United States Patent Office 3,795,621
Patented Mar. 5, 1974

3,795,621

FIRE-RESISTANT FUNCTIONAL FLUIDS

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No Drawing. Filed July 26, 1971, Ser. No. 166,310
Int. Cl. C09k 3/00
U.S. Cl. 252—78 20 Claims

ABSTRACT OF THE DISCLOSURE

Production of functional fluids, particularly aircraft hydraulic fluids, of improved fire resistance, and also reduced tendency to corrode metals, comprising (1) a functional fluid base stock, such as a phosphate ester, e.g., tri-n-butyl phenyl phosphate, or mixtures of such base stocks, such as a mixture of tri-n-butyl phosphate and tricresyl phosphate, (2) a small amount of an aryl selenide compound, preferably a chlorinated aryl selenide, e.g., 4,4'-dichlorodiphenyl diselenide, and (3) a small amount of a tertiary organic phosphine, e.g. triphenyl phosphine.

This invention relates to functional fluid compositions having improved fire resistance and is particularly directed to compositions comprising certain functional fluids and an additive amount sufficient to improve fire resistance, of certain selenium compounds, and an additive amount of certain phosphine compounds sufficient to substantially reduce metal corrosion, e.g. copper, iron or cadmium corrosion, by such functional fluids containing said selenium compounds.

Many different types of materials are employed as functional fluids and functional fluids are utilized in a wide variety of applications. Thus, such fluids have been utilized as electronic coolants, diffusion pump fluids, lubricants, damping fluids, power transmission and hydraulic fluids, heat transfer fluids and heat pump fluids. A particularly important application of such functional fluids has been their utilization as hydraulic fluids and lubricants in aircraft, requiring successful operation of such fluids over a wide temperature range, a particularly important and highly desirable property of such fluids being fire resistant.

Functional and hydraulic fluids employed in many industrial applications and particularly hydraulic fluids for aircraft must meet a number of important requirements. Thus, such hydraulic fluids particularly for aircraft use, should be operable over a wide temperature range, should have good stability at relatively high temperatures and preferably have lubricating characteristics. In addition to having the usual combination of properties making it a good lubricant or hydraulic fluid, such fluid should also have relatively low viscosity at extremely low temperatures and an adequately high viscosity at relatively high temperatures, and must have adequate stability at the high operating temperatures of use. Further, it is of importance that such fluids be compatible with and not adversely affect or corrode to any significant extent materials including metals of pumps and of hydraulic system compenents, and non-metals such as elastomeric seals of the hydraulic system in which the fluid is employed. It is particularly important in aircraft hydraulic fluids and lubricants that such fluids have as high a fire resistance as possible to prevent ignition if such fluids are accidentally or as result of damage to the hydraulic system, sprayed onto or into contact with surfaces of materials at high temperature.

While many functional and hydraulic fluid compositions have been developed having most of the aforementioned required properties, many of these compositions do not have the requisite high fire resistance desired particularly for use of such functional fluid or hydraulic fluid compositions in modern high speed aircraft or in a hydraulic system located near a high temperature jet-turbine power plant of a jet-turbine aircraft.

Thus, as an illustration, many functional and hydraulic fluids have an autoignition temperature ranging from about 450 to about 750° F. It is particularly desirable to increase the autoignition temperature of such functional and hydraulic fluids to the range of about 800 to about 1,000° F.

As described and claimed in copending application Ser. No. 129,268 of Robert S. McCord, Donald H. Nail, and Martin B. Sheratte, filed Mar. 29, 1971, now Pat. No. 3,730,897, the fire resistance, or autoignition temperature, of functional fluid or hydraulic fluid compositions, can be significantly improved by the addition to such compositions of a small amount of certain selenium compounds, in the form of certain aryl selenides and diselenides, especially chlorinated phenyl selenides and diselenides, such as 4,4'-dichlorodiphenyl diselenide and ethyl p-chlorophenyl selenide.

As pointed out in the above copending application, the aryl selenides and particularly the chlorinated aryl selenides described therein not only function to substantially increase autogenous ignition (autoignition) temperature and reduce flammability of a wide variety of functional fluids and hydraulic fluids, but in addition have the advantageous properties of being thermally stable, free from toxicity, do not have an objectionable odor, and have sufficient solubility in most functional and hydraulic fluids to effectively function as flame inhibitors. In addition, the aryl, particularly the chlorinated aryl, selenides employed according to the above application have no adverse effect on low temperature viscosity of the functional fluids, particularly when employed as hydraulic fluids in aircraft, do not adversely affect the thermal stability of the fluid, and are of relatively low cost.

Many functional fluids, e.g. phosphate esters such as tri-n-butyl phosphate, di-n-butyl phenyl phosphate and tricresyl phosphate, and mixtures of functional fluid base stocks, such as a mixture of tri-n-butyl phopshate and tricresyl phosphate, tend to corrode certain metals such as iron, cadmium, and copper and its alloys such as bronze, which are often present in components such as pumps, valves and the like, of hydraulic systems in which such fluids are employed, especially when such metals or metal components are exposed to such fluids at elevated temperatures. Although incorporation of the aryl selenides such as the chlorinated aryl selenides of the above copending application, into such fluids tends to reduce to some extent such metal attack with respect to certain metals, as for instance on iron and cadmium, and to reduce the acid number of the fluid after a period of time, as compared to the same fluid in the absence of the selenide, the corrosive attack of such fluids containing such selenide additive in concentrations required for adequate flammability protection is still often substantial and undesirable. Moreover, the incorporation of the above selenide additive into such fluids in suitable operative concentration tends to substantially increase the corrosive attack of the fluid on certain metals, particularly copper and its alloys, as compared to the corrosive effect of the same functional fluid in the absence of the selenide.

While the addition of a metal deactivator such as benzotriazole into the above functional fluids containing an aryl, e.g. chlorinated aryl, selenide of the above application, often will reduce such metal attack, the presence of such deactivators results in the formation of deposits in the functional fluids such as phosphate esters containing the above-mentioned aryl or chlorinated aryl selenides.

