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3,707,501 HYDRAULIC FLUIDS CONTAINING CERTAIN QUATERNARY PHOSPHONIUM SALTS OF PHOSPHORUS ACIDS

William F. Gentit, Mohegan Lake, and Fred Jaffe, Briar-cliff Manor, N.Y., assignors to Stauffer Chemical Com-pany, New York, N.Y.

No Drawing. Filed June 29, 1970, Ser. No. 51,001 Int. Cl. C09k 3/00; C23f 11/10

17 Claims 10 U.S. Cl. 252-78

ABSTRACT OF THE DISCLOSURE

Data obtained in a modified Boeing wear apparatus revealed that aircraft hydraulic fluids containing a phos- 15 phate ester base stock and a small percentage of methyl trioctyl phosphonium dimethyl phosphate exhibit superior wear-erosion characteristics when compared with the same formulations containing either small percentages of water or no additive.

BACKGROUND OF THE INVENTION

A number of functional fluids are known and used in 25 the hydraulic systems of aircraft. Such hydraulic systems impose stringent requirements on the hydraulic fluid. Not only must these hydraulic fluids meet stringent use requirements but they must also be adequately non-flammable to satisfy FAA requirements for fire resistance. Addi- 30 tionally, the hydraulic fluid must be capable of performance in the hydraulic system over a protracted period of time without incurring substantial damage to the various conduits, valves, pumps, etc. to which the fluid

must flow in the course of such use.

In the past, there have been reports of damage to valves and other metallic members which come into contact with phosphate ester fluids. The damage is evidenced by the wearing away of metallic parts. Several explanations have been advanced in an attempt to characterize the 40 phenomena which causes the damage and to suggest solutions The prior art speaks of cavitation, erosion, corrosion and other phenomena in reference to the wearing away of the metallic environment of a hydraulic system. One solution which has been advanced to overcome the damage problem involves maintaining a small percentage of water in the fluid. Phosphate ester fluids containing small percentages of water are known to be effective in aircraft hydraulic systems from U.S. Patent 2,470,792. Unfortunately, while the presence of a small percentage of water reduces certain types of damage when incorporated in some phosphate ester hydraulic fluids, the presence of water may have an undesirable effect on corrosion as well as stability of the fluid. For these reasons, its is the principal objective of the present invention to provide a satisfactory non-aqueous additive which will minimize damage of all types caused by the fluid in hydraulic systems.

BRIEF DESCRIPTION OF THE INVENTION

It has now been discovered that the incorporation into the hydraulic fluid compositions of a minor percentage of certain quaternary phosphonium compounds inhibits damage to the metallic environment containing the hydraulic fluid.

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DETAILED DESCRIPTION OF THE INVENTION

The quaternary phosphonium compounds which are useful for incorporation in hydraulic fluids in accordance with the present invention are represented by the following formula and description:

$$\begin{bmatrix} R' \\ R-P-R'' \\ R''' \end{bmatrix} \oplus \begin{bmatrix} X & Y' \\ Z-P & Y'' \end{bmatrix} \ominus$$

where R, R' and R" represent alkyl, aryl, alkaryl, and aralkyl groups containing from 1 to 10 carbon atoms, and R" represents alkyl or aralkyl containing from 1 to 10 carbon atoms, X represents O or S, Y' and Y" represent alkoxy, alkylthio, alkyl, aryl, alkaryl, aralkyl, aryloxy, arylthio and alkaryloxy, and Z represents oxygen

Typical compounds are illustrated as follows:

(1) methyltrioctylphosphonium dimethyl phosphate

(2) ethyltrioctylphosphonium diethylphosphonate

(3) ethyltrioctylphosphonium dimethyl phosphate

(4) butyltrioctylphosphonium dibutyl phosphate

(5) isobutyltrioctylphosphonium dimethyl phosphate

(6) benzyltriphenylphosphonium dibenzyl phosphate

(7) methylphenyldioctylphosphonium dimethyl phosphate

(8) phenyltriethylphosphonium ethyl phenylphosphonate

(9) methyldiphenyloctylphosphonium dimethyl phosphate

(10) tretraethylphosphonium diethyl phosphate

(11) methyltriphenylphosphonium dimethyl phosphate

(12) methyltributylphosphonium dimethyl phosphate

(13) methyltributylphosphonium diethyl phosphate

(14) methyltrioctylphosphonium methyl methylphos-

(15) methyltrioctylphosphonium dimethylphosphonate

(16) methyltrioctylphosphonium dimethyl phosphate

The preparation of quaternary phosphonium compounds of the type useful in the fluid compositions of the present invention are known in the prior art and requires no further explanation herein. Such salts have been found useful as polymerization catalysts, antistatic agents, stabilizers, surfactants, and in baths for dying textile materials. These compounds and further literature thereon are available from the Carlisle Chemical Works, Inc., Reading, Ohio, as shown in "Chemical Engineering News," vol. 47, No. 1, at page 7 (January 1969).

