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**FUNCTIONAL FLUID COMPOSITIONS**

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10 Claims

**ABSTRACT OF THE DISCLOSURE**

Functional fluid compositions having the ability to inhibit and control damage to mechanical members in contact with such compositions are described. These compositions comprise certain functional fluid base stocks and an amount of an organosilicon compound sufficient to inhibit and control damage.

This invention relates to functional fluid compositions having an ability to inhibit and control damage to mechanical members in contact with said fluid compositions, to functional fluid compositions which exhibit an improved tendency to resist fluid degradation and more particularly to compositions comprising certain functional fluids and an additive amount, sufficient to inhibit and control damage, of an organo silicon compound.

Many different types of materials are utilized as functional fluids and functional fluids are used in many different types of applications. Thus, such fluids have been used as electronic coolants, atomic reactor coolants, diffusion pump fluids, lubricants, damping fluids, bases for greases, power transmission and hydraulic fluids, heat transfer fluids, heat pump fluids, refrigeration equipment fluids and as filter mediums for air conditioning systems. In many of these uses there have been reports of damage to the fluid during use and to mechanical members, especially metallic members, in contact with the fluid as evidenced by a loss of weight of such members. Thus, damage has been reported in aircraft hydraulic systems, gas turbine bearings, jet turbine control systems, steam turbine bearings and steam turbine control systems. Damage has also been observed on such materials as glass, Teflon, Mylar, Plexiglas and members constructed from materials other than metals.

One particularly undesirable condition which exists during the use of a functional fluid and which can cause damage is cavitation, which can be described as a phenomenon which results in the formation and subsequent violent collapse of vapor-filled bubbles in a fluid subjected to requisite pressure changes. Bubbles can be formed when the fluid is at or below its bubble point pressure; above this pressure they collapse. Pressure changes sufficient to cause cavitation can occur in several ways; for example, a fluid flowing through a restriction, such as a partially closed valve, can encounter at the point of highest velocity a pressure far lower than both the bubble point and the valve outlet pressures. As the bubbles reach a point of higher pressure, a violent collapse occurs thereby producing shock waves which can be severe enough to damage the fluid and mechanical members in contact with the fluid. As another example, cavitation conditions can occur when a surface is moved through or vibrated in a relatively stagnant liquid.

While there are many undesirable results caused by damage, one important aspect of the problem of damage is the effect on hydraulic systems and fluids experiencing such damage. For example, the structural mechanical parts in a hydraulic system, such as pumps and valves, exhibit a marked decrease in strength, and the geometry of the parts is altered. Such changes in the case of pumps can cause a decrease in pumping efficiency and in the case

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of valves can cause faulty operations, excessive leakage or even hazardous conditions. As a result, damage necessitates premature overhaul of mechanical parts which is both costly and time consuming. In addition, as damage occurs the metal from metallic mechanical parts in contact with the functional fluid contaminates the fluids requiring premature draining of the fluids from the system, filter clogging and excessive filter replacement, and can cause a change in physical and chemical properties of the fluids. Also, metal contaminants can reduce the oxidative stability of a fluid thereby adversely affecting fluid performance. In addition to any effects resulting from contamination by metal (or other) contaminant, such damage to the fluid manifests itself in numerous ways, among which are (a) viscosity change, (b) increase in acid number, (c) formation of precipitants, (d) increase in chemical reactivity and (e) discoloration.

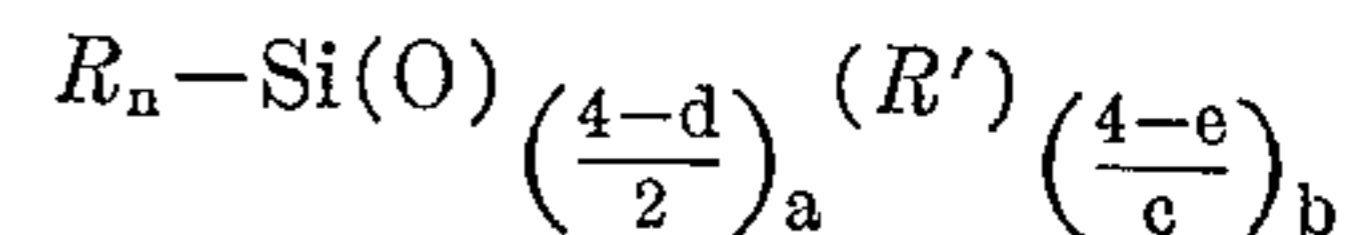
It is, therefore, an object of this invention to provide functional fluid compositions having an ability to inhibit and control damage.

It is a further object of this invention to provide functional fluid compositions having an ability to inhibit and control damage and retain the critical properties of the functional fluid used to provide such compositions.

Further objects will be apparent from the following description of the invention.

It has now been found that damage, herein defined to include damage to a functional fluid and to mechanical members in contact with said fluid, can be effectively controlled and inhibited in the many functional fluid systems described by the incorporation of an organo silicon compound, said organo silicon compound being selected from

(A) an organo silicon compound represented by the formula



wherein each R is independently selected from the group consisting of hydrogen, hydroxyl and a monovalent hydrocarbon-containing group, R' is selected from the group consisting of R and a divalent hydrocarbon-containing group, n is a number having a value of from 1 to 3, a and b are each whole numbers having a value of 0 to 1 and c is a whole number having a value of 1 to 2 provided that c is 1 only when R' is R and a is 0, d and e are each numbers having a value of 1 to n provided that the sum of d+e is equal to n and provided that the total of R+R' which are hydrogen and hydroxyl does not exceed 25% of the sum of the groups represented by R+R', and

(B) mixtures thereof.

It is an important part of this invention that the incorporation of an organo silicon compound in a functional fluid produce a functional fluid composition having the ability to inhibit and control damage without adversely affecting the other critical properties of such fluids such as viscosity, oxidative and thermal stability, corrosion resistance in the presence of metal parts and lubricating qualities of the functional fluid.

The functional fluids, to which an organo silicon compound is added to provide the compositions of this invention, hereinafter referred to as base stocks, include, but are not limited to, esters and amides of an acid of phosphorus, hydrocarbon materials including both hydrocarbon materials derived from petroleum sources and synthetic hydrocarbon oils, ether compounds which include polyphenyl ether compounds, polyphenyl thioether compounds, mixed polyphenyl ether-thioether compounds, phenoxybiphenyl compounds, phenylmercaptobiphenyl compounds, mixed phenoxyphenylmercaptobiphenyl compounds and the above ether compounds in which part or all of the phenyl

and phenylene rings are replaced with cyclic rings other than phenyl or phenylene, such as an alicyclic group, as for example, cyclohexyl, or a heterocyclic group such as thiophene, thiazole, morpholine or pyridine, mono- and dialkylthiophenes, chlorinated biphenyl, monoesters, di- and tricarboxylic acid esters, esters of polyhydric compounds, complex esters and mixtures thereof.

The concentration of an organo silicon compound in the functional fluid is adjusted in terms of the particular system and the functional fluid which is utilized in this system to provide functional fluid compositions of this invention which contain additive amounts of an organo silicon compound sufficient to inhibit and control damage. Thus, it has been found that the additive response, that is, the concentration of an organo silicon compound required to inhibit and control damage, of a base stock varies according to the base stock or blends of base stocks. Thus, for the base stocks of this invention the concentration of an organo silicon compound is from about 0.01 volume percent to about 15 volume percent, the particular concentration being that amount which will effectively inhibit and control damage. The preferred additive concentration is from about 0.025 volume percent to about 5 volume percent of an organo silicon compound, although 0.01 volume percent to about 10 volume percent have been found satisfactory and effective to inhibit and control damage. Therefore, included within the present invention are compositions comprising a functional fluid and a damage-inhibiting amount of an organo silicon compound, that is, an organo silicon compound is added, in a concentration sufficient to control and inhibit damage. The functional fluid compositions of this invention can be compounded in any manner known to those skilled in the art for the incorporation of an additive into a base stock as for example by adding an organo silicon compound to the base stock with stirring until a fluid composition is obtained or a polymeric organo silicon compound can be prepared by polymerization of at least one monomer in the base stock.

The fluid compositions of this invention having incorporated therein an organo silicon compound can be fluid compositions wherein the organo silicon compound can be fluid compositions wherein the organo silicon compound is present at a concentration which is above the solubility limits of the organo silicon compound. Thus, the fluid compositions of this invention contemplate that the organo silicon compound can be present in a state other than a completely soluble state such as suspension or dispersion, and these fluid compositions are contemplated within the scope of this invention. The preferred organo silicon compounds are those organo silicon compounds which are not totally miscible with the base stock at all concentrations. Thus, the organo silicon compound can be present at a concentration below and greater than the solubility of that particular organo silicon compound in the base stock. Although it is preferred to use organo silicon compounds which are not completely soluble in the base stock, organo silicon compounds which are completely soluble in a base stock have been found to be effective and such fluid compositions incorporating completely soluble organo silicon compounds are contemplated within the scope of this invention.

The terms "monovalent hydrocarbon-containing group" and "divalent hydrocarbon-containing group" are herein defined to include hydrocarbons which contain only carbon and hydrogen and also hydrocarbons which contain other elements in addition to carbon and hydrogen. As herein defined, a mono- and divalent hydrocarbon-containing group which contains carbon and hydrogen as well as carbon, hydrogen and other elements includes hydrocarbons which are unsaturated as well as completely saturated. Thus, the term "hydrocarbon-containing group," in addition to hydrocarbons containing only carbon and hydrogen, include hydrocarbons containing one or more elements other than carbon and hydrogen, which elements

can be substituted upon a hydrocarbon-containing group or can link two or more hydrocarbon-containing groups. It is also contemplated that a hydrocarbon-containing group can contain substitution and linkage by more than one element.

The term "monovalent hydrocarbon-containing group" can be defined by the number of carbon atoms in each R group based upon the practical problem of obtaining a concentration of an organo silicon compound represented by (A) and (B) incorporated into a fluid without adversely affecting other fluid properties with a preferred upper limit of the number of carbon atoms of about 40, and more preferably up to about 20 carbon atoms per R group. The number of elements other than carbon and hydrogen which can be present is generally up to about 10 elements per R group and more preferably up to about 5 elements per R group. With respect to the divalent hydrocarbon-containing group, R', the number of carbon atoms in R' can vary over a wide range, there being at least one carbon atom in R'. The group R' embraces many types of divalent groups among which are polymeric materials such as polyalkylene oxides which can be linked to the silicon atom through an alkylene bridge. When R' is polymeric such organo silicon compounds include by way of example block polymers such as one block consisting of a polysiloxane and a second block which is linked to the polysiloxane being a polyalkylene oxide wherein the polyalkylene oxide is linked to a silicon atom through an alkylene bridge. As is apparent from the afore-described block polymer, the number of carbon atoms present wherein R' is polymeric can vary over a wide range since the molecular weight of R' is dependent on the degree of polymerization of the monomer which is used to prepare R'. In general, it is preferred that the total number of carbon atoms in R' be adjusted so that there is a preferred upper limit of about 120 carbon atoms per silicon atom and more preferably up to about 60 carbon atoms per silicon atom in the organo silicon compound. Therefore, the preferred upper limit of the number of carbon atoms in R' when there is present more than one silicon atom is obtained by multiplying the number of silicon atoms present in the organo silicon compound times 120, which product is the preferred upper limit of the total number of carbon atoms. The number of elements other than carbon and hydrogen which can be present in R' can vary over a wide range and the number of elements present is dependent on the type of divalent radical that is attached to the silicon atom, that is, R'. In general, there is a preferred upper limit of the number of elements present in R' other than carbon and hydrogen of about 25 elements per silicon atom and more preferably up to about 15 elements per silicon atom present in the organo silicon compound.

