyl, hexyl, decyl, dodecyl, hexadecyl and the like. Also suitable are cyclohexyl, phenyl, naphthyl, tolyl, and the like. These silane reactants are produced by known reactions.

The phosphite reactant may also be prepared by known procedures. As used in this invention, the organic group, R^a, is alkyl containing from 1 to about 10 carbon atoms. It is preferable that the R^a group be a lower alkyl, i.e., about 5 carbon atoms or less, so that the alkyl halides produced may be readily removed by distillation during the reaction.

While these additives may be useful in a great many industrial organic media, they find their greatest use in automobile, railroad and aircraft engine lubricating oils, in transmission fluids and gear oils, in cutting fluids, roll oils and other metal working lubricants, in a single phase or emulsified compositions, and in other engine and machine oil compositions which must operate under heavy load conditions.

The oil medium may be a refined mineral oil of lubricating viscosity, such as paraffinic and naphthenic oils, and may include mixed mineral oil stock as well. In view of the increasing operating demands on engines developed in recent years, synthetic oils are of a special interest. These include such oils as fluid olefin polymers, polyalkylene oxides and ethers, polyacetals and silicone polymer fluids. Of particular effectiveness especially in the lubrication of jet turbine aircraft engines are the synthetic ester lubricants. These include esters of monohydric alcohols and dicarboxylic acids, of trialkylolalkanes and monocarboxylic acids, and of pentaerythritols and monocarboxylic acids wherein the number of carbon atoms in the acid may range from 1 to about 30. Suitable among these synthetic ester lubricants are di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate, dioctyl adipate, trimethylpropane trioctanoate, trimethylolbutane trihexanoate, pentaerythritol tetracaproate and pentaerythritol tetradodecanoate.

Especially preferred are mixed esters of pentaerythritol wherein two or more carboxylic acids are used. For example, with commercial valeric acid (C₅) and pelargonic acid (C₉) reacted with pentaerythritol, the ester so produced is a highly satisfactory base fluid.

The following examples are intended to illustrate the invention, although they are not intended to constitute a limitation of the scope thereof.

3

EXAMPLE I

Into a reaction flask equipped with a stirrer, thermometer, nitrogen inlet tube and a condenser, connected to a Dry Ice-acetone collector, was charged 66 grams (0.6 mole) of dimethyl phosphonate. The contents of the flask were heated to about 110° to 120° C., after which 87 grams (0.8 mole) of trimethylchlorosilane was added. The reaction mixture was held at the upper temperature for 2 hours and then an additional 87 grams of trimethylchlorosilane was added. The reaction mixture was heated for another 5 hours at 110° to 120° C. A total of 38 grams (about 60% theory) of methyl chloride was collected in the Dry-Ice-acetone trap. The reaction mixture remaining in the flask was subjected to fractional distillation leaving 35 grams of bis(trimethylsilyl)phosphonate; B.P. 78° to 82° C. (10 mm.).

Analysis.—Calc'd for $C_6H_{19}O_3PSi_2$: P, 13.9%; Si, 24.8%. Found: P, 14.1%; Si, 24.9.

EXAMPLE II

Into a reaction flask similar to that used in Example I were added 28 grams (0.2 mole) of diethyl phosphonate and 100 grams (0.43 mole) of tri-n-butylchlorosilane. The reaction mixture was heated at 145° to 150° C. for 4 hours and then at 170° to 180° C. for 7 hours. A total of 22 grams (about 85% of theory) of ethyl chloride was collected in the cold trap. The residual reaction mass was topped to 200° C. under 0.01 mm. of pressure. The residue was filtered through a diatomaceous earth filter aid to give 69 grams of clear yellow product.

Analysis.—Calc'd for $C_{24}H_{55}O_3PSi_2$: P, 6.5%; Si, 11.7%. Found: P, 6.5%; Si, 12.5%.

EXAMPLE III

Using the reactor similar to that of Example I, 107 grams (0.37 mole) of triphenyl chlorosilane was reacted with 36 grams (0.185 mole) of di-n-butyl phosphonate. The reaction mixture was heated at 175° to 195° C. for 5.5 hours. The amount of n-butyl chloride collected in the trap was about 79% theory. The remaining reaction mixture was dissolved in hot acetone, filtered and then the filtrate was concentrated by removing a portion of the acetone. Addition of iso-octane and then cooling the mixture yielded 90 grams of a white crystalline solid; M.P. 99° to 102° C.

Analysis.—Calc'd for $C_{36}H_{51}O_3PSi_2$: P, 5.2%; Si, 9.4%. Found: P, 5.2%; Si, 11.4%.

Evaluation of product

The bis(triorganosilyl)phosphonates of this invention were evaluated as both extreme pressure and antiwear agents in lubricating oils.