Lubricant compositions to which the phosphonium compositions can be added are referred to as base stocks. They include, but are not limited to, esters and amides of an acid of phosphorus, mineral oil and synthetic hydrocarbon oil base stocks, hydrocarbyl silicates, silicones, aromatic ether and thioether compounds, chlorinated biphenyl, monoesters, dicarboxylic acid esters, esters of polyhydric compounds, polyalkylene ether glycols and

alcohols as well as their esters.

The concentration of phosphonium composition required to inhibit damage will vary depending upon the particular base stock or blend of base stocks which are employed. Preferably, between about 0.1 and about 10% by weight of the phosphonium composition is employed. More preferably, between about 0.5 and about 2.0 weight percent is employed. The functional fluid composition of this invention can be compounded in any manner known 3

to those skilled in the art for incorporation of an additive into a base stock with stirring until a homogeneous fluid composition is obtained.

The functional fluid compositions which are suitable for use as base stock materials with the present invention can be esters and amides of an acid of phosphorus represented by the structure:

$$\begin{array}{c}
0 \\
-P \\
-(Y_1)_0 - R_2 \\
(Y_2)_b \\
R
\end{array}$$

wherein Y is selected from the group consisting of oxygen, sulfur and

Y₁ is selected from the group consisting of oxygen, sulfur and

and Y_2 is selected from the group consisting of oxygen, sulfur and

R, R₁, R₂, R₃, R₄ and R₅ are each selected from the 30 group consisting of alkyl, aryl, substituted aryl and substituted alkyl wherein R, R₁, R₂, R₃, R₄ and R₅ each can be identical or different with respect to any other radical, and a, b and c are whole numbers having a value of 0 to 1 and the sum of a+b+c is from 1 to 3.

Typical examples of alkyl radicals are as follows: methyl, ethyl, normal propyl, isopropyl, normal butyl, isobutyl, secondary butyl, tertiary butyl, normal amyl, isoamyl, 2-methylbutyl, 2,2-dimethyl propyl, 1-methyl butyl, diethylmethyl, 1,2-dimethyl propyl, tertiary amyl, normal 40 hexyl, 1-methylamyl, 1-ethyl butyl, 1,2,2-trimethyl propyl, 3,3-dimethyl butyl, 1,1,2-trimethyl propyl, 2-methyl amyl, 1,1-dimethyl butyl, 1-ethyl 2-methyl propyl, 1,3-dimethyl butyl, isohexyl, 3-methylamyl, 1,2-dimethyl butyl, 1methyl 1-ethyl propyl, 2-ethyl butyl, normal heptyl, 45 1,1,2,3-tetramethyl propyl, 1,2-dimethyl 1-ethyl propyl, 1,1,2-trimethyl butyl, 1-isopropyl 2-methyl propyl, 1methyl 2-ethyl butyl, 1,1-diethyl propyl, 2-methyl hexyl, 1,1-dimethyl amyl, 1-isopropyl butyl, 1-ethyl 3-methyl butyl, 1,4-dimethyl amyl, isoheptyl, 1-methyl 1-ethyl 50 butyl, 1-ethyl 2-methyl butyl, 1-methyl hexyl, 1-propyl butyl, normal octyl, 1-methyl heptyl, 1,1-diethyl 2-methyl propyl, 1,1,3,3-tetramethyl butyl, 1,1-diethyl butyl, 1,1dimethyl hexyl, 1-methyl 1-ethyl amyl, 1-methyl 1-propyl butyl, 2-ethyl hexyl, 6-methyl heptyl (iso-octyl), normal 55 nonyl, 1-methyl octyl, 1-ethyl heptyl, 1,1-dimethyl heptyl, 1-ethyl 1-propyl butyl, 1,1-diethyl 3-methyl butyl, diisobutyl methyl, 3,5,5-trimethyl hexyl, 3,5-dimethyl heptyl, normal decyl, 1-proply heptyl, 1,1-diethyl hexyl, 1,1-dipropyl butyl, 2-isopropyl 5-methyl hexyl and C11-18 alkyl 60 groups. Also included are aralkyl groups, e.g., benzyl, alpha- or beta-phenylethyl, alpha-alpha dimethyl benzyl and the like. Also included are cyclohexyl, cycloheptyl and the like.