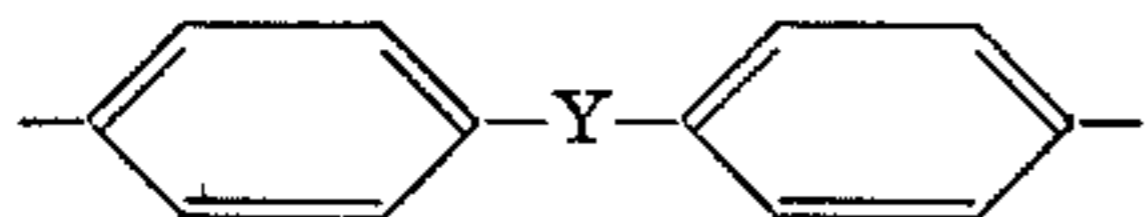
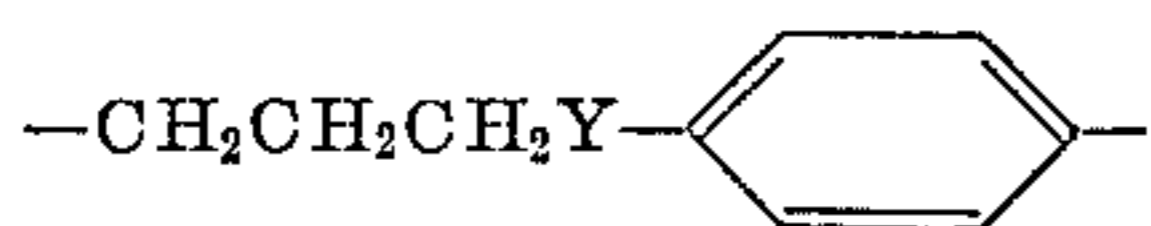
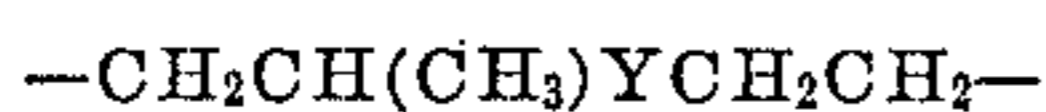
Typical examples of elements which the monovalent hydrocarbon-containing group represented by R can contain are nitrogen, oxygen, sulfur and halogen. Typical examples of elements which the divalent hydrocarbon-containing group represented by R' can contain are oxygen, nitrogen, phosphorus, sulfur, halogen, titanium, tin and aluminum. Thus, the mono- and divalent hydrocarbon-containing groups can contain by way of example oxy linkages, thio linkages, oxo groups such as aldehyde and ketone, nitrile, nitro, carboxyl, cyano, amide, hydro-sulfide and the like.

Typical examples of a "monovalent hydrocarbon-containing group" are alkyl, such as methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, octadecyl; alkenyl, such as propenyl, butenyl, heptenyl, dodecenyl and the like; cycloaliphatic, such as cyclopropyl, cyclobutyl, cyclohexyl, mono- and polymethyl cyclohexyl, mono- and polyisopropyl cyclohexyl, naphthenyl, cyclopentenyl, nonylcyclohexenyl and the like; aryl, herein defined to include mono-, di- and polynuclear hydrocarbons, such as phenyl, naphthyl and anthryl, typical examples of aryl being phenyl, alkylphenyl, xenyl, tert-amyl naphthyl, tolyl,

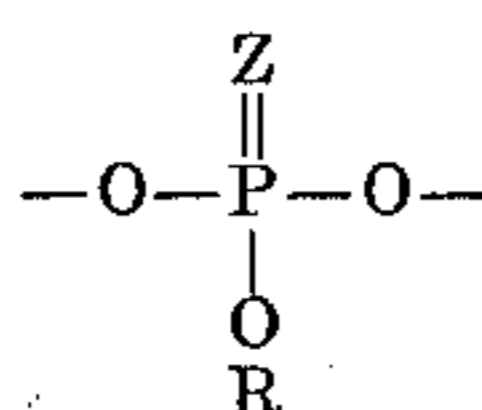
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cresyl, halogenated phenyl, o-, m- and p-2,2,2-trifluoroethylphenyl, o-, m- and p-3,3,3-trifluoropropylphenyl, o-, m- and p-4,4,4-trifluorobutylphenyl, alkylhydroxyphenyl, alkylchlorophenyl, alkylnitrophenyl, butylnitro naphthyl, cyclohexylphenyl, phenoxyphenyl, tert - butylphenoxyphenyl, aminophenyl and the like; aralkyl, such as benzyl, methylbenzyl, phenylethyl and the like; oxy-containing aliphatic, cycloaliphatic and aromatic radicals, such as alkoxy-substituted alkyl radicals, cycloalkoxy-substituted alkyl radicals, alkenoxy-substituted alkyl radicals, carboalkoxy alkyl radicals, aroxy-substituted alkyl radicals, alkoxy-substituted cyclohexyl, aroxy-substituted cyclohexyl, carboalkoxycycloalkyl radicals and the like; and heterocyclic group containing from 4 to 10 atoms optionally interrupted by from 1 to 4 hetero atoms, which can be nitrogen, sulfur or oxygen or combinations thereof, such as substituted and unsubstituted pyridyl and the like.

Typical examples of "divalent hydrocarbon-containing groups" are divalent hydrocarbon ether groups, ether herein defined to include oxy ether and thioether or combinations thereof, typical examples of which are

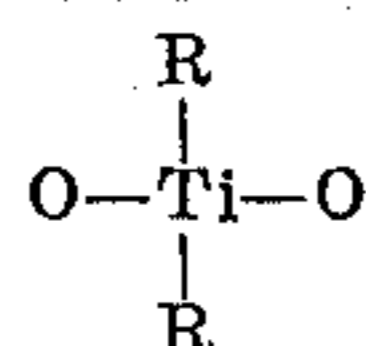


wherein Y can be oxygen or sulfur, and polymeric alkylene ethers which are linked to the silicon atoms by a carbon to silicon bond such as a polyoxyalkylene block wherein the alkylene block comprises alkylene groups of 2 to 3 carbon atoms wherein the ends of the polyoxyalkylene is linked to the silicon atoms through a carbon atom; divalent organo phosphorus groups, such as

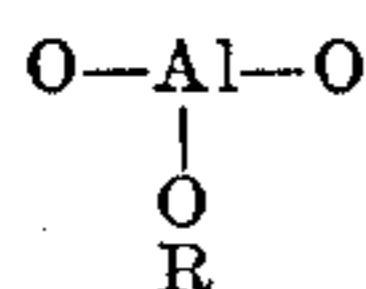


wherein Z can be oxygen or sulfur;

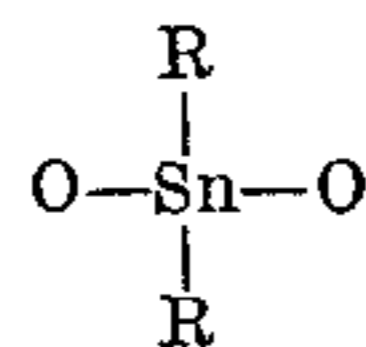
divalent oxytitanium groups, such as



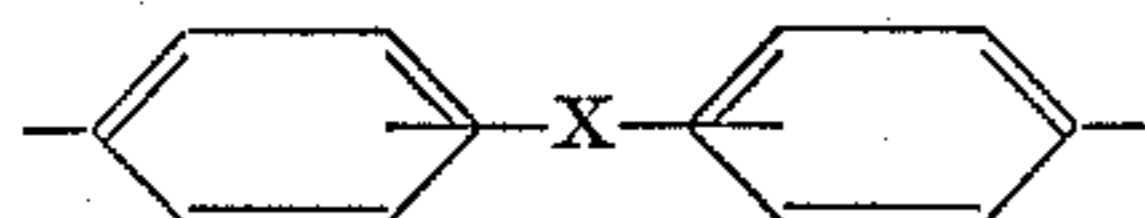
divalent oxyaluminum groups, such as



divalent oxytin groups, such as

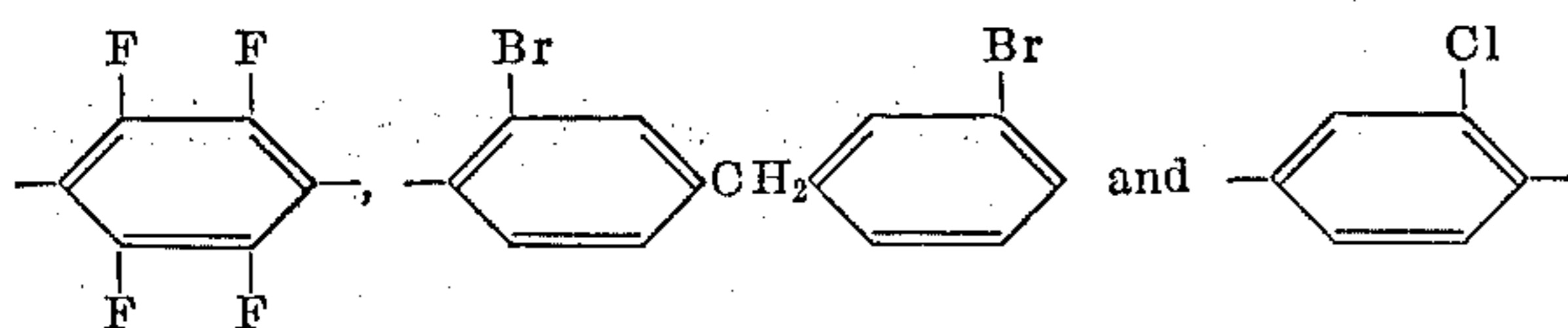


wherein R has its aforescribed significance; alkylene, such as methylene, ethylene, octadecylene, 2-methylethylene 2,2-dimethylethylene, 2-butenylene; divalent cycloaliphatic radicals, such as divalent cyclohexane; divalent aromatic radicals such as phenylene, biphenylene, naphthylene, xylene, tolylene and



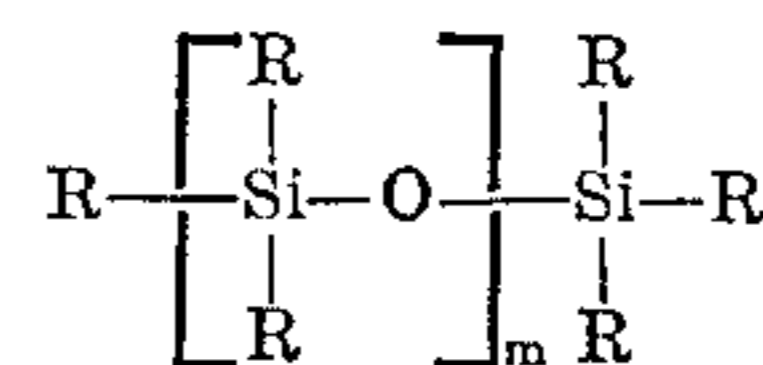
wherein X is alkylene;

and divalent haloarylene radical, typical examples of which are



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Typical examples of organo silicon compounds wherein (a) is 1 and (b) is 0 are organo polysiloxanes represented by the formula



wherein R is as aforescribed and  $m$  is a whole number having a value of 1 to 1000 or more.

