

UNITED STATES PATENT OFFICE

2,566,129

S-AMIDOMETHYLIDENE DITHIOPHOSPHORIC ACID TRIESTERS

Edwin O. Hook, Old Greenwich, Conn., and Philip H. Moss, Austin, Tex., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

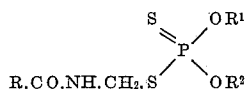
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6 Claims. (Cl. 260—461)

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This invention relates to S-amidomethylidene dithiophosphoric acid triesters and to their methods of preparation. The invention includes the novel dithiophosphoric acid triesters themselves, methods for preparing them and hydrocarbon oil compositions containing them.

We have discovered a novel class of dithiophosphoric acid triesters which, we have found, are excellent antioxidants for hydrocarbon oils. These new compounds are S-amidomethylidene dithiophosphoric acid triesters of the formula



in which R is an aliphatic hydrocarbon radical of 1-18 carbon atoms and R¹ and R² are aliphatic, cycloaliphatic or aromatic hydrocarbon radicals. These compounds are prepared by condensing an O,O-diester of dithiophosphoric acid with a reactive aliphatic carboxylic acid amide and with formaldehyde, or with the methylol derivative that is obtained by first condensing formaldehyde with an amide of an aliphatic carboxylic acid.

The O,O-diester of dithiophosphoric acid are well known compounds, and are usually prepared by condensing alcohols or phenols with phosphorus pentasulfide. Any such O,O-diester of dithiophosphoric acid may be used in preparing the new compounds of our invention, including the O,O-dialiphatic dithiophosphoric acid diesters, the O,O-diaryl dithiophosphoric acid diesters and the dicycloaliphatic dithiophosphoric acid diesters. However, when compounds having a relatively high percentage of combined phosphorus and sulfur are desired, as in the production of lubricating oil antioxidants having a high activity at relatively low temperatures which is sometimes required in turbine oils and anticorrosion oils, it is preferably to employ an O,O-dialkyl dithiophosphoric acid in which the alkyl groups are of relatively low molecular weight, such as those containing from 1 to about 8 carbon atoms. Dialkyl dithiophosphoric acids of higher molecular weight may of course be employed, such as the didecyl, didodecyl, ditetradecyl or dioctadecyl dithiophosphoric acids. Typical dicycloalkyl dithiophosphoric acid esters which may be used are those obtained by the catalytic hydrogenation of naphthenic acids to the corresponding alcohols and include the O,O-dicyclohexyl, methyl cyclopentenyl and similar alcohol esters. The O,O-dialkylphenyl dithiophosphoric acid diesters such as the 4-butyl-, 4-amyl-

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and 4-octylphenyl diesters may also be employed.

Although any carboxylic acid amide may be used, we prefer to employ the aliphatic carboxylic acid monoamides of the formula



in which R is an aliphatic hydrocarbon radical of 1-18 carbon atoms. For the purpose of obtaining a relatively high percentage of phosphorus and sulfur in the hydrocarbon oil, we usually employ acid amides of this type in which R is an aliphatic radical of 1-4 carbon atoms; i. e., acetamide, propionamide, butyramide, acrylamide, methyl acrylamide and the like. However, in cases where a higher degree of solubility in hydrocarbon oils of lubricating grade may be desirable, we can of course employ the amides of higher fatty acids such as those of 8-18 carbon atoms including lauramide, myristamide, palmitamide, stearamide and the like.

The reaction whereby our new compounds are formed is carried out simply by mixing the above two classes of compounds with formaldehyde or with a formaldehyde-yielding substance such as paraformaldehyde, trioxymethylene or the like. The reaction can be carried out at any suitable temperature from room temperature to 100° C. or higher; however, in most cases it is preferable to employ temperatures between room temperature and about 80° C. in order to avoid loss of sulfur from the dithiophosphoric acid diester by excessive evolution of hydrogen sulfide during the reaction. If desired the formaldehyde may first be reacted with the carboxylic acid amide to form the corresponding methylol derivative, which is then condensed with the O,O-dithiophosphoric acid diester. It is unnecessary to maintain any particular ratio of reacting ingredients, as the three reagents condense in equimolecular ratios; in fact, it is sometimes advantageous to employ an excessive quantity of the acid amide to function as a diluent for the reaction mixture. Of course, non-reactive diluents may be employed such as volatile hydrocarbons of the type of benzene, toluene, solvent naphtha, chlorinated hydrocarbons and the like.

The products obtained by this reaction vary from light colored tan liquids to dark brown, amorphous solids, depending on their molecular weight. Thus, when O,O-dialkyl dithiophosphoric acids in which the alkyl groups are hydrocarbon radicals of from 1 to about 8 carbon atoms are used together with lower aliphatic amides such as acetamide, propionamide and the like, the products are tan liquids that are insoluble in

water but soluble in hydrocarbon solvents. When aliphatic monocarboxylic acid amides of higher molecular weight are employed, such as lauramide or stearamide, the products are wax-like solids that are readily soluble in both paraffin base and Mid-Continent base lubricating oils.