It has now been found that by incorporation of a small amount of a tertiary organic phosphine, e.g. in the form of a triaryl phosphine such as triphenyl phosphine, into a

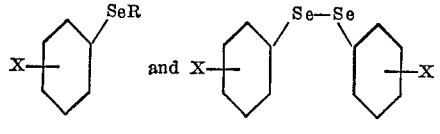
functional fluid or hydraulic fluid composition, e.g. one containing a phosphate ester or a mixture of phosphate esters as base stock, and also containing the above-noted aryl selenides, e.g. a chlorinated aryl selenide, to enhance fire resistance, the presence of the phosphine materially reduces or substantially eliminates the corrosive effect of the fluid containing such additive selenium compounds, without formation of any undesirable deposits, and without adversely affecting any of the important characteristics and properties of the functional or hydraulic fluid, particularly for use as an aircraft hydraulic fluid, and without adversely affecting the function of the selenium compound for improving the fire resistance or for increasing autoignition temperature of such functional or hydraulic fluid compositions.

As a matter of fact, it has been found that when the organic phosphine additive, e.g. triphenyl phosphine, is used in combination with the above-noted aryl, e.g. chlorinated aryl, selenide in a functional fluid, the phosphine additive exhibits two important phenomena, namely, it affords substantially complete protection to metal parts, particularly copper and its alloys, iron and cadmium, against metal attack by such fluid containing the above-noted selenides, and it interacts in a synergistic manner with the above selenide additive, so that the amount of selenide required to provide a given improvement in fire resistance or a given increase in autoignition temperature, is substantially reduced over the amount of selenide required in the absence of the tertiary organic phosphine. In addition, the reduced concentration in the fluid of the selenide compound thus permitted by the presence of the phosphine to obtain a given degree of fire resistance also tends to reduce any corrosive effect of the selenide compound and at the same time reduces the overall cost of the fluid.

Effective selenium compounds, that is aryl selenides, for use as additives in functional hydraulic fluids to reduce flammability and increase autoignition temperature of the fluid, as described in the above copending application 129,268, have the formula ArSeR, where Ar is a member selected from the group consisting of aryl and substituted aryl including a substituent selected from the group consisting of alkyl, halogen, alkoxy, aryloxy, amino and diakylamino, and R is a member selected from the group consisting of unsubstituted and substituted alkyl, aryl and aryloxy, including a substituent selected from the group consisting of halogen, amino and diakylamino; and SeAr', where Ar' has the same definition as Ar above, and Ar and Ar' are the same or different.

Thus, Ar and Ar' can be phenyl, naphthyl anthranyl, and the like, and such aryl groups can contain alkyl substituents such as methyl, ethyl, propyl, butyl, and branched chain alkyls such as isopropyl and isobutyl, and the like, halogen atoms such as chlorine and bromine, alkoxy such as methoxy, ethoxy, propoxy, and the like, aryloxy such as phenoxy and naphthoxy, amino and dialkylamino such as dimethylamino, diethylamino, and the like, such alkyl groups containing from 1 to about 10 carbon atoms. R can be alkyl such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and the like, of from 1 to about 10 carbon atoms, aryl such as phenyl, naphthyl, and the like, aryloxy such as phenoxy and naphthoxy, and substituted alkyl, aryl and aryloxy radicals containing substituents such as halogen, e.g., chlorine and bromine, amino and dialkylamino such as dimethylamino and diethylamino, and the like, such alkyl groups containing from 1 to about 10 carbon atoms.

The preferred aryl selenides according to the invention are those selected from the group having the general formulae:



where X is selected from the group consisting of H, alkyl, both straight chain and branched chain and having 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, isopropyl, pentyl, and the like, halogen such as chlorine and bromine, alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, amino and dialkylamino such as dimethylamino, diethylamino, and the like, and R is alkyl of from about 1 to about 12 carbon atoms, both straight and branched chain, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, and the like.

Compounds which have been found particularly effective according to the above copending application are the halogenated, e.g., chlorinated or brominated aryl selenides, especially the chlorinated aryl selenides, that is, selenides of the formulae noted immediately above, where X is halogen such as chlorine. The aryl nuclei of the above noted formulae each can contain one or more of the X, e.g., chloro or bromo, substituents, such as one, two or three such halogen, e.g., chlorine, atoms on each of the phenyl nuclei. The most desirable chlorinated selenides of these types have been found to be ethyl p-chlorophenyl selenide and 4,4'-dichlorodiphenyl diselenide. Other exemplary chlorinated aryl selenides having a structure as defined by the above formulae include methyl p-chlorophenyl selenide, ethyl and propyl o-chlorophenyl selenides, methyl and ethyl 2,4 dichlorophenyl, selenides, ethyl 2,4,6,-trichlorophenyl selenide, 2,2' dichlorodiphenyl diselenide, 2,4,2',4' - tetrachloro diphenyl diselenide and 2,4,6,2',4',6'-hexachloro diphenyl diselenide. Brominated analogues corresponding to the above specific examples of the chlorinated selenides and diselenides can be employed.

The tertiary organic phosphines employed as additives in combination with the above-described aryl selenides according to the invention, are phosphines having the general formula:

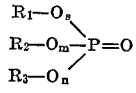


where R_a, R_b and R_c each can be aryl such as phenyl and naphthyl, and alkaryl such as cresyl, xylyl, ethyl phenyl, propyl phenyl, isopropyl phenyl, and the like, said aryl and alkaryl radicals preferably containing from 6 to about 8 carbon atoms. R_a, R_b, and R_c can be the same or different. Specific examples of the above tertiary organic phosphine additives which can be employed according to the invention are the preferred triphenyl phosphine and dicresyl phenyl phosphine, additional examples of suitable phosphines according to the invention being cresyl diphenyl phosphine, tricresyl phosphine, alpha-naphthyldiphenyl phosphine and tris-(4,3-dimethylphenyl) phosphine.

The following base stocks are illustrative of typical base stocks that can be utilized in preparing the functional fluid compositions of the present invention, and the instant invention can be practiced utilizing the various modifications of the base stocks which are set forth below:

Preferably functional fluid base stocks are employed which are selected from the group consisting of phosphorus esters, amides of an acid of phosphorus, di- and tricarboxylic acid esters, and petroleum hydrocarbons.

Phosphorus esters which can be employed according to the invention have the general formula:



where *s*, *m* and *n* can be 0 or 1, and not more than two of *s*, *m*, and *n* can be 0, where R_1, R_2 and R_3 each can be aryl such as phenyl and naphthyl, alkaryl such as cresyl, xylyl, ethyl phenyl, propyl phenyl, isopropyl phen-

yl, and the like, said aryl and alkaryl radicals preferably containing from 6 to about 8 carbon atoms, alkyl, both straight chain and branched chain of from about 3 to about 10 carbon atoms such as n-propyl, n-butyl, n-amyl, n-hexyl, isopropyl, isobutyl, and the like, and alkoxyalkyl having from about 3 to about 8 carbon atoms such as methoxy methyl, methoxy ethyl, ethoxy ethyl, methoxy propyl, and the like.

