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FUNCTIONAL FLUID COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Compositions of the class which exhibit improved resistance towards corrosion which are polyphenyl thioethers, mixed polyphenyl ether-thioethers, phenylmercaptobiphenyls and mixed phenoxyphenylmercaptobiphenyls having incorporated therein in a corrosion inhibiting amount a metal organic compound wherein the metal is selected from Group II-A metals, Group III-A metals, Group IV-A metals, Group II-B metals, Group IV-B metals, Group VI-B metals, nickel and cobalt.

This invention relates to functional fluid compositions having the ability to inhibit and control corrosion damage to mechanical members in contact with said compositions and more particularly to compositions comprising a functional fluid and corrosion inhibiting amounts of a metal compound.

Many different types of materials have been utilized as functional fluids and functional fluids are used in many different types of applications. Such fluids have been used as electronic coolants, atomic reactor coolants, diffusion pump fluids, synthetic lubricants, damping fluids, bases for greases, force transmission fluids (hydraulic fluids), heat transfer fluids, die casting release agents in metal extrusion processes and as filter mediums for air conditioning systems. Because of the wide variety of applications and the varied conditions under which functional fluids are utilized, the properties desired in a good functional fluid necessarily vary with the particular application in which it is to be utilized with each individual application requiring a functional fluid having a specific class of properties.

Of the foregoing the use of functional fluids as lubricants, particularly jet engine lubricants, has posed what is probably the most difficult area of application. As the operating temperatures for lubricants have increased it has become exceedingly difficult to find lubricants which properly function at engine temperatures for any satisfactory length of time. Thus, the requirements of a jet engine lubricant are as follows: The fluid should possess adequate temperature-viscosity properties and satisfactory storage stability and be non-corrosive and non-damaging to metal mechanical members which are in contact with the fluid. Such fluids should, in addition, possess adequate temperature-viscosity properties and satisfactory lubricity, that is, the lubricants must not become too thin at the very high temperatures to which they are subjected nor must they become too thick at lower temperatures and must at the same time be able to provide lubricity over such range of temperatures. In addition, such lubricants should not form deposits which interfere with the proper operation of a jet engine.

As the speed and altitude of operation of jet engine-containing vehicles increases, lubrication problems also increase because of increased operating temperatures and higher bearing pressures resulting from the increased thrust needed to obtain high speeds and altitudes. As the service conditions encountered become increasingly severe the useful life of the functional fluid is shortened, one

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of the factors being increased corrosion of mechanical members in contact with the functional fluid. In general, as the operating requirements of a jet engine are increased, engine temperatures increase and oil temperatures in the range of 600° F. and higher are encountered.

The useful life of any lubricant can be adjudged on the basis of many criteria such as the extent of viscosity increase, the extent of corrosion to metal surfaces in contact with the lubricant and the extent of deposits. Those skilled in the art have found many ways to improve lubricants and to thus retard or prevent the effects which shorten the useful life of a lubricant. Thus, it is a general practice to add small amounts of other materials, or additives, to lubricants in order to affect one or more of the properties of the base lubricant. It is difficult, however, especially as operating temperatures are increased, to find additives which will still perform the function for which they are added and yet not inject other problems such as increasing engine deposits.

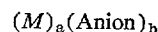
A problem which exists in functional fluid systems is the control of corrosion of mechanical members in contact with the fluid. Thus, depending upon the application, a fluid contacts various metals as for example, aluminum, copper, bronze and steel and many alloys, which alloys utilize many types of metals in the alloy composition. Corrosion of mechanical members in contact with a functional fluid adversely affects (1) the mechanical members of a system in contact with the fluid and (2) the functional fluid itself. Thus, damage to mechanical members in contact with a functional fluid results in alteration of the geometry of the mechanical members in contact with the fluid and the corrosion products resulting therefrom contaminate the fluid. The corrosion products can form deposits on the mechanical members in contact with the fluid as well as being solubilized in the functional fluid. Certain corrosion products in addition to forming deposits can promote oxidation by catalyzing the oxidation of a functional fluid, thereby promoting increased sludge and deposit formation. Thus, deposits and insoluble products interfere with the proper lubrication of mechanical members in a functional fluid system and in addition can act as insulating materials when such deposits and insoluble materials form on mechanical members. When this insulating effect occurs, the fluid does not accept heat as readily from mechanical parts at temperatures higher than the fluid and as a consequence metal fatigue and pitting of mechanical members can occur. In addition, as a consequence of the corrosion of mechanical members, the close tolerances which are required for certain mechanical members are altered, which alteration can result in an excessive rate of wear thereby causing premature removal and replacement of mechanical parts.

It has now been found that control and inhibition of corrosion damage and thus the useful life of functional fluids can be greatly extended, even under the severe conditions encountered in jet engines and other devices operating at temperatures of the order of 550° F. and higher, by the addition to functional fluids of a metal compound, said metal compound being selected from the group consisting of

(A) A metal compound wherein the metal is selected from the group consisting of Group II-A metals, Group III-A metals, Group IV-A metals, Group II-B metals, Group IV-B metals, Group VI-B metals, nickel and cobalt, and

(B) Mixtures thereof.

Typical examples of metal compounds represented by (A) are metal compounds represented by the structure



wherein M is selected from the group consisting of Group II-A metals, Group III-A metals, Group IV-A metals,

Group II-B metals, Group IV-B metals, Group VI-B metals, nickel and cobalt, a is a number having a value of at least one and b is a number having a value of from 1 to the product of a times the valence of M.

The functional fluids, to which a metal compound is added to provide the compositions of this invention, hereinafter referred to as base stocks, include, but are not limited to, polyphenyl thioethers, mixed polyphenyl ether-thioethers, mixed phenoxyphenylmercaptobiphenyls, phenylmercaptobiphenyls, any of the above-described base stocks in which part or all of the cyclic rings represented by phenyl and phenylene are replaced by a cyclic ring, other than phenyl or phenylene, such as alicyclic and heterocyclic, typical examples of which are cyclohexyl, thiophene and pyridene, and mixtures of the aforedescribed base stocks, provided that the number of sulfur atoms linking two or more of the phenyl, phenylene or cyclic rings is greater than one-third of the total number of atoms represented by sulfur and oxygen linking the phenyl, phenylene and cyclic rings. It is contemplated that mixtures of the aforedescribed base stocks can contain major amounts of one base stock even as high as 99% with the remainder being one or more base stocks.

