STABLE PHOSPHATE ESTERS
Assignee: Ethyl Corporation, Richmond, Va.
Filed: Feb. 19, 1971
Appl. No.: 117,094

U.S. Cl. 252/46.7, 252/47, 252/49.8
Int. Cl. C10m 1/30, C10m 1/38
Field of Search 252/47, 49.8, 78, 46.7

References Cited
UNITED STATES PATENTS
3,115,465 12/1963 Orloff et al. 252/49.8

Primary Examiner—Daniel E. Wyman
Assistant Examiner—Y. H. Smith
Attorney, Agent, or Firm—Donald L. Johnson; Robert A. Linn; Joseph D. Odenweller

ABSTRACT
Esters of an acid of phosphorus such as tricresyl phosphate containing a stabilizing amount of a 2,5-bis-(4-pyridyl)-1,3,4-thiadiazole are useful as lubricants or functional fluids at elevated temperatures in contact with metal surfaces.

8 Claims, No Drawings
1 STABLE PHOSPHATE ESTERS

BACKGROUND

Esters of phosphorus-containing acids such as tricresyl phosphate are used as lubricants and in other related areas such as hydraulic fluids. In many such applications they contact metal surfaces. At elevated temperatures, contact with metal surfaces can lead to severe degradation. It is an object of this invention to provide a stable ester of a phosphorus acid which can be used as a lubricant, hydraulic fluid or for any other use where such esters are normally used, and is especially useful in those applications where it contacts a metal surface at elevated temperatures.

SUMMARY

The objects of this invention are accomplished by providing an ester of an acid of phosphorus containing a stabilizing amount of a 2,5-bis(4-pyridyl)-1,3,4-thiadiazole.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A preferred embodiment of the present invention is a normally liquid ester of an acid of phosphorus suitable for use at high temperature in contact with metal surfaces containing a 2,5-bis(4-pyridyl)-1,3,4-thiadiazole. The ester can be any liquid ester of an acid of phosphorus including such acids as phosphoric, phosphonic, phosphinic, phosphorous, phosphinous, phosphinic and phosphonous acid. The ester group can be alkyl, cycloalkyl, aryl, alkaryl or aralkyl, including halogenated alkyl, cycloalkyl, aryl, alkaryl, aralkyl and the like. The preferred alkyl groups are those containing from 1 to about 50 carbon atoms, and the more preferred alkyls are those containing from about 3 to 30 carbon atoms, including their halogenated analogs. These include such alkyl groups as methyl, ethyl, 2-chloroethyl, 2-bromoethyl, propyl, isopropyl, 2-chloropropyl, 3-bromopropyl, butyl, isobutyl, 2-chlorobutyl, 2-bromobutyl, 2-chloroisobutyl, isodecyl, 2-chlorododecyl, tetradecyl, octadecyl, eicosyl, docosyl, 2-bromodocosyl, triacontyl, 2-chlorotriacontyl, tetracontyl, pentacontyl, 2-bromopentacontyl, 2-fluoropentacontyl, 2-chloropentacontyl, and the like.

Some examples of esters resulting from the above alkyl groups are trimethyl phosphate, triethyl phosphate, tributyl phosphate, tridodecyl phosphate, triecosyl phosphate, tri-triacontyl phosphate, dimethylisocyclo phosphate, methyl-dieicosyl phosphate, tri-pentacontyl phosphate, and the like, including their halogenated derivatives such as tri(2-chloropropyl)phosphate, tri(2-bromoeicosyl)phosphate, and the like.

