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PRESERVATIVE-TYPE FUNCTIONAL FLUIDS

Louis R. Stark, East St. Louis, Ill., assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

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This invention relates to fire-resistant functional fluids having outstanding preservative or rust-preventive properties which fluids are composed of the fluid triaryl phosphates containing an additive amount of a dimer acid.

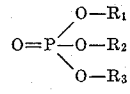
The manufacturer of hydraulically operated equipment, such as a pump, transmission, die-casting machine, etc., usually provides an initial fill of such equipment with a hydraulic fluid and operates such equipment for a short period of time on the initial fill to insure that the particular item of equipment operates satisfactorily. Additionally, this initial operation contacts the internal parts of the equipment with hydraulic fluid so that after the hydraulic fluid is drained prior to shipment or storage, a film of the hydraulic fluid remains on the internal parts of the equipment and thereby provides protection of the parts against rusting. Similar action is also taken in situations where equipment is to be removed from service for an extended period of time, as for example, when a manufacturing facility is closed down or as when one of the branches of the Armed Services, such as the Navy, "moth balls" some of its equipment.

The use of petroleum-based fluids containing suitable anti-rust additives as storage preservatives is known. With the increasing popularity of synthetic fire-resistant fluids, however, many problems are presented when these latter fluids are used to provide storage protection. The use of petroleum-based fluids as storage preservatives for equipment designed to eventually operate on a synthetic fluid is undesirable since any remaining petroleum oil could (*a*) decrease the fire resistance of a later added fire-resistant synthetic fluid, (*b*) possibly be incompatible with seals installed for use with synthetic fluids, and (*c*) be incompatible with the synthetic fluids. On the other hand, most of the synthetic fluids do not inherently possess the property of providing protection against rust formation on ferrous surfaces under storage conditions, and normal additive quantities of the anti-rust additives generally used in petroleum-based fluids do not help in providing the synthetic fluids with adequate rust inhibition properties as shown by the fact that synthetic fluids frequently require very large quantities (often as much as 20%) of the same additives as are normally used with petroleum based fluids to provide the desired level of rust protection. However, the use of such large quantities of additives results in a fluid having an unrealistic cost for most commercial applications and also greatly reduces the fire resistance of the synthetic fluids. It has now been found that synthetic fire-resistant triaryl phosphate-based fluids can be utilized as preservative fluids by adding thereto an additive amount of a hereinafter-described dimer acid. The resulting composition provides storage preservation for a period of time equal to that normally expected from petroleum-based fluids even under severe conditions of temperature and humidity.

It is an object of this invention to provide synthetic fire-resistant functional fluids having superior preservative

or rust-preventive properties. It is a further object of this invention to provide synthetic fire-resistant functional fluids which in a "fill and drain" type operation, as heretofore described, provide anti-rust protection for an extended period of time even under conditions of high temperature and high humidity. These objects will be readily apparent to those skilled in the art from the following description of the invention.

It has now been discovered that the fluid triaryl phosphates containing an additive amount, i.e. up to about 10% by weight, of a dimer acid, provide synthetic fire-resistant functional fluids having outstanding preservative or rust-preventive properties. The triaryl phosphates of this invention can be represented by the general formula:



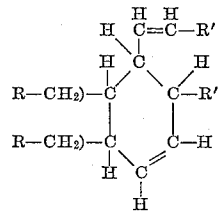
where R_1, R_2 and R_3 are each selected from phenyl, alkylphenyl, halophenyl, alkylhalophenyl, and haloalkylphenyl radicals. Of the alkyl-substituted phenyl radicals, including those radicals containing halogen substituents, the methyl-substituted phenyl radicals are preferred. Within the scope of the invention, various mixtures of triaryl phosphates can be used, and the substituted phenyl groups within a particular triaryl phosphate need not be the same. Non-limiting examples of suitable radicals are phenyl, cresyl, xylyl, ethylphenyl, isopropylphenyl, tert.-butylphenyl, amylphenyl, decylphenyl, chorophenyl, naphthyl, trifluormethylphenyl, 2,2,2-trifluorethylphenyl, methylchlorophenyl, diphenyl, and the like.