Typical examples of substituted alkyl radicals are the 65 haloalkyl radicals which can be represented by the structure:

$$C_nHal_{2n+1-m}H_mC(Hal)_2C$$
 70

where Hal refers to a halogen, m is less than or equal to 2n+1 and n may have any value from 0 to 18, and R_6 and R_7 can be hydrogen, halogen or alkyl radicals. Pre- 75

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ferred radicals are those where Hal is fluoro and include those represented by the following formulas:

o representation by the reme	
\mathbf{R}_{0}	\mathbf{R}_{6}
CF₃C—	CF₃CF₂Ċ—
Ŕ ₇	Ř,
R ₆	Re CR. (CR.)
CF₃CH₂Ċ—	CF ₃ (CF ₂) ₂ Ċ—
${f R_7}$	${f R_f}$
$CF_3(CF_2)_3C$	CF ₃ (CF ₂) ₄ C—
R,	$egin{array}{cccccccccccccccccccccccccccccccccccc$
${f R_0}$	\mathbf{R}_{0}
CF ₃ (CF ₂) ₅ C	CF3(CF2)6 C-
R ₇	$\mathbf{R}_{\mathbf{J}}$
R ₆	$\mathbf{R_6}$
CF ₃ (C₂H₅)C→	$\mathbf{CF_3}(\mathbf{C_3H_7})\mathbf{C}$ —
R_{δ}	\mathbf{R}_{0}
CF₃(C₄H₀)Ċ—	CF ₃ (C ₅ H ₁₁)C—
${f R_6}$	$\mathbf{R}_{f 0}$
CF ₃ (C ₆ H ₁₃)C—	CF3(C7H15)C-
\mathbf{R}_{0}	${f R_6}$
C F ₃ (C ₈ H ₁₇) C—	$\mathbf{CF_4CF_2}(\mathbf{C_2H_5})\mathbf{C}$
\mathbf{R}_{6}	$\mathbf{R}_{f 6}$
$\mathbf{CF_3CF_2(C_3H_7)C}$	CF ₂ CF ₂ (C ₄ H ₉)C-
$ m R_{6}$	${f R_6}$
CF ₃ CF ₂ (C ₅ H ₁₁)C-	CF3CF2(C6H13) C-
\mathbf{R}_{0}	$ m R_{6}$
CF2(C6H15)C-	CF ₃ CF ₂ (C ₈ H ₁₇) C—
$\mathbf{R_6}$	\mathbf{R}_{6}
CF ₂ (CF ₂) ₂ (C ₂ H ₅)C—	CF3(CF2)2(C3H7)C-
. R $_{6}$.	${f R_6}$
CF2(CF2)2(C4H2)C-	CF ₃ (CF ₂) ₂ (C ₅ H ₁₁)C—
$\mathbf{R_{b}}$	$\mathbf{R_6}$
CF ₃ (CF ₂) ₂ (C ₆ H ₁₃)C-	CF ₃ (CF ₂) ₂ (C ₇ H ₁₅)C—
$\mathbf{R_4}$	R ₆
CF ₃ (CF ₂) ₂ (C ₈ H ₁₇)C—	CF ₁ (CF ₂) ₃ (C ₂ H ₅) C—
R ₆	R ₆
CF ₃ (CF ₂) ₃ (C ₃ H ₇)C—	CF ₃ (CF ₂) ₂ (C ₄ H ₉) C
R ₆	
CF ₃ (CF ₂) ₃ (C ₅ H ₁₁)C—	CF ₃ (CF ₂) ₃ (C ₆ H ₁₃)C—
R ₆	
CF3(CF2)3(C7H15)C-	CF ₃ (CF ₂) ₃ (C ₈ H ₁₇)C—
CF ₃ (CF ₂) ₄ (C ₂ H ₅)C—	R ₆ CF ₃ (CF ₂) ₄ (C ₃ H ₇) C—
	and the state of the state of the state of
$\mathbf{C}\mathbf{F_3}(\mathbf{C}\mathbf{F_2})_4(\mathbf{C_4H_0})\mathbf{C}$	R ₆
المكاري الراق المسامري الروسية أراكا أأراجيك	$C F_3 (C F_2)_4 (C_5 H_{11}) C -$
R ₆	R ₀
CF ₃ (CF ₂) ₄ (C ₆ H ₁₃) Ċ—	CF ₃ (CF ₂) ₄ (C ₇ H ₁₅) Ċ
R ₆	R ₆
C F ₃ (C F ₂) ₄ (C ₈ H ₁₇) C—	$C F_3 (C F_2)_5 (C_2 H_5) \dot{C}$ —
R 6	$\mathbf{R_6}$
CF ₃ (CF ₂) ₅ (C ₃ H ₇) C	CF3(CF2)5(C4H9)C-
$\mathbf{R_0}$	R ₆
CF3(CF2)5(C5H11)C-	CF3(CF2)5(C6H13)C-