The novel products of the present invention are preferably used in lubricating oils in relatively small quantities which may vary from about 0.1% up to about 4-5% or greater, depending on the particular oil and on the degree of protection desired therein. In automobile engine lubricating oils, quantities on the order of 0.2% to 2-3% are usually incorporated into the oil. Our novel antioxidants are compatible with all of the commonly used detergents, stabilizers, sludge-inhibitors and other ingredients of compounded oils and may be used in conjunction with smaller or larger quantities of aliphatic or aromatic sulfonates such as calcium petronate, alkyl phenol sulfides such as p,p'-dibutyl-, diamyl- or dioctyl phenol mono- or polysulfides and their polyvalent metal salts, 2,4-dialkyl phenol mono- or polysulfides and their metal salts, or salts of oxygen- or sulfur-containing acids of phosphorus such as those described in U. S. Patents Nos. 2,364,284 and 2,228,658 and Reissue 22,829. These and other additives are usually employed in the oils in quantities of about 0.1-5%, most commonly in quantities of about 0.5-2%, in admixture with the antioxidants of the present invention.

The invention will be further illustrated in detail by the following specific examples. It should be understood, however, that although these examples may describe in detail some of the specific compounds of the invention, they are given also for purposes of illustration and the invention in its broader aspects is not limited thereto. In these examples the products are evaluated as lubricating oil antioxidants by dissolving a portion in an SAE 30 Mid-Continent base lubricating oil together with 0.04% of iron naphthenate, based on the Fe_2O_3 equivalent, and subjecting the oil to the Underwood oxidation test. In this test 1500 cc. of the oil is heated for 10 hours at 325° F. in an open container providing free circulation of air while portions of the oil are sprayed continuously against two freshly sanded alloy bearings. When silver-cadmium alloy bearings were used in the test with the above oil containing the iron naphthenate oxidation catalyst but no antioxidant the loss in weight due to corrosion was 1097 mg.

Example 1

A mixture of 50 grams of O,O-diethyl dithiophosphoric acid and 14 grams of acetamide was agitated while 19 grams of 37% aqueous formaldehyde solution were added with stirring. Agitation was continued at room temperature for 2½ days, after which time the condensation product was dissolved in benzene and washed with water. The product was then washed with an aqueous 1% solution of sodium carbonate, again washed with water, and dried. After removal of the benzene by vacuum distillation there remained 39 grams of a light-colored mobile liquid. The product was soluble in a Mid-Continent base lubricating oil of SAE 30 grade and was tested in this oil at 0.5% concentration by the Underwood oxidation test using silver-cadmium bearings. There was no loss in weight of the bearings after the test, indicating that the product was an effective antioxidant for the oil.

Example 2

A portion of distilled diethyl dithiophosphoric acid (N. E. 202) weighing 41 grams was agitated while 40 grams of 57.8% methylol acrylamide was introduced slowly. The reaction vessel was cooled on an ice bath as there was considerable evolution of heat during the early stages of this addition. The mixture was stirred for 5 hours and at the end of that time had become an opaque thick liquid. It was allowed to stand overnight and separated into two layers. Water and benzene were added and the water layer was separated and discarded. The benzene layer was washed with water, dried over calcium sulfate and freed of benzene under reduced pressure. There was obtained 51 grams of a dark, thick liquid that was free of hydrogen sulfide odor.

The product was tested in Mid-Continent base SAE 30 lubricating oil at a concentration of 0.5% by the Underwood oxidation test against silver-cadmium bearings. There was no bearing corrosion at the end of the test.

Example 3

One-fourth mol (15 grams) of acetamide was stirred into 10 cc. of water containing 0.2 gram of potassium carbonate. To this solution was added 24 grams (0.3 mol) of 37% aqueous formaldehyde solution and the liquid was stirred for 3 hours. There was then added 65 grams (0.25 mol) of diisobutyl dithiophosphoric acid (N. E. 260) and stirring was continued for 4 hours. The mixture was then allowed to stand overnight. The aqueous layer was then discarded and the hydrogen sulfide-free lower layer was washed with water and freed of volatile matter by heating it at reduced pressure at 95° C. There was obtained 79 grams of a tan colored liquid having a pleasant odor and good solubility in hydrocarbon lubricating oils.

The product was tested by the Underwood oxidation test against silver-cadmium bearings at a concentration of 0.5%. At the end of the test the bearing loss was 3 milligrams.