The corresponding phosphonates can also be employed, where one of *s*, *m* and *n* is 0, and the corresponding phosphinates where two of *s*, *m* and *n* are 0.

Preferred phosphorus esters are the dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates.

Examples of such phosphate esters are the dialkyl aryl phosphates in which the alkyl groups are either straight chain or branched chain and contain from about 3 to about 10 carbon atoms, such as n-propyl, n-butyl, n-amyl, n-hexyl, isopropyl, isobutyl, isoamyl, and the aryl radicals have from 6 to 8 carbon atoms and can be phenyl, cresyl or xylyl, particularly dialkyl phenyl phosphates including dibutyl phenyl phosphate, butyl amyl phenyl phosphate, butyl hexyl phenyl phosphate, butyl heptyl phenyl phosphate, butyl octyl phenyl phosphate, diamyl phenyl phosphate, amyl hexyl phenyl phosphate, amyl heptyl phenyl phosphate, and dihexyl phenyl phosphate.

Examples of triaryl phosphates to which the combination of aryl selenides, especially chlorinated selenides, and phosphine additives of the invention can be added are those in which the aryl radicals of such phosphates have from 6 to 8 carbon atoms, that is, may be phenyl, cresyl or xylyl, and in which the total number of carbon atoms in all three of the aryl radicals is from 19 to 24, that is, in which the three radicals include at least one cresyl or xylyl radical. Examples of such phosphates include tricresyl, trixylyl, phenyl dicresyl, and cresyl diphenyl phosphates.

Examples of trialkyl phosphates employed according to the invention include phosphates having alkyl groups which are either straight chain or branched chain with from about 3 to about 10 carbon atoms, such as n-propyl, n-butyl, n-amyl and n-hexyl, particularly tri-n-butyl phosphate, tri(2-ethyl hexyl) phosphate and triisononyl phosphate, the straight chain alkyl groups preferably containing from 4 to 6 carbon atoms.

Examples of alkyl diaryl phosphates which can be employed to produce the invention compositions include those in which the aryl radicals of such phosphates may have from 6 to 8 carbon atoms and may be phenyl, cresyl or xylyl, and the alkyl radical may have from about 3 to about 10 carbon atoms, examples of which are given above. Examples of the alkyl diaryl phosphates include butyl diphenyl, amyl diphenyl, hexyl diphenyl, heptyl diphenyl, octyl diphenyl, 6-methyl heptyl diphenyl, 2-ethylhexyl diphenyl, butyl phenyl cresyl, amyl phenyl xylyl, and butyl dicresyl phosphates.

Functional fluid base stocks according to the invention also include phosphonate and phosphinate esters having alkyl and aryl groups corresponding to those defined above with respect to the phosphate esters.

Examples of phosphinate esters to which the invention principles are applicable include phenyl-di-n-propyl phosphinate, phenyl di-n-butyl phosphinate, phenyl-di-n-pentyl phosphinate, p-methoxyphenyl-di-n-butyl phosphinate, tert-butylphenyl-di-n-butyl phosphinate. Examples of phosphonate esters to which the invention is applicable include aliphatic phosphonates such as an alkyl alkenyl phosphonate, e.g., dioctyl isooctene phosphonate, an alkyl alkane phosphonate such as di-n-butyl n-octane phosphonate, di-isooctyl pentane phosphonate, and dimethyl decane phosphonate, a mixed alkyl aryl phosphonate, for example, di-octyl phenyl phosphonate, di(n-amyl) phenyl phosphonate, di(n-butyl) phenyl phosphonate, phenyl butyl hexane phosphonate and butyl bis-benzene phosphonate.

Another class of phosphorus-containing compounds in which the combination of selenide and phosphine additives of the invention can be employed are the amides of acids of phosphorus, e.g. amido phosphates, including the mono-, di- and triamides of an acid of phosphorus, an example of which is phenyl N-methyl N-n-butyl-N'-methyl-N'-n-butyl phosphoro-diamidate. Additional examples are

m-cresyl-p-cresyl-N,N-dimethylphosphoroamidate,
di-m-cresyl-N,N-dimethylphosphoroamidate,
di-p-cresyl-N,N-dimethylphosphoroamidate,
phenyl-N,N-dimethyl-N',N'-dimethylphosphoro-diamidate,
N-methyl-N-butyl-N',N''-tetramethylphosphoro-triamidate,
N,N'-di-n-propyl-N''-dimethylphosphorotriamidate.

Another class of functional fluid base stocks whose auto-ignation temperature can be improved by incorporation of the aryl selenides, particularly the chlorinated aryl selenides, and whose corrosive properties can be reduced by the addition of the phosphine compounds according to the invention are the di- and tricarboxylic acid esters, particularly the dicarboxylic acid esters. Preferred types of the latter compounds are the alkyl diesters of adipic and sebacic acid, that is the diester adipates and sebacates. Such esters can contain alkyl groups, either straight chain or branched chain, containing from about 4 to about 12 carbon atoms including butyl, isobutyl, amyl, pentyl, hexyl, isohexyl, nonyl, decyl and isodecyl groups. Specific examples of these base stocks are dihexyl, di 2-ethylhexyl, dioctyl, dinonyl, didecyl and diisodecyl adipate, and the corresponding sebacates. Also, the diesters of the dicarboxylic aromatic acids, particularly the diesters of phthalic acid, that is the phthalate diesters can be employed as base stocks. The diesters of such acids can contain alkyl groups of from 4 to 12 carbon atoms, examples of which are given above with respect to the diesters of the dicarboxylic aliphatic acids, adipic and sebacic acid. Illustrative examples of the diester phthalates which can be employed are di-n-butyl phthalte, dihexyl phthalate, dioctyl phthalate, dinonyl phthalate, didecyl phthalate, and diisodecyl phthalate.

There can also be employed as functional fluid base stocks according to the invention the esters of tricarboxylic acids, particularly the aromatic tricarboxylic acids such as trimellitic acid. The triesters of such acids can contain alkyl groups of from 4 to 12 carbon atoms, illustrative examples of which are noted above with respect to the dialkyl esters of phthalic acid, specific examples of trimellitate triesters including tri-butyl, tri-hexyl, tri-octyl, tri-isooctyl, tri-nonyl, tri-decyl and tri-isodecyl trimellitate.