Typical examples of polysiloxanes are those having molecular weights from about 160 to about 100,000. Particularly preferred polysiloxanes are those having average molecular weights of 200 to about 40,000. Such polysiloxanes generally have viscosities of about 1 to about 30,000 centistokes at 77° F. Typical examples of polysiloxanes are polydimethyl siloxanes having molecular weights ranging from 200 to 40,000, polyphenylmethyl siloxanes having phenyl to methyl ratios from 0.05 to 1.5 which in general have viscosity in centistokes at 77° F. of from about 40 to 700; polychlorophenylmethyl siloxanes having a viscosity in centistokes at 77° F. of 80; polymethyl-3,3,3-trifluoropropylphenyl siloxanes; polyethylmethyl siloxanes, polydiphenylmethyl and phenylmethyl siloxanes, copolymeric siloxanes, such as copolymers of dimethyl siloxane and diphenyl siloxane, terpolymers containing dimethyl siloxane units, diphenyl units and methylphenyl siloxane units, copolymers of dimethyl siloxanes and methyl- $\beta$ -cyanomethyl siloxane, and terpolymers containing dimethyl siloxane units, diphenyl siloxane units and methyl- $\beta$ -cyanoethyl siloxane units.

When  $m$  has a value of 1 the organo silicon compounds are disiloxanes, typical examples of which are hexamethyl, hexaethyl, hexapropyl and hexabutyl disiloxanes, hexachlorophenyl disiloxane, dimethyl tetraphenyl disiloxane, hexaphenyl disiloxane, tributyl triphenyl disiloxane, hexa(alkoxy) disiloxane, such as hexa-2-ethylbutoxy disiloxane and hexa-2-ethylhexoxy disiloxane. 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.

In addition to the polysiloxanes as described above, it is also contemplated within the scope of this invention that polycyclic siloxanes can be utilized as additives, a typical example of which is a cyclic dimethyl polysiloxane, such as octamethyl cyclotetrasiloxane.

Also useful as additives are ortho silicates, silanols and silanes, that is,  $a$  is equal to 0,  $b$  and  $c$  are 1,  $n$  is equal to 3 and  $R'$  is R, typical examples of which are alkoxy-silanes, such as trimethoxysilane, tributylloxysilane, trichlorophenoxysilane, diphenoxysilane and the like. Typical silanols useful in the compositions of this invention are trimethylsilanol, triphenylsilanol, trichloromethylsilanol, tributylsilanol, trichlorophenylsilanol and triethylsilanol. Typical examples of ortho silicates are tetraoctyl ortho-silicate, tetra-2-ethylhexyl ortho-silicate, tetraisooctyl ortho-silicate and those in which the isooctyl radicals are obtained from isooctyl alcohol which is derived from the oxo process and the like.

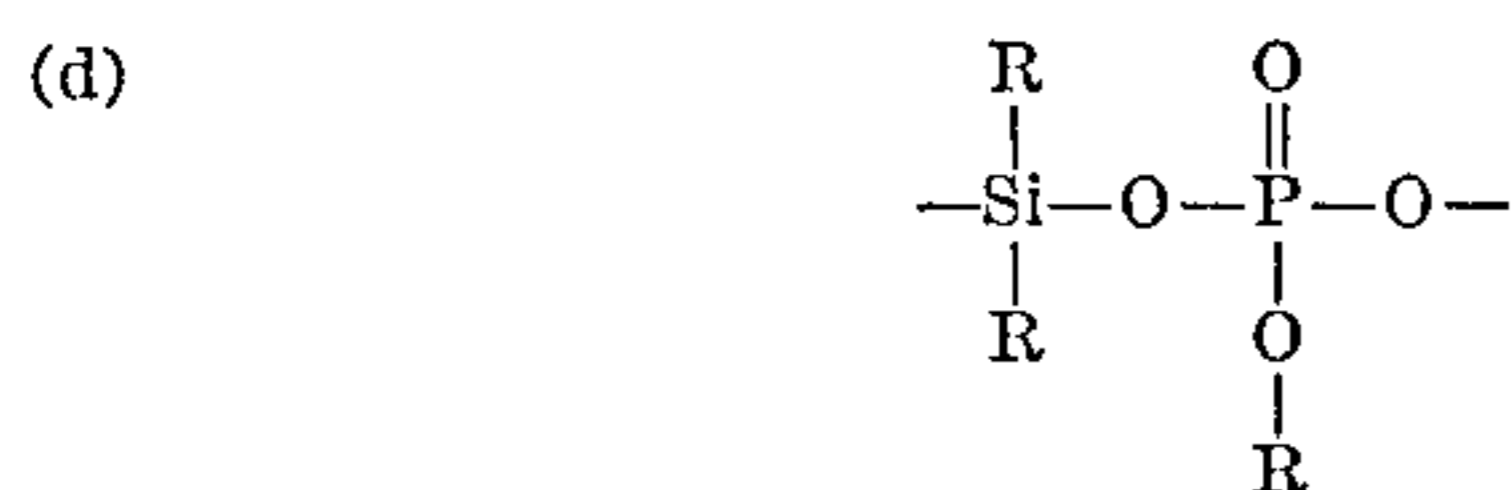
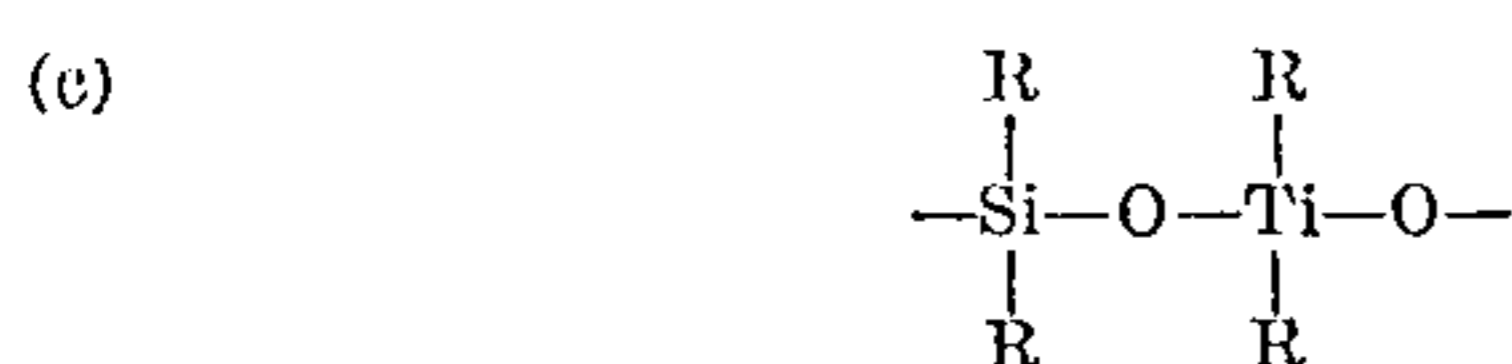
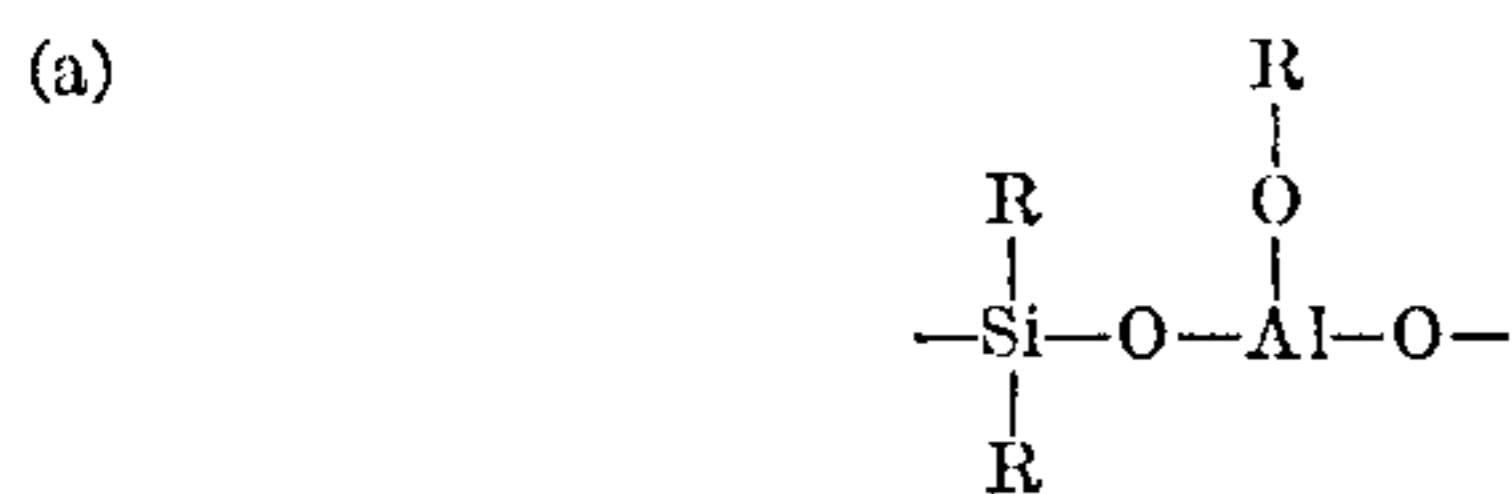
Another group of organo silicon compounds which are contemplated within the scope of this invention are organo silicarbanes, that is,  $a$  has a value of 0 and  $b$  has a value of 1 and  $R'$  is, for example, alkylene, substituted alkylene, alkylene-containing nonterminal hetero atoms, phenylene, substituted phenylene and N,N'-dialkylene urea wherein the alkyl groups are bonded to the silicon atoms.

Another example of organo silicon compounds are organo polysilanes, that is, when  $a$  and  $b$  have a value of 0 and the silicon atom is attached directly to another silicon atom. Typical examples of such polysilanes are polydimethylsilane containing from 3 to 50 silicon atoms

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and polyethylphenylsilane containing from 3 to 50 silicon atoms.

An additional group of organo silicon compounds which can be utilized within the scope of this invention are organo silicon compounds containing a metal such as phosphorus, aluminum, tin and titanium, typical examples of which are copolymers having the following repeating units:



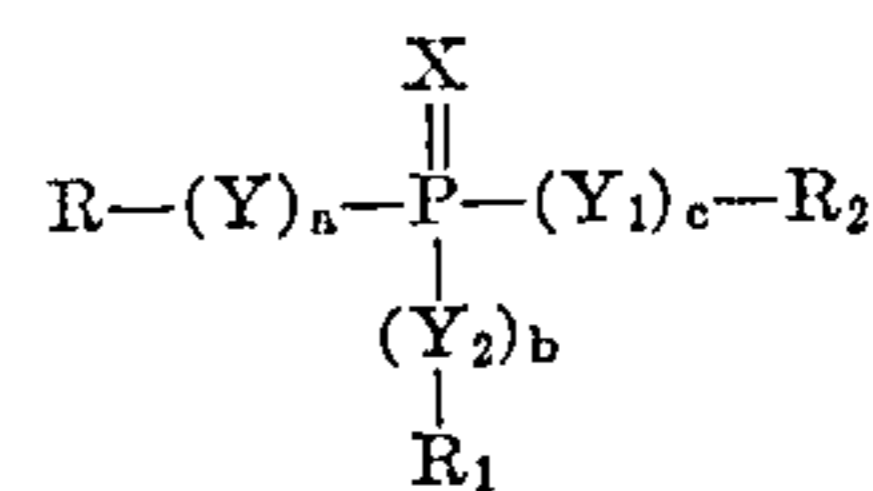
wherein R has its aforescribed significance. Whereas the above examples relate to copolymeric materials, it is contemplated that there can be more than one repeating silicon unit, that is, there can be contained in the organo metal-containing silicon compounds a block of silicon repeating units which can be, for example, a polysiloxane block.