CF3C(C3H7)2-CF3C(CH3)2-CF3C(C2H5)2-

where R₆ and R₇ have their aforedescribed significance. The halogenated alkyl radicals can be primary, second-

Other suitable fluorine-containing radicals include 10 resented by the general structure: fluorinated alkoxyalkyl radicals particularly those represented by the following formulas:

where R₆ and R₇ have their aforedescribed significance. It is also contemplated within the scope of the invention

that the hydrogen and the fluorine in the previously described haloalkyl radicals can be replaced by other halo-

gens, such as chlorine or bromine.

Typical examples of aryl and substituted aryl radicals are phenyl, cresyl, xylyl, halogenated phenyl, alkoxylated phenyl, cresyl and xylyl in which the available hydrogen 55 on the aryl or substituted aryl is partially or totally replaced by a halogen, o-, m- and p-trifluoromethylphenyl, o-, m- and p-2,2,2-trifluoroethylphenyl, o-, m- and p-3,3,3trifluoropropylphenyl and o-, m-, and p-4,4,4-trifluorobutylphenyl. Also included are isopropyl phenyl, butyl 60 phenyl, alpha-alkylbenzylphenyl and alpha,alpha-dialkylbenzylphenyl, e.g. alpha-methylbenzylphenpl, alpha,alpha dimethylbenzyl phenyl.

The orthosilicates useful as base stocks include the tetraalkyl orthosilicates such as tetra(octyl)orthosilicates, tetra 65 (2-ethylhexyl)orothosilicates and the tetra(isooctyl) orthosilicates and those in which the isooctyl radicals are obtained from isooctyl alcohol which is derived from the oxo process, and the (trialkoxysilico)trialkyl orthosolicates, otherwise referred to as hexa(alkoxy) disiloxanes, 70 such as hexa(2-ethylbutoxy) disiloxane and hexa(2-ethyl-

hexoxy) disiloxane.

The preferred tetraalkyl orthosilicates and hexa(alkoxy) disiloxanes are those in which the alkyl or alkoxy radicals have from 4 to 12 carbon atoms and in which 75 substituted aryl radicals are given above.

the total number of carbon atoms in the orthosilicate is from 16 to 60.

In addition to the hexa(alkoxy) disiloxanes referred to above, other hexa(alkoxy) disiloxanes can be used in which the aliphatic radical of the alkoxy groups are for example, 1-ethylpropyl, 1,3-dimethylbutyl, 2-methylpentyl, 1-methylhexyl, 1-ethylpentyl, 2-butylhexyl and 1-methyl-4-ethyloctyl.

The orthosilicates and alkoxy polysiloxanes can be rep-

$$R_{S}-O-S_{1}-O-X-(O)_{m}$$
 R_{10}
 R_{11}
 $O-X-(O)_{m}$
 R_{12}
 R_{12}

wherein R₈, R₉ and R₁₀ each can be alkyl, substituted 20 alkyl, aryl, substituted aryl and can be identical or different with respect to any other radical, O is oxygen, Si is silicon, X is a member of the group consisting of carbon and silicon, m is a whole number having a value of 0 or 1, n is an integer having a value of from 1 to 25 about 200 or more and when X is carbon, m is 0, n is 1 and R_{11} , R_{12} and R_{13} each can be hydrogen, alkyl, substituted alkyl, aryl and substituted aryl radicals and when X is silicon m is 1, n is an integer having a value of from 1 to about 200 or more and R_{11} , R_{12} and R_{13} each can 30 be alkyl, substituted alkyl, aryl and substituted aryl.

