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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 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 is 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 multi-functional compound selected from that group or class of metalorganic compounds which is herein referred to as the oil-soluble or oil-miscible alkyl-substituted aryl metal oxides. I have discovered that aryl metal oxides of the general class above referred to 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 falling into the general class referred to.

The oil-improving agents contemplated by this invention are all characterized by the presence of an aromatic nucleus in which at least one nuclear hydrogen has been substituted with an hydroxyl group, the hydroxyl hydrogen of which is replaced with its equivalent weight of metal. This characterizing group may be represented by the formula:

$$T'(OM)$$

in which T' represents an aromatic nucleus; and (OM) represents at least one hydroxyl group in which the hydrogen is replaced with its equivalent weight of a metal, M, the (OM) group being attached to the nucleus T'.

The aryl metal oxides corresponding to the group represented by the above formula which are otherwise unsubstituted are not miscible with mineral oil, and it is therefore important that the improving agents containing the above char-

acterizing group have additional nuclear hydrogen replaced with substituents of a solubilizing nature. In other words, it is important that the aryl nucleus carry a substituent or substituents which will render the composition as a whole miscible with mineral oil fractions. By the terms "oil-miscible" or "oil-soluble" as they are used herein I have reference to that property of remaining uniformly dispersed in the mineral oil fraction either as a true solution or as a colloidal suspension during normal conditions of handling and use.

The improving agents contemplated by this invention are characterized by the presence of alkyl substituents in the aryl nucleus, and the improving agents preferred for use in viscous mineral oils are further characterized by the presence of alkyl or aliphatic substituents in the aryl nucleus which will give other properties to the composition as a whole in addition to oil-miscibility. I have found, for example, that where the aryl nucleus is substituted with one or more aliphatic groups corresponding to certain aliphatic hydrocarbon compounds of relatively high molecular weight (herein referred to as heavy alkyl groups), a compound or composition can be obtained which will effect marked improvement in the viscosity index and the pour point as well as other important properties of viscous mineral oils.

As a general proposition, therefore, it may be said that the improving agents contemplated by this invention are aryl metal oxides having the characterizing group T'(OM) described above, in which additional nuclear hydrogen is replaced with an oil-solubilizing substituent such as a predominantly aliphatic material, such substituent comprising a sufficient proportion of the composition as a whole to render the same miscible with mineral oil fractions under normal conditions of handling and use. As a further generalization it may be said that at least one point on the aromatic nucleus T', and preferably two or more points on such nucleus, are substituted with aliphatic hydrocarbon radicals or groups, such aliphatic radicals or groups preferably being high molecular weight derivatives or heavy alkyl groups.

The simplest type of compound satisfying the above requisites may be represented by the formula:

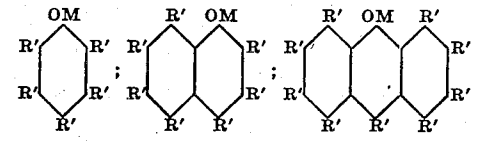
I. $R(T(OM))$

in which R represents at least one aliphatic hydrocarbon radical or group, such group or groups preferably corresponding to relatively high molecular weight aliphatic hydrocarbons and being attached to a mono or poly cyclic aromatic nucleus T and in which (OM) is as indicated above.

In addition to the aliphatic or alkyl substituent R, the compounds or compositions contemplated herein as mineral oil improving agents may have additional nuclear hydrogen replaced with other substituents which may or may not have a solubilizing effect upon the composition as a whole. Such a compound in its simplest form may be represented by the formula:

II. $R(T(OM)Y)$

in which R, T, and (OM) have the same significance indicated above and in which Y represents residual hydrogen which may be replaced by a radical from the group consisting of: chlorine, alkoxy, aroxy, aralkyl, alkaryl, aryl, nitro, and amino radicals or groups. Compounds of the above general formula-type having mono, di, and tri cyclic nuclei are illustrated by the following specific formulae:



in which at least one R' represents an aliphatic radical or group, preferably a heavy alkyl group, and in which the remaining R''s represent residual hydrogen which may be replaced with hydroxy, chlorine, alkoxy, aroxy, aralkyl, alkaryl, aryl, nitro, and amino radicals or groups.

In the foregoing examples it will be observed that the aliphatic or alkyl substituent is a monovalent aliphatic hydrocarbon group, but, as will appear from the hereinafter described synthesis of my oil-improving agent, part or all of the aliphatic hydrocarbon material may be comprised of polyvalent aliphatic hydrocarbon radicals or groups in which the several valences are attached to separate aromatic nuclear groups. Compounds of this type are included under the following general formula representation:

III. $R^v(T(OM)Y_b)_n$

in which T and (OM) have the same significance indicated above; R^v represents at least one aliphatic or alkyl radical or group, such alkyl group or groups being attached by one valence only to at least one aromatic nucleus T, v representing the valence of the aliphatic radical R^v, which may be one to four; Y_b represents a monovalent element or group selected from the class identified above in connection with Y; b represents the number of Y's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied with R^v or (OM); and n represents a whole number from one to four and indicates the total number of groups $(T(OM)Y_b)$ present in the molecule represented by the formula which are attached to the aliphatic group or groups represented by R^v through the valences v.

In the foregoing general formula representation III it will be seen that the compounds represented thereby include those materials in which all of the aliphatic substituent is monovalent ($v=1$ and $n=1$) or in which all of the aliphatic substituent is polyvalent (v and n being equal to two, three, or four); or since R^v is defined as being at least one aliphatic radical or group and may therefore include several such groups, it will be seen that this general Formula III is inclusive of compounds having aliphatic groups or radicals of different valences (from one to four) in the same molecule. Also it will be observed that since n may be any whole number from one to four, the number of aromatic nuclei T in the molecule may likewise vary from one to four. It will be seen, therefore, that the relationship between n and v in Formula III, in its broadest aspect, is such that when n is equal to one, v is equal to one; and when n is greater than one, the valence v of at least one of the R''s is equal to n (in order to tie the several nuclei or T's together) the valence of any remaining R''s being any whole number equal to or less than n.

As stated above, and as will appear more fully later from the description of their synthesis,

these materials represented by general Formula III may contain both monovalent and polyvalent aliphatic substituents. Both the polyvalent aliphatic substituent and the monovalent substituent, if both are present, may be introduced in the nucleus as part of an alkylation reaction, or all or part of the monovalent aliphatic substituent may be present in the nucleus of a hydroxy-aromatic starting material as low molecular weight aliphatic groups, such as methyl, ethyl, propyl groups, etc.

