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FUNCTIONAL FLUID COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Compositions of the class which exhibit improved oxidation resistance by the incorporation of an alkali metal compound or an antimony, bismuth or lanthanum compound or mixtures of these compounds into a class of base stocks representative of which are polyphenyl ethers, polyphenyl thioethers, mixed polyphenyl etherthioethers, phenylmercaptobiphenyls, phenoxyphenylmercaptobiphenyls and mixtures thereof. The compositions have many uses, among which are jet engine lubricants, heat transfer fluids and hydraulic fluids.

This application is a continuation-in-part of application Ser. No. 575,927, filed Aug. 26, 1966, now abandoned.

This invention relates to functional fluid compositions having improved oxidative stability, to compositions comprising a functional fluid and an oxidation improving amount of a metal compound and to functional fluid compositions having the ability to inhibit and control corrosion damage.

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 high and low temperature stability, foam resistance, good 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, primarily due to their deficiency in oxidative stability above 500° F. 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 corrosion and engine deposits.

As is seen from the foregoing characteristics of a jet engine, a functional fluid can attain temperatures of up to 600° F. and higher which can result in oxidative and thermal degradation of a lubricant. The stabilization of lubricants at these high operating temperatures through the use of additives presents an extremely complex and difficult problem since antioxidants which have been utilized in lubricating oil compositions, such as phenolic and amine derivatives, decompose at high temperatures thereby producing deposits and sludge. In addition, such decomposition products can at high temperatures promote oxidation thereby subjecting a lubricant to an increased rate of oxidative degradation. It is, therefore, a requirement for an antioxidant which is to be used in a high temperature lubricant that it perform its desired function without forming sludge or deposits. It is, thus, of particular importance that a functional fluid have improved oxidation resistance without forming sludge and deposits in the many functional fluid systems and applications as aforedescribed.

In addition to the antioxidant requirements as are set out above, an additional requirement of an antioxidant is that it must function as an antioxidant as soon as a fluid is subjected to oxidizing conditions in order to prevent initial build-up of oxidation products which over a period of time can attack metals, form insoluble products and alter the proper functioning of the functional fluid and the antioxidant itself. Thus, the extent of control of the initial rate of oxidation of a fluid can determine the effectiveness of an antioxidant over the entire time to which a functional fluid is subjected to oxidizing conditions.

Another property which determines the effectiveness of an antioxidant under the conditions as aforedescribed, in addition to the above requirements, is the continued control of oxidation of a functional fluid. Thus, an antioxidant must control oxidation of a fluid over a prolonged period of time, preferably with the same degree of control of oxidation as that exhibited during control of the initial rate of oxidation of the fluid.

Thus, it has been found that antioxidants can function initially in inhibiting oxidation of a fluid whereupon the antioxidant activity is exhausted and oxidation increases at a considerable rate. In addition, antioxidants can provide no initial inhibition of oxidative degradation, yet start to function as antioxidants only after a period of time. Both of these types of oxidation inhibitors do not provide the necessary antioxidant activity that is required for high temperature operations in functional fluid systems and particularly for use as jet engine lubricants.

The problem that arises with antioxidants which inhibit oxidation initially is that the antioxidant is exhausted after

only a short period of time. After exhaustion of the antioxidant, the fluid is oxidized at a rate whereby the usefulness of the fluid is expended in a very short period of time. The problem that arises with the second type of antioxidant, that is, an antioxidant which does not function initially is that a fluid which has been oxidized during the initial time when a fluid is subject to oxidizing conditions contains oxidation products, which oxidation products remain in the fluid. Such oxidation products can form sludge and deposits and chemically attack both the fluid and mechanical members in contact with the fluid. Thus, while an antioxidant can function after a period of time, the contaminated fluid does not have the desired properties that are required in functional fluid systems. It is, therefore, an important requirement that an antioxidant inhibit oxidative degration from the time a fluid is subjected to oxidizing conditions. In addition to inhibiting initial rate of oxidation, an antioxidant must continue to inhibit oxidative degration of a fluid over a prolonged period of time. Thus, it is preferred that the control of oxidation over a prolonged period of time generally be at about the same level as the control of oxidation during that time when a fluid is subjected initially to oxidizing conditions.

Thus, the requirements of preferred antioxidants can be defined as (1) control of the extent of viscosity increase, (2) control of deposit formation, (3) control of oxidation as soon as the fluid is subjected to oxidizing conditions, (4) continued control of oxidation as a fluid continues to be subjected to oxidizing conditions and (5) control of oxidation over extended periods of time in order to extend the useful life of a functional fluid.

In addition to the problems of limiting oxidation of a functional fluid as set out above, there exists the problem of 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 lubricating 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 the oxidative stability 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)(1) an alkali metal compound, and
(2) mixtures thereof;
(B)(1) a metal compound wherein the metal is selected from the group consisting of antimony, bismuth and lanthanum, and
(2) mixtures thereof; and
(C) mixtures of (A) and (B).

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

$$(M)_{(a)}(Anion)_{(c)}$$

wherein M is an alkali metal and a is a number having a value of at least one. Typical examples of metal compounds represented by (B) are metal compounds represented by the structure

$$(M_1)_{(b)}(Anion)_{(c)}$$

wherein M_1 is selected from the group consisting of antimony, bismuth and lanthanum, b is a number having a value of at least one and c is a number having a value of from 1 to the product of b times the valence of M_1.

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 ethers, polyphenyl thioethers, mixed polyphenyl ether-thioethers, phenoxybiphenyls, 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 mono- and divalent thiophene and pyridene, examples of which are thenyl, thenylidene, thienyl and pyridyl, and mixtures of the aforedescribed base stocks. 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.

