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3,723,319  
**FUNCTIONAL FLUIDS OF INCREASED FIRE  
 RESISTANCE**

Robert S. McCord, Pacific Palisades, Donald H. Nail, Los Angeles, and Martin B. Sheratte, Reseda, Calif., assignors to McDonnell Douglas Corporation, Santa Monica, Calif.

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23 Claims

**ABSTRACT OF THE DISCLOSURE**

Production of functional fluids, particularly aircraft hydraulic fluids, of improved fire resistance, comprising a functional fluid base stock, such as a phosphate ester, e.g., tri-n-butyl phosphate, or mixtures of such base stocks, and a small amount of a trialkyl or a trialkoxy phosphorus selenide compound, e.g., triethyl phosphorus selenide or triethoxy phosphorus selenide.

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.

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 fluid, 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 resistance.

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 materials including metals and non-metals such as elastomeric seals of the 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 or materials of 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 above 750° F., e.g., to the range of about 800 to about 1,000° F.

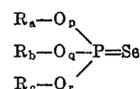
It has now been found in accordance with the present invention that the fire resistance, or autoignition temperature, of functional fluid or hydraulic fluid compositions, can be significantly improved by the addition to such compositions of a small amount of certain selenium compounds, in the form of certain trialkyl or trialkoxy phosphorus selenides, defined in greater detail hereinafter. The inclusion of such selenium-containing additives in functional and hydraulic fluid compositions generally does not adversely affect any of the above noted important characteristics of such fluids, particularly aircraft hydraulic fluids, including their desirable viscosity characteristics.

Another important feature is that certain recently developed hydraulic fluids for aircraft use have been designed particularly to have reduced density, but many of these low density fluids have inferior fire resistance to the higher density hydraulic fluids, and it has been found that the organic selenium compounds of the invention when incorporated into such low density fluids substantially increase the fire resistance and reduce the flammability of these low density hydraulic fluids.

The use of dialkyl selenides as oxidation inhibitors for orthosilicate fluids is described in U.S. Pat. 3,118,841 to Moreton. In such patent the selenide, e.g., dilauryl selenides, is employed in combination with other oxidation inhibitors such as phenyl alpha naphthylamine. However, selenides which inhibit oxidation in liquids do not necessarily function to reduce flammability, or to increase autogenous ignition temperature of a fluid, and in such patent only orthosilicates are employed as the base stock. Further, many of the selenides are toxic, thermally unstable and/or insufficiently soluble at the working temperature. Certain selenides also tend to corrode metals. Moreover, in order to effectively reduce flammability, selenium compounds should also possess the property of decomposing in the plasma condition in flames to prevent or poison continuation of the flame.

It has been found that certain trialkyl and trialkoxy phosphorus selenides as defined below, 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, relatively free from corrosion, and have sufficient solubility in most functional and hydraulic fluids to effectively function as flame inhibitors. In addition, the trialkyl and trialkoxy phosphorus selenides employed according to the invention 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.

Effective selenium compounds, that is trialkyl and trialkoxy phosphorus selenides, for use as additives in functional or hydraulic fluids to reduce flammability and increase autoignition temperature of the fluid, according to the invention have the formula:



where *p*, *q* and *r* can be 0 or 1, preferably all 0 or all 1, and *R<sub>a</sub>*, *R<sub>b</sub>* and *R<sub>c</sub>* each are alkyl, either straight chain or branched chain, of from about 1 to about 6 carbon atoms, and where *R<sub>a</sub>*, *R<sub>b</sub>* and *R<sub>c</sub>* can be the same or different, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl, isoamyl, n-hexyl, and the like. Where *R<sub>a</sub>*, *R<sub>b</sub>* and *R<sub>c</sub>* each contain more than 6 carbon atoms, solu-

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bility of the additives in the functional fluid is generally insufficient.