Further examples of alkyl esters include dimethyl hydrogen phosphate, dimethyl methylene phosphate, dibutyl methyl phosphate, di(2-chloropropyl) hydrogen phosphate, di(2-bromobutyl) bromobutyl phosphate, and the like. Also included are methyl phosphate, 2-chloropropyl phosphate, isobutyl disobutyl phosphate, trimethyl phosphate, tributyl phosphate, methyl didodecyl phosphate, triecosyl phosphate, methyl ditriacontyl phosphate, tri-tetracontyl phosphate, dimethyl pentacontyl phosphate, dimethyl phosphonite, didodecyl phosphonite, dipentacontyl phosphonite, dodecyl phosphinate, eicosyl phosphinite, triacontyl phosphinite, butyl phosphinate, 2-chloroamyl phosphinate, 2-bromooctadecyl phosphinate, 2-chloropropyl phosphinate, and the like.

The cycloalkyl esters include those in which the cycloalkyl group contains from about 6 to 8 carbon atoms, such as cyclohexyl, 3-chlorocyclohexyl, cycloheptyl, 4-bromocycloheptyl, cyclooctyl, 2-fluorocyclooctyl, 2-bromocyclooctyl, 2-chlorocyclooctyl, and the like. Exemplary esters are those listed above wherein the cycloalkyl groups are substituted for the alkyl radicals listed.

Preferred aryl and alkaryl groups include both the mono- and di-nuclear radicals containing from 6 to about 30 carbon atoms. Mononuclear aryl and alkaryl groups containing from 6 to about 30 carbon atoms are preferred. These are termed "phenyl groups" which term includes alkyl-substituted phenyl and halo-substituted phenyl. Some examples are phenyl, 4-chlorophenyl, 2-bromophenyl, 2,4-dichlorophenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 3-methyl-4-chlorophenyl, 2,4-dimethylphenyl, 2-ethylphenyl, 4-tert-butylphenyl, 3-octylphenyl, 2,4-didecylphenyl, 2,4-diocyl-3-bromophenyl, 4-ecosylphenyl, 4-triacontylphenyl, 3-tetracontylphenyl, 4-pentacontylphenyl, and the like. Typical resultant esters are triphenyl phosphate, tricyclic esters, tri(4-tert-butylyl)phenyl phosphate, phenyl dicyclohexyl phosphate, cresyl diphenyl phosphate, tri(4-chlorophenyl)phosphate, tri(3-methyl-4-bromophenyl)phosphate, tri(4-hexylphenyl)phosphate, diphenyl(4-dodecylphenyl)phosphate, 4-chlorophenyl di(4-ecosylphenyl)phosphate, diphenyl hydrogen phosphate, diphenyl phenyl phosphate, triphenyl phosphate, cresyl methyl phosphate, and the corresponding phosphonates, phosphonites, phosphinates, phosphinates and phosphinites.

Aryalkyl esters of acids of phosphorus include those in which the arylalkyl group contains from 7 to about 50 carbon atoms. Representative examples of such groups include benzyl, 2-phenylethyl, 4-hromobenzy, 4-chlorobenzyl, 2,4-dichlorobenzyl, 4-dodecylbenzy, 2-phenylbutyl, 2-cresylodecyl, 4-phenylhyd, 2-(4-bromophenyl)ethyl, 2,2-diphenylhyd, 2-phenyltetracontyl, 2-cresyltetracontyl, and the like.

The most preferred esters of a phosphorus acid are the esters of phosphoric acid. In particular, the aryl esters are preferred. Examples of these are diphenyl dodecyl phosphate, cresyl dibutyl phosphate, diphenyl eicosyl phosphate, di(4-chlorophenyl)methyl phosphate, 4-bromophenyl ditriacontylphenyl phosphate, 4-chlorophenyl di(2-chloropropyl)methyl phosphate, di(4-dodecylphenyl)dodecyl phosphate, 2-ecosylphenyl di(4-brom-2-methylphenyl)phosphate, and the like.