Whereas the incorporation of any foreign element into a base stock can alter properties of a functional fluid, the concentration of metal compounds represented by (A) and (B) in the base stock is adjusted in terms of the particular system and the base stock which is utilized in this system to provide functional fluid compositions of this invention which contain additive amounts of a metal compound represented by (A) and (B) sufficient to inhibit and control corrosion damage of mechanical members in contact with the functional fluid while not adversely affecting critical base stock properties. It has generally been found that the additive concentration of a metal compound represented by (A) and (B) for the base stocks described above is generally from about 0.001 weight percent to about 10 weight percent, preferably from about 0.01 weight percent to about 5 weight percent. Therefore, included within the present invention are compositions comprising a base stock and a corrosion inhibiting amount of a metal compound represented by (A) and (B), that is, a metal compound represented by (A) and (B) is added to the compositions at a concentration sufficient to inhibit and control corrosion damage.

The functional fluid compositions of this invention can be compounded in any manner known to those skilled in the art, as for example, by adding a metal compound represented by (A) and (B) to the base stock with stirring until a composition is obtained. It is also contemplated within the scope of this invention that compositions can be utilized which comprise a base stock and additive amounts of the metal compounds represented by (A) and (B) in which the metal is dispersed, suspended or in contact with the base stock. Thus, the compositions of this invention include the use of composition slurries such as the use of functional fluid compositions of this invention as heat transfer fluids in which the additive can be present in other than a totally solubilized form. In addition, the metal compounds can be prepared in situ, that is, in the base stocks as aforedescribed. It is also contemplated within the scope of this invention that additive concentrates can be prepared such as additive compositions containing from about 10% to about 60% of the metal compounds represented by (A) and (B) and the base stocks as aforedescribed.

Typical examples of Group II-A metals represented by M are beryllium, magnesium, calcium, strontium and barium. The preferred Group II-A metals are magnesium, calcium and barium, although all the Group II-A metals are contemplated within the scope of this invention.

Typical examples of Group III-A metals represented by M are aluminum, gallium and indium.

Typical examples of Group IV-A metals represented by M are tin and lead. The preferred Group IV-A metal

is lead, although all Group IV-A metals are contemplated within the scope of this invention.

Typical examples of Group II-B metals represented by M are zinc and cadmium. The preferred Group II-B metal is zinc, although all Group II-B metals are contemplated within the scope of this invention.

Typical examples of Group IV-B metals represented by M are titanium and zirconium.

Typical examples of Group VI-B metals represented by M are chromium and molybdenum. The preferred Group VI-B metal is chromium, although all the Group VI-B metals are contemplated within the scope of this invention.

The anion portion of the compounds of this invention can be derived from many sources and can be classified broadly as inorganic anions and hydrocarbon-containing anions. The term "hydrocarbon-containing anion" is herein defined to include hydrocarbons which contain only carbon and hydrogen and also hydrocarbons which contain other elements in addition to carbon and hydrogen. The term "hydrocarbons," which contain carbon and hydrogen as well as carbon, hydrogen and other elements, includes hydrocarbons which are completely saturated as well as hydrocarbons which have unsaturation. Thus, the term "hydrocarbon-containing," in addition to hydrocarbons containing only carbon and hydrogen, includes hydrocarbons containing one or more elements other than carbon and hydrogen, which elements can be substituted upon a hydrocarbon or can link two or more hydrocarbon groups. It is also contemplated that a hydrocarbon-containing group can contain both substitution and linkage by one or more elements.

Typical examples of elements which the hydrocarbon-containing anions can contain are boron, silicon, nitrogen, phosphorus, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine and bromine. Typical examples of hydrocarbon-containing anions are acyloxy, substituted acyloxy, aryloxy and substituted aryloxy, aryloxy and substituted aryloxy, alkoxy, substituted alkoxy, alkyl, alkenyl, alkaryl, aralkyl, aryl, substituted alkyl, substituted alkenyl, substituted aryl, cyclic anion, that is (carbon- and hetero-groups); Group III-A non-metal hydrocarbon-containing anions such as hydrocarbon-containing boron anions; Group IV-A non-metal hydrocarbon-containing anions such as hydrocarbon-containing silicon anions; Group V-A hydrocarbon anions, that is, hydrocarbon-containing nitrogen anions, such as amido and the corresponding substituted amido derivatives, hydrocarbon-containing phosphorus anions and hydrocarbon-containing arsenic anions; Group VI-A hydrocarbon-containing anions, that is, hydrocarbon-containing sulfur, selenium and tellurium anions; and Group VII-A hydrocarbon-containing anions such as hydrocarbon-containing fluorine, chlorine, bromine and iodine anions. The term "aryl" as used above in the examples of hydrocarbon-containing anions is defined to include mono-, di- and polynuclear aromatic hydrocarbons such as phenyl, naphthyl and anthryl.

Whereas all the above hydrocarbon-containing anions are contemplated within the scope of this invention, it has been found that the preferred hydrocarbon-containing anions are those anions which contain an element selected from oxygen, nitrogen and divalent sulfur, wherein the sulfur is contained in a heterocyclic ring or linking two aromatic rings or which contain two or more of any combination of elements. The term "hydrocarbon-containing anion" is in addition defined to be that anion which does not adversely affect the performance of the metal compound under the conditions to which a functional fluid composition incorporating metal compounds represented by (A) and (B) is subjected. Thus, for example, when a hydrocarbon-containing anion contains elements as described above, as for example, halogen or sulfur other than divalent sulfur as defined above in the preferred anions, such elements should be non-interfering

with respect to the performance of the metal compound in a functional fluid such that it will not completely nullify the performance and activity of the metal compound under such operating conditions and in the particular fluid system to which the functional fluid composition is subjected.