As stated above, functional fluids which have been aforedescribed can contain major amounts of one base stock even as high as 99% with the remainder being one or more base stocks. Certain of the compositions of this invention which have incorporated therein a metal compound represented by (A), (B) and (C) have been found to exhibit unique load carrying ability; that is, certain compositions exhibit greater lubricating qualities than comparative compositions of this invention. In particular it has been found that compositions comprising a polyphenyl ether, a phenoxybiphenyl or mixtures thereof having incorporated herein a polyphenyl thioether, a mixed polyphenyl ether-thioether, a phenylmercaptobiphenyl or a mixed phenoxyphenylmercaptobiphenyl or mixtures of the aforedescribed base stocks, hereinafter referred to as "sulfur-containing base stocks," in minor amounts have improved lubricating qualities, that is, the metal compounds represented by (A), (B) and (C) and the sulfur-containing base stock act synergistically to provide fluid compositions having improved lubricating qualities. Thus, the lubricating qualities of a polyphenyl ether or phenoxybiphenyl composition containing singly either a metal compound represented by (A), (B) or (C) or a minor amount of a sulfur-containing base stock as aforedescribed are not appreciably improved by the incorporation of the above additives whereas a polyphenyl ether or phenoxybiphenyl composition having present therein a metal compound represented by (A), (B) and (C) and a sulfur-containing base stock in minor amounts exhibit improved lubricating qualities.

In general it is preferred that the sulfur-containing base stock contain from 3 to 7 benzenoid rings and from 1 to 6 sulfur atoms. In addition, it is preferred that the sulfur-containing base stock contain at least one meta linkage, preferably at least 40% of the linkages between the phenyl and phenylene rings being meta. The preferred sulfur-containing base stocks are those base stocks which contain all-sulfur linking the phenyl and phenylene rings, that is, a polyphenyl thioether. The concentration of the sul-

fur-containing base stock in a polyphenyl ether or phenoxybiphenyl can vary over a wide range but in general the sulfur-containing base stock acts synergistically with the metal compounds represented by (A), (B) and (C) at a concentration of from about .001% up to about 10%. Although higher concentrations of the sulfur-containing base stock can be utilized in preparing functional fluid compositions, these compositions would then take on the characteristics of the sulfur-containing base stock. Thus, the lubricating qualities of functional fluid compositions containing over about 50% of a sulfur-containing base stock show improved lubricating qualities over a functional fluid composition which contains exclusively a polyphenyl ether or phenoxybiphenyl. This is true since in general the sulfur-containing base stocks have better lubricating qualities than the all-ether-containing base stocks. Thus, the lubricating qualities of blends are improved due to the better lubricating qualities of the sulfur-containing base stocks. However, at small concentrations, the sulfur-containing base stock in the absence of a metal compound represented by (A), (B) or (C) do not improve the lubricating qualities of an all-ether-containing base stock. The improvement in lubricating qualities utilizing a sulfur-containing base stock and a metal compound represented by (A), (B) and (C) is therefore a synergistic additive effect and not merely an effect due to blending.

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), (B) and (C) 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), (B) and (C) sufficient to improve the oxidative stability of a base stock while not adversely affecting critical base stock properties. It has generally been found that the preferred additive concentration of a metal compound represented by (A), (B) and (C) 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 an oxidation improving amount of a metal compound represented by (A), (B) and (C), that is, a metal compound represented by (A), (B) and (C) is added to the compositions at a concentration sufficient to improve the oxidative stability. 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), (B) and (C) 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), (B) and (C) 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), (B) and (C) and the base stocks as aforedescribed.

Typical alkali metals are lithium, sodium, potassium, rubidium and cesium.

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 "hydrocarbon," 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, aluminum, silicon, tin, lead, nitrogen, phosphorus, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine and bromine. Typical examples of hydrocarbon-containing anions are acyloxy, substituted acyloxy, aroyloxy and substituted aroyloxy, aryloxy and substituted aryloxy, alkoxy, substituted alkoxy, alkyl, alkenyl, alkaryl, aralkyl, aryl, substituted alkyl, substituted alkenyl, substituted aryl, cyclic anion, that is (carbo- and hetero- groups); Group III–A hydrocarbon-containing anions such as hydrocarbon-containing boron and aluminum anions; Group IV–A hydrocarbon-containing anions such as hydrocarbon-containing silicon anions, hydrocarbon-containing tin anions and hydrocarbon containing lead 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 at which a functional fluid composition incorporating metal compounds represented by (A), (B) and (C) 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 and M_1 wherein M and M_1 have the same significance as aforedescribed. 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 con-

centration of M or M_1 or both 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 or M_1 is generally up to about 60 carbon atoms per equivalent weight of M or M_1 and even more preferably up to about 48 carbon atoms per equivalent weight of M or M_1. Thus, anions which contain more than one equivalent of M or M_1 attached to a given anion, that is, *a* is greater than 1 and *c* is greater than *b*, would have a preferred upper carbon atom limitation for the anion, which limitation is obtained by multiplying the number of equivalents of M or M_1 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 and M_1 wherein M and M_1 have their aforedescribed 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 or M_1 is as a preferred upper limit about 20 elements per one equivalent of M or M_1 and more preferably is an upper limit of about 10 elements per equivalent of metal represented by M and M_1. 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 or M_1 is up to about 5 per equivalent of M or M_1 and more preferably up to about one element per equivalent of M or M_1.

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 aforedescribed 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 phosphorus-containing anion. In addition, the above-described anions can contain other metals, such as for example, titanium.

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.

Group III–A hydrocarbon-containing anions can be derived from, for example, boron and aluminum hydrocarbon-containing compounds. Typical examples of hydrocarbon boron-containing compounds which can be utilized to prepare compounds represented by (A), (B) and (C) 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-hydroxphenoxyphenyl)-di(phenoxyphenyl) boroxin.

Group IV–A hydrocarbon-containing anions can be derived, for example, from silicon, lead and tin hydrocarbon-containing compounds. Typical examples of these compounds are p-triphenyl silyl benzoic acid p-(triphenyl silyl) propionic acid, p-hydroxyphenyl, pentaethyl disiloxane, triethyl silyl benzonic, 4,4'-(tetramethyl disiloxanylene) dibenzoic acid, p-hydroxyphenyltriphenyl silicate, p-triphenyl stannyl benzoic acid, p-hydroxyphenyl pentaphenyl ditin, m-hydroxy benzyl-tribenzyl lead, p-trimethyl plumbyl benzoic acid and phenyl plumbonic acid.

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 examples of the phosphorus compounds which can be utilized to form the phosphorus hydrocarbon-containing anions include the hydrocarbon-containting 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, dimethylamonopropylamine, 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), (B) and (C).

