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MINERAL OIL COMPOSITION

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This invention has to do in a general way with mineral oil compositions and is more particularly related to compositions comprised of mineral oil and a minor proportion of an added ingredient which will improve the oil in one or more important respects.

It is well known to those familiar with the art that mineral oil fractions refined for their various uses are in and of themselves usually deficient in one or more respects, so that their practical utility is limited even in the particular field for which they have been refined. For example, mineral oil fractions refined for use as lubricants have a tendency to oxidize under conditions of use with the formation of sludge or acidic oxidation products; also the lighter fractions such as gasoline and kerosene tend to oxidize with the formation of color bodies, gum, etc. In order to prevent the formation of these products and thereby extend the useful life of the oil fraction, it is common practice to blend with such oil fractions an additive ingredient which will have the effect of inhibiting oxidation, such ingredients being generally known to the trade as oxidation inhibitors or sludge inhibitors, gum inhibitors, etc.

It is also the practice to add other ingredients to mineral oil fractions for the purpose of improving "oiliness" characteristics and the wear-reducing action of such mineral oils when they are used as lubricants, particularly when the oils are used for the purpose of lubricating metal surfaces which are engaged under extremely high pressures and at high rubbing speeds.

Other ingredients have been developed for the purpose of depressing the pour point of mineral oil fractions which have been refined for use as lubricants, such refinement leaving a certain amount of wax in the oil, which, without the added ingredient, would tend to crystallize at temperatures which would render the oil impracticable for use under low temperature conditions. Additive agents have also been developed for improving the viscosity index of lubricating oil fractions. In the case of internal combustion engines, particularly those operating with high cylinder pressures, there is a decided tendency for the ordinary lubricating oil fractions to form, under such conditions of use, carbonaceous deposits which cause the piston rings to become stuck in their slots and which fill the slots in the oil ring or rings, thus materially reducing the efficiency of the engine. Ingredients have therefore been developed which, when added to the oil, will reduce the natural tendency of the

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oil to form deposits which interfere with the function of the piston rings.

Aside from the corrosive action which attends the formation of acidic products of oxidation in mineral oil fractions of the lubricant range, it has been discovered that certain types of recently developed hard metal alloy bearing metals, such as cadmium-silver alloy bearings, are attacked by ingredients in certain types of oils, particularly oils of high viscosity index obtained by various methods of solvent-refining. This corrosive action on alloys of the above type has led to the development of corrosion inhibitors which may be used in solvent-refined oils to protect such bearing metals against this corrosive action.

In the lighter mineral oil fractions, such as those used for fuel purposes, particularly in internal combustion engines, it has been found that the combustion characteristics of the fuel may be controlled and improved by adding minor proportions of various improving agents thereto.

The various ingredients which have been developed for use in mineral oil fractions to improve such fractions in the various respects enumerated above are largely specific to their particular applications, and it has therefore been the practice to add a separate ingredient for each of the improvements which are to be effected.

It is a primary object of the present invention to provide a mineral oil composition which has been improved in one or more of the various properties enumerated above by the incorporation therein of a small quantity of a multifunctional compound or composition obtained by reacting an alkylated hydroxyaromatic compound with a phosphorus sulfide and subsequently reacting the resultant reaction product with a sulfur chloride.

We have discovered that the compounds or compositions of the class defined above, and the neutralized products or metal salts thereof, may be added in small quantities to mineral oil fractions to form mineral oil compositions or blends superior to the unblended fractions in one or more important respects, and the present invention, therefore, is broadly directed to a mineral oil composition containing a compound coming within the general class referred to.

The alkylated hydroxyaromatic compound employed in the reaction can be an alkylated hydroxy benzene as cresol, or an alkylated hydroxy polycyclic aromatic compound, such as, for example, an alkylated naphthol, viz., methyl α -naphthol. The hydroxyaromatic compound employed

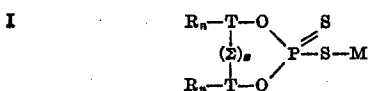
may be phenol, a cresol, a xlenol, a naphthol, etc.