Whereas all the above examples of organo silicon compounds represented by (A) and (B) have been described in separate groups, it is contemplated within the scope of this invention that any one organo silicon compound can contain more than one type of the organo silicon compounds within a group in one organo silicon compound. Thus, the organo silicon compound can be a copolymer, terpolymer or a number of monomeric units can be used to prepare a polymeric organo silicon compound. In addition, the organo silicon compound can be a block polymer wherein each block can be a specific type of polymeric organo silicon group. The organo silicon compounds which are of this type are by way of example polydimethyl siloxane glycol copolymer having a viscosity in centistokes at 77° F. of 900, polydimethyl siloxane silphenylene copolymer having a viscosity in centistokes at 77° F. of 190, a block copolymer comprising as one block a polydimethyl siloxane and as a second block a polydimethylphenylene silcarbane and a copolymer-block type organo silicon compound such as a block represented by a polydimethyl siloxane polymer as a copolymer with an oxytitanium divalent group.

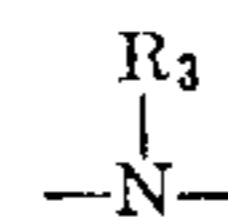
Whereas all the above-described organo silicon compounds can be incorporated into the aforescribed base stocks, the preferred organo silicon compounds are those organo silicon compounds containing at least 50% of a polysiloxane group in the organo silicon compound. Within this preferred class of organo silicon compounds are included the polymeric siloxanes, such as the polydimethyl siloxanes and the copolymers and block polymers containing at least 50% of the polysiloxane group in the organo silicon compound.

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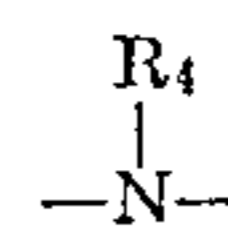
The esters and amides of an acid of phosphorus which are suitable as base stocks for the functional fluid compositions of this invention are those represented by the structure



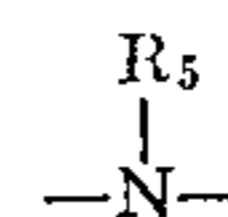
wherein Y is selected from the group consisting of oxygen, sulfur and



Y<sub>1</sub> is selected from the group consisting of oxygen, sulfur and



and Y<sub>2</sub> is selected from the group consisting of oxygen, sulfur and



R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are each selected from the group consisting of alkyl, aryl, substituted aryl and substituted alkyl wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> each can be identical or different with respect to any other radical, X is selected from the group consisting of sulfur and oxygen 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, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-amyl, isoamyl, 2-methylbutyl, 2,2-dimethylpropyl, 1-methylbutyl, diethylmethyl, 1,2-dimethylpropyl, tert-amyl, n-hexyl, 1-methylamyl, 1-ethylbutyl, 1,2,2-trimethylpropyl, 3,3-dimethylbutyl, 1,1,2-trimethylpropyl, 2-methylamyl, 1,1-dimethylbutyl, 1-ethyl-2-methylpropyl, 1,3-dimethylbutyl, isohexyl, 3-methylamyl, 1,2-dimethylbutyl, 1-methyl-1-ethylpropyl, 2-ethylbutyl, n-heptyl, 1,1,2,3-tetramethylpropyl, 1,2-dimethyl-1-ethylpropyl, 1,1,2-trimethylbutyl, 1-isopropyl-2-methylpropyl, 1-methyl-2-ethylbutyl, 1,1-diethylpropyl, 2-methylhexyl, 1,1-dimethyl amyl, 1-isopropylbutyl, 1-ethyl-3-methylbutyl, 1,4-dimethylamyl, isohexyl, 1-methyl-1-ethylbutyl, 1-ethyl-2-methylbutyl, 1-methylhexyl, 1-propylbutyl, n-octyl, 1-methylheptyl, 1,1-diethyl-2-methylpropyl, 1,1,3,3-tetramethylbutyl, 1,1-diethylbutyl, 1,1-dimethylhexyl, 1-methyl-1-ethylamyl, 1-methyl-1-propylbutyl, 2-ethylhexyl, 6-methylheptyl (isooctyl), n-nonyl, 1-methyloctyl, 1-ethylheptyl, 1,1-dimethylheptyl, 1-ethyl-1-propylbutyl, 1,1-diethyl-3-methylbutyl, diisobutylmethyl, 3,5,5-trimethylhexyl, 3,5-dimethylheptyl, n-decyl, 1-propylheptyl, 1,1-diethylhexyl, 1,1-dipropylbutyl, 2-isopropyl-5-methylhexyl and C<sub>11-18</sub> alkyl groups.

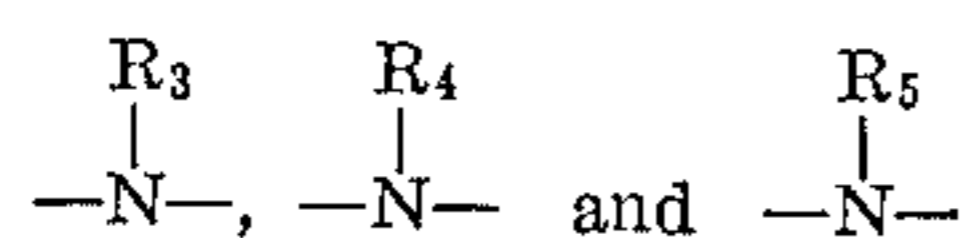
It is also contemplated within the scope of this invention that all or part of the hydrogen other than hydrogen occupying the one position in the previously described alkyl radicals can be replaced by halogens, such as fluorine, chlorine or bromine.

It is also contemplated that the above alkyl and halogenated alkyl groups can have hetero atom linkages such as oxa linking any two carbon atoms contained in the alkyl and halogenated alkyl groups.

Typical examples of aryl and substituted aryl radicals are phenyl, cresyl, xylyl, halogenated phenyl, cresyl and xylyl in which the available hydrogen 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*-3,3,3-trifluoropropylphenyl and *o*-, *m*- and *p*-4,4,4-trifluorobutylphenyl.

The preferred esters of an acid of phosphorus are those base stocks wherein *a*, *b* and *c* have a value of 1, Y, Y<sub>1</sub> and Y<sub>2</sub> are oxygen and R, R<sub>1</sub> and R<sub>2</sub> are alkyl, aryl or substituted aryl. Typical examples of these esters of an acid of phosphorus, that is, phosphates, are dibutylphenyl phosphate, triphenyl phosphate, tricresyl phosphate, tributyl phosphate, tri-2-ethylhexyl phosphate, trioctyl phosphate and mixtures of the above phosphates, such as mixtures of tributyl phosphate and tricresyl phosphate, and mixtures of isooctyldiphenyl phosphate and 2-ethylhexyldiphenyl phosphate and mixtures of trialkyl phosphates and tricresyl phosphates and the like.

The preferred amides of an acid of phosphorus are those wherein *j*, *k* and *l* have a value of 1 and Y, Y<sub>1</sub> and Y<sub>2</sub> are selected from oxygen and



respectively. Typical examples of the amides of an acid of phosphorus, that is, mono-, di- and tri-amides of an acid of phosphorus, hereinafter defined as phosphoramidates, are

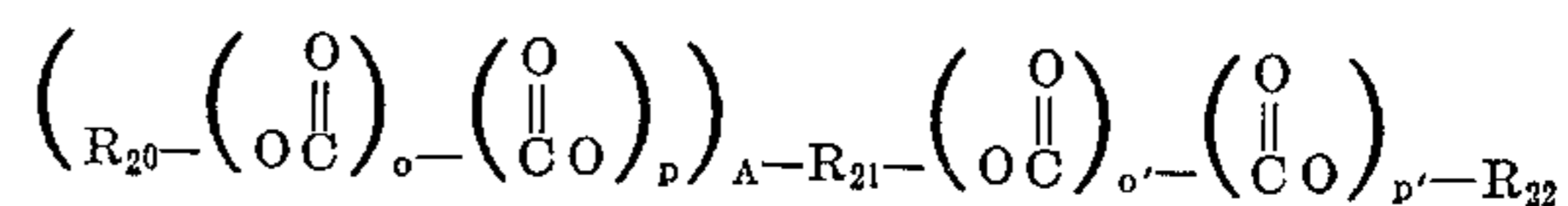
phenyl-methyl-N,N-dimethylphosphoramidate;  
phenylmethyl-N,N-di-n-butylphosphoramidate;  
mixtures of phenyl-*m*-cresyl-N,N-dimethylphosphoramidate and phenyl-*p*-cresyl-N,N-dimethylphosphoramidate;  
mixtures of *m*-cresyl-*p*-cresyl-N,N-dimethylphosphoramidate,  
di-*m*-cresyl-N,N-dimethylphosphoramidate and di-*p*-cresyl-N,N-dimethylphosphoramidate;  
di-*m*-bromophenyl-N-methyl-N-n-butylphosphoramidate;  
di-*m*-chlorophenyl-N-methyl-N-n-butylphosphoramidate;  
di- $\alpha,\alpha,\alpha$ -trifluoro-*m*-cresyl-N-methyl-N-n-butylphosphoramidate;  
di-*p*-bromophenyl-N-methyl-N-n-isoamylphosphoramidate;  
di-*p*-chlorophenyl-N-methyl-N-n-isoamylphosphoramidate;  
*p*-chlorophenyl-*m*-bromophenyl-N-methyl-N-n-isoamylphosphoramidate;  
phenyl-N-methyl-N-butyl-N'-methyl-N'-butylphosphorodiamidate;  
phenyl-N,N-di-n-butyl-N',N'-di-n-butylphosphorodiamidate;  
phenyl-N,N-dimethyl-N',N'-dimethylphosphorodiamidate;  
*m*-chlorophenyl-N-methyl-N-n-butyl-N'-methyl-N'-n-butylphosphorodiamidate;  
*m*-bromophenyl-N-methyl-N-n-butyl-N'-methyl-N'-n-butylphosphorodiamidate;  
 $\alpha,\alpha,\alpha$ -trifluoro-*m*-cresyl-N-methyl-N-n-butyl-N'-methyl-N'-n-butylphosphorodiamidate;  
*p*-chlorophenyl-N-methyl-N-isobutyl-N'-methyl-N'-isoamylphosphorodiamidate;  
*p*-bromophenyl-N-methyl-N-isobutyl-N'-methyl-N'-isoamylphosphorodiamidate;  
N-methyl-N-butyl-N'-methyl-N'-butyl-N''-methyl-N''-butylphosphorotriamidate;  
N-methyl-N-butyl-N',N''-tetramethylphosphorotriamidate;  
N-di-n-propyl-N',N''-tetramethylphosphorotriamidate;  
and  
N,N'-di-n-propyl-N''-dimethylphosphorotriamidate.