Typical examples of Group VI–A hydrocarbon-containing anions are the hydrocarbon sulful-containing anions. These anions can be derived, for example, from mercaptans and sulfonic acids, among which are thiophenol, dedecyl 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 or bromine. It is also contemplated that any of the aforedescribed anions can be substituted with Group VII–A elements.

The metal compounds represented by (A), (B) and (C) 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 organometallic compounds as there is bonding between the metal and carbon. Typical examples of these compounds are phenyl lithium and dodecyl lithium.

While the aforedescribed anions are effective and contemplated within the scope of this invention as oxidation stabilizers, 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 effetive 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 ethylendiamine tetra-acetate, dimetal ethyl-

enediamine tetra-acetic acid, dimetal ethylenediamine diacetate, metal ethylenediamine diacetic acid, trimetal nitrilotriacetate, metal nitrolotriacetic acid, metal benzoate, metal salicylate, metal acetosalicylate, metal biphthalate, 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-etheylhexanoic acid, nonanoic acid, decanoic acid, dodecanoic acid, undecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, eicosanoic acid, docosanic acid, triacontanoic acid, butenic acid, pentenic acid, hexenic acid, teracrylic acid, hypogeic acid, elaidic acid, linoleic acid, α-eleostearic acid, α-eleostearic acid, α-linolenic acid, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, 3-butenoic acid, angelic acid, senecioic acid, hydrosorbic acid, sorbic acid and 4-tetradecenoic acid.

(b) Alicyclic monocarboxylic acids

Cyclopropanecarboxylic acid, cyclopentanecarboxylic acid, hydrocarpic acid, chaulmoogric 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, indoxylic acid, 3-indoleacetic acid, cinchoninic acid, furoic acid, 2-thiophenecarboxylic acid, 2-pyrrolecarboxylic acid, 9-acridancarboxylic acid, quinaldic acid, pyrazionic acid and antipyric 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, ethidenemalonic acid, mesaconic acid, allylmalonic acid, allylsuccinic acid, teraconic acid, xeronic acid, cetylmalonic acid, pyromellitic 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 or M_1 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 aforedescribed 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), (B) and (C).

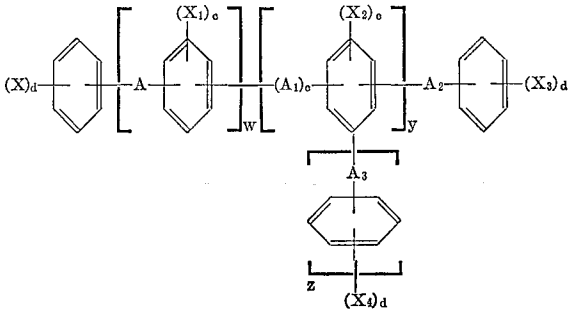
Typical examples of unsubstituted and substituted aroxy-, alkoxy- and oxyheterocyclic groups from which the metal compounds represented by (A), (B) and (C) can be derived are methyl, ethyl, propyl, t-butyl and n-butyl alcohols, isoamyl alcohol, cyclohexyl, lauryl alcohol, benzyl alcohol, acetyl alcohol, stearyl alcohol, phenol, o-, m- and p-cresol, nitrophenol, guaiacol, 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-dibutylaminomethyl-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), (B) and (C) 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 compounds 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 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, anti-foam and lubricity. As an

example of imparting an additional property by an anion, a metal anion represented by (A), (B) and (C) in which the anion is derived from a polysiloxane can impart anti-foam properties. In addition, a metal compound in which the anion is derived from a polymer such as a methacrylic and 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, A_1, A_2 and A_3 are each a chalkogen having an atomic number of 8 to 16, X, X_1, X_2, X_3 and X_4 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. Typical examples of such base stocks are 2- to 7-ring o-, m-, and p-polyphenyl ethers and mixtures thereof, polyphenyl thioethers and mixtures thereof, mixed polyphenyl ether-thioether compounds in which at least one of the chalkogens represented by A, A_1, A_2 and A_3 is dissimilar with respect to any one of the other chalkogens, phenoxybiphenyls, phenylmercaptobiphenyls, mixed phenoxy phenylmercaptobiphenyls and mixtures thereof. It is also contemplated within the scope of this invention that the phenyl and phenylene groups in the aforedescribed base stocks can be partially or totally replaced with a heterocyclic group such as thiophene and pyridene.

Typical examples of unsubstituted polyphenyl ethers, that is, when A, A_1, A_2 and A_3 are oxygen and *e* has a value of 1 are those having all their ether linkages in the meta position since the all-meta linked ethers are the best suited for many applications because of their wide liquid range and high degree of thermal stability. However, mixtures of the polyphenyl ethers, i.e., either isomeric mixtures or mixtures of homologous ethers, can also be used to obtain certain properties, e.g., lower solidification points. Examples of the polyphenyl ethers contemplated are the bis(phenoxyphenyl) ethers, e.g., bis(m-phenoxyphenyl) ether; the bis(phenoxyphenoxy)benzenes, e.g., m-bis(m - phenoxyphenoxy)benzene, m-bis(p - phenoxyphenoxy)benzene, o-bis(o-phenoxyphenoxy)benzene; the bis(phenoxyphenoxyphenyl) ethers, e.g., bis[m-(m-phenoxyphenoxy)phenyl] ether, bis[p-(p-phenoxyphenoxy)phenyl] ether, m-[(m-phenoxyphenoxy)(o-phenoxyphenoxy)] ether and the bis(phenoxphenoxyphenoxy)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 nonterminal 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 only 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 position 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 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.

Typical examples of phenoxybiphenyl compounds, that is, when *e* has a value of 0 and A, A_1, A_2 and A_3 are oxygen are 3,3′-diphenoxybiphenyl, 3,2′-diphenoxybiphenyl, 3,4′-diphenoxybiphenyl, 3,4-diphenoxybiphenyl, o-, m- and p-phenoxybiphenyl and tri- and tetra-substituted phenoxybiphenyls. It is also contemplated that mixtures of the above phenoxybiphenyls can be utilized as base stocks, for example, mixtures containing from 1 to 25% of a monophenoxybiphenyl, from 25% to 75% of a diphenoxybiphenyl having at least one phenoxy group in the meta position with respect to the biphenyl nucleus and from 1 to 40% of a tri- and/or tetra-substituted phenoxybiphenyl.