Preferred alkylated hydroxyaromatic compounds, however, are phenols, naphthols, etc. which have at least one oil-solubilizing alkyl group containing at least ten carbon atoms, and preferably at least twenty carbon atoms, attached to a nuclear carbon atom thereof. As will be described hereinafter such alkylated hydroxyaromatic compounds can be readily prepared by a Friedel-Crafts synthesis, using a halogenated aliphatic hydrocarbon and a hydroxyaromatic compound, or by reaction of an unsaturated aliphatic compound (preferably of high molecular weight) or a higher alcohol and a hydroxyaromatic compound in the presence of sulfuric acid.

The alkylated hydroxyaromatic compound, such as an alkylated phenol or an alkylated naphthol, is reacted with a phosphorus sulfide, preferably P_2S_5 , and the resultant product is then reacted with a sulfur chloride.

As indicated hereinabove, the product resulting from the reaction of the sulfur chloride with the alkylated hydroxyaromatic compound-phosphorus sulfide reaction product can be employed as such, or the metal salts of the final reaction products can be employed. The acidic product obtained from the sulfur chloride reaction may be converted to its corresponding metal salt by reaction with a suitable metal compound such as a hydroxide or an alcoholate.

Of the foregoing compositions or compounds, particularly preferred herein are the oil-soluble or oil-miscible metal salts of diaryl sulfides (selenides and tellurides) of alkyl-substituted diaryl dithiophosphoric acids, which may be represented by the general formula:



in which T represents an aromatic nucleus; R represents at least one oil-solubilizing alkyl group attached to an aromatic nucleus T and contains at least ten carbon atoms, and preferably contains at least twenty carbon atoms; n represents the number of R groups substituted on an aromatic nucleus T, and is a whole number from 1 to 4; Z represents sulfur, selenium and tellurium, x represents the number of atoms in said Z and is a whole number from 1 to 4; and M represents the hydrogen equivalent of a metal.

The aromatic nucleus T in the compounds represented by general Formula I may be mono- or polycyclic typical of which are benzene, naphthalene and anthracene.

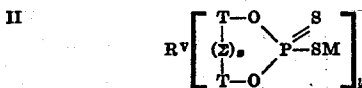
The metal substituent, M, in general Formula I may be broadly classified as follows: The alkali metals, lithium, sodium, potassium, rubidium and caesium; the alkaline earth group, beryllium, magnesium, calcium, strontium and barium; the metals zinc, cadmium and mercury; scandium, yttrium, lanthanum; aluminum, gallium, indium, thallium, titanium, zirconium, cerium, thorium, germanium, tin and lead; vanadium, columbium and tantalum; arsenic, antimony and bismuth; chromium, molybdenum, tungsten and uranium; rhenium, manganese, iron, cobalt and nickel; ruthenium, rhodium and palladium; osmium, indium and platinum.

Some of the rare earth metals are recited above; other rare earth metals suitable for the formation of the metal salts contemplated here-

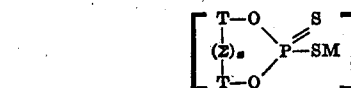
in are those now commercially available as the cerium and yttrium groups, namely, a mixture of praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thallium and lutecium.

While all of the foregoing metals are contemplated as metal constituents (M) in the metal salts of this invention, particular preference is given to barium and tin.

As indicated above, the oil-solubilizing alkyl groups (R) are preferably those which contain at least twenty carbon atoms. While each oil-solubilizing group of this type may be attached to only one aromatic nucleus T as shown in general formula I, it is also contemplated that this group may be a polyvalent aliphatic hydrocarbon group attached to separate aromatic nuclear groups (T). Compounds in which the oil-solubilizing alkyl groups may be polyvalent are included under the following general formula representation:



in which T, Z, M and x have the same significance indicated above; R^v represents at least two aliphatic or alkyl radicals or groups, each of which is attached to at least one aromatic nucleus T, v representing the valence of the aliphatic radicals R^v , which may be one to two; and y represents a whole number from one to two, and indicates the total number of groups



present in the molecule represented by general Formula II, and which are attached to the aliphatic groups represented by R^v through the valence v .