When two like or unlike molecules of a polyethenoid monocarboxylic fatty acid condense to form a dicarboxylic acid, the product by definition is a dimer acid, or the carboxylic acid is said to be dimerized. In general, the dimer acids suitable for use in this invention are produced by the condensation of two like or unlike unsaturated aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, examples of which comprise

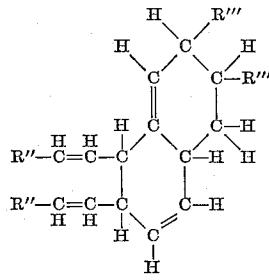
$\Delta^{9,11}$-hexadecadienoic acid
$\Delta^{9,12}$-heptadecadienoic acid
$\Delta^{8,12}$-octadecadienoic acid
$\Delta^{9,11}$-octadecadienoic acid
$\Delta^{9,12}$-octadecadienoic acid (linoleic acid)
$\Delta^{9,13}$-octadecadienoic acid
$\Delta^{9,11,13}$-octadecatrienoic acid
$\Delta^{9,12,15}$-octadecatrienoic acid (linoleic acid)

The dimer acids can be characterized as being dicarboxylic acids having either one substituted six-membered hydroaromatic ring or having two fused six-membered hydroaromatic rings, one of which does not carry the two carboxylic acid groups being disubstituted. These acids are further characterized by having two carboxylic acid groups attached to a single six-membered hydroaromatic ring through a plurality of (CH_2)-groups, the number of such groups being dependent upon the number of such groups between the carbon atom of the carboxylic acid group and the nearer carbon of the nearest double bond of the monocarboxylic acid. The substituents are alkyl or alkenyl groups, depending upon the degree of unsaturation of the monocarboxylic acid from which the dimeric

acid is derived. Thus, the dimer acids derived from a diethenoid fatty acid, or a dienoic acid, have a single six-membered hydroaromatic ring substituted in two immediately adjacent positions by two alkyl groups and in two other immediately adjacent positions by carboxylic acid groups separated from the hydroaromatic ring in one substituent by a straight-chain unsaturated aliphatic group and in the other by a straight-chain saturated aliphatic group. Consequently, dimer acids, when prepared from the individual monocarboxylic acids, are represented by two formulae; i.e.,



where R is $CH_3(CH_2)_n$—, and R' is —$(CH_2)_m$COOH, and *n* is a small number one more than the number of CH_2= groups between the terminal CH_3-group and the nearer carbon of the nearer double bond of the diethenoid monocarboxylic acid from which the dimer acid is derived, and *m* is a small number representing the number of CH_2= groups between the carbon of the carboxylic group and the nearer carbon of the nearer double bond of the diethanoid monocarboxylic acid from which the dimer acid is derived; and



where R'' is $CH_3(CH_2)_n$ and R''' is —$(CH_2)_m$COOH, and *n* and *m* have the same significance as before. Thus, the dimer acids are dicarboxylic acids derived from two molecules of polyethenoid fatty acids of drying and semi-drying oils and from fatty acids such as ricinoleic acid which, upon dehydration, become polyethenoid fatty acids. Therefore, in general, dimer acids are dicarboxylic acids derived by the condensation of two molecules of one or more polyethenoid aliphatic monocarboxylic acids.

While the dimer acids can be used in pure form, for practical reasons, impure forms are used; that is to say, the dimer acids are not presently available at commercially attractive costs in pure form. The purest form examined contained about 85% dimerized acids—the impurest sample examined contained about 45% dimerized acids. The preferred dimer acid for use in this invention is dimerized linoleic acid which is obtained by condensing linoleic acid. Linoleic acid may be condensed by heating at a temperature of 330–360° C. in the presence of a small amount of water or in an atmosphere of steam for a period of three to eight hours at pressures varying between 85 and 400 pounds per square inch. The resulting product consists essentially of the dimer, but minor proportions of the trimer are also formed. Methods for carrying out this procedure in detail may be found in the article by Charles G. Goebel, Journal of the American Oil Chemists Society, vol. 24, pp. 65–8 (1947). A well-known source of this dimerized linoleic acid is the product

sold by Emery Industries, Inc., the properties of which are given as follows:

Neutral equivalent	290–310.
Iodine value	80–95.
Color	Gardner 12 (max.).
Dimer content	Approx. 85%.
Trimer and higher	Approx. 12%.
Monomer	Approx. 3%.

Tests of several batches of material supplied by this producer indicate that the properties of this product are within the following limits:

Specific gravity, ° A.P.I	15–15.1
Specific gravity, D60/60	0.9665
Color, Lovibond	35
Kinematic viscosity at 100° F., centistokes	2462–2666
A.S.T.M. bromine No	39.3
Neutrality No	186.8–190.4
Iodine value	67–86

It will be noted that the dimer acids available from the Emery Industries, Inc., contain approximately 85% dimerized acids and about 12% trimerized and higher polymeric acids.