Typical examples of polyphenyl thioethers, that is, when A, A_1, A_2 and A_3 are sulfur and *e* has a value of 1 which can be utilized as base stocks and in addition blended in minor amounts into polyphenyl ethers and phenoxybiphenyls so as to act synergistically with a metal compound represented by (A), (B) and (C) to provide compositions having improved lubricating qualities 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, A_1, A_2 and A_3 are sulfur which can be utilized as base stocks and in addition blended in minor amounts into polyphenyl ethers and phenoxybiphenyls so as to act synergistically with a metal compound represented by (A), (B) and (C) to provide compositions having improved lubricating qualities are 3,3′-bis(phenylmercapto)biphenyl, o-, m- and p-phenylmercaptobiphenyl, 3,4-phenylmercaptobiphenyl, 3,2-diphenylmercaptobiphenyl, m - chlorophenylmercapto-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 chalkogens represented by A, A_1, A_2 and A_3 is dissimilar with respect to any other chalkogen which can be utilized as base stocks and in addition blended in minor amounts into polyphenyl ethers and phenoxybiphenyls so as to act synergistically with a metal compound represented by (A), (B) and (C) to provide compositions having improved lubricating qualities are

1-phenylmercapto-2,3-bis(phenoxy)benzene,
2-phenylmercapto-4′-phenoxydiphenyl sulfide,

2-phenoxy-3'-phenylmercaptodiphenyl sulfide,
2,2'-bis(phenylmercapto)diphenyl ether,
3,4'-bis(m-tolylmercapto)diphenyl ether,
3,3'-bis(xylylmercapto)diphenyl ether,
3,4'-bis(m-isopropylphenylmercapto)diphenyl ether,
3,4'-bis(p-tert-butylphenylmercapto)diphenyl ether,
3,3'-bis(m-chlorophenylmercapto)diphenyl ether,
3,3'-bis(m-trifluoromethylphenylmercapto)diphenyl ether,
3,4'-bis(m-perfluorobutylphenylmercapto)diphenyl ether,
2-m-tolyloxy-2'-phenylmercaptodiphenyl sulfide,
m-phenylmercaptodiphenyl ether,
3,3'-bis(phenylmercapto)diphenyl ether, 3,3'-bis (phenoxy)diphenyl sulfide,
3-phenoxy-3'-phenylmercaptodiphenyl sulfide,
3-phenylmercapto-3'-phenoxydiphenyl ether,
3,4'-bis(phenylmercapto)diphenyl ether,
m-bis(m-phenylmercaptophenoxy)benzene,
3-phenylmercapto-3'-(m-phenylmercaptophenylmercapto)diphenyl ether and mixtures thereof.

Typical examples of mixed phenoxy-thiophenoxybiphenyl, that is, where e has a value of 0 and one of the chalkogens represented by A, A_1, A_2 and A_3 is dissimilar with respect to any other chalkogen which can be utilized as base stocks and in addition blended in minor amounts into polyphenyl ethers and phenoxybiphenyls so as to act synergistically with a metal compound represented by (A), (B) and (C) to provide compositions having improved lubricating qualities are phenylmercaptophenoxybiphenyl, o-phenylmercaptophenyl-m-phenoxyphenoxybiphenyl and mixtures thereof.

It is also contemplated within the scope of this invention that the aforedescribed 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-phenoxyphenyl) sulfide. Particularly useful mixtures are those containing the above mixtures and m-bis(phenylmercapto) benzene in 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:

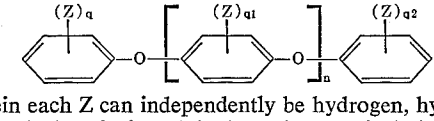
(1) 50% m-bis(phenylmercapto)benzene, 25% m-phenoxyphenyl - m - phenylmercaptophenyl sulfide, 11% bis (m-phenoxyphenyl) sulfide, 14% bis(m-phenylmercaptophenyl) sulfide.

(2) 50% m - bis(phenylmercapto)benzene, 25% m-phenoxy-m-phenylmercaptobenzene, 25% o - bis(phenylmercapto)benzene.

(3) 46% m-(m-chlorophenylmercapto)-m-phenylmercaptobenzene, 31% m-bis(phenylmercapto)benzene, 15% m-phenoxy-m-phenylmercaptobenzene, 8% m - chlorodiphenyl sulfide.

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.

It is also contemplated within the scope of this invention that a polymeric polyphenylene ether and mixture thereof can be stabilized against oxidative degradation by the incorporation of metal compounds represented by (A), (B) and (C). Typical examples of a polyphenylene ether are polyphenylene ethers represented by the structure



wherein each Z can independently be hydrogen, hydrocarbon radical, substituted hydrocarbon radical, hydrocarbonoxy, nitro, hydroxyl, halogen, primary, secondary or tertiary amino, diazo, nitrile, carboxyl, quaternary ammonium, PX_2, AsX_2 in which X is halogen, PO_3H_2, PO_2H_2, AsO_3H_2 and AsO_2H_2; and n is an integer having a value of at least 19; q and q_2 are whole numbers having a value of 1 to 5 and q_1 is a whole number having a value of 1 to 4 provided that q_1 is independently selected with respect to each phenylene group to which Z is attached.

It is also contemplated that the metal compounds represented by (A), (B) and (C) can be incorporated into the polyphenylene ethers prior to the polymerization of the starting materials which are utilized to prepare the polyphenylene ethers. In addition, the metal compounds represented by (A), (B) and (C) can be incorporated into the polyphenylene ether by mixing the compounds with the polyphenylene ether. The concentration of the metal compounds represented by (A), (B) and (C) which is incorporated into a polyphenylene ether is generally from about .001% to about 10%, preferably from about .005% to about 8%.

The preferred polyphenylene ethers are those in which Z is hydrogen, hydrocarbon radicals or hydrocarbonoxy radicals or the corresponding substituted hydrocarbon radicals or hydrocarbonoxy radicals which do not contain a tert-α-carbon atom and when Z is nitro, primary, secondary or tertiary amino, diazo, halogen, nitrile, carboxyl, quatenary ammonium, PX_2, AsX_2, in which X is halogen, PO_3H_2, PO_2H_2, AsO_3H_2 and AsO_2H_2, it is preferred that not more than two of the above groups be attached to the same phenylene or phenyl group.