Compounds of the general type last described above, which include polyvalent substituted aliphatic substituents and may also include both the monovalent and the polyvalent aliphatic substituents, are included under the subgeneric formula representation:

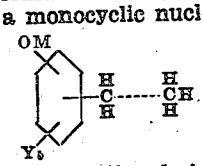
IV. $R^{v'}(T(OM)Y_{b'}R_c)_{n'}$

in which T and (OM) have the same significance as indicated above; $R^{v'}$ represents at least one polyvalent aliphatic radical or group having a valence v' of two, three, or four; $Y_{b'}$ indicates the same group of substituents as described above for Y; R_c represents monovalent aliphatic radicals or groups; b' represents the number of Y_b's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied with $R^{v'}$, (OM) and R_c; c indicates the number of R_c's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied with $R^{v'}$, (OM), and $Y_{b'}$; and n' represents a whole number from two to four and indicates the total number of the groups $(T(OM)Y_{b'}R_c)$ present in the molecule represented by the formula which are attached to the aliphatic group or groups represented by $R^{v'}$ through the valences v'.

In the above general Formulae III and IV it will be understood that since R^v and $R^{v'}$ are aliphatic hydrocarbon radicals of the chain type and are each attached by one valence only to each corresponding aromatic nucleus, the valence v or v' of such radical or radicals is of necessity never greater than the number n, which indicates the number of aromatic nuclei in the molecule and in Formula III is always equal to one when n equals one. Otherwise an R^v or an $R^{v'}$ having a valence greater than the number (n or n') of aromatic nuclei would either have some of its valences unsatisfied or else would form a condensed ring or rings by attachment at two or more points to one and the same aromatic nucleus. Such latter compounds, as already indicated from the definition of R^v or $R^{v'}$, are not considered as characterizing the product of the present invention although probably formed in some instances in minor amounts as unobjectionable by-products by certain of the methods of preparation herein disclosed.

A simple type of compound coming under general Formula III in which v and n is each equal to one and in which there is only one oil-solubilizing aliphatic group R^v may be illustrated by the following formula showing T for purposes of illustration as a monocyclic nucleus:

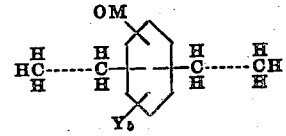
(A)



In the above formula the chain represents the oil-solubilizing alkyl substituent (R^v), and Y_b and (OM) have the same significance as has been heretofore given to these groups.

Since group R^v has been defined as "at least one", it will be apparent that there may be more than one heavy alkyl substituent attached to the nucleus T. Such a compound, where v and n are each one and in which there are two such monovalent R^v groups, may be represented by the following formula:

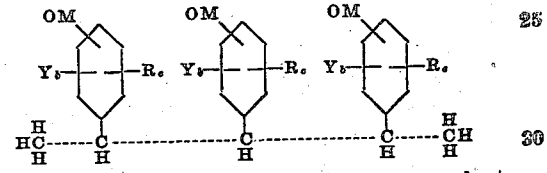
(B)



in which the chains and the substituent characters have the same significance defined above.

Compounds of the type satisfying the general Formula III and the subgeneric Formula IV in which R^v (or $R^{v'}$) is polyvalent and v (or v') and n (or n') are more than one and in which there is only one such polyvalent R^v group may be illustrated by the following formula, in which the aryl nucleus T is again indicated for illustration as being monocyclic:

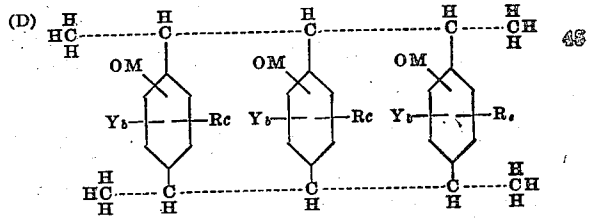
(C)



In the above Formula C, R_c is a monovalent alkyl group as defined above under Formula IV and is the same as monovalent R^v in Formula III.

Under this same type of compound indicated by Formula C there may also be more than one polyvalent R^v group (represented by the chain), such a compound in which there are, for example, two polyvalent R^v groups being illustrated by the following formula, in which the characterizing groups have the same significance described above under Formula C:

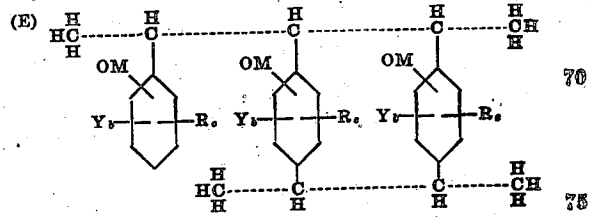
(D)



The possible molecular structure of compounds in which the aryl nucleus T is polycyclic will be obvious from the foregoing exemplary Formulae A to D inclusive, and the possible molecular structure of compounds in which v and n are equal to two and four will be readily understood from the exemplary Formulae C and D.

Another possible molecular structure of compounds coming under general Formula III is a compound having more than one polyvalent R^v, at least two of which have different valences. Such a compound may be typified by the following formula in which the symbols have the same significance as in Formula C:

(E)



As to the possible number of R^v (and R_c) groups going to make up a single molecule, this will vary with the extent to which it is desired to effect substitution of the nucleus 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 nucleus which are available for substitution. As will be apparent to those skilled in the art, the maximum possible number of R^v (and R_c) groups which can be attached to a single aromatic nucleus will vary as the nucleus is mono or poly cyclic and also as the nucleus is otherwise substituted. It will also be apparent that available valences on the nuclei may all be attached to polyvalent aliphatic substituents.

It will be understood that the oil-improving agents contemplated by this invention may be pure compounds satisfying the general Formula III described above with any one of the various mono and poly cyclic aromatic nuclei as T and the various substituents R^v (or R^v and Y) described, the only requisites being that at least one nuclear hydrogen be substituted with a metal-oxy group or hydroxyl group in which the hydroxyl hydrogen is replaced with its equivalent weight of a metal and at least one nuclear hydrogen be substituted with an oil-solubilizing aliphatic radical or group. However, in manufacturing the preferred oil-improving product of the present invention by the preferred method of procedure, as will appear more fully later on, the final oil-improving product obtained is normally or usually a mixture of different compounds corresponding to different values of n and v and to different numbers of aliphatic groups R^v.