Another source of dimer acids is the still residue from the dry distillation of castor oil in the presence of sodium hydroxide. This distillation yields approximately two equal fractions, the distillate and a second still residue, which residue contains about 45–50% dimerized acids and about 50% trimerized and higher polymeric acids. Since neither of these industrially available products are 100% dimerized acids, it is manifest that materials containing more highly polymerized acids than the dimer acids can be used. However, it is to be noted that these materials contain only small amounts, say less than 10%, of the monocarboxylic or unpolymerized fatty acids and saturated acids. Accordingly, preferred dimer acids are those containing not more than about 15% of unpolymerized unsaturated fatty acids and saturated fatty acids.

In general, the content of dimerized acids and trimerized and higher acids should be of the order of at least about 85%, with the dimer acids representing at least about 50% of the dimeric and higher polymeric acids. The Emery Industries' dimer acid contains about 85% dimerized acid, while the second still residue of the dry distillation of castor oil, in the presence of sodium hydroxide contains about 46.8% dimerized acids.

In order to demonstrate the outstanding rust-preventing properties of compositions of this invention, Federal Test Method Standard No. 791, Method 5323–T, was used, by which test the degree of protection provided by mineral or synthetic lubricating oils under conditions of specified temperature and humidity can be determined. Test panels prepared as specified in this method and dipped in formulations compounded according to this invention gave protection against rust for a period of at least thirty days.

Some typical formulations of this invention which give anti-rust protection for thirty days in the above described test are as follows:

Base stock	Dimer acid, Percent by weight
Tricresyl phosphate	3.0
Tritolyl phosphate	3.5
Cresyl diphenyl phosphate	2.7
Trixylyl phosphate	1.0
Xylyl diphenyl phosphate	4.5
Diphenyl β-naphthyl phosphate	5.0
Dicresyl phenyl phosphate	3.5
Diphenyl xylyl phosphate	6.0
Diphenyl ethylphenyl phosphate	5.0
Tri-o-chlorophenyl phosphate	7.5
Dicresyl xylyl phosphate	5.0
Phenyl dicresyl phosphate	2.3

Such results are outstanding when it is considered that using the same method test panels coated with triaryl phosphates alone (i.e. without the addition of a dimer acid) showed an average of about 40% rusting after 24 hours. Amounts of dimer acid as low as about 0.25% provide definite improvement of the anti-rust properties of the fluid triaryl phosphates and are therefore contemplated as part of the invention. Such small amounts do not however provide a minimum of about 30 days protection in the above-described rust test. For anti-rust protection of the order of 30 days about at least 2% dimer acid should be used.

The physical properties of the formulations of this invention do not differ materially from the properties of the triaryl phosphate base stocks. Thus, for example, the physical properties of both a formulation of this invention (tricresyl phosphate plus dimerized linoleic acid) and the triaryl phosphate base stock (tricresyl phosphate) are compared in the following table.

PROPERTY	Tricresyl Phosphate + 5.0% dimer acid	Tricresyl Phosphate
Viscosity, 100° F	43.7 centistokes	32.6 centistokes.
Viscosity, 210° F	5.07 centistokes	4.23 centistokes.
Specific gravity, 60°/60° F	1.154	1.163.
Flash Point, Cleveland Open Cup.	465° F	460° F.
Fire Point, Cleveland Open Cup.	565° F	695° F.
Color	Tan-Amber	Off-White.

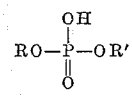
Comparisons of physical properties of other fluid triaryl phosphates suitable for use in this invention with formulations of this invention are given below. In each case of a formulation of this invention about 5.0% by weight of dilinoleic acid and about 95% by weight triaryl phosphate was used.