The hydrocarbon-containing anions can be defined by the number of carbon atoms present in the anion per equivalent weight of metal represented by M wherein M has the same significance as aforescribed. While there is no lower limit as to the number of carbon atoms or other elements that can be present in the anion portion, there is a preferred upper limit which is based upon the practical problem of obtaining a concentration of M incorporated into a fluid without adversely affecting other fluid properties. Thus, in general, it has been found that the preferred upper limit with respect to the number of carbon atoms present per equivalent weight of M is generally up to about 60 carbon atoms per equivalent weight of M and even more preferably up to about 48 carbon atoms per equivalent weight of M. Thus, anions which contain more than one equivalent of M attached to a given anion, that is, *b* is greater than *a*, would have a preferred upper carbon atom limitation for the anion, which limitation is obtained by multiplying the number of equivalents of M attached to the anion times 60. The hydrocarbon-containing anions in addition to the above can be defined by the number of elements other than carbon and hydrogen which are present per equivalent of metal represented by M wherein M has its aforescribed significance. Thus, for hydrocarbon-containing anions containing oxygen, nitrogen or divalent sulfur wherein the divalent sulfur is contained in a heterocyclic ring or linking two aromatic rings, or combinations of the above elements, the number of elements which can be present per equivalent of M is as a preferred upper limit about 20 elements per one equivalent of M and more preferably is an upper limit of about 10 elements per equivalent of metal represented by M. With respect to the hydrocarbon-containing anions which contain elements other than or in addition to oxygen, nitrogen and divalent sulfur wherein the divalent sulfur forms part of a heterocyclic ring or links two aromatic rings, the preferred upper limit of the number of these other elements present per equivalent of M is up to about 5 per equivalent of M and more preferably up to about one element per equivalent of M.

It is also contemplated within the scope of this invention that the above-described anion of the metal compounds can contain any combination of the aforescribed anions which are linked together to form one anion. Thus, for example, there can be present in one anion acyloxy, alkoxy and hydrocarbon-containing silicon anions. As another example, there can be contained in one anion alkoxy and a hydrocarbon-containing phosphorus anion.

Typical examples of inorganic anions are nitrite, nitrate, cyanate, thiocyanate, carbonate, phosphate, borate, hydride, oxides, hydroxide and the like.

The inorganic anions that are preferred are those anions which cannot be derived from strong acids.

Typical examples of Group III-A non-metal hydrocarbon-containing anions are diethyl-p-hydroxybenzene boronic acid, p-hydroxyphenyl diphenyl boroxin, m-hydroxy phenyldiphenyl boroxin, (p-hydroxyphenoxyphenyl)diphenyl boroxin and p-carboxyphenyl, ditolyl boroxin and (p-hydroxyphenoxyphenyl) - di(phenoxyphenyl) boroxin.

Group IV-A non-metal hydrocarbon-containing anions can be derived, for example, from silicon. Typical examples of these compounds are p-triphenyl silyl benzoic acid, p-(triphenyl silyl) propionic acid, p-hydroxyphenyl, pentaethyl disiloxane, triethyl silyl benzoic acid, 4,4'-(tetramethyl disiloxanylene) dibenzoic acid and p-hydroxyphenyltriphenyl silicate.

It is also contemplated that the above Group IV-A

hydrocarbon-containing anions can be derived from polymeric compounds. Typical examples of such polymeric compounds are the methyl polysiloxanes, ethyl polysiloxanes, phenyl-methyl polysiloxanes which have been reacted with an unsaturated acid such as acrylic or methacrylic acid to produce a graft polymer, that is, the acrylic or methacrylic acid is reacted with, for example, one of the methyl or ethyl groups.

Group V-A hydrocarbon-containing anions can be derived from, for example, arsenic and phosphorus compounds. Typical example of the phosphorus compounds which can be utilized to form the phosphorus hydrocarbon-containing anions include the hydrocarbon-containing esters and amides of an acid of phosphorus, which include, by example, phosphoric acids, thiophosphoric acids, phosphinic acids, thiophosphinic acids, phosphonic acids, thiophosphonic acids and the like. Typical examples of hydrocarbon-containing phosphoric acid derivatives are dialkyl phosphoric acids, dialkyl-dithiophosphoric acids, dicyclohexyl phosphoric acids, dimethylcyclohexyl phosphoric acids, di-2-phenylhexyl phosphoric acids, diphenyl phosphoric acids and di-n-dodecylphenyl phosphoric acids.

The amido anions can be derived from various nitrogen-containing compounds among which are amines. Typical amines which can be utilized to prepare the amido anions are dimethylaminoethylamine, dimethylaminopropylamine, dimethylaminobutylamine, dimethylaminoheptylamine, diethylaminopropylamine, dihexylaminoarylamine, didodecylaminopropylamine, dioctyldecylpropylamine, N-octadecyl - N-dodecylaminopropylamine, tetrahydropyrrole and the like. In addition, carbamic and dithiocarbamic acid compounds can be utilized to prepare metal compounds represented by (A) and (B).

Typical examples of Group VI-A hydrocarbon-containing anions are the hydrocarbon sulfur-containing anions. These anions can be derived, for example, from mercaptans and sulfonic acids, among which are thiophenol, dodecyl mercaptan, decyl mercaptan, octadecyl mercaptan, dialkylbenzene sulfonic acids and wax sulfonic acids derived from the sulfonation of high molecular weight aliphatic materials.

The Group VII-A hydrocarbon-containing anions are anions which contain, for example, fluorine, chlorine, bromine or iodine. It is also contemplated that any of the aforescribed anions can be substituted with Group VII-A elements.

The metal compounds represented by (A) and (B) can also be derived from organo-metallic compounds where the anion portion can be alkyl, substituted alkyl, aryl and substituted aryl, alkenyl and substituted alkenyl. These compounds are commonly referred to as organo-metallic compounds as there is bonding between the metal and carbon. Typical examples of these compounds are di(p-octylphenyl)zinc and di(octadecyl)zinc.

While the aforescribed anions are effective and contemplated within the scope of this invention as corrosion inhibitors, it has also been found that those hydrocarbon anions containing only carbon, hydrogen, oxygen, nitrogen and divalent sulfur which is contained in a heterocyclic ring or bound to two aromatic rings are more effective in also inhibiting and controlling corrosion damage to mechanical members in contact with a functional fluid. Thus, the preferred anions of this invention are, for example, acyloxy, substituted acyloxy, aroyloxy, substituted aroyloxy, aroxy, substituted aroxy, alkoxy, substituted alkoxy, and substituted and unsubstituted carbonyloxy and oxy heterocyclic groups containing from 1 to 4 hetero atoms selected from oxygen, sulfur and nitrogen and containing from 4 to 10 atoms in the heterocyclic ring.

