UNITED STATES PATENT OFFICE

ESTERS OF THE THIO ACIDS OF PHOSPHORUS

Paul L. Salzberg, Wilmington, and James H. Wernicke, Marshallton, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application February 19, 1935,
Serial No. 7,235

22 Claims. (Cl. 260—99.20)

This invention relates to new esters of the thio acids of phosphorus and more particularly to the long chain aliphatic esters of such acids.

The aliphatic esters of orthophosphoric acids are known. The orthophosphoric esters of the long molecular weight alcohols have not proved to be entirely satisfactory for commercial use for the reason that they do not have the marked surface active effect desired in compounds of this type in the uses for which they are intended to be employed. The orthophosphoric esters of the longer chain aliphatic alcohols have the desired surface active effect but are generally solids at ordinary room temperatures and are insufficiently soluble in oils and hydrocarbon solvents to enable full advantage to be taken of their desirable properties.

An object of the present invention is to provide new chemical compounds having the advantageous features of prior compounds but without all of their disadvantages. A further object of this invention is to provide long chain aliphatic esters of the thio acids of phosphorus which are new chemical compounds. A still further object is to provide methods for preparing such new chemical compounds. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

These objects may be accomplished in accordance with our invention which comprises reacting an esterifying derivative of a thio acid of phosphorus with at least one molecular proportion of an aliphatic alcohol containing at least ten carbon atoms or reacting an esterifying derivative of an acid of phosphorus with at least one molecular proportion of an aliphatic mercaptan containing at least ten carbon atoms wherein by aliphatic esters of the thio acids of phosphorus are obtained. These compounds are new chemical compounds not known heretofore and have many advantageous properties over phosphoric esters heretofore known.

By the term "thio acid of phosphorus" we intend to include the mono, di, tri and tetra thio ortho-phosphoric acids, the thio-meta-phosphoric acids, the thio-pyro-phosphoric acids, the thio-hypophosphoric acids and also the thio phosphoric, pyro and hypo acids. However, the thio phosphoric acids are generally the cheapest to manufacture and have the most desirable properties and of these the thio ortho-phosphoric acids are preferred both for ease and cheapness of manufacture and for their unusually desirable properties.

The esters of our invention contain at least one aliphatic chain of at least ten carbon atoms. They may contain 2, 3 or 4 of such chains. They may contain aliphatic chains of a lesser number of carbon atoms. These aliphatic chains may be derived from either saturated or unsaturated aliphatic alcohols and are preferably hydrocarbon chains. They may also contain phenolic radicals. In other words, the esters of our invention may be either neutral or acid esters and may be homogeneous or mixed esters.

The esters of dithio ortho-phosphoric acid may be prepared by reacting at least one molecular proportion of the desired alcohol with a mixture of phosphorus and sulphur or with P4S10. For example, two molecular proportions of decyl alcohol, when reacted with P4S10, forms didecyl dithiophosphate. An inert organic solvent such as benzene or toluene may be employed to better control the reaction. The reaction will generally be carried out under a reflux condenser at refluxing temperatures and under a slight vacuum in order to remove hydrogen sulfide which is formed. If desired, the alcohol may be first reacted with sodium to form the corresponding alcoholate before reacting with the phosphorus pentasulfide.

The monothio ortho-phosphates may be prepared by reacting one or more molecular proportions of the alcohol or alcoholate with phosphorus sulfochloride PSCl3. For example, when three molecular proportions of sodium dodecylxide were reacted with PSCl3, tridodecyl monothio ortho-phosphate was obtained. When one molecular proportion of decyl alcohol was reacted with PSCl3, the mono decyl monothio phosphate was obtained.

Still other esters of theo ortho-phosphoric acids may be prepared by reacting mercaptans such as tetradecyl mercaptan with phosphorus oxychloride POCl3. The compounds produced by this method have each alkyl chain connected to the phosphorus through a sulphur atom. The resulting product will be a mono, di or tri-thio phosphate, depending upon the molecular proportions of the mercaptan to the phosphorus oxychloride. If the phosphorus oxychloride is substituted by phosphorus pentasulfide the tetra-thio phosphate will be produced. A dithio phosphate produced by this method will be isomeric with that obtained by reacting the alcohol with phosphorus pentasulfide. It will be apparent that a variety of esters of the thio acids of phosphorus may be obtained by employing other esterifying derivatives of the acids of phosphorus in place of...
the phosphorus oxychloride, phosphorus pentasulfide, phosphorus sulfochloride, etc.