The most preferred stabilized esters are the triaryl phosphates, including the halogenated triaryl phosphates. Examples of these are tricresyl phosphate, phenyl dicyclos phosphate, cresyl diphenyl phosphate, tri(4-tert-butylphenyl)phosphate, tri(2-tert-butylphenyl)phosphate, diphenyl 4-dodecylphenyl phosphate, phenyl di(4-ecosylphenyl)phosphate, 4-chlorophenyl di(4-triacontylphenyl)phosphate, di(4-bromophenyl) 4-pentacontylphenyl phosphate, tri(4-hexylphenyl)phosphate, tri(4-oclyphenyl)phosphate, tri(2-sec-butylphenyl)phosphate, de(4-hexylphenyl)2,4-
dihexylphenyl phosphate, phenoxy(4-octylphenyl)(2,4-dioctylophenyl)phosphate, and the like. The 2,5-bis(4-pyridyl)-1,3,4-thiadiazole compounds are those having the formula:

\[
\text{R}_1\text{N} = \text{N} = \text{R}_2
\]

in which \(n\) and \(p\) are integers from 0-2 and \(\text{R}_1\) and \(\text{R}_2\) are lower alkyl groups containing 1-12 carbon atoms. Representative examples are 2,5-bis(2-methyl-4-pyridyl)-1,3,4-thiadiazole, 2,5-bis(2,6-dimethyl-4-pyridyl)-1,3,4-thiadiazole, 2,5-bis(3-ethyl-4-pyridyl)-1,3,4-thiadiazole, 2,5-bis(2-n-butyl-4-pyridyl)-1,3,4-thiadiazole, 2,5-bis(2-dodecyl-4-pyridyl)-1,3,4-thiadiazole, 2,5-bis(2-hexyl-4-pyridyl)-1,3,4-thiadiazole, 2,5-bis(2,5-diocyl-4-pyridyl)-1,3,4-thiadiazole, 2,5-bis(2,5-dimethyl-4-pyridyl)-1,3,4-thiadiazole, 2-(2-methyl-4-pyridyl)-5(4-pyridyl)-1,3,4-thiadiazole, and 2-(2-octyl-4-pyridyl)-5(4-pyridyl)-1,3,4-thiadiazole. The most preferred stabilizer is 2,5-bis(4-pyridyl)-1,3,4-thiadiazole itself.

The thiadiazoles of the present invention are known compounds and are described by: Konig et al., Ber. 87, p. 825 (1954), McMillan et al., J. Am. Pharm. Assoc. 42, p. 457 (1953) and Van der Burgh, Rec trav. chim., 74, p. 257 (1955).

The amount of stabilizer should be a stabilizing amount. This is a minor amount, sufficient to impart the required degree of stability under use conditions. Generally this is provided by adding from 0.005 to 5 weight per cent. A more preferred amount is from about 0.01 to 3 weight per cent.

The stabilizing compositions are readily made by merely adding the required amount of the 2,5-bis(4-pyridyl)-1,3,4-thiadiazole to the liquid ester and stirring until thoroughly blended. The following will serve to illustrate the preparation of some stabilized esters of this invention. All parts are by weight.

**EXAMPLE 1**

In a blending vessel place 10,000 parts of tricresyl phosphate and 10 parts of 2,5-bis(4-pyridyl)-1,3,4-thiadiazole. Stir until thoroughly blended. The resultant ester is stable at high temperatures in contact with metal surfaces and is eminently useful as a turbine bearing lubricant at installations where a fire-resistant lubricant is required.

**EXAMPLES 2 – 32**

Repeat the procedure of Example 1 substituting in order the following esters: dimethyl eicosyl phosphate tridecyl phosphate tributyl phosphate dioctyl hydrogenaphosphonate di(2-chlororopropyl) hydrogenaphosphonate di(2-bromomethyl) bromobutyl phosphonate butyl dibromobutyl phosphonate tricresyl phosphate tridecyl phosphonate tricresyl phosphinite dodecyl phosphenate 2-chlorooctyldecyl phosphenate 2-chloroecosyl phosphonite tricyclohexyl phosphate tri(3-chlorocyclohexyl)phosphate tri(2-fluorocyclooctyl)phosphate tri(cyclohexyl)phosphate dicyclosyl hydrogenaphosphonate triphenyl phosphate tri(4-tetra-butyl)phenyl phosphate phenyldicyresyl phosphate cresylidinephosphonate tri(4-chlorophenyl)phosphate tri(3-methyl-4-bromophenyl)phosphate tri(4-hexylophenyl)phosphate diphenyl(4-dodecylphenyl)phosphate 4-chlorophenyl di(4-eicosylphenyl)phosphate diphenyl hydrogenaphosphonate diphenyl phenyl phosphonate tricresyl phosphate