Typical examples of metal acyloxy, substituted acyloxy, aroyloxy, substituted aroyloxy compounds, and

substituted and unsubstituted carbonyloxy heterocyclic groups are metal acetate, metal propionate, metal cyclohexanoate, metal neodecanoate, metal neotridecanoate, metal n-tetradecanoate, metal oleate, metal bitartrate, tetra-metal ethylenediamine tetra-acetate, dimetal ethylenediamine tetra-acetic acid, dimetal ethylenediamine diacetate, metal ethylenediamine diacetic acid, tri-metal nitrilotriacetate, metal nitrilotriacetic acid, metal benzoate, metal salicylate, metal acetosalicylate, metal bipthalate, metal o-phenoxybenzoate, metal m-phenoxybenzoate, metal 1,1,3-trimethyl-2-keto valerate, metal o-phenyl azobenzoate, metal m-phenyl azobenzoate, metal p-phenyl azobenzoate, metal 5-(m-nitrophenyl azo) salicylate, metal phenylacetate, metal benzilate and metal pyrrolidine.

In addition, the acyloxy, substituted acyloxy, aroyloxy, substituted aroyl anions, substituted and unsubstituted carbonyloxy heterocyclic groups can be derived from carboxylic acids, typical examples of which are:

(A) ALIPHATIC MONOCARBOXYLIC ACIDS

Formic acid, butyric acid, isobutyric acid, nitroisobutyric acid, valeric acid, isovaleric acid, hexanoic acid, heptanoic acid, 2-ethylhexanoic acid, nonanoic acid, decanoic acid, dodecanoic acid, undecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, eicosanoic acid, docosanoic acid, triacontanoic acid, butenic acid, pentenic acid, hexenic acid, teracrylic acid, hypogeic acid, elaidic acid, linoleic acid, α -elostearic acid, α -linolenic acid, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, 3-butenic acid, angelic acid, senecioic acid, hydrosorbic acid, sorbic acid and 4-tetradecenoic acid.

(B) ALICYCLIC MONOCARBOXYLIC ACIDS

Cyclopropanecarboxylic acid, cyclopentanecarboxylic acid, hydrocarpic acid, chaumoogric acid, naphthenic acid, 2,3,4,5-tetrahydrobenzoic acid and cyclodecanecarboxylic acid.

(C) AROMATIC MONOCARBOXYLIC ACIDS

1-naphthoic acid, 2-naphthoic acid, o-toluic acid, m-toluic acid, p-toluic acid, o-nitrobenzoic acid, m-nitrobenzoic acid, p-nitrobenzoic acid, 2,3-dinitrobenzoic acid, m-hydroxybenzoic acid, p-hydroxybenzoic acid, gallic acid, anisic acid and β -phenylpropionic acid.

(D) HETEROCYCLIC MONOCARBOXYLIC ACIDS

Picolinic acid, nicotinic acid, furylacrylic acid, piperic acid, indoxyllic acid, 3-indoleacetic acid, cinchoninic acid, furoic acid, 2-thiophenecarboxylic acid, 2-pyrrolecarboxylic acid, 9-acridancarboxylic acid, quinaldic acid, pyrazionic acid and antipyrinic acid.

(E) ALIPHATIC POLYCARBOXYLIC ACIDS

Oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassylic acid, thapsic acid, maleic acid, fumaric acid, glutaconic acid, citraconic acid, itaconic acid, ethidenemalononic acid, mesaconic acid, allylmalonic acid, allylsuccinic acid, teraconic acid, xeronic acid, cetylmalonic acid, pyromellitic acid and trimellitic acid.

It is also contemplated herein to employ dimeric and trimeric polycarboxylic acids. When two like or unlike molecules of a polyethenoid monocarboxylic fatty acid condense to form a dicarboxylic acid, the product by definition is a dimer acid, or the carboxylic acid is said to be dimerized. In general, the dimer acids suitable for use in this invention are produced by the condensation of two like or unlike unsaturated aliphatic monocarboxylic acids

having between about 16 and about 18 carbon atoms per molecule, examples of which comprise

$\Delta 9,11$ -hexadecadienoic acid
 $\Delta 9,12$ -heptadecadienoic acid
 $\Delta 8,12$ -octadecadienoic acid
 $\Delta 9,11$ -octadecadienoic acid
 $\Delta 9,12$ -octadecadienoic acid (linoleic acid)
 $\Delta 9,13$ -octadecadienoic acid
 $\Delta 9,11,13$ -octadecatrienoic acid
 $\Delta 9,12,15$ -octadecatrienoic acid (linolenic acid)

It is also contemplated within the scope of this invention that the polycarboxylic acids can be utilized to prepare partial or complete metal compounds, that is, when a partial metal compound is formed the remaining available carboxylic acid groups can be reacted with other compounds, such as alcohols to form esters and amines to form amides or imides. It is also contemplated that the above carboxylic acid derivatives which contain other substituents which themselves can form a metal compound, such as hydroxy-substituted carboxylic acids can be utilized to prepare a partial or complete metal compound. In addition, as for example, in the case where the anion is a hydroxy-substituted carboxylic acid, the metal M can be attached to the anion through the hydroxyl group and in such a case the carboxylic acid group can be blocked or hindered. In addition, a metal enolate can be formed from certain carbonyl-containing compounds, such as acetyl acetone and such metal enolates are included within the scope of this invention.

Typical examples of metal alkoxides and aroxides are metal phenate, metal benzylate, metal diphenyl methoxide, metal triphenyl methoxide, metal lauryl methoxide, metal butyl methoxide and metal m,m'-phenoxyphenoxyphenate.

It is also contemplated within the scope of this invention that the carboxy group in the aforescribed carboxylic acids which can be used to prepare hydrocarbon-containing anions can be partially or totally replaced by a hydroxyl group and such compounds in turn can be utilized to prepare metal compounds as represented by (A) and (B).