In order to more clearly illustrate our invention and the preferred modes of carrying the
same into effect, the following examples are given:

Example 1

Twenty-two and two-tenths parts by weight of phosphorus pentasulfide were suspended in 258
parts by weight of toluene. To this, 74.4 parts by weight of dodecyl alcohol were added slowly.
The mixture was heated at 725 mm. under a re-
flux condenser for 18 hours. The resulting re-
action product forms stable emulsions when
mixed with water.

This reaction product was treated with the cal-
culated amount of aniline and heated under a
vacuum to remove most of the toluene. The
thick syrup which remained crystallized when
chilled in ice water. The salt was recrystallized
from toluene in which it is soluble at room tem-
peratures. The white crystals were then dis-
solved in ether and anilino hydrochloride was
precipitated by passing in dry hydrogen chloride.
The anilino hydrochloride was filtered off and
the filtrate evaporated. The oily residue became
solid when chilled to about 50° C. but melted
to an oil when warmed up to 20° C. It did not
30

Example 1

Example 1

Crystallize in an ice-salt mixture. The oil was
heated under a vacuum to remove residual sol-
vents. This oil analyzed 6.3% of phosphorus.
(Theory for didodecyl dithiolephosphate is 6.6%
phosphorus.) The didodecyl dithiolephosphate
when added to water was sufficiently soluble to
render the water acid in reaction.

The p-nitroaniline salt of the diithophosphate
was prepared by dissolving it in toluene and
reacting with p-nitroaniline. This salt was quite
soluble in toluene and alcohol at ordinary tem-
peratures.

The pyridine salt was prepared by adding the
calculated amount of pyridine to a water suspen-
sion of the didecyl dithiolephosphate and the
solution shaken. The resulting solution foamed
and exhibited a cleansing action when applied
to the skin.

The sodium salt of didecyl dithiolephosphate
made by treating didecyl dithiolephosphate with
an aqueous solution of sodium carbonate, is not
soluble in water.

Example 2

When four molecular proportions of 9,10-octa-
decyl alcohol were reacted with one molecular
proportion of phosphorus pentasulfide in ac-
cordance with the procedure of Example 1, dioct-
decyl dithiolephosphate was produced.

This compound has the formula

Example 3

When five molecular proportions of octadecyl
alcohol were reacted with one molecular propor-
tion of phosphorus pentasulfide, trioctadecyl
dithiolephosphate was obtained. This compo-
dund has the following formula

Example 4

When three molecular proportions of tetra-
decyl alcohol were reacted with one molecular propor-
tion of phosphorus sulphur chloride, tri-
tetradecyl monothiolephosphate having the formula

was obtained.

Example 5

Monotetradecyl thiometaphosphate having the formula

was obtained by treating tritetradecyl monothiole-
face of concentrated sulphuric

Example 6

Monocetyl monothiolephosphate having the formula

was prepared by reacting one mol. of cetyl al-
cohol with one mol. of FSCl in accordance with
the procedure of Example 4, followed by hy-
drolysis.

Example 7

Tridodecyl trithiolephosphate

may be made by reacting three mols of dodecyl
mercaptan with one mol. of phosphorus oxy-
chloride.

Example 8

Tridodecyl trithiolephosphate

may be obtained by reacting one mol. P2S5 with
three mols of dodecyl alcohol. This compound
is preferably obtained by reacting three mols of
dodecyl mercaptan with phosphorus trichloride
P3Cl3.

Example 9

The 0,0-dicetyl monothiolephosphate

may be obtained by reacting cetyl alcohol with
phosphorus pentasulfide in accordance with the
procedure of Example 1. The resulting product
apparently contains a substantial amount of
0,8-dicetyl monothiolephosphate having the formula
Example 10

The tetraethyl dithiopyrophosphate may be obtained by treating triethyl monothiophosphate with concentrated sulphuric acid.