Preferably  $R_a$ ,  $R_b$  and  $R_c$  are the same alkyl group. The preferred class of selenide additives according to the invention are the compounds wherein  $p$ ,  $q$  and  $r$  are all 1, that is, the trialkoxy phosphorus selenides. Specific examples of the latter class are as follows:

- (1)  $(CH_3O)_3PSe$
- (2)  $(C_2H_5O)_3PSe$
- (3)  $(CH_3CH_2CH_2O)_3PSe$
- (4)  $(iso-C_3H_7O)_3PSe$
- (5)  $(n-C_4H_9O)_3PSe$
- (6)  $(iso-C_4H_9O)_3PSe$
- (7)  $(n-C_5H_{11}O)_3PSe$
- (8)  $(iso-C_5H_{11}O)_3PSe$
- (9)  $(n-C_6H_{13})_3PSe$
- (10)  $(C_2H_5O)_2(CH_3O)PSe$
- (11)  $(C_2H_5O)_2(iso-C_3H_7O)PSe$
- (12)  $(n-C_3H_7O)_2(iso-C_4H_9O)PSe$

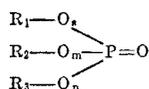
Specific examples of trialkyl phosphorus selenides are those corresponding to the specific trialkoxy phosphorus selenides (1) to (12) listed above, the respective alkoxy groups of which are changed to alkyl groups connected directly to the phosphorus atom.

Compound (2) above, namely, triethoxy phosphorus selenide has been found particularly effective according to the invention.

The following base stocks are illustrative of typical base stock 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 phenyl, 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, 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.

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Examples of triaryl phosphates to which the trialkyl or trialkoxy phosphorus selenides 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 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, tertbutylphenyl-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 isoctene 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 selenides of the invention can be employed as additives 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-dimethyl-phosphoroamidate,
- phenyl-N,N-dimethyl-N'-N'-dimethylphosphorodiamidate,
- N-methyl-N-butyl-N'-N''-tetramethylphosphorotriamidate,
- N,N'-di-n-propyl-N''-dimethyl phosphorotriamidate

Another class of functional fluid base stocks whose autoignition temperature can be improved by incorporation of the selenides of the invention are the di- and tri-carboxylic 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 in-

cluding 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 phthalate, dihexyl phthalate, dioctyl phthalate, dinonyl phthalate, didecyl phthalate, and di-isodecyl 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 selenides are added according to the invention, petroleum hydrocarbons, which can contain carbon chains of from C<sub>10</sub> to about C<sub>22</sub> 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<sub>10</sub> to about C<sub>20</sub> 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 di-isodecyl 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 di-isodecyl adipate and di-isodecyl 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 6,000 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 6,000 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 according to the invention, it is usually desirable to employ only a small amount of the trialkyl or trialkoxy phosphorus 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.

The trialkoxy phosphorus selenide and trialkyl phosphorus selenide additives of the invention can be prepared in known manner. Thus, the trialkoxy phosphorus selenide additive can be prepared generally by reacting the corresponding trialkyl phosphite with selenium powder under suitable conditions, and the trialkyl phosphorus selenide additive can be prepared by reacting the corresponding trialkyl phosphine with selenium powder under suitable reaction conditions.

The following are examples of preparation of two of the preferred selenide additives of the invention:

#### EXAMPLE 1

##### Triethoxy phosphorous selenide

Freshly distilled triethylphosphite (50 g., 0.3 mole) was treated under nitrogen with selenium shot (25.3 g., 0.32 mole). An immediate vigorous exotherm was observed, and the temperature of the mixture was controlled below 80° C. by occasional use of an ice bath. After about an hour, the reaction abated, and the mixture was then heated to 100° C. for ten minutes. The colorless product was filtered from the small amount of unreacted selenium and used without further purification. The yield was 73 g., which is almost quantitative.