The resultant esters are more stable at elevated temperatures in contact with metal than the original unstabilized ester and are useful as lubricants and hydraulic fluids.

In a similar manner, each of the other alkylsubstituted 2,5-bis(4-pyridyl)-1,3,4-thiadiazoles disclosed can be substituted in Example 1 with good results.

The excellent stability provided by the present additives was shown using a Polyveriform Test carried out at 400°F. The test ester was placed in a cell together with magnesium, copper and steel coupons. The ester was heated to 400°F. and air bubbled through it for 72 hours. After this period, the acid number, percent viscosity increase and percent pentane insolubles were measured as criteria of degradation. The ester used in the test was a triaryl phosphate in which the ary1 groups were mixtures of phenyl, hexylphenyl and octylophenyl radicals. The results obtained are shown in the following table.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Conc.</th>
<th>Acid No.</th>
<th>% Visc. Increase</th>
<th>% Pentane Insolubles</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>—</td>
<td>9.6</td>
<td>64</td>
<td>5.69</td>
</tr>
<tr>
<td>2,5-bis(4-pyridyl)-1,3,4-thiadiazole</td>
<td>0.06%</td>
<td>1.1</td>
<td>9</td>
<td>0.19</td>
</tr>
</tbody>
</table>

As the results show, the addition of only a small amount of an additive of the present invention provided an ester of an acid of phosphorus having very high stability even at elevated temperatures in contact with metal surfaces. Such esters are useful as lubricants, especially for stationary turbine installations and as hydraulic fluids where a fire-resistant fluid of good viscosity properties is needed.

I claim:
1. A normally liquid ester of an acid of phosphorus suitable for use as a lubricant or hydraulic fluid at high temperatures in contact with metal surfaces selected from the group consisting of hydrocarbyl and halogenated hydrocarbyl esters of an acid of phosphorus containing a stabilizing amount of a compound selected from the group consisting of 2,5-bis(4-pyridyl)-1,3,4-thiadiazole and alkylsubstituted 2,5-bis(4-pyridyl)-1,3,4-thiadiazoles.
2. A composition of claim 1 wherein said 2,5-bis(4-pyridyl)-1,3,4-thiadiazole is compound.
3,816,311

3. A composition of claim 2 wherein said acid is phosphoric acid.
4. A composition of claim 3 wherein said phosphate ester is an aryl phosphate aryl being selected from the group consisting of phenyl, alkylphenyl and halo-phenyl.
5. A composition of claim 4 wherein said aryl is a triaryl phosphate.

6. A composition of claim 5 wherein said triaryl phosphate is tricresyl phosphate.
7. A composition of claim 5 wherein said triaryl phosphate is phenyl dicresyl phosphate.
8. A composition of claim 5 wherein said triaryl phosphate is cresyl diphenyl phosphate.

* * * * *
In column 4, Claim 2 should read -- A composition of Claim 1 wherein said compound is 2,5-bis(4-pyridyl)-1,3,4-thiadiazole. -- In column 5, Claim 4 should read -- A composition of Claim 3 wherein said ester is an aryl phosphate, said aryl being selected from the group consisting of phenyl, alkylphenyl and halophenyl. -- Column 5, in Claim 5, line 1, insert "phosphate" after "aryl".

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.  C. MARSHALL DANN
Attesting Officer  Commissioner of Patents