There can also be employed as functional fluid base stocks to which the combination aryl selenides and tertiary phosphines are added according to the invention, petroleum hydrocarbons, which can contain carbon chains of from C_{10} to about C_{24} carbon atoms. A typical example of such a petroleum hydrocarbon is the red petroleum hydrocarbon liquid according to military specification MIL–H–5606B, understood to contain carbon chains of about C_{10} to about C_{20} carbon atoms, generally employed as a hydraulic fluid in military aircraft.

It is also contemplated within the scope of the present invention that mixtures of individual functional or hydraulic fluid components are included to form a single base stock. Thus, for example blends of esters of an acid of phosphorus can be employed, e.g., a blend of tri-n-butyl phosphate and tricresyl phosphate, blends of an ester of an acid of phosphorus and a dicarboxylic acid diester such as the aliphatic diesters of adipic, sebacic or phthalic acid, e.g., a mixture of tri-n-butyl phosphate and diisodecyl adipate and/or diisodecyl phthalate, or a combination or blend of dicarboxylic acid diesters and/or

tricarboxylic acid triesters can be employed, such as a blend of diisodecyl adipate and diisodecyl phthalate.

Thus, there can be employed as functional fluid base stocks a blend or mixture of a phosphorus ester such as a phosphate and an alkyl diester of phthalic acid, with or without an alkyl diester of adipic acid and/or of sebacic acid, wherein said alkyl groups contain from about 4 to about 12 carbon atoms, as described and claimed in the copending application, Functional Fluid Compositions, M. B. Sheratte, Ser. No. 129,270, filed Mar. 29, 1971. In addition, functional fluid base stocks can be utilized comprising a blend or mixture of a phosphorus ester such as a phosphate and an alkyl diester of adipic acid and/or of sebacic acid, as defined above, and as described and claimed in the copending application, Functional Fluids, M. B. Sheratte, Ser. No. 129,269, filed Mar. 29, 1971.

The functional or hydraulic fluid base stocks employed and described above, can also contain other additives such as viscosity index improvers, in a small amount ranging from 0 to about 10%, generally about 2 to about 10%, by weight of the composition. Examples of the latter are polyalkyl acrylates and methacrylates, the polyalkyl methacrylates generally being preferred, and in which the alkyl groups may contain from about 4 to about 12 carbon atoms, either straight or branched chain, and having an average molecular weight ranging from about 2,000 to about 15,000. Specific examples of such viscosity index improvers are polybutyl methacrylate and poly n-hexyl acrylate, having an average molecular weight between about 2,000 and about 12,000. Other additives such as corrosion inhibitors, stabilizers, metal deactivators, and the like, can also be employed.

For greatest effectiveness in substantially reducing the flammability, and for correspondingly substantially increasing the autoignition temperature of the above functional fluid base stocks, it is usually desirable to employ only a small amount of the aryl selenide or halogenated aryl selenide in the functional or hydraulic fluid base stock. Generally, there can be employed as little as 0.25% and up to about 5% of the selenide additive of the invention, preferably from about 0.5 to about 2% of such selenide, in the functional fluid base stock, based on the weight of the composition. It has been found that an optimum amount of such selenide additive ranges from about 0.8 to about 2% by weight of the composition. However, as previously noted, and demonstrated hereinafter, the amount of the selenide additive employed can be reduced to a substantial proportion as result of the presence of the phosphine additive, and still obtain a comparable reduction in flammability.

The amount of tertiary organic phosphine additive incorporated in the functional fluid base stock together with the small amount of the aryl selenide additive, can range from about 0.1 to about 5% by weight of the composition. In preferred practice, however, there is employed an amount of such phosphine ranging from about 0.1 to about 2% by weight of the composition. As previously noted, this small amount of the above-defined phosphine incorporated with the aryl selenide in the functional fluid base stock, particularly phosphate ester, effectively minimizes or eliminates corrosion by the fluid, of copper and its alloys such as bronze, iron and steel, cadmium such as cadmium plate, and also aluminum and its alloys, and titanium and its alloys. It is found undesirable, however, to employ the above-noted phosphine additive when the functional fluid to be contacted with magnesium and its alloys at temperatures above 150° F.

Preparation of the above-noted aryl selenides, particularly the chlorinated aryl selenides as represented by 4,4'-dichlorodiphenyl diselenide and ethyl p-chlorophenyl selenide, is described in the above copending application 129,268, and such disclosure is incorporated herein by reference.

The above-noted tertiary organic phosphines such as, e.g. triphenyl phosphine and dicresyl phenyl phosphine, are generally prepared by preparation of the appropriate Grignard reagent, such as R_aMgCl, e.g. C_6H_5MgCl, where R_a has the values defined above, that is aryl or alkaryl, and reaction of such aryl or alkaryl magnesium halide with PCl_3 to produce the corresponding tertiary organic phosphine, e.g. triaryl phosphine such as triphenyl phosphine. Where one or more of R_a, R_b and R_c as defined above are different, a mixture of the appropriate aryl and/or alkaryl magnesium halide compounds in appropriate molar proportion is employed to produce the mixed tertiary organic phosphine. Thus, for example, triphenyl phosphine can be produced by reaction of phenylmagnesium chloride with PCl_3 in ether, as follows:

$$3C_6H_5MgCl + PCl_3 \rightarrow (C_6H_5)_3P + 3MgCl_2$$

Triphenyl phosphine is a white solid melting at 86° C. It has a slight phosphine odor, which is completely masked when disolved in tributyl phosphate.

Similarly, dicresyl phenyl phosphine can be prepared by reacting two mols of cresyl magnesium chloride and one mol of phenyl magnesium chloride, with one mol of PCl_3.

The following are examples illustrating practice of the invention by incorporation of aryl selenide and phosphine additives into functional fluid base stocks according to the invention, the percentages being in terms of percent by weight, unless otherwise indicated.

EXAMPLE 1

To one portion of a functional fluid blend comprising about 80% tri-n-butyl phosphate, about 11% tricresyl phosphate, and a small amount of polybutyl methacrylate viscosity index improver, is added 0.8% 4,4'-dichlorodiphenyl diselenide, such fluid designated fluid I, and to another portion of the same functional fluid blend is added 0.8% 4,4'-dichlorodiphenyl diselenide and 0.5% triphenyl phosphine, the latter fluid blend being designated fluid II.

The above two fluids I and II, together with a control of the above fluid blend containing no selenide or phosphine additive, are subjected to a closed oxidation-corrosion test at 325° F. on bronze, iron and cadmium plate, placing all three metal samples in each of the above three fluids, and the corrosive effect of the respective fluids on each of these respective metals is measured over a period of 32 hours by determining the weight changes in mg./cm.² on each of the respective metals at the end of this period, and the acid number of the respective fluids following the above 32 hour test at 325° F. is also determined.