#### EXAMPLE 2

##### Triethyl phosphorus selenide

Freshly distilled triethyl phosphine (59 g., 0.5 mole) was dissolved in 200 ml. anhydrous benzene under nitrogen, and then treated with selenium shot (40 g., 0.51 mole). The exothermic reaction was controlled by occasional immersion of the flask in an ice bath. When the reaction had abated, the flask was heated under reflux for two hours.

The colorless solution was then filtered, and the benzene was removed under vacuum. The white crystalline product, triethyl phosphorus selenide, had M.P. 108-110° C., and was used without further purification.

The following are examples illustrating practice of the invention by incorporation of trialkoxy phosphorus selenide and trialkyl phosphorus selenide additives according to the invention into functional fluid base stocks. In the examples below the term "AIT" means autoignition temperature, the autoignition temperature of the functional fluid compositions of the invention according to the examples below being determined in accordance with standard method of test for autoignition temperature in accordance with ASTM D 2155 procedure. All percentages are in terms of percent by weight of the functional fluid compositions.

#### EXAMPLE 3

To aliquot portions of tri-n-butyl phosphate, designated Fluid A in the table below, is added varying minor amounts of triethoxy phosphorus selenide, and the autoignition temperature of the various aliquot portions of the resulting fluid compositions, and of a control of Fluid A with no such selenide, is obtained.

The results of such tests are noted in the table below.

TABLE

Fluid	Additive	Additive concentration (percent)	AIT (° F.)
A	Triethoxy phosphorus selenide	0	730
A	do	0.5	820
A	do	1.3	910
A	do	2.0	930

From the table above, it is seen that incorporation of the above noted small amounts of the triethoxy phosphorus selenide additive in Fluid A substantially increases the AIT of the control Fluid A from an AIT of 730° F., e.g. to 910° F. employing 1.3% of the selenide additive, and to about 930° F. employing 2% of such selenide, on the order of 200° F. above the AIT of the control fluid, and that increasing proportions of the selenide additive in the fluid generally increases the AIT thereof.

## EXAMPLE 4

To di-n-amyl pentane phosphonate fluid is added 5% triethoxy phosphorus selenide, and the autoignition temperature of the resulting fluid composition and of a control of such fluid in the absence of any selenide, is obtained.

The AIT of the fluid containing the 5% selenide additive noted above is 780° F., about 200° F. higher than the AIT of only 590° F. for the control fluid containing no selenide.

## EXAMPLE 5

The procedure of Example 3 is repeated, employing in place of triethoxy phosphorus selenide, triethyl phosphorus selenide, triethyl phosphorus selenide.

Results similar to those of Example 3 are obtained.

## EXAMPLE 6

The procedure of Example 3 is repeated, employing in place of Fluid A of Example 3, 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.

Results comparable to those of Example 3 are obtained, that is, the addition of the triethoxy phosphorus selenide in varying proportions ranging from about 0.5 to about 2.0% to the above functional fluid blend substantially increases AIT over the AIT of 740° F. for the functional fluid control in the absence of such selenide, to values between about 850 and 950° F., and the AIT of the functional fluid blend increases with increasing amount of the selenide additive incorporated in the functional fluid blend.

## EXAMPLE 7

To a blend of a functional fluid containing about 70% di-isodecyl adipate and 30% tri-n-butyl phosphate are respectively added the selenide compounds (3), (4) and (6) above, and the corresponding tripropyl, triisopropyl and triisobutyl phosphorus selenides, each in amounts respectively of 0.5, 1.0 and 1.8%, to respective portions of the functional fluid blend.

For each of these trialkoxy and trialkyl phosphorus selenide additives incorporated in the functional fluid blend of this example, AIT is substantially increased in the range of about 800 to about 950° F., well above the less than 700° F. value for the control, in the absence of any selenide additive, and in each case for each of such selenide additives, the AIT increases with increasing amount of additive incorporated, up to the 1.8% level.

## EXAMPLE 8

The procedure of Example 8 is repeated, employing in place of Fluid A of Example 3, a functional fluid blend comprising 70% di-isodecyl adipate and 30% tri-n-butyl phosphate.