In order to demonstrate the outstanding properties of the compositions of this invention, various metal salts were blended into base stocks and the resulting functional fluid compositions evaluated for oxidative stability and control of metal corrosion.

One of the major bench scale methods used for evaluating the oxidative stability of a lubricant is the procedure given in Federal Test Method, Standard No. 791, Method No. 5308 according to which the lubricant to be tested is heated at a specific temperature (500° F.) in the presence of certain metals and oxygen and the viscosity increase of the lubricant is determined. In addition, information as to the corrosivity of a lubricant to metals and the degree of sludge and deposit formation can also be obtained.

Various functional fluid compositions containing a metal compound represented by (A), (B) and (C) were tested according to the above procedure except that the temperature was held at 650° F. with an air rate of 10 liters per hour in Examples 1 through 47 and at 500° F. and an air rate of 5 liters per hour in Examples 48 through 51. The metal specimens used were, as specified in said procedure, steel, copper, silver, titanium, magnesium alloy and aluminum alloy. The viscosity of the fluid before and after testing was determined at 100° F.

In Table I the percent stabilization is determined by the following formula:

$$\text{Degree of Stabilization } (D) = \frac{V_1 \text{ minus } V_2}{V_1} \times 100$$

and in addition

$$\frac{V_1}{V_2} = \frac{100}{100-D}$$

wherein V_1 is the percent viscosity increase of the heat base stock after a certain test time and at a defined test temperature; V_2 is the percent viscosity increase of the base stock plus metal compound determined at the same test time and under the same test conditions as the neat base stock. V_1/V_2 relates to the extended usable life of the functional fluid as measured by the number of times that the percent viscosity increase is reduced over a given period of time. In Examples 1 through 45 the degree of stabilization was determined after a test time of 24 hours at a test temperature of 650° F. In Exam-

ples 46 and 47 the degree of stabilization was determined after a test time of 48 hours at a test temperature of 650° F. and in Examples 48 through 51 the degree of stabilization was determined after a test time of 48 hours at a test temperature of 500° F.

In addition, in Table I the percent reduction in the initial rate of oxidation is determined by the following formula:

$$\text{Percent reduction}=\frac{Rb-Rb+a}{Rb}\times 100$$

wherein Rb is the initial rate of oxidation of the base stock expressed as the change in viscosity in centistokes per hour determined at approximately 7 hours; $Rb+a$ is the rate of oxidation in centistokes per hour of the base stock plus additive determined at 7 hours.

In Table I "R Initial" is the rate of oxidation of the fluid after approximately 7 hours, "R_{48}" is the rate of oxidation of the fluid in centistokes per hour determined after 48 hours, and "R Final" is the rate of oxidation of the fluid in centistokes per hour when the oxidation and corrosion test was continued beyond a 48 hours period. The test duration of R Final is given in parentheses next to the R Final rate of oxidation.

In Table I the base stocks that were used are as follows: in Examples 1 through 45 the base stock was a mixture of 5-ring polyphenyl ethers, in Examples 46 and 47 the base stock was bis(m-phenylmercaptophenyl) sulfide, and in Examples 48 through 51 the base stock was a mixture of m-bis(phenylmercapto)benzene, m-bis(phenylmercaptophenyl) sulfide, m-phenylmercaptophenyl-m-phenoxyphenyl sulfide and m-bis(phenoxyphenyl) sulfide.

A bearing test was run which was modified from MIL-L-27502. The test time was 100 hours using an Erdco bearing. The test conditions for Example 52 were a bearing temperature of 600° F., a bulk oil temperature of 600° F. and an oil in temperature of 550° F. The test conditions for Example 53 are the same as for Example 52 except the bearing temperature was increased to 650° F. In Table II the base stock that was used was a mixture of 5-ring polyphenyl ethers. The stabilizer that was used was potassium p-phenylazobenzoate.

TABLE II

Example No.	Concentration by Weight	Overall Rating	Final Viscosity, cs. at 100° F.
52	0.00	[1] 79.3	[1] 20,000
53	0.12 4	[2] 61.8	[2] 412

[1] Test terminated and viscosity determined at 62½ hours.
[2] Deposit rating and viscosity determined at 100 hours.

A Ryder load test was run to determine the lubricating qualities of compositions comprising a polyphenyl ether, a metal compound represented by (A), (B) and (C) and a minor amount of a sulfur-containing base stock. The Ryder load test consists of subjecting a test lubricant (held at 165° F.) to a series of controlled tests at increasing gear tooth loads in a test machine which uses a set of spur gears (one of which has wider teeth than the other) as the test gears. After each loading, the narrow gear of the test gears is examined to determine the scuffed area on each tooth. The load carrying ability of the scuff-limit load of the lubricant is defined as the tooth load on the narrow test gear at which the average per-