As has been emphasized hereinabove, it is important that the oil-improving agents as represented by general Formulae III and IV have nuclear hydrogen in the aromatic nucleus T substituted with predominantly aliphatic material which comprises a sufficient proportion of the composition as a whole to render the same miscible with the mineral oil fraction in which the improving agent is used under normal conditions of handling and use. It appears from the results of my research that there is a critical range in the degree of alkylation of these improving agents below which the product or agent will not satisfy the requirements for oil-miscibility. Expressing this in another way, it appears that the hydroxyaromatic constituent from which the metal oxide is derived should not exceed a certain percentage of such alkylated hydroxyaromatic composition as a whole. This critical range of alkylation may be roughly expressed as the ratio by weight of $(T(OH))_n$ to $R^v(T(OH))_n$.

The degree of alkylation and the critical range within which operative or preferred compounds can be obtained may also be expressed as the number of carbon atoms contained in the aliphatic substituents for each aryl nucleus in a given molecule or molecular structure.

The critical range in the degree of alkylation of the aryl nucleus in the improving agents contemplated herein may vary with: (*a*) the mineral oil fraction in which the improving agent is to be used; (*b*) the aryl nucleus T (mono or poly cyclic); (*c*) the hydroxyl content of the aryl nucleus from which the metal oxide is derived (mono or poly hydric); (*d*) the character of aliphatic material comprising the substituent (straight or branched chain); (*e*) mono or poly substitution of the aryl nucelus; and (*f*) other substituents on the nucleus T, which may be of positive or negative or of neutral solubilizing activity.

In general it may be said that a polycyclic nucleus appears to require a higher degree of alkylation than a monocylic nucleus; that a polyhydric nucleus requires a higher degree of alkylation than a monohydric nucleus; and that branched chain aliphatic substituents have a somewhat greater solubilizing action than straight chain solubilizing substituents.

In view of the foregoing variables it would be impracticable and probably misleading to attempt to give an expression and figure which would indicate accurately the proper ratio of hydroxyaromatic constituent to the alkylated hydroxyaromatic constituent which would express a degree of aliphatic substitution satisfying all cases taking these variables into account. As a guide for preparing these improving agents, however, my research indicates that for a product having pour depressing and V. I. improving properties in addition to other valuable properties the ratio, expressed as:

VII. $$\frac{(T(OH))_n}{R^v(T(OH))_n}$$

should not be greater than .17 when the weight of the hydroxyaromatic nucleus or component $(T(OH))_n$ is expressed in terms of its chemically equivalent weight of phenol (C_6H_5OH). However, for mere oil-solubility with inhibition of oxidation I have found that this ratio may be raised as high as .40 by poly-substituting the nucleus with branched chain aliphatic groups. In general it may be said that in the preferred improving agents contemplated herein the ratio by weight of the hydroxyaromatic component in the product to the corresponding alkylated hydroxyaromatic nucleus or component therein should not be greater than about seventeen parts by weight of the former to about 100 parts by weight of the latter, or about seventeen per cent, when the weight of the hydroxyaromatic nucleus or component is expressed in terms of its chemically equivalent weight of phenol. It will be observed that the ratio as represented by the Formula VII above does not take into account any other substituent in the nucleus than the aliphatic substituents and the hydroxyl group; but since the aliphatic substituent is primarily relied upon in the agents contemplated herein as the solubilizing substituent, it is believed that the foregoing expression and limits will serve as a working guide for the preparation of oil-soluble materials and the preferred multifunctional materials.

As stated above, the degree of alkylation may also be expressed by the number of carbon atoms contained in the aliphatic substituent for a given hydroxyaromatic nucleus T. As a general guide here it may be said that the aliphatic substituents represented by R^v in the above general Formula III should, for the preferred multifunctional materials contemplated herein, contain at least thirty carbon atoms for each aromatic nucleus T. The above limit is representative of preferred materials, but metal phenates which are oil-soluble and which have oxidation inhibiting action when admixed with oils have been prepared from di-tertiary amyl phenol which it will be observed is poly-substituted with a branched chain hydrocarbon and has only ten carbon atoms in the alkyl substituents.

The ratio of seventeen per cent, which I may term the "phenolic ratio", represents what I consider a maximum figure for the preferred prod-

ucts contemplated herein, and in general it will be found that this figure will be lower, the actual ratio, of course, being dependent upon the variable factors enumerated above. For example, as will later appear, an improving agent of the preferred type in which the aliphatic substituent is derived from petroleum wax (a predominantly straight chain aliphatic hydrocarbon of at least twenty carbon atoms) and in which the aromatic nucleus was derived from phenol otherwise unsubstituted may have a phenolic ratio, as expressed above, not substantially greater than about thirteen per cent.

A further general guide for the synthesis of the preferred improving agents for viscous oils is to alkylate the aromatic nucleus so it is polysubstituted with aliphatic hydrocarbon radicals or groups preferably of relatively high molecular weight.

As has been previously indicated, it is one of the primary objects of the invention to provide an oil-improving agent which will have multifunctional improving activity in a mineral oil. My research indicates that compounds satisfying the requisites of general Formula III above may be blended in minor proportions with mineral oil fractions, particularly of the viscous or lubricating oil type, to effect marked improvement in several important properties. The improvement effected may be varied somewhat with the aliphatic substituent, petroleum wax and aliphatic hydrocarbons of similar characteristics such as ester wax, for example, giving products which effect a marked improvement in viscosity index and pour point in addition to other properties to be hereinafter pointed out. The effectiveness may also be varied with other substituents in the aryl nucleus—for example, alkoxy groups may contribute to solubility—and the properties of the agents may also be varied with the character of the metal substituent in the hydroxyl group. In general it appears that the salt of any metal satisfying the requisites of Formula III above will act to inhibit oxidation in mineral oils and reduce the formation of harmful oxidation products. Certain of the metals, such, for example, as lead and zinc, may serve to increase the load-carrying capacity of lubricating oils.

The procedure whereby the oil-improving agents contemplated herein can be prepared may be broadly described as involving the substitution of the hydroxyl hydrogen in an alkylated hydroxyaromatic compound with a metal and may be indicated by the following general equation:

$$(a) \qquad R^a(T(OH)Y_b)_n \xrightarrow{M} R^a(T(OM)Y_b)_n$$

This substitution may be effected in various ways some of which will be described hereinafter with specific examples.