As to the possible number of R^v groups going to make up a single molecule, this will vary with the extent to which it is desired to effect substitutions of the aromatic nuclei with oil-solubilizing aliphatic groups for obtaining the desired properties in the product and is, of course, limited by the number of valences on the aromatic nuclei which are available for substitution. It will be apparent to those skilled in the art that the maximum possible number of R groups which can be attached to a single aromatic nucleus will vary as the nucleus is mono- or polycyclic and also as the nucleus is otherwise substituted. It will also be apparent that available valences on the nuclei may all be attached to oil-solubilizing polyvalent aliphatic groups.

It will be understood that the preferred oil-improving agents contemplated by this invention may be pure compounds satisfying the general formula representation II above, or may be mixtures of such compounds. In synthesizing the preferred oil-improving agents of the present invention, however, the final oil-improving product is normally or usually a mixture of different compounds corresponding to different values of v and y and to different numbers of aliphatic groups R^v . This will be more apparent from the following discussion, and illustrations, of the synthesis of the metal salts contemplated herein:

It will also be understood that the preferred oil-improving metal salts of this invention, represented by general Formulae I and II above, may be characterized by the presence of substituent

groups other than those already shown. For example, the aryl nuclei may carry other groups such as halogen, hydroxyl, alkoxy, aroxy, aralkyl, aryl, nitro, nitroso, keto, ether alcohol and ester. The methods for introducing such groups are known to those familiar with the art.

While the preferred metal salts of the diaryl sulfides, selenides and tellurides of alkyl-substituted diaryl dithiophosphoric acids are contemplated broadly by the present invention, the aryl sulfides of this class are particularly preferred. For this reason, the preparation of said diaryl sulfides will be described at length hereinbelow. It will be understood, however, that the corresponding selenides and tellurides can be similarly prepared from the existing selenides and tellurides corresponding to the sulfides, such as the sulfur halides, used in the preparation of the diaryl sulfides described above.

The preferred metal salts of diaryl sulfides of alkyl-substituted diaryl dithiophosphoric acids are prepared from alkylated hydroxyaromatic compounds or alkyl halides and hydroxyaromatic compounds, phosphorus pentasulfides (P_2S_5), sulfurizing agents and suitable metal compounds. For example, a hydroxyaromatic compound may be alkylated with one or more alkyl groups (R) and then reacted with P_2S_5 to form an alkyl-substituted diaryl dithiophosphoric acid. The acid so obtained may be directly reacted with a suitable sulfurizing agent, such as elemental sulfur or a sulfur halide, to form the corresponding sulfide of said alkyl-substituted diaryl dithiophosphoric acid; or, the acid may be first converted to its corresponding alkali metal salt by reaction with an alkali metal, and then reacted with said sulfurizing agent. The indirect procedure through the alkali metal salt is preferred. Finally, the sulfide of said dithiophosphoric acid is converted to its corresponding metal salt by reaction with a suitable metal compound, such as a hydroxide or an alcoholate.

Another procedure by which the preferred metal salts of this invention can be obtained involves a modification in the preparation of the intermediate product, the alkyl-substituted diaryl dithiophosphoric acid. We have recently discovered that the alkyl-substituted diaryl dithiophosphoric acids prepared by reacting a hydroxyaromatic compound and an alkyl halide in the presence of a Friedel-Crafts catalyst and then reacting the Friedel-Crafts reaction mixture with P_2S_5 followed by removal of the Friedel-Crafts complex, provides a particularly stable dithiophosphoric acid. This is discussed in detail in our copending application Serial No. 489,086, filed May 29, 1943 (now Patent No. 2,386,207 dated October 9, 1945). The dithiophosphoric acid formed by this procedure is then converted to the desired metal salt by the manner outlined above, and the desired metal salts obtained are also particularly stable.