The results of these tests are noted in Table 1 below.

TABLE 1

Selenide additive, percent	Triphenyl phosphine, percent	Weight changes (mg./cm.²) Bronze	Iron	Cadmium plate	Acid number
0	0	−0.18	−9.6	−1.10	12
0.8	0	−0.75	−0.04	−0.61	2.25
0.8	0.5	0	−0.01	0	0.18

From Table 1 above it is noted that addition of the 4,4'-dichlorodiphenyl diselenide additive in the functional fluid, forming fluid I, increases the corrosive effect of the fluid on bronze at the end of the test period to 0.75 mg./cm.², from 0.18 mg./cm.² for the control, but upon the addition of 0.5% triphenyl phosphine to the fluid containing the selenide additive, forming fluid II, the corrosive effect of the fluid containing the 4,4'-dichlorodiphenyl diselenide additive on the bronze is completely eliminated, as indicated by a weight change of 0 for this fluid at the end of the test.

Also, with respect to the corrosive effect of the various fluids on iron, it is noted that fluid I containing only the

selenide additive has a corrosive effect corresponding to a weight change of 0.04 mg./cm.^{2}, as compared to 9.6 mg./cm.^{2} for the control in the absence of selenide, but when 0.5% of triphenyl phosphine is incorporated, forming fluid II, the corrosive effect of the resulting fluid on the iron corresponds to a weight change of only 0.01 mg./cm.^{2}.

In the case of cadmium plate, it is noted that fluid I containing the above selenide additive has a corrosive effect corresponding to 0.61 mg./cm.^{2}, as compared to 1.10 mg./cm.^{2} for the control, whereas fluid II, containing 0.5% triphenyl phosphine in addition to the selenide, has no corrosive effect on the cadmium plate as indicated by the value of 0 for the weight change in this test as noted in the above table.

In addition, the acid number of the control at the end of these tests on bronze, iron and cadmium plate is very high, the acid number for fluid I containing only the selenide additive being 2.25, whereas the acid number for the fluid II containing 0.5% triphenyl phosphine in combination with 0.8% of the selenide additive is substantially reduced to only 0.18.

The results of these tests, as demonstrated in Table 1 above, show that the presence of triphenyl phosphine in combination with the additive 4,4'-dichlorodiphenyl diselenide in the above functional fluid substantially reduces the corrosive attack of the fluid on each of the bronze, iron and cadmium plate samples, as compared to the control fluid and also as compared to the fluid containing only the selenide, and also the fluid containing the phosphine additive, as indicated by its relatively low acid number at the end of these tests, prevents acid build-up in the fluid as compared to the control fluid and also the fluid containing only the selenide.

EXAMPLE 2

The procedure of Example 1 is repeated but employing in place of triphenyl phosphine, dicresyl phenyl phosphine, and carrying out the oxidation-corrosion tests for each of the three fluids at 325° F. on bronze, iron and cadmium plate for a period of 34 hours.

The results of these tests are noted in Table 2 below.

TABLE 2

Selenide additive, percent	Dicresyl phenyl phosphine, percent	Weight change (mg./cm.^{2}) Bronze	Iron	Cadmium plate	Acid number
0	0	−0.22	−10.3	−1.35	12
0.8	0	−0.85	−0.50	−0.80	3.40
0.8	0.5	0	−0.02	0	0.21

It is noted from Table 2 above that the results obtained employing dicresyl phenyl phosphine in place of the triphenyl phosphine in Example 1, for the 34 hour corrosion-oxidation test of the present example, are quite similar to the results obtained in Example 1, as shown in Table 1.

The results tabulated in Table 2 above, show that the presence of dicresyl phenyl phosphine in combination with the additive 4,4'-dichlorodiphenyl diselenide in the functional fluid of Example 1, reduces the corrosive attack of the fluid on each of the bronze, iron and cadmium plate samples as compared to the control fluid, and significantly also as compared to the fluid containing only the selenide, and also that the fluid containing the phosphine additive, as shown by its low acid number following the corrosion tests, prevents acid build-up and prevents formation of deposits in the fluid, as compared to the control fluid and to the fluid containing only the selenide.

EXAMPLE 3

To aliquot portions of the functional fluid blend I of Example 1 above, and containing 0.8% of the selenide additive 4,4'-dichlorodiphenyl diselenide, is added, respectively, 0.2%, 0.5% and 1.0% of the phosphine additive triphenyl phosphine.

The resulting three fluids, together with a control of fluid I, containing the selenide additive but no phosphine additive, are again tested for the effect of the presence of the phosphine additive on reduction of corrosion of fluid I containing the selenide additive 4,4'-dichlorodiphenyl diselenide, on bronze, iron and cadmium plate in a 32 hour test, according to the procedure of Example 1, and also obtaining the acid number of the respective fluids following the corrosion test.

The results of this test are noted in Table 3 below.

TABLE 3

Triphenyl phosphine, percent	Weight changes (mg./cm.^{2}) Bronze	Iron	Cadmium plate	Acid number
0	−0.75	−0.04	−0.61	2.25
0.2	−0.27	−0.01	−0.33	0.92
0.5	0	−0.01	0	0.18
1.0	0	0	0	0.14

It will be seen from Table 3 above that increasing amounts of triphenyl phosphine from 0.2% to 1.0%, and particularly from 0.2% to 0.5%, substantially reduces the corrosive effect of fluid I containing the selenide additive on both bronze and cadmium plate, reducing the amount of corrosion from 0.75 mg./cm.^{2} for the control fluid to 0 corrosion for the fluid containing 0.5 and 1% of the phosphine in the case of bronze, and from 0.61 mg./cm.^{2} for the control, to 0 corrosion for the fluids containing 0.5 and 1% phosphine additive on cadmium plate. On iron, corrosion is reduced from 0.04 mg./cm.^{2} for the control to 0 for the fluid containing 1.0% of the phosphine.

Further, it is noted that acid number is substantially reduced from 2.25 for the control following the above test, down to 0.18 and 0.14, respectively, for the fluids containing 0.5 and 1.0% of the phosphine additive.

EXAMPLE 4

The test of Example 3 above is repeated, except employing in place of the phosphine additive triphenyl phosphine, the phosphine additive dicresyl phenyl phosphine.