The metal substituents in the hydroxyl group of the improving agents described herein may be broadly classified as the metals belonging to the silver, copper, tin, aluminum, iron, alkali and alkaline earth analytical groups, which include: silver, mercury, lead, and thallium; bismuth, copper, and cadmium; arsenic, antimony, and tin; iron, cobalt, nickel, and manganese; barium, calcium, strontium, and magnesium; and sodium, potassium, and lithium, respectively. Other desirable metals include: titanium, cerium, thorium, vanadium, molybdenum, tungsten, uranium, and platinum.

The general reaction described and illustrated above has shown an alkylated or an aliphatic-substituted hydroxyaromatic compound as the starting material. Compounds of this nature, which satisfy the requirements of high alkylation for the preferred improving agents discussed above, or mixtures of such compounds can be readily prepared by alkylating a mono or poly cyclic, mono or poly hydric, substituted or unsubstituted hydroxyaromatic compound with aliphatic compounds or predominantly aliphatic materials.

The starting material for the hydroxyaromatic constituent in the alkylation reaction to obtain an alkylated hydroxyaromatic product

$$R^v(T(OH)Y_b)_n$$

in which Y_b, if present, is residual hydrogen, may be a mono or poly cyclic hydroxyaromatic compound otherwise unsubstituted; or such compounds containing alkyl substituents; or in certain special cases (to be hereinafter described) the starting material may be an alkyl-aryl ether or an aralkyl-aryl ether. For obtaining an alkylated hydroxyaromatic product containing a "Y" substituent, in adidtion to or in place of residual hydrogen, the starting material for the hydroxyaromatic constituent may be a mono or poly cyclic hydroxyaromatic compound in which part of the nuclear hydrogen is substituted with a member or members of the group consisting of chlorine, hydroxy, alkoxy, aroxy, aryl, alkaryl, and aralkyl groups,

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, guiacol, alpha and beta naphthol, alpha and beta methyl naphthol, tolyl naphthol, xylyl naphthol, benzyl naphthol, anthranol, phenyl methyl naphthol, phenanthrol, monomethyl ether of catechol, methoxy phenol, phenoxy phenol, anisole, beta naphthyl methyl ether, chlorphenol, and the like. Preference in general is to the monohydroxy phenols otherwise unsubstituted, particular preference being given to phenol and alpha and beta naphthol.

The alkylation of the hydroxyaromatic compound 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.

I have found the Friedel-Crafts type of alkylation reaction to be particularly adapted to the step of preparing the alkylated hydroxyaromatic compounds from which the improving agents described herein are synthesized because it affords a convenient means of controlling the degree of alkylation and obtaining the desired "phenolic ratio" for use in the preferred mineral oil compositions contemplated by this invention.

In this reaction an appropriate mono or poly chlorine-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 poly chlorine-substituted aliphatic compounds may be used. However, as will be readily understood by those skilled in the art, since it is usually very 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, I prefer to employ a mixture of such hydrocarbons, such as a suitable petroleum fraction, as the starting material for my preferred improving agents, converting it into a mixture of different chlorine (or other halide) 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 by this invention as preferred sources for the alkyl or aliphatic substituent R^v in Formula III 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. Special preference is given to petroleum wax of melting point not substantially less than about 120° F. Such specially preferred aliphatic hydrocarbon materials commonly have molecular weights of about 250 and have at least twenty carbon atoms in their molecules.

As stated above, the Friedel-Crafts synthesis affords a convenient means of controlling the "degree of alkylation" of the product. This is accomplished by controlling: (*a*) the chlorination of the aliphatic hydrocarbon and (*b*) the reacting proportions of the chlorinated aliphatic hydrocarbon and the hydroxyaromatic compound used in the Friedel-Crafts reaction. As is well known to those skilled in the art, the replacement of nuclear hydrogen in the hydroxyaromatic compound with an aliphatic group is, in the Friedel-Crafts synthesis, effected by reaction of such nuclear hydrogen with chlorine in the chlorinated aliphatic compound, the substitution being effected with evolution of HCl. It will thus be seen that the number of chlorine substituents in a chlorinated aliphatic compound corresponds to the number of valences (*v* in general Formula III) which will be satisfied by or attached to hydroxyaromatic nuclei in the product of the reaction. For example, in a reaction where a quantity of pure monochloraliphatic hydrocarbon containing say three atomic proportions of chlorine is reacted with one molecular proportion of hydroxyaromatic compound, the resulting alkylated product, $R^v(T(OH)Y_b)_n$, is one in which *v* and *n* are equal to one and there are three aliphatic groups R^v attached to one nucleus T. On the other hand, assuming a reaction in which a quantity of pure trichlor-aliphatic hydrocarbon containing three atomic proportions of chlorine is reacted with one molecular proportion of hydroxyaromatic compound, the product would be one in which *v* and *n* of general Formula III are each equal to three, and the solubilizing action of a single aliphatic group would be distributed among three nuclear hydroxyaromatic groups. It is due to this latter condition that I consider it preferable that the number of valences "*v*" (in R^v of Formulae III, etc.) be maintained within the range of from one to four hereinabove specified. In other words, it appears that the required oil-solubilizing and oil-improving action of the aliphatic substituent R^v, particularly where the agent is to be used for multifunctional activity in viscous oils, is not obtained with materials predominantly comprised of a compound or compounds $R^v(T(OM)Y_b)_n$ (Formula III) in which *v* and *n* are greater than four. Hence, for use in the Friedel-Crafts reaction the chlorinated high molecular weight aliphatic material should be a compound, or should be predominantly comprised of compounds, in which the chlorine content is not greater than a tetrachlor compound.

As will be readily apparent to those skilled in the art, the chlorination of an aliphatic material such as a liquid petroleum fraction or a crystalline petroleum wax will normally or usually result in a mixture of mono- and poly-chloraliphatic hydrocarbon compounds. Consequently, the product of a Friedel-Crafts reaction between such chlorinated material and a hydroxyaromatic compound will be a mixture of different compounds corresponding to different values of *v* and *n* in the formula $R^v(T(OH)Y_b)_n$ and the final metal oxide derived therefrom according to the reaction of Equation *a* above will likewise be a mixture of compounds corresponding to different values of *n* and *v* in the formula $R^v(T(OM)Y_b)_n$ (general Formula III). It will be understood, therefore, that the specific values for *v* and *n* in the above formula, as well as the formula itself, relate to the different specific compounds present in such a mixture which characterize it as a product of the present invention.