Examples of the hydroxyaromatic compounds which may be used as starting material for the alkylation reaction are: phenol, resorcinol, hydroquinone, catechol, cresol, xylenol, hydroxydiphenyl, benzylphenol, phenyl-ethyl-phenol, phenol resins, methyl hydroxydiphenyl, guaiacol, alpha- and beta-naphthol, methyl alpha- and methyl beta-naphthol, tolyl naphthol, xylol naphthol, benzyl naphthol, anthranol, phenyl methyl naphthol, phenanthrol, monomethyl ether of catechol, anisole, beta-naphthyl methyl ether, chlorphenol and the like. Preference in general is to the monohydroxyphenols otherwise unsub-

stituted, particular preference being given to phenol and to alpha- and beta-naphthol.

The alkylation of the hydroxyaromatic compounds may be accomplished in various ways, such as by a Friedel-Crafts synthesis, using a halogenated aliphatic hydrocarbon, or by reaction with unsaturated high molecular weight aliphatic compounds or higher alcohols in the presence of H_2SO_4 as a catalyst. The Friedel-Crafts type of alkylation reaction is particularly well adapted to the step of preparing the alkylated hydroxyaromatic compounds from which the improving agents contemplated herein are synthesized, inasmuch as it affords a convenient means of controlling the desired degree of alkylation, and, accordingly, the desired degree of oil-solubility.

In this reaction an appropriate mono- or polychlorine-substituted aliphatic compound or material is reacted with the desired hydroxyaromatic compound in the presence of a catalytic amount of aluminum chloride. Pure or substantially pure mono- or polychlorine substituted compounds may be used. However, as will be readily understood, since it is usually extremely difficult to prepare or obtain high molecular weight aliphatic hydrocarbons in a pure or substantially pure state and since it is equally difficult to prepare the chlorine (or other halogen) substitution products of such hydrocarbons in a pure or substantially pure state, we prefer to employ a mixture of such hydrocarbons, such as a suitable petroleum fraction, as the starting material. This material is converted into a mixture of different chlorine (or other halogen) substitution products by any suitable method for use in the alkylation step. In general it may be said that the high molecular weight aliphatic hydrocarbons contemplated herein as preferred sources for the alkyl or aliphatic substituent R' in general Formula II above, may be pure or mixed compounds typified by those which characterize the heavier products of petroleum, such as heavy petroleum oils of the lubricant type, petrolatum and crystalline petroleum wax or other compounds or materials which will result in relatively long-chain aliphatic substituents. Particular preference is given to petroleum wax characterized by a melting point not substantially less than about $120^\circ F.$ ($49^\circ C.$), molecular weight of about 350 and at least about twenty carbon atoms in their molecules.

For example, a wax-substituted phenol prepared by a Friedel-Crafts procedure (such as that described in Patent 2,280,039 in which one of the present inventors, O. M. Reiff, is a co-inventor), in which a quantity of chlorwax containing three atomic proportions of chlorine, sixteen per cent chlorine in the chlorwax, is reacted with one mol of phenol, may, for brevity herein be designated as "wax phenol (3-16)." Parenthetical expressions of this type (A-B) will be used hereinafter in connection with the alkylated hydroxyaromatic compounds to designate (A) the number of atomic proportions of chlorine in chlor-aliphatic material reacted with one mol of hydroxyaromatic compound in the Friedel-Crafts reaction, and (B) the chlorine content of the chlor-aliphatic material. In the above example $A=3$ and $B=16$. This same designation will also apply to the oil improving agents, of this invention, derived from these alkylated hydroxyaromatic compounds.

It will be apparent that the "wax" substituent of a "wax-phenol," such as the illustration used above, is a wax hydrocarbon group and is dis-

tinguished from the hydrocarbon material known as wax by the loss of one or more hydrogen atoms.

The alkylated hydroxyaromatic compounds obtained by the Friedel-Crafts reaction may then be reacted with P_2S_5 as outlined in application Serial No. 390,586, filed April 26, 1941, in which one of the present inventors, O. M. Reiff, is a co-inventor. Also the reaction with P_2S_5 to form the corresponding alkyl-substituted dithiophosphoric acid may be carried out by the novel procedure described in our copending application Serial No. 489,086, filed May 29, 1943 (now Patent No. 2,386,207 dated October 9, 1945); in this procedure an alkyl halide, as a chlorwax, and a hydroxyaromatic compound are reacted in the presence of a Friedel-Crafts catalyst, and the Friedel-Crafts reaction mixture (containing said catalyst) is then reacted with P_2S_5 followed by removal of the Friedel-Crafts catalyst, or corresponding complex.