Typical examples of substituted aryl radicals are o-, mand p-chlorophenyl, o-, m- and p-bromophenyl, o-, mand p-fluorophenyl, alpha,alpha,alpha-trichlorocresyl, alpha,alpha,alpha-trifluorocresyl, xylyl and o-, m- and pcresyl. Typical examples of alkyl and haloalkyl radicals

are those heretofore described.

The siloxanes or silicones useful as base stocks are represented by the general structure:

wherein R₁₄, R₁₅, R₁₆, R₁₇, R₁₈ and R₁₉ can each be alkyl, substituted alkyl, aryl and substituted aryl radicals and nis a whole number from about 0 to about 2000 or more. Typical examples of alkyl and haloalkyl radicals are those heretofore described. Typical examples of the siloxanes are poly(methyl)siloxane, poly(methyl, phenyl)siloxane, poly(methyl, chlorophenyl)siloxane and poly(methyl, 3,3,3-trifluoropropyl)siloxane.

Typical examples of substituted aryl radicals and o-, m- and p-chlorophenyl, o-, m- and p-bromophenyl, o-, mand p-fluorophenyl, alpha, alpha, alpha-trichlorocresyl, alpha,alpha,alpha-trifluorocresyl, o-, m- and p-cresyl and

xylyl.

Dicarboxylic acid esters which are suitable as base stocks are represented by the structure:

wherein R_{20} and R_{22} are each selected from the group consisting of alkyl, substituted alkyl, aryl and substituted aryl and R₂₁ is a divalent radical selected from the group consisting of alkylene and substituted alkylene, and are prepared by esterifying dicarboxylic acids such as adipic acid, azelaic acid, suberic acid, sebacic acid, hydroxysuccinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, 2,2-dimethyl heptanol, 1-methyl cyclohexyl methanol, etc.

Typical examples of alkyl, aryl substituted alkyl and

Polyesters which are suitable as base stocks are represented by the structure:

wherein R₂₃ is selected from the group consisting of hydrogen and alkyl, R24 and R25 are each selected from the group consisting of alkyl, substituted alkyl, aryl and substituted aryl, a is a whole number having a value of 0 to 1, Z is a whole number having a value of 1 to 2 and when Z is 1, R₂₆ is selected from the group consisting of hydrogen, alkyl acyloxy and substituted acyloxy and when Z is 2, R_{26} is oxygen, and are prepared by esterifying such polyalcohols as pentaerythritol, dipentaerythritol, trimethylolpropane, trimethylolethane and neopentyl glycol with such acids as propionic, butyric, isobutyric, n-valeric, caproic, n-heptylic, caprylic, 2-ethylhexanoic, 2,2-dimethylheptanoic and pelargonic. Typical examples of alkyl, substituted alkyl, aryl and substituted aryl radicals are given above.

Other esters which are also suitable as base stocks are the mono esters.

Another class of base stocks which are suitable as base stocks for this invention are represented by the structure:

$$X$$
 A_3
 A_3
 A_3

wherein A, A₁, A₂, and A₃ are each a chalcogen having an atomic number of 8 to 16, X, X₁, X₂, X₃ and X₄ each are selected from the group consisting of hydrogen, alkyl, haloalkyl, halogen, arylalkyl and substituted arylalkyl m, n and o are whole numbers, each having a value of 0 50 to 8 and a is a whole number having a value of 0 to 1 provided that when a is 0, n can have a value of 1 to 2. Typical examples of alkyl and substuted alkyl radicals are given above. Typical examples of such base stocks are 2to 7-ring ortho-, meta- and para-polyphenyl ethers and 55 mixtures thereof, 2- to 7-ring ortho-, meta- and para-polyphenyl thioethers and mixtures thereof, mixed polyphenyl ether-thioether compounds in which at least one of the chalcogens represented by A, A1, A2 and A3 is dissimilar with respect to any one of the other chalcogens, dihalogen- 60 ated diphenyl ethers, such as 4-bromo-3'-chlorodiphenyl ethers and bisphenoxy biphenyl compounds and mixtures thereof.

Hydrocarbon oils including mineral oils derived from petroleum sources and synthetic hydrocarbon oils are 65 suitable base stocks. The physical characteristics of functional fluids derived from a mineral oil are selected on the basis of the requirements of the fluid systems and therefore this invention includes as base stocks mineral oils having a wide range of viscosities and volatilities such 70 as naphthenic base, paraffinic base and mixed base mineral oils.