TABLE I

Ex. No.	Metal salt	Concentration in milli-equivalents per 100 grams of base stock	Degree of stabilization	Percent reduction in initial rate of oxidation	Rate of oxidation, cs./hour: R initial	R_{48}	R final	Net change in rate of oxidation R_{48}–R initial	Net change in metal mg./cm.²: Cu	Ag
1	Neat base stock	0.00	0	0	16.5	[1] 42		[1] 29.5	−1.20	
2	Potassium cyclohexanoate	1.0	93	84	2.6	2.5		−0.1	+0.12	
3	Potassium acetate	1.0	91.5	77	4.0	3.6		−0.4	+0.02	
4	Potassium neodecanoate	1.0	95.5	82	3.0	1.6		−1.4	+0.24	
5	Potassium neotridecanoate	1.0	99	92	0.3	0.8		+0.5	+0.02	
6	Potassium oleate	1.0	95.5	88	2	1.7		−0.3	−0.60	
7	Potassium bitartrate	1.0	95.5	85	2.5	1.5		−1.0	+0.25	
8	Potassium thiocyanate	1.0	84.5							
9	Tetrapotassium ethylene diamine tetraacetate	1.0	92	73	4.5	2.7		−1.8	+0.56	
10	Dipotassium ethylene diamine diacetate	1.0	92	76	4.0	3.1		−0.9	+0.15	
11	Potassium ethylene diamine diacetate acid	1.0	90	73	4.5	4.7		+0.2	−0.12	
12	Potassium nitrilo triacetic acid	1.33	95.5	87	2.2	1.8		−0.4	+0.35	
13	Potassium benzoate	1.0	95	82	3.0	1.7		−1.3		
14	Potassium salicylate	1.0	92.5	79	3.5	3.1		−0.4	+0.58	
15	Potassium acetosalicylate	1.0	88	72	4.8	6.1		+1.3	+0.59	
16	Potassium m-phenoxybenzoate	1.0	95.5	86	2.3	1.7		−0.6		
17	Potassium o-phenyl azobenzoate	1.0	95.5	84	2.7	1.6		−1.1		
18	Potassium m-phenyl azobenzoate	0.94	95	85	2.4	2.4		0.00	[2] +0.57	
19	Potassium p-phenyl azobenzoate	2.0	3	76	4.0	2.7		−1.3		
20	Potassium phenyl acetate	1.0	94.5	84	2.6	2.2		−0.4	+0.37	
21	Potassium benzilate	0.74	95.5	85	2.5	1.4		−1.1	+0.40	
22	Lithium m-phenoxybenzoate	1.0	95	80	3.2	1.9		−1.3		
23	Lithium m-phenyl azobenzoate	2.0	94	82	3.0	2.2		−0.8	−0.46	
24	Lithium p-phenyl azobenzoate	0.47	91.5	82	3.0	3.7		+0.7		
25	Sodium o-phenoxybenzoate	1.0	96	90	1.6	2.0		+0.4		
26	Sodium 5-(m-nitrophenylazo)-salicylate	1.0	87						−0.75	
27	Rubidium m-phenyl azobenzoate	0.47	94.5	80	2.3	2.2		−0.1		
28	Rubidium p-phenyl azobenzoate	1.0	94	85	2.5	2.4		−0.1	[3] +0.22	
29	Potassium benzylate	0.3	97	91	1.4	1.4	1.5(75)	0.00		
30	do	2.0	97	90	1.6	1.4	2.5(307)	−0.2	[4] +0.30	
31	Potassium m-phenoxybenzylate	1.0	95.5	83	2.8	1.4		−1.4		
32	Lithium benzylate	1.0	93	73	4.5	2.4		−2.1		
33	Potassium diphenyl methoxide	1.0	96	88	2.0	1.6		−0.4	+0.55	
34	Potassium triphenyl methoxide	1.0	95	86	2.3	1.8		−0.5	+0.30	
35	Potassium t-butoxide	1.0	97	82	3.0	1.3	4.9(141)	−1.7	[5] +0.77	
36	do	2.0	96.5	82	3.0	1.3	2.3(307)	−1.7		
37	Potassium p-azobenzene sulfonate	3.0	48.5							
38	m,m'-phenoxyphenoxy potassium phenate	1.0	95.5	85	2.5	1.6		−0.9	+0.21	
39	Lathanum m-phenoxybenzoate	1.0	91.5	76	4.0	4.4		+0.4		
40	Lathanum m-phenylazobenzoate	1.0	91	74	4.3	4.4		+0.1		
41	Bismuth m-phenoxybenzoate	1.0	92	79	3.5	4.8		+1.3	−0.25	
42	Bismuth m-phenylazobenzoate	1.0	91						+0.12	
43	Potassium 3,5-dichloro anthranilate	2.0	57							
44	Potassium pentachloro phenate	2.0	86.5	48	8.5				[6] −2.20	
45	Potassium trichloro acetate	2.0	47							
46	Neat	0.0	00	00	5.3	7.8		+2.5	−14.4	−1.80
47	Potassium t-butoxide	3.0	69.5	36	3.4	2.5		−0.9	−0.4	−0.50
48	Neat	0.0	00	00					−2.13	−0.92
49	Potassium t-butoxide	0.1	65						−0.61	0.36
50	Potassium triphenyl methoxide	2.0	80						−0.80	−0.10
51	Potassium diphenyl methoxide	0.5	69						−0.85	−0.10

[1] Rate of oxidation determined at 25 hours test time.
[2] Copper weight change determined at 120 hours.
[3] Weight loss of copper determined at 65 hours.
[4] Copper weight determined at 300 hours.
[5] Copper weight change determined at 141 hours.
[6] Copper weight change determined at 29 hours.

cent of tooth area scuffed is 22½% for the narrow test gear. The test equipment and basic test procedure, which were first developed by E. A. Ryder, are described in ASTM Bulletin No. 184 entitled "A Test for Aircraft Gear Lubricants."

The Ryder load test utilizes the Ryder Gear Erdco universal tester which includes a Ryder Gear machine, a drive system, a support and load oil system, a test oil system and the necessary instrumentation and controls. The test gears are special spur gears made of AMS 6260 steel, case hardened and ground, having 28 teeth, 3½ inches pitch diameter, 8 inch diametral pitch, 22.5° pressure angle with 0° tip relief.

In reporting the results from the Ryder load test, the scuffed area of each gear tooth is measured and is multiplied by 100 divided by the total working area of the gear tooth. The average percent of tooth area scuffed is the algebraic average of the percent of scuffed area of all 28 teeth of the test gear. The percent of tooth area scuffed is estimated visually to the nearest 5% of each individual tooth with the aid of a grid mounted in the left eye base of a microscope which is part of the test equipment.

As noted above the load carrying ability or the scuff-limit load of a lubricant has been defined as the gear tooth load at which the average percent of tooth area scuffed is 22.5% for the narrow test gear by plotting the average percent of the area scuffed for the narrow test gear versus the load oil pressure. From the plot thereby obtained, the load oil pressure is read at which the average percent of tooth area scuffed is 22.5%. Then the load carrying ability of the lubricant is determined by the following formula:

$$P=\frac{kL}{W_2}$$

where P equals load carrying ability of the lubricant, pounds per inch; k equals Ryder gear machine constant, which is 18.55; L equals load oil pressure, pounds per square inch gage; and W_2 equals the effective tooth width in inches, and is the actual contact width of the gear tooth which is determined by multiplying the gross tooth width by the ratio of effective tooth width to gross tooth width as determined by visual examination.