The alkyl-substituted dithiophosphoric acid obtained by the foregoing procedures may then be converted to their corresponding alkali metal salts by reaction with an alkali metal or alkali metal compound, before conversion to their sulfides. Similarly, the acid per se may be converted to the corresponding sulfide by reaction with a sulfurizing agent. The sulfur halides are preferred for forming the desired mono- and poly-disulfides; sulfur monochloride, for example, forming the disulfide, and sulfur dichloride forming the monosulfide. The higher sulfides, such as the tri- and tetra-sulfides can be prepared by using an appropriate amount of elementary sulfur in combination with sulfur monochloride in this reaction. A somewhat more expensive means may also be employed for forming the tetrasulfides, such means involving reacting an alkyl tetrasulfide, such as tertiary butyl tetrasulfide, with the disulfide formed from sulfur mono-chloride.

To prepare the final products, the preferred improving agents contemplated herein, the diaryl sulfides of alkyl-substituted diaryl dithiophosphoric acids obtained above are substituted with metal. This substitution with metal may be accomplished through the use of a metal hydroxide, particularly for the formation of the alkali metal salts, and through the use of a metal alcoholate.

The synthesis of the preferred improving agents of this invention will be better understood from the following illustrative examples wherein the preparation of typical metal salts is described.

EXAMPLE 1

BARIUM SALT OF THE DISULFIDE OF WAX-SUBSTITUTED DIPHENYL DITHIOPHOSPHORIC ACID (3-14)

(a) Preparation of chlorwax

Petroleum wax of A. S. T. M. melting point of 126° F. (52° C.) was chlorinated by introducing chlorine at about 150° F. (c. 65° C.) until 14% by weight of chlorine was absorbed.

(b) Preparation of dithiophosphoric acid of wax-phenol (3-14)

One hundred grams of the chlorwax obtained in (a) were mixed with 12.3 grams of phenol, and 3 grams of $AlCl_3$ were added at about 65° C. at a rate slow enough to avoid excessive foaming caused by the evolution of hydrogen chloride. The reaction temperature was then raised to

about 175° C. and the mixture was stirred for about one hour at this temperature to complete the reaction. The product at this stage was the aluminum phenate of wax phenate of wax-phenol (3-14).

A solvent refined mineral oil (207 grams) of Saybolt Universal viscosity (S. U. V.) of 45 seconds at 210° F. was then added, followed by 7.4 grams of P_2S_5 . The resulting mixture was then heated for about four hours longer at about 175° C. The reaction with P_2S_5 was largely completed after one hour at this temperature as indicated by the decrease in the amount of H_2S evolved; however, the reaction mixture was heated longer to insure completion of the reaction. The reaction mixture was then cooled to about 100° C., and water was carefully added to decompose the aluminum chloride complex. The color of the reaction mixture was lightened at this point by the addition of 5 grams of zinc dust. Small amounts of butanol were added to break emulsions formed on the addition of water. Several washings with water were required to obtain a water extract free of aluminum chloride. The product was filtered through Hi-Flo, and the butanol distilled from the filtrate by using reduced pressure. The product obtained was a 1:3 blend in mineral oil, which contained 0.6% phosphorus and 1.0% sulfur, and had a neutralization number (N.N.) of 6.3. These values approximate the theoretical values for the dithiophosphoric acid of wax-phenol (3-14), also known as wax-substituted diphenyl dithiophosphoric acid (3-14).

(c) Preparation of the disulfide of dithiophosphoric acid of wax-phenol (3-14)

One hundred grams of the mineral oil blend obtained in (b) were reacted with 34 grams of a butanol solution of sodium butylate, which was formed by dissolving 1.13 grams of metallic sodium in 33 grams of butanol. The reaction mixture was heated for one hour at 100° C., then cooled to room temperature (about 20-25° C.), and 3.33 grams of sulfur monochloride were added at a rate slow enough to avoid appreciable rise in temperature, thereby avoiding discoloration of the product. This reaction mixture was stirred for about one hour at about 20-25° C., and the reaction product formed therein was the disulfide of dithiophosphoric acid of wax-phenol (3-14), also described as the disulfide of wax-substituted diphenyl dithiophosphoric acid (3-14).