However, in the case of a pure compound corresponding to general Formula III or in mixtures thereof, I have, as previously stated, discovered that for a satisfactory product, the ratio by weight of hydroxyaromatic component $(T(OH))_n$ to the corresponding alkylated hydroxyaromatic nucleus or component $(R^v(T(OH))_n)$ should not be greater than a certain critical maximum ratio which varies with constituents, conditions of use, and properties desired, as discussed in detail hereinabove.

The above-mentioned ratio of hydroxyaromatic component to the corresponding alkylated hydroxyaromatic component,

$$\left(\frac{(T(OH))_n}{R^v(T(OH))_n}\right)$$

in which the hydroxyaromatic component is calculated as phenol and which is therefore herein referred to as the phenol content or "phenolic ratio", is usually calculated from the weight of the hydroxyaromatic compound used up in the alkylation reaction and from the total weight of alkylated compound resulting from such alkylation reaction, as will be readily understood by those skilled in the art.

For example, when the Friedel-Crafts synthesis is used for alkylation, the aliphatic hydrocarbon material is first chlorinated until the weight of chlorine absorbed indicates that the average composition of the chlorinated product corresponds roughly to say a dichlor-aliphatic hydrocarbon. Such a product will, of course, contain some mono- and tri-chlor compounds and probably some tetrachlor compounds. The reacting proportions (based on atomic proportions of chlorine to one mole of hydroxyaromatic compound) are then selected so that the theoretical product of the Friedel-Crafts reaction will give the approximate phenolic ratio desired. After the Friedel-Crafts reaction and purification of the product the weight of aliphatic material in the chlorinated aliphatic starting material is subtracted from the weight of the alkylated or aliphatic-substituted product to obtain the weight of hydroxyaromatic material $((T(OH))n)$ actually combined or used up in the alkylation synthesis. From this value and the weight of the alkylated product

$$(R^v(T(OH))_n)$$

the phenolic ratio or phenol content can be readily calculated. If there are other substituents (Y_b) on the hydroxyaromatic nucleus in addition to the mono- or poly-valent aliphatic groups, a deduction should be made for them before calculating the phenolic ratio, an operation which will be apparent to those skilled in the art.

In the foregoing description of the Friedel-Crafts alkylation reaction I have referred to a hydroxyaromatic compound as a starting material. This same reaction may be used with an alkyl-aryl ether or an aralkyl-aryl ether which undergoes a substantial rearrangement during Friedel-Crafts alkylation to form an alkylated hydroxyaromatic compound in which the alkyl group of the ether replaces one of the nuclear hydrogen atoms.

In the event it is desired to obtain a product $R^v(T(OM)Y_b)_n$ which contains an alkoxy group as the substituent Y_b, it is preferable that the alkylation be effected with a hydroxyaromatic compound containing such alkoxy or aroxy group as a substituent and a high molecular weight unsaturated aliphatic hydrocarbon (such as polymerized isobutylene, dodecylene, tetradecylene, octadecylene, melene, etc.) or a higher alcohol (such as cetyl alcohol, myricyl alcohol, ceryl alcohol, octadecyl alcohol, etc.) using H_2SO_4 as a catalyst. By this procedure, the hydroxyaromatic ether can be alkylated without substantial rearrangement taking place. As an alternative procedure, polyhydric phenols can be alkylated by reaction with alcohols or unsaturates or by Friedel-Crafts reaction followed by substitution of one hydroxy with a low molecular weight alkyl group. In carrying out this latter procedure, the alkylated polyhydric phenol is treated with an alkali alcoholate to introduce alkali metal into the OH group followed by treating with the desired alkyl halide, whereby the substitution is effected.

When it is desired to obtain a nitro or amino group as the substituent "Y_b" in general Formula III, the hydroxyaromatic compounds are alkylated when free of nitro or amino groups, and such alkylation is followed by nitration of the alkylated compound to introduce the nitro substituent. The amino group can be obtained by reduction of the nitro group.

PREPARATION OF WAX-SUBSTITUTED ARYL OXIDES

(1) Alkylation of Phenol

A paraffin wax melting at approximately 120° F. and predominantly comprised of compounds having at least twenty carbon atoms in their molecules is melted and heated to about 200° F., after which chlorine is bubbled therethrough until the wax has absorbed about sixteen per cent of chlorine, such product having an average composition between a monochlor wax and a dichlor wax. Preferably the chlorination is continued until about one-sixth the weight of the "chlorwax" formed is chlorine. A quantity of chlorwax thus obtained, containing three atomic proportions of chlorine, is heated to a temperature varying from just above its melting point to not over 150° F., and one mole of phenol (C_6H_5OH) is admixed therewith. The mixture is heated to about 150° F., and a quantity of anhydrous aluminum chloride corresponding to abut three per cent of the weight of chlorwax in the mixture is slowly added to the mixture with active stirring. The rate of addition of the aluminum chloride should be sufficiently slow to avoid violent foaming, and during such addition the temperature should be held at about 150° F. After the aluminum chloride has been added, the temperature of the mixture may be increased slowly over a period of from fifteen to twenty-five minutes to a temperature of about 250° F. and then should be more slowly increased to about 350° F. To control the evolution of HCl gas the temperature of the mixture is preferably raised from 250° F. to 350° F. at a rate of approximately one degree per minute, the whole heating operation occupying approximately two hours from the time of adding the aluminum chloride. If the emission of HCl gas has not ceased when the final temperature is reached the mixture may be held at 350° F. for a short time to allow completion of the reaction. But, to avoid possible cracking of the wax, the mixture should not be heated appreciably above 350° F., nor should it be held at that temperature for any extended length of time.

It is important that all unreacted or non-alkylated hydroxyaromatic material (phenol) remaining after the alkylation reaction be removed. Such removal can be effected generally by water-washing, but it is preferable to treat the water-washed product with super-heated steam, thereby insuring complete removal of the unreacted material and accomplishing the dry-out of the product in the same operation.

The wax-substituted phenol thus obtained may be characterized by the general formula

$$R^v(T(OH)Y_b)_n$$

in which R^v represents at least one aliphatic group or radical characteristic of paraffin wax having a valence v of from one to four; T represents a monocyclic aromatic nucleus; Y_b represents residual hydrogen, "b" being a number corresponding to the number of valences on the nucleus T not satisfied by R^v and (OH); and n is a number from one to four corresponding to the valences v on the aliphatic group or groups R^v which are satisfied by the nuclear group or groups $T(OH)Y_b$.

A wax-substituted phenol prepared according to the above procedure, in which a quantity of chlorwax containing three atomic proportions of chlorine (sixteen per cent chlorine in the chlorwax) is reacted with one mole 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 mole 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 metal oxides derived from these alkylated hydroxyaromatic compounds.

