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3,730,898

FUNCTIONAL FLUID COMPOSITIONS OF INCREASED FIRE RESISTANCE

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35 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 selenophene or tellurophene compound, preferably a chlorinated selenophene or a chlorinated tellurophene, e.g., tetrachloroselenophene or tetrachlorotellurophene.

This invention relates to functional fluid composition 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 or tellurium 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

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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 or tellurium compounds, in the form of certain selenophenes and tellurophenes, especially chlorinated selenophenes and chlorinated tellurophenes, defined in greater detail hereinafter. The inclusion of such selenium or tellurium-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 hydraulic fluids have inferior fire resistance to the higher density hydraulic fluids, and it has been found that the selenium- and tellurium-containing additives 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.

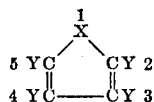
The use of dialkyl selenides as oxidation inhibitors for orthosilicate fluids is described in U.S. Pat. 3,118,841 to Moreton. In such patent the selenide, e.g., dilauryl selenide, is employed in combination with other oxidation inhibitors such as phenyl alpha naphthylamine. However, selenides which inhibit oxidation in liquids do not necessarily function to reduce flammability, or to increase autogenous ignition temperature of a fluid. Further, many of the selenides are toxic, thermally unstable, insufficiently soluble at the working temperature, or have an objectionable odor. 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 selenophenes and tellurophenes, and particularly the chlorinated selenophenes and tellurophenes of the invention, 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, 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 selenophenes and tellurophenes, particularly the chlorinated selenophene and tellurophene derivatives, 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 and tellurium compounds for use as additive in functional or hydraulic fluids to reduce flammability and increase autoignition temperature of the fluid, according to the invention, are the 5-membered un-

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saturated selenium and tellurium heterocyclic compounds having the general formula:



where X is Se or Te, and Y is H or halogen such as Cl or Br.

Thus, specific examples of selenium and tellurium compounds within the above definition which can be employed according to the invention, include unsubstituted selenophene and tellurophene, wherein all of the Y's above are hydrogen.

It has been found that the halogenated selenophenes and tellurophenes, particularly the chlorinated derivatives, wherein at least one Y is halogen, e.g. chlorine or bromine, including both the partially halogenated and especially the completely halogenated, selenophenes and tellurophenes, and wherein 1, 2, 3 or all 4 Y's are halogen such as chlorine or bromine, are particularly effective functional fluid additives according to the invention. Also, halogen substituted selenophenes and tellurophenes can be employed having mixed halogen substituents, e.g., 1 or more of the Y's can be chlorine and one or more of the Y's in the same compound can be bromine. Further, mixtures of the above defined selenophenes, or of the above defined tellurophenes, or a combination of selenophenes and tellurophenes can be employed.

Specific examples of the above defined selenophenes and tellurophenes which can be employed according to the invention are as follows:

- (1) selenophene
- (2) tellurophene
- (3) 2-chloroselenophene
- (4) 3-chloroselenophene
- (5) 2,3-dichloroselenophene
- (6) 2,5-dichloroselenophene
- (7) 2,3,4-trichloroselenophene
- (8) 2,3,5-trichloroselenophene
- (9) tetrachloroselenophene
- (10) 2-chloro 3-bromoselenophene
- (11) 2,3-dichloro 4-bromoselenophene

Specific examples of halogenated tellurophenes correspond to those of compounds (3) to (11) above, wherein selenium is replaced by tellurium.

Specific examples of brominated selenophenes are those corresponding to compounds (3) to (9) above, wherein chlorine in each of such compounds is replaced by bromine, and specific examples of brominated tellurophenes correspond to the above specific brominated selenophenes, wherein selenium is replaced by tellurium.

Compounds which have been found especially effective and which are preferred according to the invention are tetrachloroselenophene, compound (9) above, and its tellurium analogue, tetrachlorotellurophene.

Selenophene, tellurophene and their halogenated derivatives employed as additives for functional fluids according to the invention, can be prepared in known manner. Thus, selenophene can be prepared by reacting selenium with acetylene under suitable reaction conditions, and tellurophene can be prepared in a similar manner employing tellurium.

Partially chlorinated derivatives of selenophene and tellurophene can be prepared in known manner by reacting selenophene or tellurophene with chlorine gas under suitable conditions and controls to obtain the desired degree of partial chlorination, e.g., substitution by 1, 2 or 3 chlorine atoms. Partially brominated derivatives of selenophene and tellurophene can be prepared in a similar manner employing bromine in place of chlorine. However, this procedure cannot be employed for preparing the completely halogenated, that is the tetrachlorinated or

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tetrabrominated derivatives of selenophene and tellurophene.

Thus, tetrachloroselenophene can be prepared by reacting substantially equimolar portions of selenium powder and hexachlorobutadiene, under heat and pressure, and tetrachlorotellurophene is prepared in a similar manner but employing tellurium powder.