Typical examples of phosphinate esters are

phenyl-di-n-propyl phosphinate,  
phenyl-di-n-butyl phosphinate,

phenyl-di-*sec*-butyl phosphinate,  
phenyl-di-n-pentyl phosphinate,  
phenyl-di-neopentyl phosphinate,  
phenyl-di-n-hexyl phosphinate,  
5 phenyl-di-n-butyl thiophosphinate,  
p-methoxyphenyl-di-n-butyl phosphinate,  
m-chlorophenyl-di-n-butyl phosphinate,  
phenyl-(n-propyl-n-pentyl) phosphinate,  
phenyl-(n-propyl-n-butyl) phosphinate,  
10 phenyl-(n-propyl-n-hexyl) phosphinate,  
phenyl-(n-butyl-pentyl) phosphinate,  
phenyl-(n-butyl-n-hexyl) phosphinate,  
phenyl-(n-butyl-n-pentyl) phosphinate,  
phenyl-(neopentyl-n-propyl) phosphinate,  
15 phenyl-(neopentyl-n-butyl) phosphinate,  
phenyl-(neopentyl-n-hexyl) phosphinate,  
thiophenyl-di-n-propyl phosphinate,  
thiophenyl-di-n-pentyl phosphinate,  
cresyl-di-n-pentyl phosphinate,  
20 tert-butylphenyl-di-n-butyl phosphinate,  
n-butylphenyl-di-n-butyl phosphinate,  
sec-butylphenyl-di-n-butyl phosphinate,  
ethylphenyl-di-n-butyl phosphinate,  
xylyl-di-n-butyl phosphinate,  
25 thiophenyl-di-n-hexyl phosphinate,  
thiophenyl-di-n-butyl phosphinate,  
thiophenyl-di-n-propyl thiophosphinate,  
thiophenyl-di-n-butyl thiophosphinate,  
thiophenyl-di-n-pentyl thiophosphinate,  
30 thiophenyl-di-n-hexyl thiophosphinate,  
thiophenyl-(n-propyl-n-butyl) phosphinate,  
thiophenyl-(propyl-n-pentyl) phosphinate,  
thiophenyl-(n-propyl-n-hexyl) phosphinate,  
thiophenyl-(n-butyl-n-pentyl) phosphinate,  
35 thiophenyl-(n-butyl-n-hexyl) phosphinate,  
thiophenyl-(n-pentyl-n-hexyl) phosphinate,  
thiophenyl-(n-propyl-n-butyl) thiophosphinate,  
thiophenyl-(n-propyl-n-pentyl) thiophosphinate,  
thiophenyl-(n-propyl-n-hexyl) thiophosphinate,  
40 thiophenyl-(n-butyl-n-pentyl) thiophosphinate,  
thiophenyl-(n-butyl-n-hexyl) thiophosphinate and  
thiophenyl-(n-pentyl-n-hexyl) thiophosphinate.

Di- and tricarboxylic acid esters which are suitable as base stocks are represented by the structure

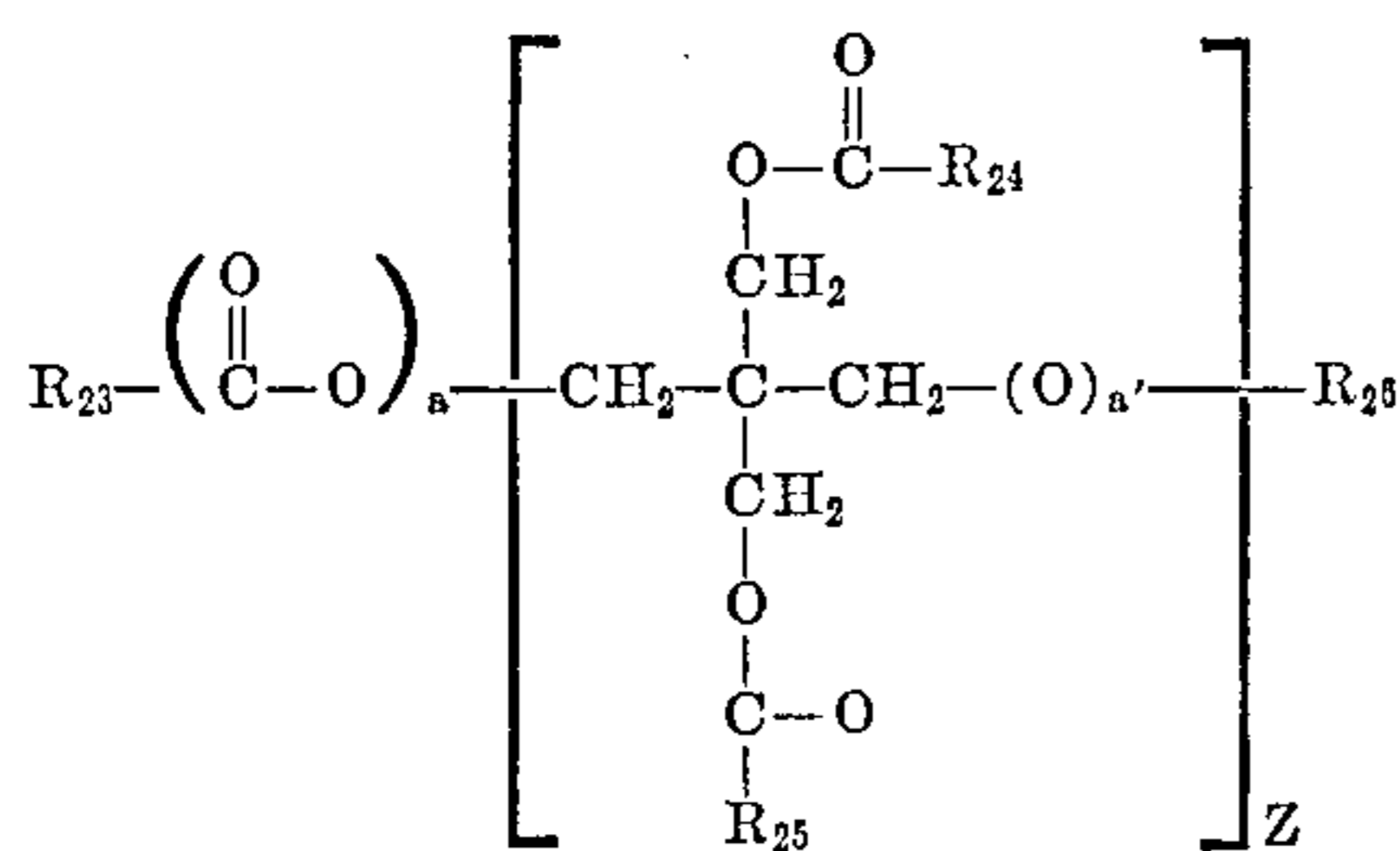


45 wherein *o*, *o'*, *p* and *p'* each are whole numbers having the value of 0 to 1 provided that the sum of each of *o*+*p* and *o'*+*p'* is 1; A is a whole number having a value of 1 to 2; R<sub>20</sub> and R<sub>22</sub> each can be alkyl, cycloalkyl, substituted alkyl, alkenyl, substituted alkenyl, aralkyl, substituted aralkyl, aryl and substituted aryl; and R<sub>21</sub> can be a hydrocarbon radical and a substituted hydrocarbon radical. Typical examples of alkyl, aryl, substituted alkyl and substituted aryl radicals are given above.

Typical examples of di- and tricarboxylic acid esters are di(2-ethylhexyl) azelate, di(2-ethylhexyl) sebacate, diisooctyl sebacate, 2-ethylhexyl 3:5:5 trimethylhexyl sebacate, diisooctyl azelate, di(3:5:5 trimethylhexyl) sebacate, di(1-methyl-4-ethyloctyl) sebacate, diisodecyl azelate, diisotridecyl azelate, di(1-methyl-4-ethyloctyl) glutarate, di(2-ethylhexyl) adipate, di(3-methylbutyl) azelate, di(3:5:5 trimethylhexyl) azelate, di(2-ethylhexyl) adipate, di(C<sub>10</sub> oxo) adipate, bis (diethylene glycol monobutyl ether) adipate, di(isooctyl/isodecyl) adipate, diisotridecyl adipate, triethylene glycol di(2-ethylhexanoate), hexanediol 1,6-di(2-ethylhexanoate) and dipropylene glycol dipelargonate. Additional examples are mixtures of esters made from an aliphatic di-basic acid and a technical mixture of alcohols such as a mixture of alcohols obtained by the oxo process.

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



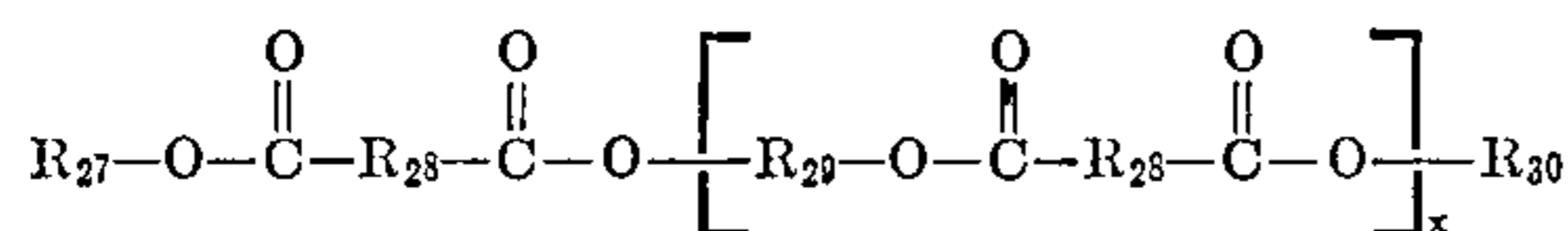
wherein  $R_{23}$  is selected from the group consisting of hydrogen and alkyl,  $R_{24}$  and  $R_{25}$  are each selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, aralkyl, aryl and substituted aryl,  $a$  is a whole number having a value of 0 to 1,  $Z$  is a whole number having a value of 1 to 4 and when  $Z$  is a 1,  $a'$  is 0 and  $R_{26}$  is selected from the group consisting of acyloxy and substituted acyloxy and when  $Z$  is 2 to 4,  $a'$  is 1 and  $R_{26}$  is selected from the group consisting of acyl and substituted acyl.

Typical polyester compounds can be prepared by the reaction of an acid compound with a polyhydroxy compound which polyhydroxy compound can be trimethylolpropane, trimethylolethane, pentaerythritol, dipentaerythritol, tripentaerythritol and tetrapentaerythritol.

The acids which may be utilized are aliphatic monocarboxylic acids, alicyclic monocarboxylic acids, aromatic monocarboxylic acids and heterocyclic monocarboxylic acids, such as propionic, butyric, isobutyric, n-valeric, caproic, n-heptylic, caprylic, 2-ethylhexanoic, 2,2-dimethylheptanoic and pelargonic. Examples of esters of this type are esters of trimethylolpropane (1 mole) with monocarboxylic acids (3 moles), e.g., trimethylolpropane tri-n-octanoate; esters of pentaerythritol (1 mole) with monocarboxylic acids (4 moles); esters of di- or tripentaerythritol (1 mole) with monocarboxylic acids (6 or 8 moles). Typical examples of alkyl, substituted alkyl, aryl and substituted aryl radicals are given above.

Other esters which are also suitable as base stocks are hydrocarbon monesters containing one ester group, typical examples of which are isooctyl stearate and 2-ethylhexyl octoate.