Wax-phenol (3–16) as obtained by the above procedure had a phenol content or a "phenolic ratio" of about thirteen per cent. My research indicates that this phenolic ratio of thirteen per cent may be considered as representing about the maximum for satisfactory miscibility and multifunctional activity in viscous oils of the aryl metal oxides in which the alkyl substituent is derived from wax and the hydroxyaromatic constituent is derived from phenol (C_6H_5OH).

(2) Formation of Wax-Substituted Metal Phenates (Alkylated Aryl Metal Oxides)

The substitution of the hydroxyl hydrogen of the alkylated hydroxyaromatic compound or product with its equivalent weight of metal may be effected in various ways of which the following are illustrative examples.

Example A

The wax-substituted aryl alkali metal oxides can be prepared by the reaction of a wax-hydroxyaromatic compound with finely divided alkali metal at elevated temperatures and in the presence of a non-oxidizing gas. The reaction is carried out with rapid stirring of the mixture to maintain the alkali metal in a fine state of subdivision thereby accelerating the reaction. When using metallic sodium the reaction mixture may be heated to 500° F. for a two-hour period and the potassium oxides can be formed by heating the reaction mixture to 400° F. for a one-hour period. Examples of reacting proportions are as follows:

	Parts by weight
(a) Wax-phenol (13.2% combined phenol)	500
Sodium or equivalent amount of potassium	16
(b) Wax-naphthol (15.7% combined naphthol)	500
Sodium or equivalent amount of potassium	12½

Example B

Wax(alkyl)-substituted aryl oxides of the alkali and alkali earth metals and metals from the silver, copper, aluminum, tin and iron analytical groups can be readily prepared by the reaction of the wax-hydroxyaromatic compound with the desired alkyl metal oxide (metal alcoholate). The reaction mixture is heated to about 300° F. during a one-hour period, allowing the alcohol released to distill off, thereby obtaining an alkyl-substituted aryl metal oxide as the finished product. Anhydrous methyl and ethyl alcohols are considered preferable for preparing the alcoholates for use in this reaction. Illustrative reacting proportions are:

	Parts by weight
(a) Wax-phenol (13.2% combined phenol)	500
Alkyl sodium oxide; or equivalent amount of other alkali alcoholate	16
(b) Wax-phenol (13.2% combined phenol)	500
Calcium in form of alkyl calcium oxide or equivalent amount of other alkaline earth metal alcoholate	14

In forming the alkyl-substituted aryl oxides of the metals other than alkali metals through the use of alcoholates of such metals, the preferred procedure is to first form the alkyl oxides (alcoholates) of such metals by double decomposition of alkyl sodium oxide with an alcohol-soluble salt (such as a chloride) of the desired metal. The alkyl (wax)-substituted hydroxyaromatic compound is then added to the alkyl metal oxide mixture without separating the pure alkyl oxide of the desired metal from the alkali salt, and the mixture is heated during one hour at 300° F., allowing the alcohol to distill to complete the formation of the alkyl-substituted aryl oxide of the desired metal. The reaction product is then purified by diluting the mixture with a light mineral oil to aid the separation of the alkali salt, which is removed by settling, filtering or centrifuging, after which the diluent is distilled to obtain the finished product.

Example C

The wax-aryl lead oxide can be readily prepared by reacting a wax-substituted hydroxyaromatic compound, such as wax-substituted phenol, with litharge in the presence of a non-oxidizing gas and heating the mixture with stirring to a temperature of about 500° F. during a period of one hour. The reaction product may then be diluted with a light mineral oil, such as Stoddard solvent, after which the unreacted litharge can be settled out and separated. The refined product is obtained by removing the diluent by distillation. The proportions used in this reaction should be substantially as follows:

	Grams
Wax phenol of 13.2% combined phenol content	500
Litharge	78.3

Example D

The alkyl(wax)-substituted aluminum oxide may be formed by a modification of the Friedel-Crafts reaction which is employed in the formation of the alkyl(wax)-substituted hydroxyaromatic compound described hereinabove, using the theoretical amount of anhydrous aluminum chloride required to convert completely the hydroxyaromatic compound to the aryl metal oxide, carrying out the reaction as described in connection with the formation of wax phenol except that the mixture is heated to only 200° F. to complete the reaction and form wax-substituted aluminum aryl oxide as the end product. The product is not water-washed but purified by removing the hydrogen chloride gas under vacuum or by blowing the product with a non-oxidizing gas, such as nitrogen. The purification step can be aided by use of a diluent, such as Stoddard solvent, whereby any non-alkyl-substituted aluminum oxide can be settled out. The diluent is removed by distillation to give the finished product. For the preparation of a wax-substituted aluminum phenate according to this procedure the following proportions of reactants may be used:

	Parts by weight
Chlorwax of 16% chlorine content	500
Phenol	70.6
Anhydrous aluminum chloride	33.4

The conversion of wax hydroxyaromatic compounds to wax aryl metal oxides results in considerable increase in viscosity with the formation of tough and waxy materials. With an increase in metal content the tendency is toward the formation of a rubber-like product, and on this account it is often desirable to use diluents in the preparation of the compounds for the purpose of reducing the viscosity of the mixtures. In the event the compounds are being prepared for incorporation in a particular oil it is convenient to employ as a diluent a quantity of the same oil with which the compounds are to be blended.

As has been previously pointed out, the alkyl substituent in these alykyl-substituted aryl metal oxides should be of relatively high molecular weight. In order to obtain compounds having pour depressant and viscosity index improving properties along with other improved properties, such as sludge inhibition, etc., I have found that the alkyl substituents should preferably be in the nature of petroleum wax or an aliphatic hydrocarbon of correspondingly high molecular weight, and for that reason the wax-substituted

compounds are considered preferable for the purpose of this invention. Although the wax-substituted products are considered preferable for the reasons just stated I have prepared oil-miscible alkyl-substituted aryl metal oxides from alkylated hydroxyaromatic compounds in which the alkyl substituent was derived from Transil oil (a highly refined viscous paraffin base white oil having a Saybolt viscosity of eighty-two seconds at 100° F. and specific gravity of 0.8498) and from di-tertiary amyl phenol.