Example 11

Tridodecyl tetra thio o-phosphate having the formula may be obtained by reacting three mols of dodecyl mercaptan with one mol. of phosphorus pentasulphide.

Example 12

Tetradodecyl trithiophosphate may be obtained by reacting four mols of tetradodecyl alcohol with one mol. of phosphorus trithiophetarbromide PbSBr₃.

Example 13

Tetraecosyl penta-thiophosphate may be obtained by reacting two mols of ecosyl alcohol and two mols of ecosyl mercaptan with one mol. of phosphorus trisulfitetarbromide.

Example 14

One gram molecular weight of phosphorus pentasulphide was suspended in 2580 parts by weight of toluene. To this four gram molecular weights of the mixture of alcohols obtained by the carboxylic reduction of coconut oil were added slowly. The mixture was heated at 725 mm. at the reflux temperature under a reflux condenser for 18 hours. The resulting mixture of esters and mixed esters of thio phosphoric acid was an oil which formed stable emulsions when mixed with water. This oil blends readily with lubricating oil and in this respect offers an advantage over a pure didodecyl dithio phosphate which blends less readily with lubricating oil.

The above examples are merely illustrative of some of the compounds embraced within our invention and the preferred modes of preparing such compounds. Other similar compounds may be prepared from other alcohols such as decyl, undecenyl, hexacosenyl, octacosyl, eicosyl, ricinoleyl, abetyl and the like alcohols and mercaptans. Also, mixtures of esters containing mixed esters may be prepared by reacting a mixture of such alcohols with an esterifying derivative of a thio acid of phosphorus or a mixture of the corresponding mercaptans with an esterifying derivative of an acid of phosphorus. When such mixtures are employed, it will, in general, be desirable to employ such a mixture obtainable from the alcohols obtained by the carboxylic reduction of a natural fatty oil such as sperm oil and coconut oil or the acids present therein. Other mixtures of esters comprising mixed esters may be obtainable by reacting an esterifying derivative of a thio acid of phosphorus with such an alcohol or mixture of alcohols admixed with other alcohols or phenols. Our invention also includes esters prepared from secondary alcohols derived from the olefins obtained by cracking paraffin wax hydrocarbons.

If pure mixed esters are desired, they may be obtained by reacting one or two mols of an alcohol or mixture of alcohols containing at least ten carbon atoms with the esterifying derivative of a thio acid of phosphorus or their corresponding mercaptans with an esterifying derivative of an acid of phosphorus and then reacting the resulting product with one or more mols of a different alcohol, a phenol or mercaptan.

Our invention embraces the acid esters and their salts such as the alkali, alkaline earth, calcium, zinc, lead or ammonium salts. By "ammonium salts", we intend to include the salts of amines such as, for example, monododecyl amine, diethyl amine, cyclohexylamine, triphenylamine, aniline, nitroaniline, pyridine, naphthaline, o-toluidine, diphenyl guanidine and the like as well as the salts of ammonia.

In the above examples, we have disclosed toluene as a diluent for the reaction. We may use other inert solvents or no solvents at all. We prefer to use a solvent which is effective for the solution of both the alcohol and the resulting thiophosphate but which is a non-solvent for impurities in the reagents. For example, such solvents as chlorobenzene, carbon tetrachloride, benzene and the like or mixtures of such solvents such as a mixture of carbon tetra chloride and toluene will be found to be satisfactory.