Tetrabromoselenophene and tetrabromotellurophene can be prepared in a manner similar to that noted above for tetrachloroselenophene and tetrachlorotellurophene, employing hexabromobutadiene in place of hexachlorobutadiene.

The following is an example of preparation of tetrachloroselenophene:

EXAMPLE 1

Tetrachloroselenophene

Equivalent amounts of selenium powder (70 grams, 1 mole) and hexachlorobutadiene (260 grams, 1 mole) were heated under autogenous pressure at 250° C. for 24 hours. The mixture, after cooling, was poured into a solution of sodium bisulfite.

Selenium powder was precipitated together with tetrachloroselenophene. Solid materials were filtered off and the tetrachloroselenophene was dissolved in ether. After filtering the ether solution of tetrachloroselenophene from the selenium, the removal of the ether from such solution and distillation of the residual liquid, there was obtained 100 grams pure tetrachloroselenophene. Approximately 35 grams of selenium was recovered.

EXAMPLE 2

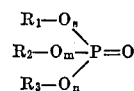
Tetrachlorotellurophene

The procedure of Example 1 was followed employing in place of selenium powder, tellurium powder in the same molecular proportion as noted in Example 1. The resulting product was tetrachlorotellurophene.

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 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, 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 phosphates 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 selenophenes and tellurophenes, especially the halogenated derivatives, 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 selenophenes and tellurophenes 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'-dimethylphosphoro-diamidate,
N-methyl-N-butyl-N',N''-tetramethylphosphorotriamidate,
N,N'-di-n-propyl-N''-dimethylphosphorotriamidate.

Another class of functional fluid base stocks whose autoignition temperature can be improved by incorporation of the selenophenes and tellurophenes, particularly the halogenated derivatives 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 these 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 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 selenophenes and tellurophenes hereof are added according to the invention, petroleum hydrocarbons, which can contain carbon chains of from C₁₀ to about C₂₄ carbon atoms. A typical example of such petroleum hydrocarbon is the red petroleum hydrocarbon liquid according to military specification MIL-H-5606B, understood to contain carbon chains of about C₁₀ to about C₂₀ 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 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 invention additive, that is, selenophene, tellurophene, or halogenated selenophene or tellurophene, 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 or telluride additive of the invention, preferably from about 0.5 to about 2% of such selenide or telluride additive in the functional fluid base stock, based on the weight of the composition. It has been found that an optimum amount of such additive ranges from about 0.8 to about 2% by weight of the composition.

The following are examples illustrating practice of the invention by incorporation of the selenophenes and tellurophenes described herein as 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 methods 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 composition.

EXAMPLE 3

To aliquot portions 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, designated Fluid A, is added varying amounts of tetrachloroselenophene, 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

Additive	Additive concentration, percent	AIT (° F.)
Fluid:		
A-----Tetrachloroselenophene-----	0	740
A-----do-----	0.5	800
A-----do-----	1.0	860
A-----do-----	1.3	870
A-----do-----	1.6	885
A-----do-----	2.0	890

From the table above, it is seen that incorporation of, for example, 1.0% by weight of the above selenophene additive in Fluid A increases the AIT of the control Fluid A from an "AIT" of 740° F. for the control, to 860° F., and that increased proportions of the selenophene additive increases AIT further, e.g., at 1.6% to 885° F. and at 2.0% to 890° F., substantially higher than the 740° F. value for the control fluid.

EXAMPLE 4

The procedure of Example 3 is repeated except employing in place of tetrachloroselenophene, tetrachlorotellurophene, in varying amounts corresponding to those set forth in the table above.

Increases in AIT of the fluid samples containing the tellurophene additive over the control fluid in the absence

of such additive, comparable to those of Example 3, are obtained.

EXAMPLE 5

The procedure of Example 3 is repeated, employing each of the respective compounds (3), (5) and (7) and their tellurophene analogues, each such additive being employed in amounts ranging from 0.5 to 2.0% by weight in respective portions of the fluid composition A.

For each of the tellurophene additives noted above and incorporated in Fluid A, AIT is substantially increased from the AIT of 740° F. for the control, in the absence of any additive, to an AIT ranging from about 800 to about 900° R., with AIT increasing as the amount of additive in each case is increased up to the 2.0% level.

EXAMPLE 6

The procedure of Example 3 is repeated, employing in place of tetrachloroselenophene, tetrabromoselenophene and tetrabromotellurophene, respectively, each in proportions noted in the table of Example 3.

Increased AIT values for the additive-containing samples of Fluid A, comparable to the increased AIT values set forth in the table of Example 3 are obtained, respectively, for each of the above brominated selenophene and tellurophene compounds.