As will appear from the foregoing description, the oil-improving agents contemplated by this invention are characterized by the general Formula III ($R^v(T(OM)Y_b)_n$ described hereinabove; such chemical compounds or products may also be characterized as oil-miscible "alkylated or alkyl-substituted aryl metal oxides" or "alkylated hydroxyaromatic compounds in which the hydroxyl hydrogen has been replaced with its equivalent weight of metal", it being understood that the terms "alkyl" and "alkylated" are used herein in a broad sense to include polyatomic or polyvalent, as well as monovalent aliphatic radicals or groups.

To demonstrate the effectiveness of compounds or products of the type described above in the mineral oil compositions contemplated by this invention, I 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 alkylated-aryl metal oxides.

POUR TEST

This series of tests was conducted with a mineral lubricating oil fraction having a Saybolt viscosity of 244 seconds at 130° F. and an A. S. T. M. pour point of +20° F. The alkyl-substituted aryl metal oxides used were derived from wax-substituted phenolic compounds obtained by condensing chlorwax of substantially sixteen per cent chlorine with the phenolic compound in the ratio of one molecular proportion of phenolic compound to a quantity of chlorwax containing three atomic proportions of chlorine. The aryl constituents of the oxides used in these tests were phenol and alpha and beta naphthol. The oxides obtained from phenol are listed in the table as wax (metal) phenates and those obtained from the naphthols as wax (metal) naphtholates. To demonstrate the improved effectiveness contributed by the metal substituent in these improving agents I have also prepared and tested blends of the same oil with the corresponding wax-substituted hydroxyaromatic compounds. The results of these tests are listed below.

Table I

Improving agent	Per cent by weight	A. S. T. M. pour point
	Per cent	°F.
None		+20
Wax phenol	1/8	0
Wax cupric phenate	1/8	−15
Wax stannous phenate	1/8	−15
Wax aluminum phenate	1/8	−10
Wax zinc phenate	1/8	−10
Wax ferric phenate	1/8	−10
Wax cobaltous phenate	1/8	−15
Wax calcium phenate	1/8	−5
Wax magnesium phenate	1/8	−15
Wax potassium phenate	1/8	−20
Wax sodium phenate	1/8	−20
Wax beta naphthol	1/8	+10
Wax sodium naphtholate	1/8	−15

From the foregoing results it will be observed that the alkyl-substituted aryl metal oxides contemplated by this invention, when present in a mineral lubricating oil in amounts as small as one-eighth of one per cent, are effective in depressing the pour point of the oil as much as 40° F. It will also be observed that the metal substituent in these compounds contributes materially to the pour depressing action, since the same quantity of the wax-substituted hydroxyaromatic compound corresponding to the oxide depresses the pour point only 20° F.

SLUDGE INHIBITION

To further demonstrate the improved properties present in the mineral oil compositions contemplated by this invention I have subjected blends of the same mineral lubricating oil fraction described above and various representative wax-substituted aryl metal oxides to an accelerated oxidation test in which the samples of oil blends are heated to a temperature of 350° F. in an open container, during which time they are continuously stirred with a steel propeller. The extent of sludge or tar precipitation obtained in this oxidation test is expressed as the "tar number", such numbers being comparative between the various samples and representative of the sludge forming characteristics of the oil. In carrying out this test I have employed both wax- and Transil oil-substituted aryl metal oxides prepared in accordance with the procedures outlined above. The phenol condensation product obtained with chlorinated Transil oil is referred to in the table below as "Transil oil phenol", and the sodium oxide of this condensation product is referred to as "Transil oil sodium phenate".

The results obtained in these tests, which are indicated in the table below as tar numbers, clearly show that the mineral oil compositions containing the compounds contemplated by this invention are inhibited against the formation of sludge.

Inhibitor blended with motor oil of Saybolt viscosity of 244 sec. @ 130° F.	Concen. by weight	Tar numbers on oil blends evaluated by accelerated oxidation test at 350° F.					
		Start	7 days	10 days	11 days	12 days	14 days
	Per cent						
None		0	18				
Wax phenol	1/2	0	18				
Transil oil phenol	1/2	0	18				
Wax lead phenate	1/2	0	Trace				
Wax lead phenate	1	0	0		1		
Wax stannous phenate	1/2	0	0.2				
Wax aluminum phenate	1/2	0	0.3		1		
Wax zinc phenate	1/2	0	Trace				
Wax calcium phenate	1/2	0	0.5				
Wax potassium phenate	1/2	0	0	Trace		11	
Wax sodium phenate	1/2	0	0				0
Transil oil sodium phenate	1/2	0	0				
Wax beta naphthol	1/2	0	18				
Wax sodium beta naphtholate	1/2	0	0				
Wax alpha naphthol	1/2	0	19				
Wax sodium alpha naphtholate	1/2	0	7	19			

It will be seen from the foregoing table that the alkyl-substituted hydroxyaromatic compounds have no sludge inhibiting properties but that the corresponding metal oxides are highly effective inhibitors.

OPERATION TEST

In addition to the foregoing tests I have also made tests of an oil and oil blends containing representative improving agents of the type con-

templated by this invention to determine the comparative behavior of the unblended oil and the improved oil compositions under actual operating conditions. This test was carried out in a single cylinder C F R engine cooled with a diethylene glycol-water mixture held at a temperature of about 390°. The engine was operated continuously over a time interval of twenty-eight hours at a speed of about 1200 R. P. M., which is equivalent to a road speed of about twenty-five miles per hour. The oil temperature was held at about 150° F. during the test.

The improving agents used were wax-cobaltous phenate (3–16) having a combined phenol content of 13.2 per cent and di-ter-amyl cobaltous phenate having a combined phenol content of forty per cent. The conditions observed at the end of the test were: (*a*) the extent to which the piston rings were stuck, (*b*) the extent to which the slots in the oil rings were filled with deposit, (*c*) the amount of carbonaceous deposits in the oil, and (*d*) the neutralization number (acidity) of the oil at the end of the test. The oil used was a lubricating oil stock of 120 seconds Saybolt Universal viscosity at 210° F. and the results, which are recorded below, show a marked improvement in mineral oil compositions of the type contemplated by this invention over the oil alone.

Oil	Ring condition								Carbon deposits	Neutral number
	Degrees stuck					Percent slots filled				
	1	2	3	4	5	3	4	5		
Oil alone	360	360	360	360	360	60	40	20	19.53	1.6
Oil+½% wax cobaltous phenate	15	0	0	0	0	0	0	0	9.90	0.4
Oil alone	360	270	360	360	0	20	60	5	16.2	2.2
Oil+½% di-amyl cobaltous phenate	240	360	0	0	0	0	0	0	7.13	1.1

It will be apparent from the foregoing description that I have developed a new class of mineral oil compositions characterized by the presence in a minor proportion of an alkyl-substituted aryl metal oxide 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 aryl constituents in the oxides; also by the degree of alkylation of the aryl nucleus. As to the degree of alkylation, it is important that the aryl nucleus 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 the mineral oil fraction with which it is blended and the properties desired in the final oil composition. The alkylated aryl metal oxides described herein may be used in amounts ranging from ⅛ per cent to five per cent, and in general compositions of the desired improved properties may be obtained with these improving agents in amounts of from ⅛ per cent to two per cent.