The synthetic hydrocarbon oils include but are not limited to those oils derived from oligomerization of

alpha olefins of from 4 to 20 carbon atoms by acid catalyzed dimerization and by oligomerization using trialuminum alkyls as catalysts.

Chlorinated biphenyls are also useful as base stocks. It is also contemplated within the scope of the invention that mixtures of two or more of the aforedescribed base stocks can be utilized as base stocks.

The fluid compositions of this invention when utilized as a functional fluid can also contain acid acceptors, dyes 10 pour point depressants, antioxidants, antifoam agents, viscosity index improvers such as polyalkyl acrylates, polyalkyl methacrylates, polycyclic polymers, polyurethanes, polyalkylene oxides and polyesters, lubricity agents, water and the like. Particularly desirable combinations of base stocks as well as additives are set forth in Belgian Patent No. 728,309, which is hereby incorporated by reference.

It is also contemplated that the base stocks as aforementioned can be utilized singly or as a fluid composition containing two or more base stocks in varying proportions. The base stocks can also contain other fluids which include, in addition to the functional fluids, desired fluids derived from coal products, synthetics, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and mixtures thereof), alkylene oxide type polymers (e.g., propylene oxide polymers), and derivatives including alkylene oxide polymers prepared by polymerizing the alkylene oxide in the presence of water or alcohol, e.g., ethyl alcohol, alkyl benzenes, e.g., monoalkyl benzene such as dodecyl benzene, tetradecyl benzene, etc.) and dialkyl benzene (e.g., n-nonyl 2-ethyl hexyl benzene); polyphenols, (e.g., biphenyls and terphenyls), halogenated benzene, halogenated lower alkyl benzene and mono-halogenated diphenyl ethers.

However, in the preferred form of the present invention, the phosphonium composition of the present invention is combined with a phosphate functional fluid base stock. The base stock will consist primarily of trialkylphosphates being present in amounts from 50 to 90% by weight and preferably from 65 to 75% by weight. The trialkylphosphates which give optimum results are those wherein each of the alkyl group contains from 3 to 12 carbon atoms, preferably from 4 to 9 carbon atoms. The alkyl groups should be of a straight chain configuration. A single trialkyl phosphate may contain the alkyl group in all three positions or may possess a mixture of different alkyl groups. Mixtures of various trialkyl phosphates can be used. Suitable species of trialkyl phosphates which may be employed as the base stock composition include tripropyl phosphates, tributyl phosphates, trihexyl phosphates, trioctyl phosphates, dipropyl octyl phosphates, dibutyl octyl phosphates, dipropyl hexyl phosphate, dihexyl octyl phosphate, dihexyl propyl phosphate, and propyl butyl octyl phosphate.

The trialkyl phosphates can be combined with at least one triaryl phosphate comprising tricresyl phosphate, trixylenyl phosphate, ethyl phenyl dicresyl phosphate or isopropylphenyl diphenyl phosphate, phenyl-bis (4-alphamethylbenzylphenyl) phosphate. In one preferred embodiment, tricresyl phosphate and trixylenyl phosphate are employed. The triaryl phosphates in this instance function as a thickener for the trialkyl phosphates. Thus, the amount of tricresyl phosphate may range between 0 and 25% by weight while the trixylenyl phosphate may range between 0 and 25% by weight. The preferred range of the triaryl phosphates will be from 5 to 15% tricresyl phosphate and from 5 to 15% by weight trixylenyl phosphate. The combined mixture of tricresyl phosphate and trixylenyl phosphate are blended together to provide a viscosity of between 145 and 230 Saybolt Universal Seconds measured at 100° F. This blend of materials can then be combined with a trialkyl phosphate in any known manner.

A conventional polymeric material is then blended with a mixture of trialkyl phosphate and triaryl phosphate maolefins such as polybutenes and oils derived from high 75 terial which functions as a viscosity index improver. The 9

polymeric material suitable with the present invention can be a mixture of from 10 to 55% by weight polymethacrylates, polyacrylates, each containing an alkyl moiety having from 1 to 20 carbon atoms. The polymeric materials may be within a solvent carrier such as di-2-ethylhexyl sebacate, dioctyl adipate, di-2-ethyl hexyl adipate, or other conventional carriers. The polymeric materials may be any combination of these materials. This material is thoroughly blended with a combination of ingredients to form a uniform material. The amount of material incorporated 10 therein may range between 5 and 20% by weight.