(d) Preparation of barium salt of (c)

Eight grams of barium hydroxide octahydrate ($Ba(OH)_2 \cdot 8H_2O$) were added to the reaction mixture obtained in (c) and the resulting mixture was heated to about 150° C. After stirring the mixture at this temperature for about one hour in order to remove all of the water of reaction, the temperature was then lowered to about 80° C., followed by adding 3.73 grams of barium oxide (BaO) dissolved in methanol in order to introduce more barium. Part of the methanol was distilled off during the introduction of the solution; the temperature was then raised to 125° C. to completely remove the methanol. The reaction mixture was then filtered with the aid of Hi-Flo to obtain the finished product which was approximately a 1:3 blend in mineral oil. The product so obtained is the barium salt of the disulfide of wax-substituted diphenyl dithiophosphoric acid (3-14).

EXAMPLE 2

BARIUM SALT OF THE TETRASULFIDE OF WAX-SUBSTITUTED DIPHENYL DITHIOPHOSPHORIC ACID (3-14)

(a) Preparation of the tetrasulfide of wax-substituted diphenyl dithiophosphoric acid (3-14)

One hundred grams of the mineral oil blend of wax-substituted diphenyl dithiophosphoric acid (3-14) obtained as described in Example 1 (b) were reacted with 34 grams of a butanol solution of sodium butylate (NaOC_4H_9), which was formed by dissolving 1.13 grams of metallic sodium in 33 grams of butanol. This reaction mixture was heated for one hour at about 100° C., and the butanol was then distilled off. Chlorobenzene, 35 cc., was added as a diluent and the reaction mixture was cooled to room temperature. Then, 1.7 grams of elementary sulfur and 3.33 grams of sulfur monochloride were added at a rate slow enough to avoid appreciable rise in temperature. The reaction mixture was stirred for about one hour to complete the formation of the tetrasulfide.

(b) Preparation of barium salt of (a)

Eight grams of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ were added to the reaction mixture obtained in (a) and the resulting mixture was heated to about 150° C. for one hour to remove all of the water of reaction. The temperature was then lowered to about 80° C., and 3.73 grams of BaO dissolved in methanol were added. The mixture was heated to about 125° C. to complete the reaction and to distill off methanol. The mixture was then filtered with the aid of Hi-Flo to obtain the finished product in approximately a 1:3 blend in mineral oil.

EXAMPLE 3

STANNOUS SALT OF THE DISULFIDE OF WAX-SUBSTITUTED DIPHENYL DITHIOPHOSPHORIC ACID (3-14)

One hundred grams of the mineral oil blend of wax-substituted diphenyl dithiophosphoric acid (3-14) obtained as described in Example 1 (b) were converted to the disulfide derivative of reaction with sulfur monochloride as described in 1 (c). The free acid was then converted to the sodium salt by adding 1.13 grams of metallic sodium in solution in butanol, and heating the mixture to about 100° C. A butanol solution containing 4.7 grams of stannous chloride was then added and the mixture was heated to reflux temperature for about one hour to complete the formation of the stannous salt. Butanol was then distilled off and the remaining reaction mixture was filtered with the aid of Hi-Flo to obtain the finished product, approximately a 1:3 blend in mineral oil.

It will be apparent to those skilled in the art that the metal salts of this invention can be obtained in the free state just as readily as they are obtained in mineral oil blends in the foregoing examples. To obtain a metal salt per se, a light hydrocarbon diluent, such as kerosene, Stoddard solvent, etc., is used in place of a mineral oil and is distilled off before or after the formation of the metal salt.

To demonstrate the effectiveness of the metal salts of the type described above in the mineral oil compositions contemplated by this invention, we have conducted several comparative tests, the results of which are listed below, with representative mineral oils alone and with the same oils blended with various representative metal salts

of diaryl sulfides of alkyl-substituted diaryl dithiophosphoric acids.