Results generally corresponding to those of Example 3 are obtained.

## EXAMPLE 9

The procedure of Example 3 is repeated, employing triethoxy phosphorus selenide and triethyl phosphorus selenide in respective portions of each of the following functional fluids, in each fluid varying the proportion of each of such selenide additives in the amounts noted in Example 3:

(I) A red petroleum hydrocarbon liquid containing hydrocarbon chains ranging from C<sub>10</sub> to C<sub>20</sub> (MIL-H-5606B).

(II) A blend of a functional fluid containing 50% di-isodecyl adipate, 30% tri-n-butyl phosphate and 20% di-butyl phenyl phosphate.

(III) A blend of a functional fluid containing 50% di-isodecyl adipate, 40% tri-n-butyl phosphate and 10% tri-isodecyl-tri-mellitate.

(IV) A blend of a functional fluid containing 39% tri-n-butyl phosphate, 47% di-isodecyl adipate and 10% diisodecyl phthalate.

For each of the functional fluids (I), (II), (III) and (IV) above, incorporation of the triethoxy phosphorus selenide or triethyl phosphorus selenide substantially increases AIT from that of the control, in the absence of any selenide additive, the AIT increasing in each case with increasing amount of triethoxy or triethyl phosphorus selenide additive incorporated, up to the 2.0% level, the incorporation of such additive in the above noted fluids (II), (III) and (IV) particularly increasing the AIT of such fluids from the 600 to 700° F. range to the 800 to 900° F. range.

## EXAMPLE 10

The procedure of Example 3 is repeated employing in place of Fluid A of Example 3, phenyl-N-methyl-N-n-butyl-N'-methyl-N'-n-butyl phosphorodiamidate.

Results comparable to those of Example 3 are obtained.

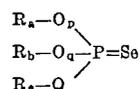
In each of the Examples 3 to 10 above, a substantial improvement in autoignition temperature, and corresponding reduction inflammability is obtained, by incorporating the trialkoxy and trialkyl phosphorus selenides of the invention into the various functional fluids and blends thereof set forth in the examples, and such reduction in flammability is obtained without reducing the high temperature thermal stability of the functional fluid and without any increase in low temperature viscosity of the fluid, employing the selenium compounds of the invention having relatively good solubility in such fluids and high effectiveness therein, and which are relatively free from toxicity.

From the foregoing, it is seen that the invention provides novel functional fluid compositions containing certain organo-selenium compounds which function effectively as flame retardants or flame inhibitors in such fluids.

While we have described particular embodiments of our 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.

We claim:

1. A composition consisting essentially of a major portion of a functional fluid base stock selected from the group consisting of phosphorus esters, amides of an acid of phosphorus, and di- and tricarboxylic acid esters, and an amount ranging from about 0.25 to about 5% by weight of said composition, of a selenium compound having the formula:



where  $p$ ,  $q$  and  $r$  are each an integer of 0 to 1, and  $R_a$ ,  $R_b$  and  $R_c$  are each alkyl of from about 1 to about 6 carbon atoms.

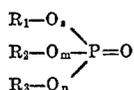
2. A composition as defined in claim 1, said selenium compound being present in an amount ranging from about 0.5 to about 2% by weight of said composition.

3. A composition as defined in claim 1, said selenium compound being selected from the group consisting of trialkyl phosphorus selenides wherein  $p$ ,  $q$  and  $r$  are each 0, and trialkoxy phosphorus selenides wherein  $p$ ,  $q$  and  $r$  are each 1.

4. A composition as defined in claim 3, wherein said selenium compound is a trialkoxy phosphorus selenide.

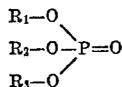
5. A composition as defined in claim 3, said selenium compound being present in an amount ranging from about 0.5 to about 2% by weight of said composition.