Thereafter, a rust inhibitor with a solvent carrier, such as an alkyl succinate acid and their derivatives, is blended with the material. This latter material can be present in amounts between 0.01 and 0.5% by weight. Thereafter, a corrosion inhibitor such as benzotriazole, quinizarin or the like in an amount ranging between 0.001 and 0.5% by weight is added to the mixture and thoroughly blended therewith. Then, a dye which may range between 5 and 20 parts per million is added thereto and blended therewith in a conventional manner. As is conventional, a silicone antifoaming agent is added thereto and can be present in an amount ranging between 5 and 50 parts per million.

This invention can be better appreciated by the following non-limiting examples:

Example 1

A base stock material consisting of tricresyl phosphate in an amount of 10.45 weight percent is thoroughly 30 blended with 8.55 weight percent of trixylenyl phosphate to attain a viscosity of 155 Saybolt Universal Seconds measured at 100° F. This blend of materials is blended with 68.96 weight percent of tributyl phosphate until the materials are thoroughly intermixed. Thereafter, 12 35 weight percent of a mixture of about 40% of a polyalkyl methacrylate and about 60% di-2-ethyl hexyl sebacate solvent carrier are thoroughly blended therewith. 3,4epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate is blended into the mixture at an additive level of 1.0% by 40 weight. A conventional alkyl succinic acid rust inhibitor in an amount of 0.02 weight percent within a solvent carrier is blended therewith. Then, 0.02 weight percent of benzotriazole is thoroughly blended therewith along with a conventional dye and antifoam agent in an amount of 45 10 parts per million and 15 parts per million, respectively. Thereafter, trioctylmethylphosphonium dimethyl phosphate is blended into the mixture at various additional levels including 5%, 3%, 1.0% and 0.5% by weight.

The compositions described in Example 1 as well as 50 other compositions were tested in the apparatus hereinafter described.

The apparatus is a modified Boeing wear apparatus designed to simulate the constricted flow in the servo valve of an aircraft hydraulic system. The apparatus consists of an air-driven piston-type hydraulic pump, accumulator, filter, flow meter, heat exchanger, reservoir and wear device. The wear device is constructed of 52100 steel hardened to R_c62. The fluid enters the device through a 0.085 inch I.D. nozzle at 2500 p.s.i.g. and 0.15 g.p.m. and impinges on a flat plate 0001 inch from the noozle The wear device is disassembled after 24 test hours and the amount of wear on the flat plate is visually estimated with the naked eye and with the aid of a microscope The results are as follows:

PERCENT METHYLTRIOCTYLPHOSPHONIUM DIMETHYL PHOSPHATE (1)

	Relative
Phosphate ester fluid (by wt.):	wear
None	
0.5	Minor.
1.0	Negligible.
3.0	Do.
5.0	Do.

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The above results illustrate the utility of methyltrioctylphosphonium dimethylphosphate to reduce the wear characteristics of a phosphate ester hydraulic ffuid and thereby inhibit damage to hydraulic systems.

Examples 2-16

Typical phosphonium compounds 2 through 16 hereinabove described when incorporated in the phosphate ester base stock of Example 1 also reduce the wear characteristics of the fluid.

In addition to use in aircraft hydraulic fluids, the phosphonium compounds described herein are useful in a wide range of lubricant compositions. The term "lubricant" as employed herein is intended to include fluids employed primarily for their lubricity as well as those employed as pressure transmission agents. The phosphonium compounds are useful as extreme pressure additives in fluids including aircraft gas turbine lubricants, as additives in fire-resistant industrial lubricants including gear and cutting oils and in brake fluids.

What is claimed is:

1. A hydraulic fluid which comprises:

- (1) a major amount of a base stock material selected from the group consisting of the esters and amides of an acid of phosphorus, mineral oils, synthetic hydrocarbon oils, orthosilicates, alkoxy polysiloxanes, silicones, polyphenyl ethers, polyphenyl thioethers, chlorinated biphenyls, esters of dicarboxylic acids and monohydric alcohols, esters of monocarboxylic acids and monohydric alcohols, esters of monocarboxylic acids and polyhydric alcohols, and mixtures thereof, polyalkylene ether alcohols and esters thereof, and
- (2) a wear inhibiting amount of a phosphonium compound in accordance with the formula:

where R, R' and R" each represent alkyl, aryl, alkaryl and aralkyl groups containing from 1 to 10 carbon atoms, and R" represents alkyl or aralkyl groups containing from 1 to 10 carbon atoms, X represents an oxygen or sulfur atom, and Y' and Y" represent lower alkoxy, lower alkyl, phenyl lower alkylphenyl, phenyl lower alkyl, phenoxy and lower alkylphenoxy, and Z represents oxygen.