Typical examples of unsubstituted and substituted aroxy-, alkoxy- and oxyheterocyclic groups from which the metal compounds represented by (A) and (B) can be derived are methyl, ethyl, propyl, n-butyl and tert-butyl alcohols, isoamyl alcohol, cyclohexanol, lauryl alcohol, benzyl alcohol, cetyl alcohol, stearyl alcohol, phenol, o-, m- and p-cresol, nitrophenol, gluaicol, saligenin, thymol, o-, m- and p-hydroxy acetophenone, o-, m- and p-hydroxy diphenyl, o-, m- and p-cyclohexyl phenol, catechol, resorcinol, pyrogallol, o-, m- and p-aminophenol, α - and β -naphthol, 8-octyl- β -naphthol, 6-dodecyl- α -naphthol, 3,5,5-dimethyl-N-hexyl phenol, N-decyl phenol, aceto phenol, nonyl phenol, alkaryl substituted phenols, alkyl resorcinol, octyl catechol, thiophene-3-ol, 2,3'-quinoxaline diol, triisobutyl pyrogallol, 2-pyridinol, 2,6-di-sec-butyl-p-amino phenol, 4-N,N-dibutyl aminomethyl-2,6-di-sec-butyl phenol, o-, m- and p-phenoxy phenols, o-, m-, p-[(o-, m-, p-phenoxy)phenoxy]phenols, hydroxy quinolines, such as 2-hydroxy quinoline, 3-hydroxy quinoline, 6-hydroxy quinoline, 7-hydroxy quinoline and 8-hydroxy quinoline.

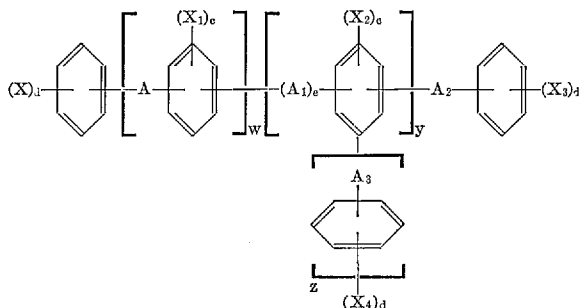
It is also contemplated that polymeric compounds can be utilized to prepare the metal compounds represented by (A) and (B) in which part or all of the available sites are attached to a metal to form a metal compound. A site is defined as a group such as hydroxyl or carboxyl which is capable of uniting with a metal cation to form a metal compound. Typical examples of such polymeric compounds are copolymers of lauryl methacrylate and acrylic acid copolymers of isooctyl acrylate and methacrylic acid, polymers prepared from esters of acrylic acid and methacrylic acid, polyesters and hydroxy-substituted polyphenylene oxides. The compounds and mixtures of com-

pounds which can be utilized to prepare the anions can contain many sites which can be attached to the metal. However, the metal can be attached to less than the total number of available sites and the use of such metal compounds are contemplated within the scope of this invention.

It is also contemplated within the scope of this invention that the compounds represented by (A) and (B) can contain two or more metals represented by M. Typical examples of compounds containing a metal represented by M which can be interacted with the same or different metal represented by M to form a compound represented by (A) and (B) having two or more M's are tin and lead hydrocarbon-containing compounds, such as p-triphenyl stannyl benzoic acid, p-hydroxyphenyl pentaphenyl ditin, m-hydroxybenzyl-tribenzyl lead, p-trimethyl plumbyl benzoic acid and phenyl plumbonic acid.

It is also contemplated within the scope of this invention that the anion portion can impart other properties to the functional fluid compositions. Typical examples of such other properties which can be imparted are adjustment of viscosity, antifoam and lubricity. As an example of imparting an additional property by an anion, a metal anion represented by (A) and (B) in which the anion is derived from a polysiloxane can impart antifoam properties. In addition, a metal compound in which the anion is derived from a polymer such as a methacrylic acid ester polymer can alter the viscosity properties of a functional fluid. As a further example, the metal anions in which the anion is derived from a hydrocarbon phosphorus-containing anion can impart lubricity and load carrying ability to a functional fluid composition.

Examples of base stocks which are suitable as base stocks of this invention are represented by the structure



wherein A, A₁, A₂ and A₃ are each a chalcogen selected from oxygen and sulfur, X, X₁, X₂, X₃ and X₄ each are selected from the group consisting of hydrogen, alkyl, haloalkyl, halogen, phenyl, alkaryl, hydroxyl, alkoxy, aralkyl and substituted aralkyl; w, y and z are whole numbers each having a value of 0 to 8; c is a whole number having a value of from 1 to 4; d is a whole number having a value of from 1 to 5 and e is a whole number having a value of 0 to 1 provided that when e is 0, y can have a value of 1 to 2 and provided that the phenyl and phenylene groups in the aforescribed base stocks can be partially or totally replaced with a cyclic group other than a phenyl or phenylene group, such as alicyclic or heterocyclic such as thiophene and pyridene, and provided that the number of sulfur atoms linking two or more of the phenyl, phenylene or cyclic rings is greater than one-third of the total number of hetero atoms represented by sulfur and oxygen linking the phenyl, phenylene or cyclic rings. Typical examples of such base stocks are polyphenyl thioethers and mixtures thereof, mixed polyphenyl ether-thioether compounds in which at least one of the chalcogens represented by A, A₁, A₂ and A₃ is dissimilar with respect to any one of the other chalcogens, phenylmercaptobiphenyls, mixed phenoxyphenylmercaptobiphenyls and mixtures thereof.

Typical examples of polyphenyl thioethers, that is, when A, A₁, A₂ and A₃ are sulfur and e has a value of 1 are

- o-bis-(phenylmercapto)benzene,
 - m-bis-(phenylmercapto)benzene,
 - bis(m-phenylmercaptophenyl)sulfide,
 - m-phenylmercaptophenyl-p-phenylmercaptophenyl sulfide,
 - the trisphenylmercaptobenzenes,
 - such as 1,2,4-trisphenylmercaptobenzene,
 - m-bis(p-phenylmercaptophenylmercapto)benzene,
 - m-bis(m-phenylmercaptophenylmercapto)benzene,
 - bis[m-(m-phenylmercaptophenylmercapto)phenyl] sulfide,
 - m-(m-chlorophenylmercapto)m-phenylmercaptobenzene,
 - m-chlorodiphenyl sulfide,
 - bis(o-phenylmercaptophenyl) sulfide,
 - m-bis(m-phenylmercaptophenylmercapto)benzene,
 - 1,2,3-tris(phenylmercapto)benzene,
 - o-bis(o-phenylmercaptophenylmercapto)benzene,
 - m-bis(p-phenylmercaptophenylmercapto)benzene
- and mixtures thereof.