EXAMPLE 7

The procedure of Example 3 is repeated employing as functional fluid, tri-n-butyl phosphate, and tetrachloroselenophene and tetrachlorotellurophene respectively, each in proportions noted in the table in Example 3.

Improvement in AIT of the fluid containing various proportions of the selenophene and tellurophene additives, comparable to those of Example 3 are obtained.

EXAMPLE 8

To respective portions of tri-n-butyl phosphate are added compounds (3), (5) and (7), and their bromine analogues, each in amounts respectively of 0.5, 1.0 and 1.8% by weight, to respective portions of the tri-n-butyl phosphate functional fluid.

For each of the halogenated selenophene additives noted above, AIT is substantially increased in the range of about 800 to 950° F., well above the 730° F. value for the control, in the absence of any selenide additive, and in each case for each of such additives, the AIT increases with increasing amount of additive incorporated.

EXAMPLE 9

The procedure of Example 3 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, and tetrachloroselenophene and tetrachlorotellurophene, respectively in the amounts noted in Example 3.

Results comparable to those of Example 3 are obtained.

EXAMPLE 10

To a blend of a functional fluid containing about 70% di-isodecyl adipate and 30% tri-n-butyl phosphate, are respectively added the halogenated selenophenes (4), (6), (8) and (10) noted above, each in amounts respectively of 0.5, 1.0 and 2.0%, to respective portions of the functional fluid blend.

For each of the selenophene additives (4), (6), (8) and (10) added to the functional fluid blend of this example, AIT is substantially increased in the range of about 800 to 900° 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 the above additives, the AIT increases with increasing amounts of additive incorporated, up to the 2.0% level.

EXAMPLE 11

The procedure of Example 3 is repeated employing tetrachloroselenophene and tetrachlorotellurophene, respec-

tively, in each of the following functional fluids, in each fluid varying the proportion of the selenophene or tellurophene additive in the amounts noted in Example 3.

(I) A red petroleum hydrocarbon liquid containing hydrocarbon chains ranging from C₁₀ to C₂₀ (MIL-H-5606B).

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

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

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

For each of the functional fluids (I), (II), (III) and (IV) above, incorporation of the selenophene or tellurophene additive substantially increases AIT from that of the control, in the absence of any selenide additive, the AIT increasing in each case with increasing amounts of the selenophene or tellurophene additive incorporated, up to the 2.0% level, incorporation of such additives 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 12

The procedure of Example 3 is repeated by incorporation of tetrachloroselenophene and tetrachlorotellurophene in di-n-amyl pentane phosphonate fluid, each such

The AIT of the fluids containing the selenophene and tellurophene additives noted above is substantially increased to values in excess of about 750° F., substantially higher than the AIT of only 590° F. for the control fluid containing no selenophene or tellurophene compound.

EXAMPLE 13

The procedure of Example 3 is repeated employing as the functional fluid, phenyl-N-methyl-N-n-butyl-N'-methyl-N'-n-butyl phosphorodiamidate.

Increases in AIT comparable to those of Example 3 are obtained.

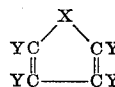
In each of the Examples 3 to 13 above, a substantial improvement in autoignition temperature and corresponding reduction in flammability is obtained, by incorporating the selenophene or tellurophene additives of the invention into the various functional fluids and blends thereof set forth in the examples, 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 certain organo-selenium and organo-tellurium compounds having relatively good solubility in such fluids and high effectiveness therein, and which are relatively free from toxicity and are relatively odor-free. Further the selenophene and tellurophene additives of the invention are substantially colorless, and hence when incorporated in functional fluids such as phosphate esters, such additives produce a minimum change in appearance or color of the fluid.

From the foregoing it is seen that the invention provides novel functional fluid compositions containing certain organo-selenium or organo-tellurium compounds which function efficiently 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 functional fluid 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, di- and tricarboxylic acid esters, and petroleum hydrocarbons containing carbon chains of from C₁₀ to about C₂₄ carbon atoms; and an amount ranging from about 0.25% to about 5% by weight of said composition of a compound having the formula:



where X is a member selected from the group consisting of Se and Te, and Y is a member selected from the group consisting of H and a halogen.

2. A composition as defined in claim 1, said 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, wherein at least one Y of said compound is halogen.

4. A composition as defined in claim 1, wherein all 4 Y's of said compound are halogen.

5. A composition as defined in claim 1, wherein X of said compound is selenium and at least one Y is a halogen selected from the group consisting of chlorine and bromine.

6. A composition as defined in claim 1, wherein X of said compound is selenium and all 4 Y's of said compound are halogen selected from the group consisting of chlorine and bromine.

7. A composition as defined in claim 1, wherein each Y of said compound is hydrogen.

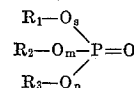
8. A composition as defined in claim 1, wherein said compound is selected from the group consisting of tetrachloroselenophene and tetrachlorotellurophene.