The compounds of our invention may be employed as flotation agents for the separation of various types of minerals, or as parasiticides or as acid inhibitors in metal pickling baths or as corrosion inhibitors to retard the attack of metals by oxygen in aqueous solutions or in lubricants for bearings which operate under high pressures or as accelerators for the vulcanization of rubber. Our compounds will have advantages over similar compounds for these purposes. For example, didodecyl dithiophosphate has the advantage over dimyl dithiophosphate in that the aniline salt of didodecyl dithiophosphate is more soluble in hydrocarbon solvents than the aniline salt of dimyl dithiophosphate. Also, the sodium salt of didodecyl is substantially insoluble in water, whereas the sodium salt of dimyl dithiophosphate is readily soluble in water. The dithiophosphates are generally oils at ordinary temperatures, whereas, the corresponding phosphates, such as didodecyl o-phosphate, are solids. This is an advantage for many technical applications such as their use as flotation agents, in pharmaceuticals and as acid corrosion inhibitors. Furthermore, the sulphur content of our compounds renders them more effective for many technical applications than the corresponding phosphates containing no sulphur; for example, when employed as parasiticides, flotation agents, or as acid inhibitors. Furthermore, our compounds are more desirable as assistants for use in extreme pressure lubricants over the corresponding phosphates containing no sulphur and the lower molecular weight dithiophosphates because of their great solubility in the oils and their higher degree of oiliness.

While we have disclosed the preferred embodiments of our invention, it will be readily apparent that many variations and modifications may be 

---

Example 10

The tetraethyl dithiopyrophosphate may be obtained by treating triethyl monothiophosphate with concentrated sulphuric acid.

Example 11

Tridodecyl tetra thio o-phosphate having the formula may be obtained by reacting three mols of dodecyl mercaptan with one mol. of phosphorus pentasulphide.

Example 12

Tetradodecyl trithiophosphate may be obtained by reacting four mols of tetradodecyl alcohol with one mol. of phosphorus trithiophetarbromide PbSBr₃.

Example 13

Tetraecosyl penta-thiophosphate may be obtained by reacting two mols of ecosyl alcohol and two mols of ecosyl mercaptan with one mol. of phosphorus trisulfitetarbromide.

Example 14

One gram molecular weight of phosphorus pentasulphide was suspended in 2580 parts by weight of toluene. To this four gram molecular weights of the mixture of alcohols obtained by the carboxylic reduction of coconut oil were added slowly. The mixture was heated at 725 mm. at the reflux temperature under a reflux condenser for 18 hours. The resulting mixture of esters and mixed esters of thio phosphoric acid was an oil which formed stable emulsions when mixed with water. This oil blends readily with lubricating oil and in this respect offers an advantage over a pure didodecyl dithio phosphate which blends less readily with lubricating oil.

The above examples are merely illustrative of some of the compounds embraced within our invention and the preferred modes of preparing such compounds. Other similar compounds may be prepared from other alcohols such as decyl, undecenyl, hexacosyl, octacosyl, eicosyl, ricinoleyl, abetyl and the like alcohols and mercaptans. Also, mixtures of esters containing mixed esters may be prepared by reacting a mixture of such alcohols with an esterifying derivative of a thio acid of phosphorus or a mixture of the corresponding mercaptans with an esterifying derivative of an acid of phosphorus. When such mixtures are employed, it will, in general, be desirable to employ such a mixture obtainable from the alcohols obtained by the carboxylic reduction of a natural fatty oil such as sperm oil and coconut oil or the acids present therein. Other mixtures of esters comprising mixed esters may be obtainable by reacting an esterifying derivative of a thio acid of phosphorus with such an alcohol or mixture of alcohols admixed with other alcohols or phenols. Our invention also includes esters prepared from secondary alcohols derived from the olefins obtained by cracking paraffin wax hydrocarbons.

If pure mixed esters are desired, they may be obtained by reacting one or two mols of an alcohol or mixture of alcohols containing at least ten carbon atoms with the esterifying derivative of a thio acid of phosphorus or their corresponding mercaptans with an esterifying derivative of an acid of phosphorus and then reacting the resulting product with one or more mols of a different alcohol, a phenol or mercaptan.

Our invention embraces the acid esters and their salts such as the alkali, alkaline earth, calcium, zinc, lead or ammonium salts. By "ammonium salts", we intend to include the salts of amines such as, for example, monododecyl amine, diethyl amine, cyclohexylamine, triphenylamine, aniline, nitroaniline, pyridine, naphthaline, o-toluidine, diphenyl guanidine and the like as well as the salts of ammonia.