Typical examples of phenylmercaptobiphenyls, that is, where e has a value of 0 and A, A₁, A₂ and A₃ are sulfur are 3,3'-bis(phenylmercapto)biphenyl, o-, m- and p-phenylmercaptobiphenyl, 3,4 - phenylmercaptobiphenyl, 3,2-diphenylmercaptobiphenyl, m-chloro-phenylmercapto-3'-phenylmercaptobiphenyl and mixtures thereof.

Typical examples of mixed polyphenyl ether-thioethers, that is, where e has a value of 1 and at least one of the chalcogens represented by A, A₁, A₂ and A₃ is dissimilar with respect to any other chalcogen provided that the number of chalcogens represented by A, A₁, A₂ and A₃ is greater than one-third sulfur are

- 1,2-phenylmercapto-3-bis(phenoxy)benzene,
- 2-phenylmercapto-4'-phenoxydiphenyl sulfide,
- 2-phenoxy-3'-phenylmercaptodiphenyl sulfide,
- 2,2'-bis-(phenylmercapto)di-phenyl ether,
- 3,4'-bis(m-tolylmercapto)diphenyl ether,
- 3,3'-bis(xylylmercapto)diphenyl ether,
- 3,4'-bis(m-isopropylphenylmercapto)diphenyl ether,
- 3,4'-bis(p-tert-butylphenylmercapto)diphenyl ether,
- 3,3'-bis(m-chlorophenylmercapto)diphenyl ether,
- 3,3'-bis(m-trifluoromethylphenylmercapto)diphenyl ether,
- 3,4'-bis(m-perfluorobutylphenylmercapto)diphenyl ether,
- 2-m-tolylloxy-2'-phenylmercaptodiphenyl sulfide,
- m-phenylmercaptodiphenyl ether,
- 3,3'-bis(phenylmercapto)diphenyl ether,
- 3-phenoxy-3'-phenylmercaptodiphenyl sulfide,
- 3,4'-bis(phenylmercapto)diphenyl ether,
- m-bis(m-phenylmercaptophenoxy)benzene,
- 3-phenylmercapto-3'-(m-phenylmercaptophenylmercapto) diphenyl ether

and mixtures thereof.

Typical examples of mixed phenoxy-phenylmercaptobiphenyl, that is, where e has a value of 0 and one of the chalcogens represented by A, A₁, A₂ and A₃ is dissimilar with respect to any other chalcogen provided that the number of chalcogens represented by A, A₁, A₂ and A₃ is greater than one-third sulfur are phenylmercaptophenoxybiphenyl, o-phenylmercaptophenyl-m-phenoxyphenoxybiphenyl and mixtures thereof.

It is also contemplated within the scope of this invention that the aforescribed base stocks can be blended together to provide mixtures comprising two or more of the above base stocks. A typical mixture of a polyphenyl thioether and a mixed polyphenyl ether-thioether is one which contains by weight from about 45% to about 55% m-phenoxyphenyl m-phenylmercaptophenyl sulfide, from about 25% to about 35% bis(m-phenylmercaptophenyl) sulfide and from about 18% to about 25% bis(m-phenyl-

mercaptophenyl) ether. Particularly useful mixtures are those containing the above mixtures and m-bis(phenylmercapto)benzene is about equal weight proportions. Typical examples of mixtures containing polyphenyl thioethers, mixed polyphenyl ether-thioether and halogenated polyphenyl ethers which are suitable as lubricants under high temperature conditions are as follows in weight percent:

(1)		Percent
m-Bis(phenylmercapto)benzene	-----	50
m-Phenoxyphenyl-m-phenylmercaptophenyl sulfide	-----	25
Bis(phenylmercaptophenyl) ether	-----	11
Bis(m-phenylmercaptophenyl) sulfide	-----	14
(2)		
m-Bis(phenylmercapto)benzene	-----	50
m-Phenoxy-m-phenylmercaptobenzene	-----	25
o-Bis(phenylmercapto)benzene	-----	25
(3)		
m - (m - Chlorophenylmercapto)-m-phenylmercapto- benzene	-----	46
m-Bis(phenylmercapto)benzene	-----	31
m-Phenoxy-m-phenylmercaptobenzene	-----	15
m-Chlorodiphenyl sulfide	-----	8

It is also contemplated that any of the individual base stocks as described above or mixtures thereof in admixture with additives of this invention can also be utilized to provide compositions of this invention.

In order to demonstrate the outstanding properties of a composition of this invention, various metal salts were blended into a base stock and the resulting functional fluid composition evaluated for control of metal corrosion. One of the major bench scale methods used for measuring the control of corrosion of a lubricant composition is a procedure given in Federal Test Method 791, Method No. 5308 according to which the lubricant composition to be tested is heated at a specified temperature (500° F.) in the presence of certain metals and oxygen and the viscosity increase of the lubricant is determined. Information as to the corrosivity of a lubricant to metals and the degree of sludge and deposit formation is determined.

In Table I, Examples 1 through 14, the compounds represented by (A) and (B) were tested in a base stock which was a mixture comprising a 3-ring polyphenyl thioether, a 4-ring polyphenyl thioether and a mixed polyphenyl ether-thioether containing a total number of sulfur atoms linking the phenyl and phenylene rings which was greater than one-third of the total number of sulfur and oxygen atoms linking the phenyl and phenylene rings. The temperature of the test was 500° F. and an air rate of 5 liters per hour was used. The duration of the test was 48 hours. The metal specimens that were used as specified in said procedure were steel, copper, silver, titanium, magnesium alloy and aluminum alloy. A negative sign on the copper and silver loss indicates that metal was lost.