Complex esters which are suitable as base stocks are represented by the structure



wherein  $R_{27}$  and  $R_{30}$  are each selected from the group consisting of hydrogen, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl and a carbocyclic radical containing from 6 to 10 carbon atoms;  $R_{28}$  and  $R_{29}$  are each selected from the group consisting of alkylene, substituted alkylene, alkenylene, substituted alkenylene, phenylene and substituted phenylene;  $x$  is a whole number having a value from 1 to about 80.

Typical examples of complex esters can be obtained by esterifying dicarboxylic acids with a mixture of monohydric alcohol and a glycol to give complex esters. Complex esters which can be employed can be prepared by esterifying a dicarboxylic acid (1 mole) with a glycol (2 moles) and a monocarboxylic acid (2 moles) or with 1 mole each of a glycol, a dicarboxylic acid and a monohydric alcohol or with 2 moles each of a monohydroxy monocarboxylic acid and a monohydric alcohol. Still other complex esters may be prepared by esterifying a glycol (1 mole) with a monohydroxy monocarboxylic acid (2 moles) and a monocarboxylic acid (2 moles).

Other complex esters which are suitable as base stocks are prepared by polymerizing a dihydroxy compound with a dicarboxylic acid and reacting the terminal hydroxy

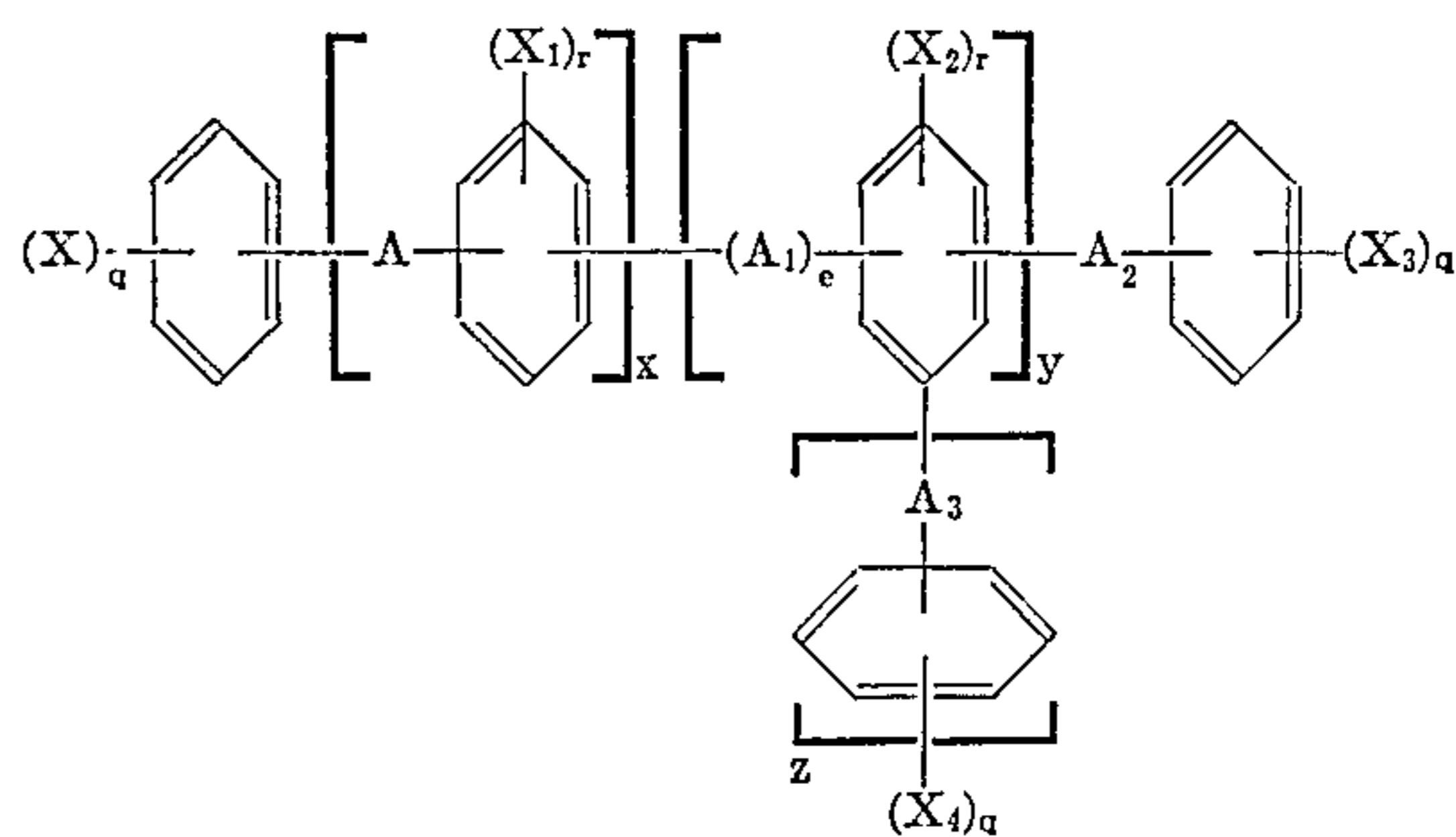
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and acid radical with a mixture of a monocarboxylic acid and a monohydric alcohol. Specific examples of polymers which may be utilized as additives within the scope of this invention are polymers prepared by the polymerization of adipic acid and 1,2-propane diol in the presence of minor amounts of short-chain monocarboxylic acids and a monohydric alcohol to give molecular weights of the polymers thereby produced of from about 700 to about 40,000 or higher.

The mono-, di- and polyhydric alcohols, and the monocarboxylic acids employed in the preparation of the complex esters can also contain ether oxygen linkages.

Specific examples of suitable complex esters are esters prepared from methylene glycol (1 mole), adipic acid (2 moles) and 2-ethylhexanol (2 moles); esters prepared from tetraethylene glycol (1 mole), sebacic acid (2 moles), and 2-ethylhexanol (2 moles); esters prepared from 2-ethyl-1:3 hexanediol (1 mole), sebacic acid (2 moles) and 2-ethylhexanol (2 moles); esters prepared from diethylene glycol (1 mole), adipic acid (2 moles) and n-butanol (2 moles); esters prepared from polyglycol 200 (1 mole), sebacic acid (2 moles) and ethylene glycol mono(2-ethylbutyl) ether (2 moles); esters prepared from sebacic acid (1 mole), tetraethylene glycol (2 moles) and caproic acid (2 moles); esters prepared from triethylene glycol (1 mole), adipic acid (1 mole), n-caproic acid (1 mole) and 2-ethylhexanol 1 mole; ester prepared from sebacic acid (1 mole), lactic acid (2 moles) and n-butanol (2 moles); ester prepared from tetraethylene glycol (1 mole), lactic acid (2 moles) and butyric acid (2 moles); complex esters prepared from neopentyl glycol (2 moles), dicarboxylic acid (1 mole) and monocarboxylic acids (2 moles) and complex esters prepared from neopentyl glycol (1 mole) dicarboxylic acids (2 moles) and monohydric neoalcohols, e.g., 2,2,4-trimethylpentanol (2 moles).

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



wherein A,  $A_1$ ,  $A_2$  and  $A_3$  are each a chalcogen having an atomic number of 8 to 16; each  $q$  is a whole number having a value of 1 to 5; each  $r$  is a whole number having a value of 1 to 4; X,  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  each are selected from the group consisting of hydrogen, alkyl, haloalkyl, halogen, arylalkyl and substituted arylalkyl,  $x$ ,  $y$  and  $z$  are whole numbers each having a value of 0 to 8 and  $e$  is a whole number having a value of 0 to 1 provided that when  $e$  is 0,  $y$  can have a value of 1 to 2. Typical examples of alkyl and substituted alkyl radicals are given above. Typical examples of such base stocks are 2- to 7-ring ortho-, meta- and para-polyphenyl ethers and 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,  $A_1$ ,  $A_2$  and  $A_3$  is dissimilar with respect to any one of the other chalcogens, dihalogenated diphenyl ethers, such as 4-bromo-3'-chlorodiphenyl ethers and bisphenoxybiphenyl compounds and mixtures thereof. It is also contemplated within the scope of this invention that the phenyl and phenylene groups in the afore-

described aromatic ether compounds can be partially or totally replaced by a cyclic ring other than phenyl or phenylene such as an alicyclic group or heterocyclic group such as thiophene or pyridine. Such heterocyclic groups can contain from 4 to 10 atoms optionally interrupted by from 1 to 4 hereto atoms such as oxygen, nitrogen and sulfur.

Examples of the polyphenyl ethers contemplated are the bis(phenoxyphenyl) ethers, e.g., bis(m-phenoxyphenyl) ether, the bis(phenoxyphenoxy)benzenes, e.g., m-bis(m-phenoxyphenoxy)benzene, m - bis(p - phenoxyphenoxy)benzene, o-bis(o-phenoxyphenoxy)benzene, the bis(phenoxyphenoxyphenyl) ethers, e.g., bis [m-(m-phenoxyphenoxy)phenyl] ether, bis[p-(p-phenoxyphenoxy)phenyl] ether, m - [(m - phenoxyphenoxy)(o-phenoxyphenyl) ether, m - [(m - phenoxyphenoxy) (o-phenoxybenzenes, e.g., m-bis[m-(m-phenoxyphenoxy)phenoxy]benzene, p-bis[p-(m-phenoxyphenoxy)phenoxy]benzene, m-bis[m-(p-phenoxyphenoxy)phenoxy]benzene and mixtures thereof with other polyphenyl ethers.

Typical examples of polyphenyl thioethers and mixed polyphenyl ethers and thioethers are

2-phenylmercapto-4'-phenoxydiphenyl sulfide,  
2-phenoxy-3'-phenylmercaptodiphenyl sulfide,  
o-bis(phenylmercapto)benzene,  
phenylmercaptobiphenyl,  
bis(phenylmercapto)biphenyl,  
m-(m-chlorophenylmercapto)-m-phenylmercaptobenzene,  
phenylmercapto(phenoxy) biphenyl,  
m-chlorodiphenyl sulfide,  
bis(o-phenylmercaptophenyl) sulfide,  
m-bis(m-phenylmercaptophenylmercapto)benzene,  
1,2,3-tris(phenylmercapto)benzene,  
1-phenylmercapto-2,3-bis(phenoxy)benzene,  
o-bis(o-phenylmercaptophenylmercapto)benzene,  
m-bis(p-phenylmercaptophenylmercapto)benzene,  
2,2'-bis(phenylmercapto)diphenyl ether,  
3,4'-bis(m-tolylmercapto)diphenyl ether,  
3,3'-bis(xylylmercapto)diphenyl ether,  
3,4'-bis(m-isopropylphenylmercapto)diphenyl ether,  
3,4'-bis(p-tert-butylphenylmercapto)diphenyl ether,  
3,3'-bis(m-chlorophenylmercapto)diphenyl ether,  
3,3'-bis(m-trifluoromethylphenylmercapto)diphenyl ether,  
3,4'-bis(m-perfluorobutylphenylmercapto)diphenyl ether,  
2-m-tolylloxy-2'-phenylmercaptodiphenyl sulfide,  
o-bis(phenylmercapto)benzene,  
bis(m-phenylmercaptophenyl)sulfide,  
m-phenylmercaptophenyl-p-phenylmercaptophenyl sulfide,  
the trisphenylmercaptobenzenes such as  
1,2,4-trisphenylmercaptobenzene,  
3,3'-bis(phenylmercapto)diphenyl,  
m-bis(p-phenylmercaptophenylmercapto)benzene,  
m-bis(m-phenylmercaptophenylmercapto)benzene,  
bis[m-(m-phenylmercaptophenylmercapto)phenyl]sulfide,  
3,3'-bis(phenylmercapto)diphenyl ether,  
3,3'-bis(phenoxy)diphenyl sulfide,  
3-phenoxy-3'-phenylmercaptodiphenyl sulfide,  
3-phenylmercapto-3'-phenoxydiphenyl ether,  
3,4'-bis(phenylmercapto)diphenyl ether,  
m-bis(m-phenylmercaptophenoxy)benzene,  
3-phenylmercapto-3'-(m-phenylmercaptophenylmercapto)diphenyl ether.