In the above examples, we have disclosed toluene as a diluent for the reaction. We may use other inert solvents or no solvents at all. We prefer to use a solvent which is effective for the solution of both the alcohol and the resulting thiophosphate but which is a non-solvent for impurities in the reagents. For example, such solvents as chlorobenzene, carbon tetrachloride, benzene and the like or mixtures of such solvents such as a mixture of carbon tetra chloride and toluene will be found to be satisfactory.

The compounds of our invention may be employed as flotation agents for the separation of various types of minerals, or as parasiticides or as acid inhibitors in metal pickling baths or as corrosion inhibitors to retard the attack of metals by oxygen in aqueous solutions or in lubricants for bearings which operate under high pressures or as accelerators for the vulcanization of rubber. Our compounds will have advantages over similar compounds for these purposes. For example, didodecyl dithiophosphate has the advantage over dimyl dithiophosphate in that the aniline salt of didodecyl dithiophosphate is more soluble in hydrocarbon solvents than the aniline salt of dimyl dithiophosphate. Also, the sodium salt of didodecyl is substantially insoluble in water, whereas the sodium salt of dimyl dithiophosphate is readily soluble in water. The dithiophosphates are generally oils at ordinary temperatures, whereas, the corresponding phosphates, such as didodecyl o-phosphate, are solids. This is an advantage for many technical applications such as their use as flotation agents, in pharmaceuticals and as acid corrosion inhibitors. Furthermore, the sulphur content of our compounds renders them more effective for many technical applications than the corresponding phosphates containing no sulphur; for example, when employed as parasiticides, flotation agents, or as acid inhibitors. Furthermore, our compounds are more desirable as assistants for use in extreme pressure lubricants over the corresponding phosphates containing no sulphur and the lower molecular weight dithiophosphates because of their great solubility in the oils and their higher degree of oiliness.

While we have disclosed the preferred embodiments of our invention, it will be readily apparent that many variations and modifications may be
made therein without departing from the spirit of our invention. Accordingly, the scope of our invention is to be limited solely by the appended claims construed as broadly as is permissible in view of the prior art.

We claim:
1. An aliphatic ester of a thio-acid of phosphorus in which at least one aliphatic radical contains at least 10 carbon atoms.
2. An aliphatic ester of a thio phosphoric acid in which at least one aliphatic radical contains at least 10 carbon atoms.
3. An aliphatic ester of a thio o-phosphoric acid in which at least one aliphatic radical contains at least 10 carbon atoms.
4. An alkyl ester of a thio-acid of phosphorus in which at least one alkyl radical contains at least 10 carbon atoms.
5. An alkyl ester of a thio phosphoric acid in which at least one alkyl radical contains at least 10 carbon atoms.
6. An alkyl ester of a thio o-phosphoric acid in which at least one alkyl radical contains at least 10 carbon atoms.
7. An aliphatic ester of a dithio-acid of phosphorus in which at least one aliphatic radical contains at least 10 carbon atoms.
8. An aliphatic ester of a dithio phosphoric acid in which at least one aliphatic radical contains at least 10 carbon atoms.

9. An aliphatic ester of dithio orthophosphoric acid in which at least one aliphatic radical contains at least 10 carbon atoms.
10. A dialiphatic ester of a thio-acid of phosphorus, each aliphatic group containing at least 10 carbon atoms.
11. A dialiphatic ester of a thio o-phosphoric acid, each aliphatic group containing at least 10 carbon atoms.
12. A dialiphatic ester of a dithio-acid of phosphorus, each aliphatic group containing at least 10 carbon atoms.
13. A dialiphatic ester of dithio o-phosphoric acid, each aliphatic group containing at least 10 carbon atoms.
15. A dodecyl ester of a thio o-phosphoric acid.
17. A dodecyl ester of dithio o-phosphoric acid.
18. A didodecyl ester of a thio-acid of phosphorus.
19. A didodecyl ester of a thio o-phosphoric acid.
20. A didodecyl ester of a dithio acid of phosphorus.
21. Didodecyl dithio o-phosphoric acid.
22. Di-(9,10-octadecenyl) dithio ortho-phosphate.

PAUL L. SALZBERG
JAMES H. WERNITZ.