Substantially similar results are obtained with respect to reduction of corrosion of the respective fluids containing 0.2%, 0.5% and 1.0% of dicresyl phenyl phosphine as in the case of the corresponding fluids in Example 3, containing 0.2%, 0.5% and 1.0% of triphenyl phosphine, as represented by a comparison of the reduction in corrosivity on bronze, iron and cadmium plate, of fluid I containing 0.8% selenide additive 4,4'-dichlorodiphenyl diselenide and 0.5% triphenyl phosphine, and the corresponding fluid containing 0.8% of such selenide, and 0.5% dicresyl phenyl phosphine, as shown in Table 4 below.

TABLE 4

Phosphine additive	Wt. percent	Weight changes (mg./cm.^{2}) Bronze	Iron	Cadmium plate	Acid number
Triphenyl phosphine	0.5	0	−0.01	0	0.18
Dicresyl phenyl phosphine	0.5	−0.01	−0.02	−0.01	0.21

EXAMPLE 5

The testing procedure of Example 3 is repeated, except employing in place of the functional fluid blend of Example 3, a blend of functional fluids consisting essentially

of 50% diisodecyl adipate and 50% dibutyl phenyl phosphate.

A substantial reduction in corrosivity on bronze, iron and cadmium plate, and a substantial reduction in acid number of the respective fluids following the test, is observed, for the fluid containing the 0.8% of the selenide 4,4'-dichlorodiphenyl diselenide, upon incorporation therein of 0.2%, 0.5% and 1.0%, respectively, of the triphenyl phosphine additive.

EXAMPLE 6

The tests of Examples 1 to 5 are repeated, except employing ethyl p-chlorophenyl selenide in place of 4,4'-dichlorophenyl diselenide.

Reduction in corrosivity and acid number results are comparable to the corresponding results of Examples 1 to 5, for the fluids containing ethyl p-chlorophenyl selenide together with the phosphine additive.

EXAMPLE 7

To three aliquot portions of the functional fluid blend of Example 1 above, containing about 80% tri-n-butyl phosphate, about 11% tricresyl phosphate, and a small amount of polybutyl methacrylate viscosity index improver, is added, respectively 0.9% of ethyl p-chlorophenyl selenide, 0.3% of ethyl p-chlorophenyl selenide, and a combination of 0.3% ethyl p-chlorophenyl selenide and 1.0% triphenyl phosphine. The autoignition temperature (AIT) of the resulting fluid compositions is obtained, the autoignition temperature of such functional fluid compositions being determined in accordance with standard methods of test for autoignition temperature in accordance with ASTM D2155 procedure.

The results of such tests are noted in Table 5 below, in which the terms "selenide" and "phosphine" designate the above-noted specific selenide and phosphine additives, respectively.

TABLE 5

Additive concentration:	AIT (° F.)
Control	730
0.9% selenide	930
0.3% selenide	820
0.3% selenide+ 1.0% phosphine	920

From the table above, it is seen that the addition of 0.3% of the selenide additive in the absence of phosphine, increases the AIT of the control fluid containing no selenide from an AIT of 730° F., to 820° F., and when incorporating 0.9% of the selenide in the absence of phosphine, the AIT is increased to 930° F. On the other hand, by incorporating with the fluid containing 0.3% of the selenide, 1.0% of the phosphine additive, the resulting fluid has an AIT of 920° F., 100° F. higher than the 820° value for the fluid containing 0.3% selenide in the absence of phosphine, and closely matching the 930° F. AIT for the fluid containing 0.9% selenide and in the absence of any phosphine.

The above Table 5 illustrates the synergistic effect of the phosphine additive on the fluid containing the selenide, in substantially increasing the autoignition temperature and correspondingly reducing flammability over a fluid containing a comparable amount of selenide only, thus improving the AIT and performance of the fluid, while reducing the concentration of selenide required, and at the same time the phosphine additive serves to protect the above-noted metals such as copper, iron and cadmium, against corrosive attack by the fluids containing the selenide additives, as demonstrated in Examples 1 to 6 above.

EXAMPLE 8

The test procedure of Example 1 is repeated, but employing as the functional fluid a blend of 56% tri-n-butyl phosphate, 35% diisodecyl adipate and 5% poly-n-hexyl acrylate having an average molecular weight of about 2,000 as viscosity index improver, with one portion of the fluid containing 0.8% of 4,4'-dichlorodiphenyl diselenide, and the other portion containing such selenide and also 1.0% of triphenyl phosphine.

The corrosivity of the fluid containing only the 0.8% of the selenide on the metals in Example 1, and the acid number of such fluid containing only this selenide, are substantially reduced by incorporation of the 1.0% triphenyl phosphine, comparable to the results obtained in Example 1.

EXAMPLE 9

The test procedure of Example 8 is repeated but employing as the functional fluid a blend of 39% tri-n-butyl phosphate, 47% diisodecyl adipate, 10% diisodecyl phthalate, and a small amount of oxidation inhibitor, with one portion of the fluid containing 0.8% of 4,4'-dichlorodiphenyl diselenide, and another portion containing 0.8% of 4,4'-dichlorodiphenyl diselenide together with 1.0% of triphenyl phosphine.

The presence of the 1.0% of triphenyl phosphine in the above-noted fluid blend containing the selenide additive substantially reduces corrosivity on bronze, iron and cadmium plate, and the acid number is also substantially reduced, as compared to the fluid containing only the selenide additive, similar to the results obtained in Example 8.

EXAMPLE 10

The test procedure of Example 1 is repeated employing as the functional fluid tri-n-butyl phosphate instead of the blend of Example 1.

Reduction in corrosivity and acid number of the resulting fluid by addition of triphenyl phosphine to the fluid containing the additive 4,4'-dichlorodiphenyl diselenide, are comparable to the results obtained in Example 1.

EXAMPLE 11

The procedures of Examples 1 and 2 are repeated employing, respectively, (a) phenyl ethyl selenide and (b) 4,4'-di(seleno ethyl) diphenyl ether, in place of 4,4'-dichlorodiphenyl diselenide, each such selenide additive (a) and (b) being employed in an amount of 1.0% by weight in the respective portions of the functional fluid blend.

Reduction in corrosivity and acid number results comparable to those of Examples 1 and 2 are obtained for the fluids containing the respective (a) and (b) selenides, together with the phosphine additives.