Other base stocks which are suitable are mono- and dialkylthiophenes. Typical examples of thiophenes are

2,5-(1-hexyl-1-methylnonyl)thiophene,  
2,4-(1-hexyl-1-methylnonyl)thiophene,  
2-tert-butyl thiophene,  
2,5-tert-butyl thiophene,  
2,5-(1,1-dimethylpropyl)thiophene,  
2,5-(1-butyl-1-octylnonyl)thiophene,

2,5-(1-propylcyclobutyl)thiophene,  
2-tert-butyl-4-(1-octyl-1-methyloctadecyl)thiophene,  
2,5-(1-methylcyclohexyl)thiophene,  
2,5-(1-octyl-1-methyldecyl)thiophene,  
2,5-(1,1-dimethyltridecyl)thiophene,  
2,3-(1,1-dimethyltridecyl)thiophene,  
2,4-(1,1-dimethyltridecyl)thiophene,  
2,4-(1-methylcyclopentyl)thiophene and  
2,5-(1-n-dodecylpentyl)thiophene.

Hydrocarbon materials, including both hydrocarbon materials derived from petroleum sources such as, for example, mineral oils, fuel oils and kerosene types and synthetic hydrocarbon oils, are 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 as naphthenic base, paraffinic base and mixed base mineral oils. In addition, lower boiling hydrocarbon material, such as fuel oil and kerosene types, are often pumped at pressures whereby pump surfaces can be damaged, such as the pumping of jet fuels and these fuels are included within the term "hydrocarbon materials."

The synthetic hydrocarbon oils include but are not limited to those oils derived from oligomerization of olefins such as polybutenes and oils derived from high alpha olefins of from 8 to 20 carbon atoms by acid catalyzed dimerization and by oligomerization using tri-aluminum alkyls as catalysts.

Another base stock which is suitable is chlorinated biphenyl having from about 20 to about 45% by weight chlorine.

It is also contemplated within the scope of this invention that mixtures of individual compounds which are included in a generic type of base stock can be utilized as a base stock within the scope of this invention. For example, two different polyesters can be blended together to form a base stock. In addition, it is contemplated within the scope of this invention that the various generic types of base stocks can be blended together to form base stocks. Thus, a mixture of 5-ring polyphenyl ethers can be blended with a polycarboxylic acid ester to form a base stock.

An additional example of the use of various generic type base stocks which can be blended together to form a base stock is a base stock prepared by blending from about 10% to about 50% of a hydrocarbon oil with from about 30% to 60% of a chlorinated biphenyl and from about 5% to about 25% of an ester of acid of phosphorus such as a triarylphosphate. In addition, it is contemplated that other additives and materials such as blending agents can be added to the above base stocks. Thus, for example, a blending agent such as tri- or tetrachlorobenzene can be added to the above mixture comprising a hydrocarbon oil, an ester of an acid of phosphorus and a chlorinated biphenyl.

The invention can be better appreciated by the following non-limiting examples. In Examples 1 through 23 a nickel specimen was immersed in a test fluid and a 20 kilohertz vibration induced into the specimen. The test duration was 45 minutes. In the following examples, the temperature during the test was 85° C. except in those examples followed by an asterisk (\*). In those examples designated by an asterisk, the test temperature was 30° C. Relative weight loss is defined to mean the total weight loss of the metal specimen when tested in the fluid containing the additive present divided by the weight loss of the metal specimen when the fluid is tested without any additive present times 100. Thus, a relative weight loss under 100 indicates that less metal was removed from the specimen when the additive was present in a given base stock and therefore demonstrates that the fluid compositions which incorporate an organo silicon compound inhibit and control damage.

TABLE I

Ex. No.	Fluid composition	Additive	Vol. percent additive in fluid	Relative weight loss
1	85.15% dibutylphenyl phosphate, 11% acryloid VI improver, 1% epoxidized soybean oil, 0.50% bis(1,2-phenylmercapto) ethane.	Polydimethyl siloxane <sup>1</sup>	2.0	83
2	do	do <sup>2</sup>	0.25	69
3	do	do <sup>2</sup>	0.05	79
4	do	do <sup>3</sup>	0.05	31
5	do	do <sup>4</sup>	0.01	53
6	do	Polychlorophenylmethyl siloxane <sup>5</sup>	0.01	82
7	Tributyl phosphate	Polydimethyl siloxane <sup>1</sup>	1.0	84
8	do	do <sup>2</sup>	5.0	60
9	do	do <sup>3</sup>	0.5	27
10	do	do <sup>4</sup>	0.5	50
11	Dibutylphenyl Phosphate	Tetrakis-2-ethylhexyl silicate	0.5	94
12	do	Hexa-2-ethylbutoxy disiloxane	0.5	96
13	do	Polydimethyl siloxane <sup>2</sup>	0.25	85
14	do	Polyphenylmethyl siloxane <sup>6</sup>	5.0	97
15	Triresyl phosphate	Polymethyl siloxane <sup>2</sup>	0.25	25
16	47.8% 2-ethylhexyl diphenyl phosphate, 47.8% iso-octyl diphenyl phosphate, 4.2% acryloid VI improver.	do <sup>2</sup>	0.25	81
17	1:1 tributyl phosphate, triresyl phosphate.	do <sup>2</sup>	0.25	86
18	70% tributyl phosphate, 22.5% triresyl phosphate, 7.5% 2-ethylhexyl sebacate.	do <sup>2</sup>	0.75	79

<sup>1</sup> Molecular weight = Approx. 236.

<sup>2</sup> Molecular weight = Approx. 1,200.

<sup>3</sup> Molecular weight = Approx. 3,950.

<sup>4</sup> Molecular weight = Approx. 16,000.

<sup>5</sup> Viscosity in centistokes at 25° C. = 80.

<sup>6</sup> Phenyl to methyl ratio = 0.75.

It is an important part of this invention that the use of an organo silicon compound controls and inhibits fluid damage. Several methods which are used to determine the degree of fluid degradation are the change in optical absorbance of a fluid after being subjected to an ultrasonic vibration and the physical properties, such as viscosity change and acid number increase, of the fluid determined prior to and after a given run. In Table II the outstanding ability of the functional fluid compositions of this invention is demonstrated with regard to inhibiting and controlling fluid damage. In Table II the relative inhibition of fluid degradation of a fluid subjected to an ultrasonic vibration was obtained by dividing the optical absorbance of the fluid compositions with additives by the optical absorbance of fluid compositions without additives times 100. The relative decrease in viscosity increase was obtained by dividing the viscosity change of the fluid composition with additives by the viscosity change of the fluid composition without additives times 100. Thus, a relative optical absorbance and relative viscosity decrease below 100 indicates that there has been less fluid damage when the additive was present in a given base stock. In all of the following examples the runs with and without additives were at the same temperatures and for the same duration, that is, 45 minutes at a test temperature of 85° C. A nickel specimen was immersed in the test fluid and a 20 kilohertz vibration was induced into the specimen.

TABLE II

Ex. No.	Base stock	Additive	Concentration, volume percent	Relative optical absorbance	Relative viscosity decrease
19	{ 85.15% dibutylphenyl phosphate 11% acryloid VI improver 1% epoxidized soybean oil 0.50% bis(1,2-phenylmercapto) ethane.	Polydimethyl siloxane <sup>1</sup>	0.25	89	86.5
20	{ 68% chlorinated biphenyl 32% dibromoethyl benzene	do <sup>2</sup>	4.0	24	
21	{ 68% chlorinated biphenyl 32% dibromoethyl benzene	Polyphenylmethyl siloxane <sup>3</sup>	4.0	81	
22	{ 10% triresyl phosphate 90% chlorinated biphenyl	Polydimethyl siloxane <sup>2</sup>	4.0	32	
23	Diphenyl ether	do <sup>2</sup>	4.0	38	

<sup>1</sup> Molecular weight = Approx. 1,200.

<sup>2</sup> Molecular weight = Approx. 236.

<sup>3</sup> Viscosity in centistokes at 77° F. = 710.

The test method as employed to determine relative damage has been found to correlate quite well to actual test runs on simulated hydraulic system test stands, such as the Fairey Test Stand. The Fairey Test Stand is a closed loop hydraulic system wherein the test conditions simulate the actual fluid pressures and temperatures as could exist on an aircraft. Such test stand has been in

use for the purpose of testing hydraulic fluids and hydraulic components. In addition, the hydraulic system test stands for determining damage have correlated quite well with the hydraulic system of commercial aircraft where damage levels have been determined.

The data in the previous examples demonstrate the significant inhibition of damage obtained by the incorporation of an organo silicon compound into a base stock. In addition, the physical properties and the performance characteristics such as lubricity, fire resistance, and viscosity were essentially unaffected by the additive, an important consideration since a base stock is selected from a given fluid system because of its physical properties or characteristics and deviations from these properties and characteristics can bring about inferior fluid performance.

As is demonstrated by Table I, the organo silicon compounds are effective in inhibiting and controlling damage to mechanical members in contact with such fluids which contain the organo silicon compounds of this invention. It is of particular importance that the inhibition and control of damage is accomplished without adversely affecting any of the critical properties of the functional fluids.

The effectiveness of the organo silicon compounds for inhibiting and controlling the degradation of the base stocks is well illustrated by Table II. In particular Table

II effectively demonstrates that the organo silicon compounds at low concentrations are effective in preventing degradation of the base stock as is evidenced by the relative decrease in optical absorptivity and viscosity change of the fluid. This inhibition of degradation of the base stock is of particular importance in the many uses of functional fluids wherein the original required fluid char-



acteristics are maintained during use by the incorporation of the organo silicon compounds. Thus, the incorporation of an organo silicon compound into a base stock to inhibit and control fluid damage is of particular importance in that fluid damage manifests itself in numerous ways among which are viscosity change, increase in acid number, formation of insoluble materials, increased reactivity and discoloration. In a fluid system the particular properties of a fluid have to be maintained in order to continue useful operation of the particular system in which the fluids are employed. Thus, changes in viscosity can be produced by fluid degradation whereby polymeric products with high molecular weights are produced in the system. Such high molecular weight products often become insoluble in the particular base stock which results in the precipitation or sludging of the insoluble material. Such precipitation and sludging plugs filters and deposits on moving parts which have to be lubricated by the fluid thereby causing inadequate lubrication and interference with the proper functioning of the mechanical parts. Increased chemical reactivity is observed on fluid degradation as well as build-up in acid number of the fluid. Such increased chemical reactivity and high acid number allows the particular system which incorporates the fluid to be chemically attacked by the fluid thereby causing pitting, wear and alterations of the close tolerances of the mechanical members of said fluid. Thus, premature overhaul of mechanical parts can be a direct consequence of fluid degradation. It is, therefore, of particular importance that fluid degradation is controlled and inhibited so as to extend the useful life of a fluid in a functional fluid system.