POUR TEST

These tests were conducted with a mineral lubricating oil fraction having a Saybolt Universal viscosity (S. U. V.) of 67 seconds at 210° F., and an A. S. T. M. pour point of 20° F. The results for the blank oil and the oil blends are listed below in Table I.

Table I

Improving Agent	A. S. T. M. Pour Test	
	Me%	1/4%
Barium salt of wax-substituted diphenyl dithiophosphoric acid disulfide (3-14)	-25°	-20°
Barium salt of wax-substituted diphenyl dithiophosphoric acid tetrasulfide (3-14)	-15°	-25°
Stannous salt of wax-substituted diphenyl dithiophosphoric acid disulfide (3-14)	0°	-15°
Barium salt of wax-substituted α -dinaphthyl dithiophosphoric acid disulfide (3-12)	-10°	+5°

The improvement produced by the improving agents of the present invention in the viscosity index of mineral oils to which they are added is clearly shown by the illustrative data shown in Table II.

Table II

Compound Added	Per cent Conc.	Kinematic Vls. at—		V. I.
		100° F.	210° F.	
None	0	30.17	4.80	79.8
Barium salt of wax-substituted diphenyl dithiophosphoric acid disulfide (3-14)	2	33.78	5.20	88.6
Barium salt of wax-substituted diphenyl dithiophosphoric acid tetrasulfide (3-14)	2	34.45	5.29	91.1
Stannous salt of wax-substituted diphenyl dithiophosphoric acid disulfide (3-14)	2	33.7	5.23	91.6
Barium salt of wax-substituted α -dinaphthyl dithiophosphoric acid disulfide (3-12)	2	32.68	5.09	87.3

The effectiveness of the preferred metal salts contemplated herein in stabilizing motor oils against the deleterious effects of oxidation is indicated by an accelerated test in a single-cylinder Lauson engine operated at an oil temperature of 290° F. and a jacket temperature of 212° F. A motor oil having a S. U. V. of 45 seconds at 210° F. was used with and without the addition agents, and the neutralization number (N. N.) and the Saybolt Universal viscosity at 210° F. were determined after 36 hours. The results of these tests are tabulated in Table III below.

Table III

Compound Added	Per cent Conc.	N. N.	S. U. V. at 210° F.
None	0	9.75	58.3
Barium salt of wax-substituted diphenyl dithiophosphoric acid disulfide (3-14)	1	1.5	47.5
Stannous salt of wax-substituted diphenyl dithiophosphoric acid disulfide (3-14)	1	5.1	56.0
Barium salt of wax-substituted α -dinaphthyl dithiophosphoric acid disulfide (3-12)	1	4.8	57.8

It will be apparent from the foregoing description that we have developed a new class of mineral oil compositions characterized by the pres-

ence in a minor proportion of a metal salt of a diaryl sulfide of an alkyl-substituted diaryl dithiophosphoric acid as an improving agent. The improved properties obtained and the degree of improvement effected in a particular property may be varied with the metal substituents and the number of sulfur atoms in the sulfide group; also by the degree of alkylation of the aryl nuclei. As to the degree of alkylation, it is important that the aryl nuclei be sufficiently alkylated to provide a final product which is "soluble" or "miscible" in the particular mineral oil fraction with which it is to be blended; that is, one which will remain uniformly dispersed in the oil in sufficient amount to effect the desired improvement. The amount of improving agent used may be varied depending upon the mineral oil or mineral oil fraction with which it is blended and the properties desired in the final oil composition. The metal salts described herein may be used in amounts ranging from about $\frac{1}{4}$ per cent to about 5 per cent, and in general compositions of the desired improved properties may be obtained with these improving agents in amounts of from $\frac{1}{4}$ per cent to 1 per cent.

It is to be understood that while we have described certain preferred procedures which may be followed in the preparation of the metal salts of diaryl sulfides (selenides and tellurides) of alkyl-substituted diaryl dithiophosphoric acids used as improving agents in the mineral oil compositions contemplated herein and have referred to various representative constituents in these salts, such procedure and examples have been used for illustrative purposes only. The invention, therefore, is not to be considered as limited by the specific examples given but includes within its scope such changes and modifications as fairly come within the spirit of the appended claims.