Table

COMPOSITION	Viscosity, centistokes		Specific Gravity, 60°/60° F.
	100° F.	210° F.	
Cresyl diphenyl phosphate	17.9	3.29	1.205
Cresyl diphenyl phosphate + dimer acid	23.1	3.85	1.200
Dicresyl phenyl phosphate	24.6	3.79	
Dicresyl phenyl phosphate + dimer acid	31.9	4.50	
Diphenyl β-naphthyl phosphate	63.4	6.15	1.242
Diphenyl β-naphthyl phosphate + dimer acid	84.1	7.41	1.238
Diphenyl α-naphthyl phosphate	64.7	6.20	1.246
Diphenyl α-naphthyl phosphate + dimer acid	86.2	7.62	1.232
Dicresyl α-naphthyl phosphate	176.0	8.55	1.202
Dicresyl α-naphthyl phosphate + dimer acid	232.6	10.41	1.186
Dicresyl p-xenyl phosphate	235.8	10.31	1.183
Dicresyl p-xenyl phosphate + dimer acid	310.6	13.35	1.164
Dicresyl o-xenyl phosphate	257.6	9.45	1.190
Dicresyl o-xenyl phosphate + dimer acid	340.0	11.46	1.168
Tris(2,4-dimethylphenyl) phosphate	201.3	7.71	
Tris(2,4-dimethylphenyl) phosphate + dimer acid	274.0	9.32	
Tris(p-tert.-butyl phenyl) phosphate	750.4	15.43	
Tris(p-tert.-butyl phenyl) phosphate + dimer acid	1,008.1	18.80	
Tris(meta-isopropylphenyl) phosphate	42.7	5.53	
Tris(meta - isopropylphenyl) phosphate + dimer acid	56.4	6.80	
Meta-isopropylphenyl diphenyl phosphate	17.7	3.41	
Meta-isopropylphenyl diphenyl phosphate + dimer acid	24.5	4.08	
di(o-Chlorophenyl) phenyl phosphate	33.1	4.51	
di(o-Chlorophenyl) phenyl phosphate + dimer acid	44.1	5.50	

It has also been found that anti-rust protection, as measured by the method hereinbefore described, for as long as sixty days and at least forty-five days can be

obtained with the basic fluid formulations of this invention by incorporating therein an additive amount of an alkaryl acid ester of phosphorus which can be represented by the formula:



where R is an alkylphenyl radical and where R′ is hydrogen or an alkylphenyl radical. By "alkylphenyl radical" is meant a phenyl radical containing one or two like or unlike substituents, such as amyl, and their various isomers. It is preferred that the alkyl substituents be on the 2 and/or 4 positions of the phenyl nucleus, and it is particularly preferred that they contain from three to six carbon atoms.

These acid esters are prepared by reacting phosphorus pentoxide with an alkyl phenol in a molar ratio of about 1:3, the reaction product being an equi-weight mixture of the mono(alkyl-substituted phenyl) acid ester of phosphorus and the di-(alkyl-substituted phenyl) acid ester of phosphorus, thus;

$$3R''OH + P_2O_5 \rightarrow (R''O)(HO)_2PO + (R''O)_2(HO)PO$$

which esters are readily separable by means well known in the art. However, from the standpoint of economy, it is not necessary to separate said esters since the mixture so obtained can be used.

Non-limiting examples of such preferred compounds are the mixture of mono- and di-(2,4-di-tert.-amyl phenyl) acid esters of phosphorus prepared from phosphorus pentoxide and 2,4-di-tert.-amyl phenol, the mixture of mono- and di-(2,4-di-isoamyl phenyl) acid esters of phosphorus obtained from phosphorus pentoxide and 2,4-di-isoamyl phenol, the mixture of mono- and di-(2-isoamyl phenyl) acid esters of phosphorus obtained from phosphorus pentoxide and 2-isoamyl phenol, the mixture of mono- and di-(2,4-di-tert.-butyl phenyl) acid esters of phosphorus obtained from phosphorus pentoxide and 2,4-di-tert.-butyl phenol, the mixture of mono-and di-(2-n-hexyl phenyl) acid esters of phosphorus obtained from phosphorus pentoxide and 2-n-hexyl phenol, the mixture of mono- and di-(4-isopropyl phenyl) acid esters of phosphorus obtained from phosphorus pentoxide and 4-isopropyl phenol. Other mixtures of mono- and di-(alkyl-substituted phenyl) acid esters of phosphorus which are operable in the compositions of this invention include the products of phosphorus pentoxide and, respectively, 2-ethyl phenol, 4-isobutyl phenol, 4-isoamyl phenol, 2,4-di-tert.-butyl phenol, 2-ethylhexyl phenol, 2-n-octyl phenol, 2-nonyl phenol, 2-decyl phenol, and 2-dodecyl phenol. It is to be understood that either the mono-(alkyl-substituted phenyl) acid esters of phosphorus or the di-(alkyl-substituted phenyl) acid esters of phosphorus can be employed per se, and that any mixture thereof is contemplated.

When using the above defined alkaryl acid esters of phosphorus in the fluid formulations of this invention an additive amount, i.e. up to about 5% by weight, is used. The addition of these acid phosphates in the fluid compositions of this invention does not measurably alter the physical properties of such compositions since the dimer acid content can be decreased somewhat, in proportion to the amount of acid ester of phosphorous used. Preferably the total of dimer acid plus acid ester of phosphorous should be, for anti-rust protection of the order of 45–60 days, at least about 2.5%. Thus the dimer acid content can be in the range of about 1–10% and the amount of acid ester of phosphorous can be in the range of about 0.1–5%.