TABLE I

Ex. No.	Metal Salt	Concentration, percent Additive in Base Stock	Net Change in Metal, mg./cm. ²	
			Cu	Ag
1.....	Neat.....	0.00	-2.13	-0.72
2.....	Magnesium benzoate.....	0.1	-0.38	-0.07
3.....	Calcium m-phenoxybenzoate.....	0.1	-1.97	-0.13
4.....	Barium m-phenoxybenzoate.....	0.1	-1.18	-0.13
5.....	Aluminum benzoate.....	0.1	-0.71	-0.27
6.....	Lead benzoate.....	0.2	-0.22	-0.19
7.....	do.....	0.025	-0.21	-0.19
8.....	Lead hydroxide monobenzoate.....	0.1	-0.32	-0.13
9.....	Lead m-phenoxybenzoate.....	0.2	-0.61	-0.16
10.....	Zinc benzoate.....	0.1	-0.49	-0.16
11.....	Zinc m-phenoxybenzoate.....	0.1	-0.29	-0.13
12.....	Zirconium benzoate.....	0.1	-1.59	-0.24
13.....	Chromium benzoate.....	0.1	-0.64	-0.39
14.....	Nickel benzoate.....	0.1	-0.93	-0.17

The data in the previous examples demonstrate the significant inhibition of corrosion damage obtained by the functional fluid compositions of this invention which have incorporated therein the metal compounds represented by (A) and (B). In addition the critical physical properties and performance characteristics, such as lubricity, fire resistance and viscosity, were not adversely affected, an important consideration since a base stock is selected for a given fluid system because of its physical properties and characteristics and critical deviations from these properties and characteristics can bring about inferior fluid performance. In particular, Table I demonstrates that the incorporation of a metal compound represented by (A) and (B) can bring about a reduction in both copper and silver corrosion as evidenced by the reduction in weight loss of the metal specimens. In many of the examples, the percent improvement in the control of copper and silver corrosion was in the order of 80% and in some cases higher. The control and inhibition of copper corrosion is of particular importance since mechanical members in contact with the fluid which are corroded can exhibit pitting and loss of metal, which loss of metal alters the geometry and close tolerances which are necessary for the proper operation of a particular system. The control of copper corrosion utilizing the functional fluid compositions of this invention extend the life of the actual fluid system and in addition the functional fluid itself.

In addition to control of corrosion to mechanical members in contact with the fluid, the incorporation of the metal compound into a base stock inhibits and controls damage to the fluid itself. The inhibition and control of corrosion damage prevents corrosion products from contaminating the fluid which contamination product can cause an increased rate of oxidation of the fluid. The metal salts which can result from corrosion can act as pro-oxidants thereby increasing fluid damage which manifests itself in numerous ways, among which are viscosity change, increase acid number, formation of insoluble materials, increased reactivity and discoloration. In a fluid system the particular properties of a fluid have to be maintained in order to continue useful operation of the particular system in which the fluids are employed. Thus, changes in viscosity can be produced by fluid degradation whereby polymeric products with high molecular weights are produced in the system. Such high molecular weight products often become insoluble in the particular base stock which results in the precipitation or sludging of the insoluble material. Such precipitation and sludging plugs filters and deposits on moving parts which have to be lubricated by the fluid thereby causing inadequate lubrication. Increased chemical reactivity is observed on fluid degradation as well as a build-up of the acid number of the fluid. Such increased chemical reactivity and high acid number allows the particular system which incorporates the fluid to be chemically attacked by the fluid thereby causing additional pitting, wear and alterations of the close tolerances of the mechanical members of said fluid. Thus, premature overhaul of mechanical parts can be a direct consequence of fluid degradation. Thus, it is of particular importance that corrosion damage of mechanical members in contact with fluid be inhibited and controlled in order to prevent damage to mechanical members and in addition fluid degradation which can be a direct consequence of contamination of a fluid with corrosion products.

As a result of the improved control of corrosion by functional fluids which incorporate the metal compounds of this invention, lubrication of gas turbine engines is obtained over extended periods of time. Thus, this invention relates to a novel method of lubricating gas turbine engines which comprises maintaining on the bearings and other points of wear a lubricating amount of a composition of this invention.

As a result of the excellent inhibition and control of damage utilizing the functional fluid composition of this

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

The pumps may be of various types, including centrifugal pumps, jet pumps, turbine vane, liquid piston gas compressors, piston-type pump, more particularly the variable-stroke piston pump, the variable-discharge or variable displacement piston pump, radial-piston pump, axial-piston pump, in which a pivoted cylinder block is adjusted at various angles with the piston assembly, for example, the Vickers axial-piston pump, or in which the mechanism which drives the pistons is set at an angle adjustable with the cylinder block; gear-type pump, which may be spur, helical or herringbone gears, variations of internal gears, or a screw pump; or vane pumps. The valves may be stop valves, reversing valves, pilot valves, throttling valves, sequence valves, relief valves, servo valves, non-return valves, poppet valves or unloading valves. Fluid motors are usually constant- or variable-discharge piston pumps caused to rotate by the pressure of the hydraulic fluid of the system with the power supplied by the pump power source. Such a hydraulic motor may be used in connection with a variable-discharge pump to form a variable-speed transmission. It is, therefore, especially important that the frictional parts of the fluid system which are lubricated by the functional fluid be protected from damage. Thus, damage brings about seizure of frictional parts, excessive wear and premature replacement of parts.

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

The fluid compositions of this invention when utilized as a functional fluid can also contain one or more dyes, pour point depressants, metal deactivators, acid scavengers, antioxidants, defoamers in concentration sufficient to impart antifoam properties, such as from about 10 to about 100 parts per million, viscosity index improvers such as polyalkylacrylates, polyalkylmethacrylates, polycyclic polymers, polyurethanes, polyalkylene oxides, polyalkylene polymers, polyphenylene oxides, polyesters, lubricity agents and the like.