2. A composition in accordance with claim 1 wherein said base stock material is selected from the group of esters and amides of an acid of phosphorus having the formula:

$$\begin{array}{c}
O \\
P - (Y_1)_c - P_2 \\
(Y_2)_b \\
\downarrow
\end{array}$$

wherein Y is selected from the group consisting of oxygen, sulfur and

 \mathbf{Y}_1 is selected from the group consisting of oxygen, sulfur and

Y₂ is selected from the group consisting of oxygen, sulfur

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R, R₁, R₂, R₃, R₄ and R₅ are each selected from the group consisting of alkyl, aryl, substituted aryl and substituted 75 alkyl; and a, b and c are whole numbers having a value

of 0 to 1 such that the sum a+b+c has a value from 1 to 3

3. A composition in accordance with claim 2 wherein said ester of an acid of phosphorus is a trialkyl phosphate.

4. A composition in accordance with claim 2 wherein said ester of an acid of phosphorus is a mixture of tri-

alkyl phosphates and triaryl phosphates.

5. A composition in accordance with claim 4 wherein said trialkyl phosphates are present in an amount between 10 about 50 and about 90% by weight and said triaryl phosphates are present in an amount up to about 50% by weight.

6. A composition in accordance with claim 4 containing a viscosity index improver admixed therewith, said 15 viscosity index improver being selected from the group consisting of polymethacrylates and polyacrylates.

7. A composition in accordance with claim 1 wherein said phosphonium compound is present in an amount be-

tween about 0.1% and about 10% by weight.

8. A composition in accordance with claim 1 wherein said phosphonium compound is present in an amount between about 0.5% and 2.0% by weight.

9. A composition in accordance with claim 1 containing an alkyl succinate rust inhibitor admixed therewith.

10. A composition in accordance with claim 1 containing a corrosion inhibitor admixed therewith, said corrosion inhibitor being selected from the group consisting of benzotriazole and quinizarin.

11. A composition in accordance with claim 10 where-

in said corrosion inhibitor is benzotriazole.

12. A composition in accordance with claim 1 containing a 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate acid acceptor.

13. A composition in accordance with claim 2 con- 35 taining a dye and a silicone antifoaming agent admixed therewith.

14. The composition of claim 1 wherein Y' and Y" are selected from the group consisting of lower alkyl and phenyl.

15. The composition of claim 1 wherein said phosphonium compound is methyltrioctylphosphonium di-

methyl phosphate.

16. A method of operating a hydraulic pressure device wherein a displacing force is transmitted to a displaceable member by means of a hydraulic fluid comprising a major amount of base stock material selected from the group consisting of the esters and amides of an acid of phosphorus, mineral oils, synthetic hydrocarbon oils, ortho-

silicate, alkoxy polysiloxanes, silicones, polyphenyl ethers, polyphenyl thioethers, chlorinated biphenyls, esters of dicarboxylic acids and monohydric alcohols, esters of monocarboxylic acids and monohydric alcohols and esters of monocarboxylic acids and polyhydric alcohols and mixtures thereof, polyalkylene ether alcohols and esters thereof, and a wear inhibiting amount of a phosphonium compound in accordance with the formula:

$$\begin{bmatrix} \mathbf{R}' \\ \mathbf{R} - \mathbf{P} - \mathbf{R}'' \\ \mathbf{R}''' \end{bmatrix} \oplus \begin{bmatrix} \mathbf{X} & \mathbf{Y}' \\ \mathbf{Z} - \mathbf{P} & \mathbf{Y}'' \end{bmatrix} \ominus$$

where R, R' and R" each represent alkyl aryl, alkaryl or aralkyl group containing from 1 to 10 carbon atoms, and R" represents alkyl or aralkyl groups containing from 1 to 10 carbon atoms, X represents oxygen or sulfur, Y' and Y" represent lower alkoxy, lower alkyl, phenyl, lower alkylphenyl, phenyl lower alkyl, phenoxy and lower alkylphenoxy, and Z represents oxygen.

17. The method of claim 16 wherein said phosphonium compound is methyltrioctylphosphonium dimethyl phos-

phate.

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U.S. Cl. X.R.

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