The Ryder gear test

This test is used to evaluate the load-carrying capacity of a lubricant. The test apparatus consists of a machine having meshed gears rotating at a specific speed. Each gear has 28 individual teeth. The teeth of the gears are indexed for the purpose of recording. The machine is started under no load conditions; and the load is applied after the machine has reached the rated speed. At 5-minute intervals, the surfaces of each tooth of one gear are microscopically examined for scuffing. The test is rated at that load at which 22.5% of the total-active gear tooth face area is scuffed. Each gear tooth is considered an individual test in itself. Since the percent scuff varies from tooth to tooth, the average of all 28 individual teeth is used to determine the failure load. The results of the Ryder test are listed below in Table I. The evaluation of a lubricant additive is based on the failure load with relation to the percent of phosphorus atoms present in the lubricant composition test sample. The higher the failure load, the more effective the lubricant. A lubricant which can carry more than 3000 lb./in.² at phosphorus concentrations of less than 0.10%, for example, is considered very effective.

4

The base fluid used in this test consists of a pentaerythritol ester prepared from a mixture of commercial valeric acid and pelargonic acid.

The results are tabulated in Table I, below:

TABLE I

Additive	Conc. Percent P	Ryder Rig lbs./in. ² (avg.)
None.....		2,581
Product of Ex. I.....	0.08	3,897
Product of Ex. II.....	0.05	3,536

Four-ball test

This test is used to investigate the relative ability of oils to lubricate sliding metal surfaces under boundary lubrication conditions. The test equipment consists of three steel balls placed in a ball cup containing the test lubricant. A fourth ball is held in a vertical chuck attached to a rotating spindle above the other three balls. At the start of the test, the fourth ball is lowered against the three balls in common contact therewith and rotated. The force with which the fourth ball is held against the other three balls during the rotation may be varied thus increasing or decreasing the load.

In this test, the additives of this invention were tested in lubricants for 1 hour, at 400° F. The fourth ball was rotated against the three balls at 600 r.p.m. under a load of 10 kg. The results of the test are reported as average wear scar diameters. The results are tabulated in Table II below:

TABLE II

Additive	Conc. Percent P	Four-Ball Test Scar Diameter, mm.
None.....		0.730
Product of Ex. I.....	0.03	0.284
Product of Ex. II.....	0.03	0.250
Product of Ex. III.....	0.03	0.361

The results of these tests show that the presence of the bis(triorganosilyl)phosphonates provides excellent extreme pressure properties to lubricating compositions. The lubricating compositions contemplated in this invention may contain a number of additional components such as detergents, pour point depressants, antioxidants, antifoam agents and the like, since the additives of the instant invention are compatible therewith.

The above invention has been described in terms of specific embodiments and examples which are not intended to represent limitations to the instant invention except as appearing in the following claims.

We claim:

1. An organic lubricant composition comprising a major proportion of a lubricating oil and in an amount effective to provide extreme pressure properties thereto a bis(triorganosilyl)phosphonate wherein the organo group is selected from the group consisting of alkyl, cycloalkyl, alkylene, aralkyl, aryl, alkaryl and substituted derivatives thereof, said substituents being selected from the group consisting of amino, hydroxy, sulfhydryl and halogen.

2. The organic composition of claim 1 wherein the number of carbon atoms of the alkyl substituents is in the range of about 1 to about 20 carbon atoms.

3. The organic composition of claim 1 wherein the said phosphonate is a bis(trialkylsilyl)phosphonate having 1 to 20 carbon atoms.

4. The composition of claim 3 wherein the trialkylsilyl group is trimethylsilyl.

5. The organic composition of claim 3 wherein the trialkylsilyl group is tri-n-butylsilyl.

6. The organic composition of claim 1 wherein the said phosphonate is bis(triarylsilyl)phosphonate.

7. The composition of claim 6 wherein the triarylsilyl group is triphenylsilyl.

8. A lubricant composition comprising a major pro-

5

portion of a synthetic ester lubricant and a bis(triorgano-silyl)phosphonate in an amount effective to provide extreme pressure properties thereto wherein the organo group is selected from the group consisting of alkyl, cycloalkyl, alkylene, aralkyl, aryl, alkaryl, and substituted derivatives thereof, said substituents being selected from the group consisting of amino, hydroxy, sulfhydryl and halogen.

9. The lubricating oil composition of claim 8 wherein the lubricant is an ester of pentaerythritol and a monocarboxylic acid having 1 to 30 carbon atoms.

10. The composition of claim 9 wherein the monocarboxylic acid is a mixture of acids.

6

References Cited

UNITED STATES PATENTS

2,488,449	11/1949	Trautman	252—49.9 X
2,515,024	7/1950	Trautman	252—49.8
2,957,931	10/1960	Hamilton et al.	260—448.2 X
3,115,519	12/1963	Crouse et al.	252—56 X

DANIEL E. WYMAN, *Primary Examiner*.

W. H. CANNON, *Assistant Examiner*.

U.S. Cl. X.R.

252—49.9; 260—448.2