EXAMPLE 12

The procedure of Example 1 is repeated employing in place of the functional fluid blend in Example 1, the following fluids:

(a) a blend of 70% diisodecyl adipate and 30% tri-n-butyl phosphate
(b) a blend of 50% diisodecyl adipate, 30% tri-n-butyl phosphate and 20% dibutyl phenyl phosphate
(c) a blend of 50% diisodecyl adipate, 40% tri-n-butyl phosphate and 10% tri-isodecyl-tri-mellitate
(d) a blend of 50% tri-n-butyl phosphate and 50% diisodecyl phthalate
(e) a red petroleum hydrocarbon liquid containing hydrocarbon chains ranging from C_{10} to C_{20} (MIL–H–5606–B)
(f) phenyl - N - methyl - N - n-butyl-N'-methyl-N'-n-butyl phosphorodiamidate.

In each of the above six fluids (a), (b), (c), (d), (e), and (f), a substantial reduction in corrosivity of the respective fluids on bronze, iron and cadmium plate, and a substantial reduction of the acid number of the respective fluids is obtained, by incorporation of the additive triphenyl phosphine in each of the above fluids also containing the selenide additive 4,4'-dichlorodiphenyl diselenide.

EXAMPLE 13

The procedure of Example 1 is repeated employing in place of triphenyl phosphine the following phosphine additives:

(1) cresyl diphenyl phosphine
(2) tricresyl phosphine
(3) alpha-naphthyl-diphenyl phosphine
(4) tris-(3,4-dimethylphenyl) phosphine.

Incorporation of the above phosphine additives (1) to (4), respectively, in the functional fluid blend of Example 1, namely fluid I containing the selenide additive 4,4'-dichlorodiphenyl diselenide, substantially reduces corrosivity of the respective fluids on bronze, iron and cadmium plate, and the resulting fluids containing the phosphine additives (1) to (4) have substantially reduced acid numbers in comparison with the corresponding fluids containing only the selenide additive and in the absence of the phosphine additive.

EXAMPLE 14

The following composition is prepared:

	Weight percent
Tri-n-butyl phosphate	50.0
Di-n-butyl phenyl phosphate	9.0
Diisodecyl adipate	33.0
Poly n-hexyl acrylate viscosity index improver, m.w.=2,000	4.5
Diepoxide oxidation inhibitor (Unox 221)	2.2
4,4'-dichlorodiphenyl diselenide	0.8
Triphenyl phosphine	0.5
	100.0

To 99.5% by weight of the above composition is added 0.5% by weight of water, and the resulting composition is designated A.

The properties of composition A are noted below.

Results of closed oxidation-corrosion tests at 250° F. for 168 hours are set forth in Tables 6 and 7 below, the metals of Table 6 all being inserted in the same fluid A above in one test and the metals of Table 7 all being inserted in another portion of fluid A in another test, the acid number of the fluid A in each of the tests being determined after the 168 hour test period.

TABLE 6

Fluid A

Weight change (mg./cm.²):	
Copper	−0.31
Iron	0
Magnesium	+7.6
Aluminum	0
Cadmium plate	0
Acid number	0.29

TABLE 7

Fluid A

Weight change (mg./cm.²):	
Bronze	0
Iron	0
Titanium	0
Aluminum	0
Cadmium plate	0
Acid number	0.25

The fluid A shows practically complete freedom from corrosive attack on the metals of Tables 6 and 7, except for magnesium, although the corrosion value in Table 6 for magnesium is within aircraft specification standards, and a low acid number for fluid A is obtained in both tests reported in Tables 6 and 7.

	° F.
Flash point	390
Fire point	400

(flash point and fire point obtained by standard Cleveland open cup procedure)

Autoignition temperature (AIT), 900° F. (obtained by ASTM D 2155 procedure)

Hot manifold flammability—lowest temperature of ignition 1275° F. (AMS 3150 C procedure)

High pressure spray flammability—ignites at a location no closer than 45 inches from spray nozzle and flame is self extinguishing

Rubber compatibility—rubber swell and hardness change after 1 week immersion of EPR (ethylene-propylene rubber) in fluid A at 160° F.—ΔH (change in hardness) −12 (Shore A scale), swell 22%

Viscosity at:		
210° F.	cs. (centistokes)	3.85
100° F.	cs.	12.2
0° F.	cs.	120
−40° F.	cs.	600
−65° F.	cs.	2250
Density at 77° F.	gm./ml.	0.966

The above values for flash point, fire point, AIT, hot manifold flammability and high pressure spray flammability indicate generally improved fire and flammability resistance of fluid A, and the above change in hardness and swell values for EPR in fluid A show satisfactory perforance within aircraft specification standards for contact of fluid A with EPR, an important rubber used widely in the manufacture of seals for aircraft hydraulic systems. The above viscosity values show operability and pumpability of fluid A both at high operating temperatures of 210° F. and at very low temperatures of −65° F., and the above density value of 0.966 of fluid A shows low density of the fluid, an important economic criterion especially for use of the fluid in the hydraulic system of modern large commercial aircraft.

A pump test of fluid A is carried out at 225° F. hottest point for about 500 hours in a New York Airbrake 3,000 p.s.i. pump, with steel, bronze and aluminum components. At various time intervals during the test the viscosity of a sample of the fluid at 100° F. and its acid number are measured. This data is set forth in Table 8 below.

TABLE 8

Time (hrs.)	Viscosity at 100° F. (cs.)	Acid number
100	10.85	0.12
214	8.47	0.18
358	8.36	0.34
430	8.23	0.40
502	8.23	0.49

The data of Table 8 above indicates that the fluid A remains relatively stable, and the pump condition after the test is classified as good to excellent with no apparent wear on the pump components, comparable to the condition of the pump when carrying out a pump test under the same operating conditions using the functional fluid blend of Example 1 above, containing no selenide and no phosphine additives.

A Shell 4-ball wear test of steel on steel of fluid A shows only a 0.80 mm. scar diameter, indicating good wear characteristics of fluid A on steel.

In accordance with the invention, by incorporation of the above-defined tertiary organic phosphine additive in a functional fluid, such as a phosphate ester, containing a selenide additive as defined above, a substantial improvement in auto-ignition temperature and corresponding reduction in flammability is obtained as result of the presence of the selenide while at the same time substantially reducing the corrosive effect of the fluid containing the selenide additive on various metals, particularly copper and its alloys, employed as components in hydraulic fluid systems, including pumps, valves and the like, without adversely affecting any of the advantageous characteristics of the functional fluid, e.g. without reducing the

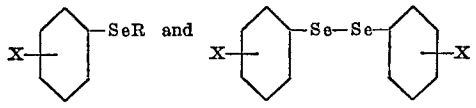
high temperature thermalstability of the functional fluid and without any increase in low temperature viscosity of the fluid.