This application is a continuation-in-part application of our copending application Serial No. 495,766, filed July 22, 1943.

We claim:

1. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of a metal salt of a diaryl sulfide of an alkyl-substituted diaryl dithiophosphoric acid, the alkyl substituent of which is an oil-solubilizing alkyl group containing at least about ten carbon atoms.

2. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt of a diaryl sulfide of an alkyl-substituted diaryl dithiophosphoric acid, the alkyl substituent thereof having at least twenty carbon atoms.

3. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt of a diaryl sulfide of a wax-substituted diaryl dithiophosphoric acid.

4. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt of a diaryl disulfide of a wax-substituted diaryl dithiophosphoric acid.

5. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible

metal salt of a diaryl tetrasulfide of a wax-substituted diaryl dithiophosphoric acid.

6. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt of a disulfide of a wax-substituted diphenyl dithiophosphoric acid.

7. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt of a tetrasulfide of a wax-substituted diphenyl dithiophosphoric acid.

8. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible barium salt of the disulfide of a wax-substituted diphenyl dithiophosphoric acid.

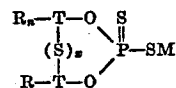
9. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible stannous salt of the disulfide of a wax-substituted diphenyl dithiophosphoric acid.

10. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible barium salt of the tetrasulfide of a wax-substituted diphenyl dithiophosphoric acid.

11. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an intimate mixture of oil-soluble metal salts of diaryl sulfides of alkyl-substituted diaryl dithiophosphoric acids, said metal salts in said mixture differing from each other with respect to the nature of the alkyl substituents, the said alkyl substituents being attached to the aryl nuclei and having at least twenty carbon atoms.

12. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an intimate mixture of oil-soluble metal salts of diaryl sulfides of alkyl-substituted diaryl dithiophosphoric acids, said metal salts in said mixture differing from each other with respect to the nature of the alkyl substituents, the said alkyl substituents being attached to the aryl nuclei and comprising essentially aliphatic hydrocarbon groups having a composition corresponding substantially to the different aliphatic hydrocarbons contained in paraffin wax.

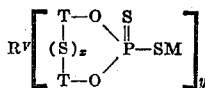
13. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt having the general formula:



in which: T represents an aromatic nucleus; R represents at least one oil-solubilizing alkyl group containing at least about ten carbon atoms; n represents the number of R groups attached to an aromatic nucleus T, and is a whole number from 1 to 4; x is the number of sulfur atoms and is a whole number from 1 to 4; and M represents the hydrogen equivalent of a metal.

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14. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt having the general formula:



in which: T represents an aromatic nucleus; R^v represents at least two polyvalent hydrocarbon groups, each of said groups having at least twenty carbon atoms and a valence *v* from 1 to 2; *x* is a whole number from 1 to 4; M represents the hydrogen equivalent of a metal and *y* is a whole number from 1 to 2.

15. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, from about 1/8 per cent to about 1 per cent, of a metal salt of a diaryl sulfide of an alkyl-substituted diaryl dithiophosphoric acid, the alkyl substituent of which is an oil-solubilizing alkyl group containing at least about ten carbon atoms.

16. A composition of matter comprising a mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt of a diaryl sulfide of an alkyl-substituted diaryl dithiophosphoric acid, the alkyl substituent of which is an oil-solubilizing alkyl group containing at least about ten carbon atoms.

17. An improved mineral oil composition comprising a mineral oil having admixed therewith

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a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt of a diphenyl sulfide of an alkyl-substituted diphenyl dithiophosphoric acid, the alkyl substituent thereof having at least 20 carbon atoms.

18. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion, sufficient to stabilize said mineral oil against oxidation, of an oil-miscible metal salt of a diphenyl sulfide of a wax-substituted diphenyl dithiophosphoric acid.

19. An improvement agent for hydrocarbon lubricating oils comprising a neutralized diaryl sulfide of an alkyl substituted diaryl dithiophosphoric acid, said alkyl substituent containing at least ten carbon atoms.

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