In Table III the base stock that was used in Example 54 was a 4-ring polyphenyl ether. In Examples 55 through 57 a mixture of 5-ring polyphenyl ethers was used as the base stock.

on the order of about 10 times less than the base stock percent viscosity increase for the same period of time. Of equal significance are the results set out in Table II since the bearing test correlates quite well with actual gas turbine performance in measuring the overall deposit rating and viscosity changes which would be expected to occur in actual use. Thus, the test of the neat base stock had to be terminated at the end of 62.5 hours with a substantial increase in viscosity. The compositions of the invention maintained the required temperature-viscosity relationship and did not become too thick on prolonged use thereby maintaining proper lubricating of mechanical parts in contact with the fluid.

In addition to the control of viscosity increase, the functional fluid compositions incorporating the metal compounds represented by (A), (B) and (C) exhibit a high degree of oxidative stabilization. As is noted from the examples in Table I, the degree of stabilization in the great majority of cases is of the order of 90% and higher. As compared to the base stock, the effectiveness of the compositions of this invention is readily apparent since the base stock has zero stabilization. It is, as mentioned above, of particular importance to maintain a high degree of stabilization in order to maintain the critical fluid properties over a given period of time.

Of equal significance is the percent reduction in the initial rate of oxidation. As is well illustrated by the examples in Table I, the magnitude of the percent reduction of the initial rate of oxidation is in the order of 70–90% and in some cases higher, which percent reduction demonstrates that the metal compounds represented by (A), (B) and (C) are providing control and inhibition of oxidation as soon as the base stock is subjected to oxidizing conditions. This is of particular importance since oxidation products which build-up when a base stock is subjected to initial oxidizing conditions without control of oxidation can contaminate the fluid and adversely affect critical fluid properties. Thus, the oxidation of a base stock has to be controlled initially in order to maintain critical fluid properties.

Of equal significance is, as is set out in Table I, the rate of oxidation at the end of 48 hours, that is, R_{48}, and the net change in rate of oxidation, that is, $R_{48}-R$ Initial. The effectiveness of an antioxidant over a continued period of time can be measured by the rate of oxidation of a base stock at two given points of time. Thus, it is preferred that an antioxidant function initially and in addition continue to function as an antioxidant over a given

TABLE III

Ex. No.	Sulfur-Containing Base Stock	Concentration, percent	Metal Salt	Concentration, percent	Ryder Load Test Result, lbs/in.
54	m-Bis(phenylmercapto)benzene	10			2,030
55			Potassium m,m'-phenoxy-phenoxy phenate	0.7	2,085
56	m-Bis(phenylmercapto)benzene	3	do	0.3	2,563
57	Mixture of: m-bis(phenylmercapto)-diphenyl sulfide; m-(phenylmercapto)phenoxy diphenyl sulfide; m-bis(phenoxy)diphenyl sulfide.	3	do	0.3	2,505

As is demonstrated by Table I and II, it is clearly evident that the incorporation of the metal compounds represented by (A), (B) and (C) into a base stock provides a functional fluid composition which has a high degree of resistance towards oxidative degradation and, therefore, a greatly extended useful life. In regard to the extension of useful life, it has been found that the test procedure described above correlates quite well with the results obtained under full-scale aircraft gas turbine bearing tests and under conditions of actual use. It has been found that the magnitude of change in viscosity of 100° F. as measured by the test procedure is representative of the extent of increased service life obtainable under actual conditions. Thus, for example, the decrease in percent viscosity increase of a composition incorporating a metal compound represented by (A), (B) and (C) was

period of time whereby the rate of oxidation is maintained about constant or reduced as the fluid is continued to be subjected to oxidizing conditions. The effectiveness of the metal compounds represented by (A), (B) and (C) in fluid compositions is significantly demonstrated by the fact that the rate of oxidation, R_{48}, is essentially the same or less than R Initial. The net change in rate of oxidation, in addition, shows that oxidation is being controlled and inhibited over a long period of time and in the majority of cases, the rate of oxidation is decreasing as a function of time, as is shown by a negative $R_{48}-R$ Initial. Thus, a negative $R_{48}-R$ Initial indicates that the antioxidant is becoming even more effective as a function of time.

Another requirement which is of equal significance in determining antioxidant activity is the continued control

of the oxidation of a base stock over a prolonged period of time. The net change in rate of oxidation as indicated above was determined at 48 hours. In order to determine the high degree of activity of the metal compounds represented by (A), (B) and (C) in functional fluid compositions over prolonged periods of time, certain compositions were tested beyond the 48 hour period. Of particular significance are Examples 30 and 36 wherein the rate of oxidation at 307 hours was 2.5 and 2.3, respectively. Thus, as indicated by R Final of these two examples, oxidation was still being controlled and inhibited after 307 hours. This outstanding effectivesss is even more pronounced when a comparison is made between these two examples and the rate of oxidation of the base stock. As is noted from Example 1, the rate of oxidation was 42, which rate of oxidation was determined at 25 hours. Thus, the far superiority of functional fluid compositions incorporating the metal compounds represented by (A), (B) and (C) over prolonged and extended periods of time is well illustrated by the examples set forth. In addition to the control and inhibition of oxidative degradation of a base stock, the outstanding effectiveness of the metal compounds represented by (A), (B) and (C) in inhibiting and controlling copper and silver corrosion is well illustrated in Table I. The control of copper corrosion is of particular importance since inhibition and control of corrosion damage prevents corrosion products from contaminating the fluid, which products can cause an increased rate of oxidation of the fluid.

The outstanding effectiveness of the combination of a metal compound represented by (A), (B) and (C) and a sulfur-containing base stock when incorporated in minor amounts into polyphenyl ethers in increasing the lubricating qualities of the compositions of this invention is well illustrated by the data of Table III. In particular, the data of Table III demonstrates that a sulfur-containing base stock acts synergistically when a metal compound represented by (A), (B) and (C) to provide functional fluid compositions having improved lubricating qualities. Thus, Example 57 clearly demonstrates the synergism which is obtained by the incorporation of a metal compound represented by (A), (B) and (C) and a sulfur-containing base stock in minor amounts into an all-ether base stock. Of particular importance is the comparison between Example 57 and Examples 54, 55 and 56 wherein the Ryder load test result demonstrated that the combination of the two additives increased the lubricating qualities as measured by the Ryder load test in the range of from about 500 to 700 pounds per inch. Of even more importance is the fact that the concentration of the sulfur-containing base stock and the metal salt when combined into the ether base stock was less than the individual concentrations when these two additives were tested separately. The results of the Ryder load test clearly demonstrate the synergistic activity of the two additives when incorporated into an all-ether base stock.