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

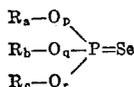


where  $s$ ,  $m$  and  $n$  are each an integer of 0 to 1, and not more than two of  $s$ ,  $m$  and  $n$  are 0, and  $R_1$ ,  $R_2$  and  $R_3$  are each a member selected from the group consisting of aryl, alkaryl, alkyl of from about 3 to about 10 carbon atoms, an alkoxyalkyl having from about 3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

7. A composition consisting essentially of a major portion of a functional fluid base stock comprising a phosphate ester having the formula:



where  $R_1$ ,  $R_2$  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, and an amount ranging from about 0.25 to about 5% by weight of said composition of a selenium compound having the formula:



where  $p$ ,  $q$  and  $r$  are each an integer of 0 to 1, and  $R_a$ ,  $R_b$  and  $R_c$  are each alkyl of from about 1 to about 6 carbon atoms.

8. A composition as defined in claim 7, wherein said phosphate ester is selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates, and said selenium compound is selected from the group consisting of trialkyl phosphorus selenides wherein  $p$ ,  $q$  and  $r$  are each 0, an trialkoxy phosphorus selenides wherein  $p$ ,  $q$  and  $r$  are each 1.

9. A composition as defined in claim 8, wherein said selenium compound is present in an amount ranging from about 0.5 to about 2% by weight of said composition.

10. A composition as defined in claim 7, wherein said base stock comprises a mixture of a phosphate ester selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates, and a dicarboxylic acid ester, and said selenium compound is selected from the group consisting of trialkyl phosphorus selenides wherein  $p$ ,  $q$  and  $r$  are each 0, and trialkoxy phosphorus selenides wherein  $p$ ,  $q$  and  $r$  are each 1.

11. A composition as defined in claim 10, wherein said dicarboxylic acid ester is selected from the group consist-

ing of the alkyl diesters of adipic and sebacic acid, containing alkyl groups of from about 4 to about 12 carbon atoms.

12. A composition as defined in claim 10, wherein said dicarboxylic acid ester is an alkyl diester of phthalic acid containing alkyl groups of from about 4 to about 12 carbon atoms.

13. A composition as defined in claim 12, wherein said mixture includes 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.

14. A composition as defined in claim 7, wherein said phosphate ester is selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates, and said selenium compound is triethoxy phosphorus selenide.

15. A composition as defined in claim 14, said selenium compound being present in an amount ranging from about 0.5 to about 2% by weight of said composition.

16. A composition as defined in claim 7, wherein said base stock comprises a mixture of said phosphate ester, said phosphate ester selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates and a dicarboxylic acid diester 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 said selenium compound is triethoxy phosphorus selenide.

17. A composition as defined in claim 7, said base stock comprising a mixture of said phosphate ester, said phosphate ester selected from the group consisting of dialkyl aryl, triaryl, trialkyl, and alkyl diaryl phosphates, and an alkyl diester of phthalic acid containing alkyl groups of from about 4 to about 12 carbon atoms, and said selenium compound being triethoxy phosphorus selenide.

18. A composition as defined in claim 17, wherein said mixture includes 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.

19. A composition as defined in claim 7, said base stock comprising a member selected from the group consisting of di-*n*-butyl phenyl phosphate, tri-*n*-butyl phosphate and tricresyl phosphate, and mixtures thereof, and said selenium compound is triethoxy phosphorus selenide.

20. A composition as defined in claim 19, said base stock comprising a mixture of tri-*n*-butyl phosphate and tricresyl phosphate.

21. A composition as defined in claim 19, said base stock including a member selected from the group consisting of diisodecyl adipate and diisodecyl phthalate, and mixtures thereof.

22. A composition as defined in claim 19, said base stock including a mixture of di-isodecyl phthalate and diisodecyl adipate.

23. A composition as defined in claim 19, said base stock being a mixture of tri-*n*-butyl phosphate, diisodecyl adipate and diisodecyl phthalate.

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LEON D. ROSDOL, Primary Examiner

H. A. PITLICK, Assistant Examiner

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