Typical formulations containing the base stock, dimer acid and alkaryl acid ester of phosphorus, which provide

anti-rust protection for from 45 to 60 days in the aforedescribed rust test are the following.

Component:	Percent by weight
Tricresyl phosphate	95.0
Dimerized linoleic acid	2.5
Diamylphenyl acid phosphate	2.5
Tricresyl phosphate	97.0
Dimerized linoleic acid	2.7
Diamylphenyl acid phosphate	0.3
Cresyl diphenyl phosphate	97.0
Dimerized linoleic acid	2.7
Diamylphenyl acid phosphate	0.3

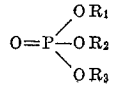
If desired, oxidation inhibitors can also be added to the fluids of this invention, examples of which are alpha- or beta-naphthol, N-phenyl alpha-naphthylamine, p-amino-diphenyl amine, N,N'-diphenyl benzidine, N,N'-di-2-naphthyl p-phenylene diamine, phenothiazine and the silica analog of phenothiazine. The amount of such inhibitors which is generally not more than about 1% by weight. Also, for some applications, it may be desirable to add small amounts of various other functional additives such as viscosity index improvers, e.g., a polymerized methacrylate ester, an alkylated polystyrene, or the polyether condensation products of ethylene oxide or propylene oxide, or both, with a glycol such as ethylene glycol, propylene glycol, butanediol, etc., or with an aliphatic alcohol such as butanol, octanol, decanol, tridecanol, etc., pour point depressors, detergents, other corrosion- and rust-inhibiting agents, anti-wear and lubricity agents, anti-foaming agents such as the silicone polymers, and the like.

By "fluid" triaryl phosphate is meant those triaryl phosphates which are fluid, i.e., mobile, at ordinary temperatures, i.e., above about 30° F. Such triaryl phosphates are known to the art, and thus need not be specifically enumerated. Thus, for example, triphenyl phosphate would not meet the above definition, as it is a solid below about 121° F., a fact well known to the art, and therefore is not contemplated within the scope of this invention.

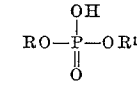
While this invention has been described with reference to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

What is claimed is:

1. A fire-resistant functional fluid composition comprising a major amount of a fluid triaryl phosphate represented by the structure

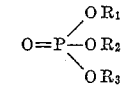


where R_1, R_2 and R_3 are selected from the group consisting of phenyl, alkylphenyl, halophenyl, haloalkylphenyl, and alkylhalophenyl, in which any alkyl substituent has up to 10 carbon atoms, from about 0.25% to about 10% by weight of a dimer acid produced by the condensation of unsaturated aliphatic monocarboxylic acids having between about 16 and 18 carbon atoms, and from about 0.1% to about 10% by weight of an acid ester of phosphorus represented by the structure

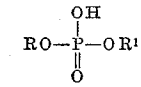


where R is alkylphenyl having up to 12 carbon atoms in the alkyl substituent and R^1 is selected from the group consisting of hydrogen and alkylphenyl having up to 12 carbon atoms in the alkyl substituent.

2. A fire-resistant functional fluid composition comprising a major amount of a fluid triaryl phosphate represented by the structure



where R_1, R_2 and R_3 are alkylphenyl, having up to 10 carbon atoms in the alkyl substituents, from about 0.25% to about 10% by weight of dilinoleic acid, and from about 0.1% to about 10% by weight of an acid ester of phosphorus represented by the structure



where R and R^1 are alkylphenyl having 3 to 6 carbon atoms in the alkyl portion thereof.

3. A fire-resistant functional fluid composition comprising a major amount of tricresyl phosphate, from about 2–10% by weight of dilinoleic acid and from about 2–10% by weight of diamylphenyl acid phosphate.

4. A fire-resistant functional fluid composition comprising by weight, about 95% tricresyl phosphate, about 2.5% dilinoleic acid and about 2.5% diamylphenyl acid phosphate.

5. A fire-resistant functional fluid composition comprising, by weight, about 97% cresyl diphenyl phosphate, about 2.7% dilinoleic acid and about 0.3% diamylphenyl acid phosphate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,080,299	Benning et al.	May 11, 1937
2,631,979	McDermott	Mar. 17, 1953

FOREIGN PATENTS

205,453	Australia	Dec. 21, 1956
790,231	Great Britain	Feb. 5, 1958