9. A composition as defined in claim 2, wherein said compound is selected from the group consisting of tetrachloroselenophene and tetrachlorotellurophene.

10. A composition as defined in claim 1, said base stock comprising a petroleum hydrocarbon containing carbon chains of from C₁₀ to about C₂₄, and said compound being a member selected from the group consisting of tetrachloroselenophene and tetrachlorotellurophene.

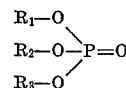
11. A composition as defined in claim 1, said base stock comprising a petroleum hydrocarbon containing carbon chains of from C₁₀ to about C₂₀, and said compound being a member selected from the group consisting of tetrachloroselenophene and tetrachlorotellurophene, said compound being present in an amount ranging from about 0.5 to about 2% by weight of said composition.

12. 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, R₁, R₂ and R₃ 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.

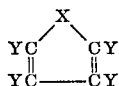
13. A functional fluid composition consisting essentially of a major portion of a functional fluid base stock, said base stock comprising a phosphate ester having the general formula:



where R₁, R₂ and R₃ are each a member selected from the group consisting of aryl, alkaryl, alkyl of from about 3 to

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about 10 carbon atoms, and alkoxyalkyl having from about 3 to about 8 carbon atoms, and about 0.25 to about 5% by weight of said composition of a compound having the formula



where X is a member selected from the group consisting of Se and Te, and Y is a member selected from the group consisting of H and a halogen.

14. A composition as defined in claim 13, wherein said base stock comprises a phosphate ester selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates.

15. A composition as defined in claim 13, wherein said base stock comprises a phosphate ester selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates, said 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 13, wherein said base stock comprises a phosphate ester selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates, and wherein X of said compound is selenium and at least one Y is a halogen selected from the group consisting of chlorine and bromine.

17. A composition as defined in claim 13, wherein said base stock comprises a phosphate ester selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates, and wherein said compound is selected from the group consisting of tetrachloroselenophene and tetrachlorotellurophene.

18. A composition as defined in claim 13, 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.

19. A composition as defined in claim 18, wherein said dicarboxylic acid ester is 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.

20. A composition as defined in claim 18, wherein said dicarboxylic acid ester is an alkyl diester of phthalic acid containing alkyl groups of from about 4 to about 12 carbon atoms.

21. A composition as defined in claim 20, 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.

22. A composition as defined in claim 13, wherein said base stock comprises a phosphate ester selected from the group consisting of dialkyl aryl, triaryl, trialkyl and alkyl diaryl phosphates, and said compound is tetrachloroselenophene.

23. A composition as defined in claim 22, said compound being present in an amount ranging from about 0.5 to about 2% by weight of said composition.

24. A composition as defined in claim 13, 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 diester selected from the group consisting of the alkyl diesters of adipic and sebacic acid, containing alkyl groups

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of from about 4 to about 12 carbon atoms, and said compound is a member selected from the group consisting of tetrachloroselenophene and tetrachlorotellurophene.

25. A composition as defined in claim 13, said base stock comprising a mixture of a 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 compound being a member selected from the group consisting of tetrachloroselenophene and tetrachlorotellurophene.

26. A composition as defined in claim 25, 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.

27. A composition as defined in claim 13, 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.

28. A composition as defined in claim 13, 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 compound is a member selected from the group consisting of tetrachloroselenophene and tetrachlorotellurophene.

29. A composition as defined in claim 28, said base stock comprising a mixture of tri-n-butyl phosphate and tricresyl phosphate.

30. A composition as defined in claim 28, said base stock including a member selected from the group consisting of diisodecyl adipate and diisodecyl phthalate, and mixtures thereof.

31. A composition as defined in claim 28, said base stock including a mixture of diisodecyl phthalate and diisodecyl adipate.

32. A composition as defined in claim 28, said base stock being a mixture of tri-n-butyl phosphate, diisodecyl adipate and diisodecyl phthalate.

33. A composition as defined in claim 34, said base stock comprising a mixture of tri-n-butyl phosphate, di-n-butyl phenyl phosphate and diisodecyl adipate.

34. A composition as defined in claim 1, including about 2 to about 10% by weight of a viscosity index improver selected from the group consisting of polyalkyl acrylates and polyalkyl methacrylates in which the alkyl groups contain from about 4 to about 12 carbon atoms, and having an average molecular weight ranging from about 6,000 to about 15,000.

35. A composition as defined in claim 17, including about 2 to about 10% by weight of a viscosity index improver selected from the group consisting of polyalkyl acrylates and polyalkyl methacrylates in which the alkyl groups contain from about 4 to about 12 carbon atoms, and having an average molecular weight ranging from about 6,000 to about 15,000.

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