Example 4

A solution of 31.6 grams (0.1 mol) of crude di-(methylisobutylcarbiny) dithiophosphoric acid and 6 grams of acetamide in 40 grams of ethanol was heated to 50° C. and agitated while 10 grams of 37% aqueous formaldehyde was added. The agitation was continued while the mixture cooled to room temperature after which the mixture was allowed to stand overnight. It was then washed with water and stripped of volatile material by heating at reduced pressure. The product, a dark brown liquid free of hydrogen sulfide odor, was tested at 0.5% concentration in SAE 30 Mid-Continent base lubricating oil by the Underwood oxidation test against silver-cadmium bearings. The bearing loss at the end of the test was 6 milligrams.

Example 5

A solution of 25 grams (0.55 mol) of technical formamide and 48 grams (0.59 mol) of 37% formalin containing 0.2 gram of potassium carbonate was stirred for 1½ hours. This reaction was very slightly exothermic. 130 grams (0.5 mol) of crude diisobutyl dithiophosphoric acid (N. E. 260) was added and the solution stirred for 6 hours. This reaction was very mildly exothermic. By washing with water, drying and stripping the liquid there was obtained 120 grams of ester.

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The product, a light-colored oil free of hydrogen sulfide, was found to possess good solubility in hydrocarbon lubricating oils. It was tested in Mid-Continent oil of SAE 30 grade at a concentration of 0.5% against silver-cadmium bearings. There was no bearing loss at the end of the test.

Example 6

A solution of 31.3 grams (0.1 mol) of methyl-oistearamide in 110 cc. of ethyl alcohol was heated to 45° C. and agitated while 18.6 grams of diethyl dithiophosphoric acid were added. Agitation was continued at the same temperature for 4 hours after which the mass was allowed to stand at room temperature for two days. It was then diluted with benzene and washed with water containing a little sodium dioctyl sulfosuccinate, and stripped of volatile material by heating on a steam bath at reduced pressure. The product was a light tan waxy solid that was easily soluble in lubricating oil.

The product was tested in a Mid-Continent base SAE 30 lubricating oil at 1% concentration against silver-cadmium bearings. The bearing loss at the end of the test was 15 milligrams.

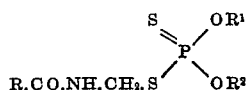
Example 7

In cases where a higher percentage of sulfur in the oil is desired thioamides may be employed. Thus, for example, N-(O,O-di-n-propyl dithiophosphato methyl) thioacetamide was prepared by the following procedure:

A solution of 19 grams (0.25 mol) of thioacetamide in 70 cc. of ethyl alcohol was prepared and 0.4 gram of potassium carbonate in 4 cc. of water was added. This solution was stirred as 24 grams (0.3 mol) of 37% aqueous formaldehyde solution was poured in. After 90 minutes there was added 59 grams (0.25 mol) of distilled di-n-propyl dithiophosphoric acid, whereupon a clear, colorless solution was obtained. This was allowed to stand at room temperature for 2½ days after which it was washed three times with water and then stripped of volatile material by heating at reduced pressure on a steam bath. There was obtained 76 grams of an almost colorless liquid that was free from hydrogen sulfide. It was tested at 0.5% concentration in a Mid-Continent base SAE 30 lubricating oil against silver-cadmium bearings. At the end of the test the bearing loss was 6 milligrams.

What we claim is:

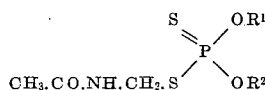
1. Triesters of dithiophosphoric acid of the formula



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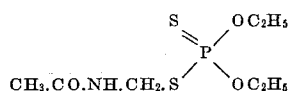
in which each of R, R¹ and R² is an aliphatic hydrocarbon radical of 1-18 carbon atoms.

2. Triesters of dithiophosphoric acid of the formula

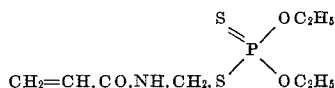


in which each of R¹ and R² is an aliphatic hydrocarbon radical of 1-18 carbon atoms.

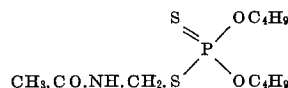
3. A triester of dithiophosphoric acid having the formula



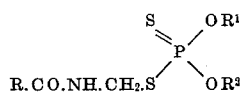
4. A triester of dithiophosphoric acid having the formula



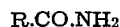
5. A triester of dithiophosphoric acid having the formula



6. A method of preparing a dithiophosphoric acid triester of the formula



in which each of R, R¹ and R² is an aliphatic radical of 1-18 carbon atoms which comprises mixing together an O,O-dialkyl dithiophosphoric acid in which each alkyl radical contains from 1 to 18 carbon atoms, an acid amide of the formula



in which R is an aliphatic hydrocarbon radical of 1-18 carbon atoms, and formaldehyde and allowing the mixture to react at a temperature between room temperature and about 100° C. until a dithiophosphoric acid triester is formed.

EDWIN O. HOOK.
PHILIP H. MOSS.

No references cited.