As a result of the excellent stabilization of functional fluid compositions of this invention which incorporate the organo silicon compounds, lubrication of gas turbine engines can be obtained over extended periods of time. Thus, this invention relates to a novel method of lubricating gas turbine engines which comprises maintaining on the bearings and other points of wear lubricating amounts of compositions of this invention.

In addition, due to the excellent physical properties of the compositions of this invention having incorporated therein an organo silicon compound, heat transfer systems can be developed wherein a liquid heat exchange medium is utilized to exchange heat with another material wherein said material is at a given temperature. Thus, the function of the liquid heat exchange medium, can be any one or a combination of the following: transfer heat, accept heat and maintain a material at a given temperature.

As a result of the excellent inhibition and control of damage utilizing the functional fluid compositions within the scope of this invention, improved hydraulic pressure devices can be prepared in accordance with this invention which comprise in combination a fluid chamber and an actuating fluid composition in said chamber, said fluid comprising a mixture of one or more of the base stocks hereinbefore described and a minor amount, sufficient to inhibit damage, of an organo silicon compound. In such a system, the parts which are so lubricated include the frictional surfaces of the source of power, namely the pump, valves, operating pistons and cylinders, fluid motors, and in some cases, for machine tools, the ways, tables and slides. The hydraulic system may be of either the constant-volume or the variable volume type of system.

The pumps may be of various types, including centrifugal pumps, jet pumps, turbine vane, liquid piston gas compressors, piston-type pump, more particularly the variable-stroke piston pump, the variable-discharge or variable displacement piston pump, radial-piston pump, axial-piston pump, in which a pivoted cylinder block is adjusted at various angles with the piston assembly, for example, the Vickers Axial-Piston Pump, or in which the mechanism which drives the pistons is set at an angle adjustable with the cylinder block; gear-type pump, which may be spur, helical or herringbone gears, variations of

internal gears, or a screw pump; or vane pumps. The valves may be stop valves, reversing valves, pilot valves, throttling valves, sequence valves, relief valves, servo valves, non-return valves, poppet valves or unloading valves. Fluid motors are usually constant- or variable-discharge piston pumps caused to rotate by the pressure of the hydraulic fluid of the system with the power supplied by the pump power source. Such a hydraulic motor may be used in connection with a variable-discharge pump to form a variable-speed transmission. It is, therefore, especially important that the frictional parts of the fluid system which are lubricated by the functional fluid be protected from damage. Thus, damage brings about seizure of frictional parts, excessive wear and premature replacement of parts.

The fluid compositions of this invention when utilized as a functional fluid can also contain dyes, pour point depressants, metal deactivator, acid scavengers, antioxidants, viscosity index improvers such as polyalkylacrylates, polyalkylmethacrylates, polycyclic polymers, polyurethanes, polyalkylene oxides and polyesters, lubricity agents and the like.

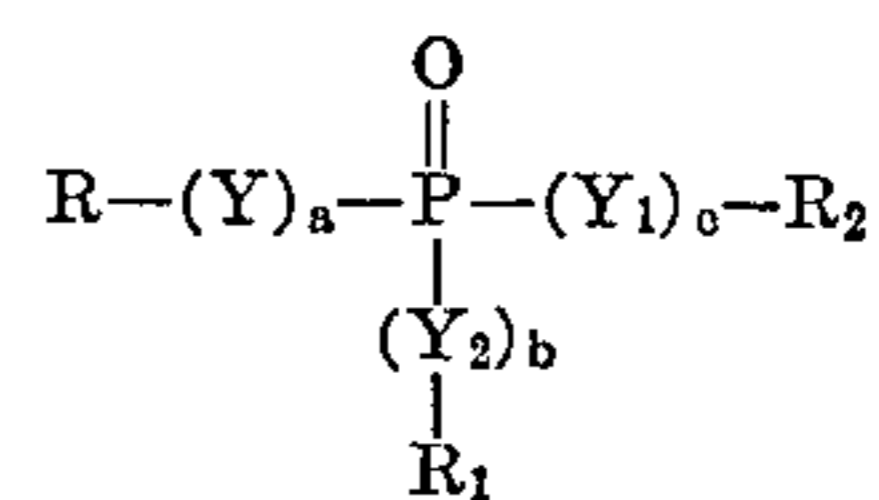
It is also contemplated within the scope of this invention that the base stocks as aforedescribed can be utilized singly or as a fluid composition containing two or more base stocks in varying proportions. The base stocks can also contain other fluids which include, in addition to the functional fluids described above, fluids derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and the 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 alcohols, e.g., ethyl alcohol, alkyl benzenes (e.g., monoalkyl benzene such as dodecylbenzene, tetradecylbenzene, etc.), and dialkylbenzenes (e.g., n-nonyl 2-ethylhexylbenzene); polyphenyls (e.g., biphenyls and terphenyls), halogenated benzene, halogenated lower alkylbenzene and mono-halogenated diphenyl ethers.

While this invention has been described with respect 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.

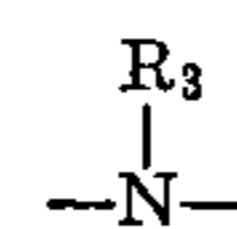
The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. In the method of operating a hydraulic pressure device wherein a displacing force is transmitted to a displaceable member by means of a hydraulic fluid the method of inhibiting cavitation damage which comprises employing as the hydraulic fluid a composition consisting essentially of

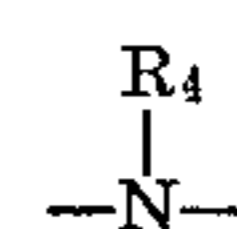
(A) a major amount of phosphorus-containing base stocks represented by the structure



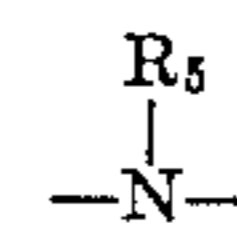
wherein Y is oxygen, or



Y<sub>1</sub> is oxygen, or



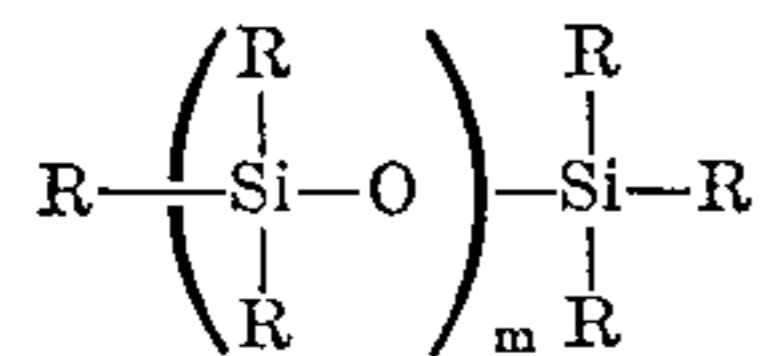
and Y<sub>2</sub> is oxygen, or



R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are each selected from alkyl groups containing from 1 to 18 carbon atoms, phenyl, cresyl, xylyl and lower alkyl substituted

phenyl, bromophenyl, chlorophenyl groups and wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> 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, and mixtures thereof, and

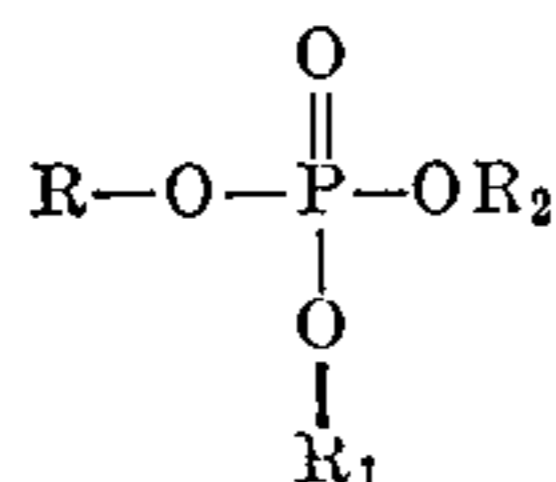
(B) a damage inhibiting amount in the range of from .025 to 5 volume percent of a material represented by the formula



wherein R is a member of the group consisting of methyl, phenyl, chlorophenyl and cyanoethyl and m is an integer having a value of from 1 to 1000.

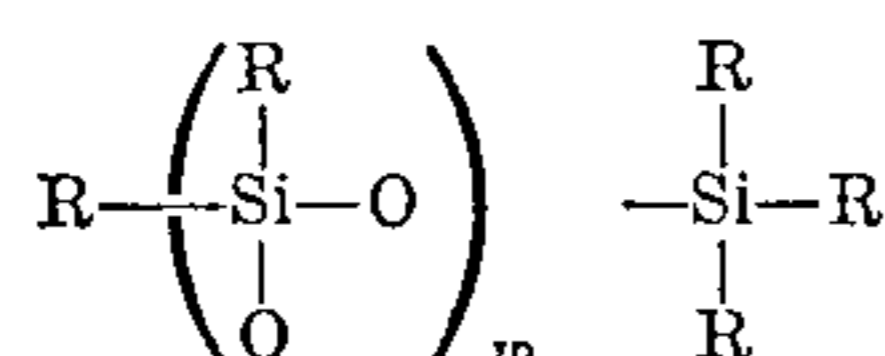
2. In the method of operating a hydraulic pressure device wherein a displaceable force is transmitted to displaceable member by means of a hydraulic fluid the method of inhibiting cavitation damage which comprises employing as the hydraulic fluid a composition consisting essentially of

(A) a major amount of phosphorus-containing base stocks represented by the structure



wherein R, R<sub>1</sub> and R<sub>2</sub> are each selected from alkyl groups containing from 1 to 18 carbon atoms, phenyl, cresyl, xylyl, lower alkyl substituted phenyl, bromophenyl and chlorophenyl groups, and wherein R, R<sub>1</sub> and R<sub>2</sub> each can be identical or different with respect to any other radical, and mixtures thereof, and

(B) a damage inhibiting amount in the range of from .025 to 5 volume percent of a material represented by the formula



wherein R is a member of the group consisting of methyl, phenyl, chlorophenyl and cyanoethyl and m is an integer having a value of from 1 to 1000.

3. A method of claim 2 wherein (B) is a polydimethyl

siloxane having a molecular weight of from about 250 to about 40,000.

4. A method of claim 2 wherein the phosphorus-containing base stock is a mixture of triaryl phosphate, diarylalkyl phosphate, aryldialkyl phosphate and trialkylphosphate.

5. A method of claim 2 wherein the phosphorus-containing base stock comprises a major amount of dibutylphenyl phosphate.

10 6. A method of claim 1 wherein the phosphorus-containing base stock is N-alkyl-N-alkyl-N'-alkyl-N'-alkyl arylphosphorodiamidate.

7. A method of claim 2 wherein the phosphorus-containing base stock is a mixture of isooctyldiphenyl phosphate and 2-ethylhexyl diphenyl phosphate.

8. A method of claim 2 wherein the phosphorus-containing base stock is tributyl phosphate.

9. A method of claim 2 wherein the phosphorus-containing base stock is tricresyl phosphate.

20 10. A method of claim 2 wherein the phosphorus-containing base stock is a mixture of tributyl phosphate and tricresyl phosphate.

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U.S. Cl. X.R.

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