From the foregoing, it is seen that the invention provides novel functional fluid compositions containing a combination of certain organo-selenium compounds, together with certain tertiary organic phosphines, which have improved fire resistance and reduced corrosivity on certain metals.

While I have described particular embodiments of my invention for purposes of illustration, it will be understood that various changes and modifications within the spirit of the invention can be made, and the invention is not to be taken as limited except by the scope of the appended claims.

I claim:

1. A functional fluid composition consisting essentially of (1) a major portion of a functional fluid base stock selected from the group consisting of phosphorus esters, amides of an acid of phosphorus, di- and tricarboxylic acid esters, and petroleum hydrocarbons; (2) a small amount of a selenium compound sufficient to increase the autoignition temperature of said base stock, said selenium compound being selected from the group of compounds having the formulae:



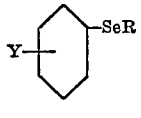
where X is halogen, there being from 1 to 3 X substituents on each phenyl nucleus, and R is alkyl of from about 1 to about 12 carbon atoms, and (3) a small amount of a tertiary organic phosphine having the formula:



where R_a, R_b and R_c are each a member selected from the group consisting of aryl and alkaryl, wherein R_a, R_b and R_c contain from 6 to about 8 carbon atoms, said selenium compound being present in an amount ranging from about 0.25 to about 5%, and said phosphine being present in an amount ranging from about 0.1 to about 5%, by weight of said composition.

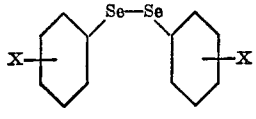
2. A composition as defined in claim **1**, said selenium compound being present in an amount ranging from about 0.5 to about 2% and said phosphine being present in an amount ranging from about 0.1 to about 2%, by weight of said composition.

3. A composition as defined in claim **1**, wherein said selenium compound has the formula:



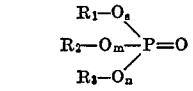
where X is halogen and R is alkyl of from about 1 to about 12 carbon atoms, there being from 1 to 3 X substituents on the phenyl nucleus, and where R_a, R_b and R_c of said phosphine are each a member selected from the group of phenyl and cresyl.

4. A composition as defined in claim **1**, where said selenium compound has the formula:



where X is halogen, there being from 1 to 3 X substituents on each phenyl nucleus, and where R_a, R_b and R_c of said phosphine are each a member selected from the group of phenyl and cresyl.

5. A composition as defined in claim **1**, wherein said base stock is a phosphorus ester having the formula:



where *s*, *m* and *n* are each an integer of 0 to 1, and not more than two of *s*, *m* and *n* are 0, R_1, R_2 and R_3 are each a member selected from the group consisting of aryl, alkaryl, alkyl of from about 3 to about 10 carbon atoms, and alkoxyalkyl having from about 3 to about 8 carbon atoms.

6. A composition as defined in claim **5**, wherein *s*, *m* and *n* are each 1, and said phosphorus ester is a phosphate ester.

7. A composition as defined in claim **1**, wherein said base stock consists essentially of a phosphate ester selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates, said alkyl groups containing from about 3 to about 10 carbon atoms and said aryl groups containing from 6 to 8 carbon atoms, the total number of carbon atoms in all three aryl groups in said triaryl phosphates being from 19 to 24.

8. A composition as defined in claim **7**, wherein said base stock additionally contains a dicarboxylic acid ester selected from the group consisting of the alkyl diesters of adipic and sebacic acid, containing alkyl groups of from about 4 to about 12 carbon atoms, and an alkyl diester of phthalic acid containing alkyl groups of from about 4 to about 12 carbon atoms.

9. A composition as defined in claim **7**, wherein said mixture additionally contains an alkyl diester of phthalic acid containing alkyl groups of from about 4 to about 12 carbon atoms, and a dicarboxylic acid ester selected from the group consisting of the alkyl diesters of adipic and sebacic acid, containing alkyl groups of from about 4 to about 12 carbon atoms.

10. A composition as defined in claim **7**, wherein said selenium compound is a member selected from the group consisting of ethyl p-chlorophenyl selenide and 4,4'-dichlorodiphenyl dieselenide, and said phosphine is selected from the group consisting of triphenyl phosphine and dicresyl phenyl phosphine.

11. A composition as defined in claim **8**, wherein said selenium compound is a member selected from the group consisting of ethyl p-chlorophenyl selenide and 4,4'-dichlorodiphenyl diselenide, and said phosphine is selected from the group consisting of triphenyl phosphine and dicresyl phenyl phosphine.

12. A composition as defined in claim **1**, said base stock consisting essentially of a member selected from the group consisting of di-n-butyl phenyl phosphate, tri-n-butyl phosphate and tricresyl phosphate, and mixtures thereof, said selenium compound is a member selected from the group consisting of ethyl p-chlorophenyl selenide, and 4,4'-dichlorodiphenyl diselenide, and said phosphine is selected from the group consisting of triphenyl phosphine and dicresyl phenyl phosphine.

13. A composition as defined in claim **12**, said selenium compound being 4,4'-dichlorodiphenyl diselenide and said phosphine being triphenyl phosphine.

14. A composition as defined in claim **12**, said base stock consisting essentially of a mixture of tri-n-butyl phosphate and tricresyl phosphate.

15. A composition as defined in claim **12**, said base stock additionally containing a member selected from the group consisting of diisodecyl adipate and diisodecyl phthalate, and mixtures thereof.

16. A composition as defined in claim **12**, said base stock consisting essentially of a mixture of di-n-butyl phenyl phopshate, tri-n-butyl phosphate and diisodecyl adipate.

17. A composition as defined in claim **12**, said selenium compound being present in an amount ranging from about 0.5 to about 2% and said phosphine being present

in an amount ranging from about 0.1 to about 2%, by weight of said composition.

18. A composition as defined in claim **12**, said base stock additionally containing a mixture of diisodecyl phthalate and diisodecyl adipate.

19. A composition as defined in claim **15**, wherein said phosphate is tri-n-butyl phosphate.

20. A composition as defined in claim **1**, wherein said base stock consists essentially of a mixture of a dialkyl phthalate and a member selected from the group consisting of a dialkyl adipate and a dialkyl sebacate, containing alkyl groups of from about 4 to about 12 carbon atoms, said selenium compound is a member selected from the group consisting of ethyl p-chlorophenyl selenide and 4,4'-dichlorodiphenyl diselenide, and said phosphine is selected from the group consisting of triphenyl phosphine and dicresyl phenyl phosphine.

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U.S. Cl. X.R.

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