It is also contemplated within the scope of this invention that the base stocks as aforescribed can be utilized singly or as a fluid composition containing two or more base stocks in varying proportions. The base stocks can also contain other fluids which include, in addition to the functional fluids described above, fluids derived from coal products and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and mixtures thereof), alkylene oxide-type polymers (e.g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxide in the presence of water or alcohols, e.g., ethyl alcohol, alkylbenzenes (e.g., monoalkylbenzene such as dodecylbenzene, tetradecylbenzene, etc.), and dialkylbenzenes (e.g., *n*-nonyl 2-ethylhexylbenzene); polyphenyls

(e.g., biphenyls and terphenyls), halogenated benzene, halogenated lower alkylbenzene, halogenated biphenyls, halogenated diphenyl ethers, trialkyl phosphine oxides, diarylalkyl phosphonates, trialkyl phosphonates, aryldi-alkyl phosphonates, triaryl phosphonates, di- and tri-carboxylic acid esters, such as di-2-ethylhexyl adipate, di-2-ethylhexyl sebacate, polyesters, such as trimethylolpropane, pentaerythritol, dipentaerythritol esterified with acids such as butyric, propionic, caproic and 2-ethylhexanoic and complex esters such as are obtained by esterifying a dicarboxylic acid with a glycol and a monocarboxylic acid, and polyphenyl ethers, typical examples of which are bis(phenoxyphenyl) ethers, e.g., bis(*m*-phenoxyphenyl) ether; the bis(phenoxyphenoxy)benzenes, e.g., *m* - bis(*m*-phenoxyphenoxy)benzene, *m*-bis(*p*-phenoxyphenoxy)benzene, *o* - bis(*o* - phenoxyphenoxy)benzene; the bis(phenoxyphenylphenyl) ethers, e.g., bis[*m*-(*m* - phenoxyphenoxy)phenyl] ether, bis[*p* - (*p*-phenoxyphenoxy)phenyl] ether, *m* - [(*m*-phenoxyphenoxy)(*o*-phenoxyphenoxy) ether and the bis(phenoxyphenoxyphenoxy) benzenes, e.g., *m* - bis[*m* - (*m*-phenoxyphenoxy)phenoxy]benzene, *p* - bis[*p* - (*m*-phenoxyphenoxy)phenoxy]benzene, *m* - bis[*m* - (*p*-phenoxyphenoxy)phenoxy]benzene and 1,3,4-triphenoxybenzene. It is also contemplated that mixtures of the polyphenyl ethers can be used. For example, mixtures of polyphenyl ethers in which the non-terminal phenylene rings (i.e., those rings enclosed in the brackets in the above structural representation of the polyphenyl ethers contemplated) are linked through oxygen atoms in the meta and para positions, have been found to be particularly suitable as lubricants because such mixtures possess lower solidification points and thus provide compositions having wider liquid ranges. Of the mixtures having predominantly meta and para linkages, a preferred polyphenyl ether mixture of this invention is the mixture of 5-ring polyphenyl ethers where the non-terminal phenylene rings are linked through oxygen atoms in the meta and para positions and composed, by weight, of about 65% *m* - bis(*m*-phenoxyphenoxy)benzene, 30% *m* - [(*m* - phenoxyphenoxy)(*p*-phenoxyphenoxy)]benzene and 5% *m* - bis(*p*-phenoxyphenoxy)benzene. Such a mixture solidifies at about -10° F. whereas the three components solidify individually at temperatures above the normal room temperatures.

Examples of substituted polyphenyl ethers are 1-(*p*-methylphenoxy) - 4 - phenoxybenzene, 2,4-diphenoxy-1-methylbenzene, bis[*p* - (*p* - methylphenoxy)phenyl] ether, bis[*p* - (*p*-tert-butylphenoxy)phenyl] ether and mixtures thereof. The aforescribed fluids can be added in amounts such that the final base stock has a total number of sulfur atoms linking the phenyl, phenylene and cyclic rings in the aforescribed base stocks, greater than one-third of the total number of sulfur and oxy linkages linking the phenyl, phenylene and cyclic rings.

While this invention has been described with respect to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

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

1. A composition comprising

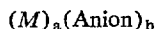
(A) a major amount of a base stock selected from the group consisting of

- (1) polyphenyl thioethers,
- (2) mixed polyphenyl ether-thioethers,
- (3) phenylmercaptobiphenyls,
- (4) mixed phenoxyphenylmercaptobiphenyls and
- (5) mixtures of any combination of (1), (2), (3) and (4), provided that the total number of sulfur linkages in a mixed polyphenyl ether-thioether compound linking the aryl and arylene rings is greater than one-third of the sum of the total number of oxy and sulfur linkages linking the aryl and arylene rings; and

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(B) a corrosion inhibiting amount of a material selected from the group consisting of

(1) a metal compound represented by the structure



wherein M is selected from the group consisting of Group II-A metals, Group III-A metals, Group IV-A metals, Group II-B metals, Group IV-B metals, Group VI-B metals, nickel and cobalt, a is a number having a value of at least one and b is a number having a value of from 1 to the product of a times the valence of M, anion is a member of the class consisting of carbonate, oxide, hydroxide, halide and hydrocarbon-containing anions selected from the group consisting of acyloxy, aryloxy, aroxy, alkoxy, and a carbonyloxy carbon-containing heterocyclic group having from 4 to 10 atoms optionally interrupted by from 1 to 4 hetero atoms selected from the group consisting of oxygen, sulfur and nitrogen, and an oxy carbon-containing heterocyclic group having from 4 to 10 atoms optionally interrupted by from 1 to 4 hetero atoms selected from the group consisting of oxygen, nitrogen and sulfur.

2. A composition of claim 1 wherein the metal compound contains from 1 to about 60 carbon atoms per equivalent of metal.

3. A composition of claim 2 wherein the metal compound contains from 1 to about 48 carbon atoms per equivalent of metal.

4. A composition of claim 3 wherein the anion is an aroxy group.

5. A composition of claim 3 wherein the anion is an alkoxy group.

6. A composition of claim 1 wherein M is selected from the group consisting of magnesium, calcium, barium, zirconium, nickel, zinc, cadmium and lead.

7. A composition of claim 2 wherein M is selected from the group consisting of magnesium, calcium, barium, zirconium, nickel, zinc, cadmium and lead.

8. A composition of claim 1 wherein M is selected from the group consisting of magnesium, calcium, barium,

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zirconium, nickel, zinc, cadmium and lead and anion is carbonate, oxide or hydroxide.

9. A composition of claim 1 wherein the base stock is selected from the group consisting of unsubstituted polyphenyl thioethers, unsubstituted mixed polyphenyl ether-thioethers containing from 3 to 10 aromatic rings and mixtures thereof.

10. A composition of claim 3 wherein the base stock is selected from the group consisting of unsubstituted polyphenyl thioethers, unsubstituted mixed polyphenyl ether-thioethers containing from 3 to 10 aromatic rings and mixtures thereof.

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