It is, therefore, readily apparent that the requirements of an antioxidant are highly complex and many factors have to be considered in order to determine the true effectiveness of an antioxidant. Thus, in a fluid system, the particular properties of a fluid have to be maintained in order to continue the 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 fluid 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 causes deposits to form on moving parts which are lubricated by the fluid thereby causing inadequate lubricating and interference with the proper functioning of the parts. Increased chemical reactivity is observed on fluid degradation as well as a build-up in acid number of the fluid. Such increased chemical reactivity and high acid number allows the particular system which incorporates the fluid to be chemically attacked by the fluid thereby causing pitting, wear and alterations of the close tolerances of mechanical members in contact with said fluid. Thus, premature overhaul of mechanical parts can be a direct consequence of fluid degradation. It is, therefore, of particular importance that a base stock be stabilized against oxidation and corrosion so as to extend the useful life of a fluid in a functional fluid system.

As a result of the excellent stabilization of 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 compositions within the scope of this invention, improved hydraulic pressure devices can be prepared in accordance with this invention which comprise in combination a fluid chamber and an actuating fluid composition in said chamber, said fluid comprising a mixture of one or more of the base stocks hereinbefore described and a minor amount, sufficient to inhibit 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), (B) and (C), 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 dyes, pour point depressants, metal deactivator, acid scavengers, antioxidants, defoamers in concentration sufficient to impart anti-foam properties, such as from about 10 to about 100 parts per million, viscosity index improvers such as polyalkyl-

ates, 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 aforedescribed can be utilized singly or as a fluid composition containing two or more base stocks in varying proportions. The base stocks can also contain other fluids which include, in addition to the functional fluids described above, fluids derived from coal products and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and 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 biphenyl, monohalogenated diphenyl ethers, trialkyl, phosphine oxides, diarylalkyl phosphonates, trialkyl phosphonates, aryldialkyl phosphonates, triaryl phosphonates, di- and tricarboxylic acid esters, such as di-2-ethylhexyl adiphate, 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 mixtures thereof.

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 ethers,

(2) polyphenyl thioethers,

(3) mixed polyphenyl ether-thioethers,

(4) phenylmercaptobiphenyls,

(5) phenoxybiphenyls,

(6) mixed phenoxyphenylmercaptobiphenyls, and

(7) mixtures of any combination of (1), (2), (3), (4), (5) and (6); and

(B) an oxidation improving amount of up to 5% by weight of the composition of a compound selected from the group consisting of

(1) (a) an alkali metal compound represented by the structure

$$(M)_{(a)}(\text{Anion})$$

wherein M is an alkali metal, Anion is a hydrocarbon-containing anion selected from the group consisting of acyloxy, aroyloxy, 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, 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, sulfur and nitrogen and *a* is a number having a value of at least one,

(b) an alkali metal inorganic compound wherein the inorganic anion is selected from the group consisting of thiocyanate, phosphate, nitrite, carbonate and hydroxide, and

(c) mixtures thereof;

(2) (a) a metal compound represented by the structure

$$(M_1)_{(b)}(\text{Anion})_{(c)}$$

wherein M_1 is selected from the group consisting of bismuth and lanthanum, wherein Anion is as above-described, *b* is a number having a value of at least 1 and *c* is a number having a value of from 1 to the product of *b* times the valence of M_1,

(b) a metal inorganic compound selected from the group consisting of lanthanum oxide and bismuth oxide, and

(c) mixtures thereof; and

(3) mixtures of (1) and (2).

2. A composition of claim **1** wherein the compound is (B)(1) and (B)(1)(a) is an alkali metal compound wherein Anion contains from 1 to 60 carbon atoms per equivalent of M.

3. A composition of claim **1** wherein the compound is (B)(2) and (B)(2)(a) is a metal compound wherein the Anion contains from 1 to 60 carbon atoms per equivalent of M_1.

4. A composition of claim **2** wherein the Anion is phenoxy phenoxide.

5. A composition of claim **2** wherein the Anion is selected from the group consisting of phenoxyphenoxide and diphenoxy phenoxide.

6. A composition of claim **1** wherein M is selected from the group consisting of lithium, sodium and potassium.

7. A composition of claim **2** herein M is selected from the group consisting of lithium, sodium and potassium.

8. A composition of claim **1** wherein M_1 is bismuth.

9. A composition of claim **3** wherein M_1 is bismuth.

10. A composition of claim **1** wherein the base stock is (A)(1) and (A)(1) is an unsubstituted polyphenyl ether having from 3 to 8 aromatic rings and mixtures thereof.

11. A composition of claim **2** wherein the base stock is (A)(1) and (A)(1) is an unsubstituted polyphenyl ether having from 3 to 8 aromatic rings and mixtures thereof.

12. A composition of claim **1** wherein the base stock is a polyphenylene ether polymer containing at least 17 benzenoid rings.

References Cited

UNITED STATES PATENTS

2,057,212	10/1936	Shoemaker et al.	252—42.7
2,079,051	5/1937	Sullivan et al.	252—25
2,197,833	4/1940	Reiff	252—42.7
2,335,017	11/1943	McNab et al.	252—42.7 XR
2,348,317	5/1944	Waugh	252—42.7
3,065,173	11/1962	Blake et al.	252—25 XR
3,080,321	3/1963	Blake et al.	252—52 XR
3,096,375	7/1963	Campbell et al.	252—45 XR
3,163,603	12/1964	Le Suer	252—33.6
3,213,025	10/1965	Hedenburg	252—52 XR
3,274,107	9/1966	Wilson et al.	252—46.4
3,314,887	4/1967	Carlson et al.	252—42.7
3,321,403	5/1967	Campbell et al.	252—45 XR

FOREIGN PATENTS

851,651	10/1960	Great Britain.

OTHER REFERENCES

Versene, Techincal Bulletin No. 1, Bersworth Chemical Co., Farmingham, Mass., copyright 1949, pp. 1(a) and 2 most pertinent.

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