It is to be understood that while I have described certain preferred procedures which may be followed in the preparation of the alkylated aryl metal oxides used as improving agents in the mineral oil compositions contemplated by this invention and have referred to various representative constituents in these improving compounds, such procedures 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.

I claim:

1. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible aryl metal oxide in which the oxygen of the metal oxide group is directly attached to the nucleus and in which part of the nuclear hydrogen has been replaced with a mineral oil solubilizing substituent.

2. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible aryl metal oxide in which the oxygen of the metal oxide group is directly attached to the nucleus and in which part of the nuclear hydrogen has been substituted with predominantly aliphatic organic material, said last-mentioned substituent comprising a sufficient proportion of the substituted aryl metal oxide to render same miscible with said oil under normal conditions of handling and use.

3. An improved mineral oil composition comprising a mineral oil having admixed therewith in minor proportion: an oil-miscible wax-substituted hydroxyaromatic compound in which the hydroxyl hydrogen is replaced with its equivalent weight of metal.

4. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted aryl metal oxide in which the alkyl substituent and the metal oxide substituent are attached at different points on the nucleus.

5. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted aryl metal oxide in which the alkyl substituent is a high molecular weight aliphatic hydrocarbon derivative.

6. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted aryl metal oxide in which the alkyl substituent is derived from an aliphatic hydrocarbon having at least twenty carbon atoms.

7. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted aryl metal oxide in which the alkyl substituent is derived from petroleum wax.

8. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible substituted aryl metal oxide in which the substituent is a high molecular weight aliphatic hydrocarbon group and in which the aryl nucleus is poly-substituted with said substituent.

9. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible substituted aryl metal oxide in which the substituent is derived from an aliphatic hydrocarbon having at least twenty carbon atoms and in which the aryl nucleus is poly-substituted with said aliphatic derivative.

10. An improved mineral oil composition com-

prising a mineral oil having admixed therewith a minor proportion of an oil-miscible substituted aryl metal oxide in which the substituent is derived from petroleum wax and in which the aryl nucleus is poly-substituted with said wax derivative.

11. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted metal phenate.

12. In improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted metal naphtholate.

13. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted metal phenate in which the alkyl substituent is a high molecular weight aliphatic hydrocarbon derivative.

14. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted metal naphtholate in which the alkyl substituent is a high molecular weight aliphatic hydrocarbon derivative.

15. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted metal phenate in which the alkyl substituent is a high molecular weight aliphatic hydrocarbon derivative and in which the aryl nucleus is poly-substituted with said aliphatic derivative.

16. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted metal naphtholate in which the alkyl substituent is a high molecular weight aliphatic hydrocarbon derivative and in which the aryl nucleus is poly-substituted with said aliphatic derivative.

17. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible wax-substituted metal phenate.

18. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible wax-substituted metal naphtholate.

19. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkyl-substituted aryl metal oxide in which the metal substituent is selected from the group consisting of copper, tin, aluminum, zinc, chromium, manganese, iron, cobalt, calcium, magnesium, potassium, and sodium.

20. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an alkylated phenol in which hydroxyl hydrogen has been replaced by its equivalent weight of metal and in which the alkyl substituent is derived from petroleum wax, the proportion by weight of phenol in the alkylated phenol constituent being in the neighborhood of about thirteen per cent.

21. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkylated hydroxyaromatic compound in which the hydroxyl hydrogen has been replaced by its equivalent weight of metal and in which the proportion by weight of the hydroxyaromatic constituent in said alkylated-hydroxyaromatic constituent is chemically equivalent to not more than forty per cent phenol.

22. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible alkylated hydroxyaromatic compound in which the hydroxyl hydrogen has been replaced with its equivalent weight of metal and in which the proportion by weight of the hydroxyaromatic constituent in said alkylated-hydroxyaromatic constituent is chemically equivalent to not more than seventeen per cent phenol.

23. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of a product obtained by: chlorinating petroleum wax until about one-sixth the weight of the reaction product is chlorine; reacting the chlorinated wax with a hydroxyaromatic compound in the proportions of one mole of the latter to an amount of the chlorinated wax containing at least two atomic portions of chlorine to form a wax-substituted hydroxyaromatic compound; and substituting the hydroxyl hydrogen with a metal to form a wax-substituted aryl metal oxide of said metal.

24. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith a minor proportion, from about one-sixteenth per cent to about five per cent of an oil-miscible alkyl-substituted aryl metal oxide.

25. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith a minor proportion, from about one-sixteenth per cent to about five per cent of an oil-miscible alkyl-substituted aryl metal oxide in which the alkyl substituent is derived from an aliphatic hydrocarbon having at least twenty carbon atoms.

26. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith a minor proportion, from about one-sixteenth per cent to about five per cent of an oil-miscible alkyl-substituted aryl metal oxide in which the alkyl substituent is derived from petroleum wax.

27. A composition of matter comprising a mineral oil fraction and in admixture therewith a minor proportion of an oil-miscible metalorganic compound having the general formula

$$R^v(T(OM)Y_b)_n$$

in which: T represents an aromatic nucleus; (OM) represents at least one hydroxyl group in which the hydroxyl hydrogen is replaced with its equivalent weight of a metal, said group being attached to the nucleus T; R^v represents at least one aliphatic group having a valence v of one to four, and attached by one valence only to at least one nucleus T; Y represents a monovalent radical selected from the group consisting of residual hydrogen, and chlorine, alkoxy, aroxy, aralkyl, alkaryl, aryl, nitro, and amino radicals; b represents the number of Y's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied by R^v or (OM); and n is a whole number from one to four; the substituent R^v comprising a sufficient proportion of the metalorganic compound to render the same miscible with said oil under normal conditions of handling and use.

28. A composition of matter comprising a mineral oil fraction and in admixture therewith a minor proportion of an oil-miscible metalorganic compound having the general formula

$$R^v(T(OM)Y_b)_n$$

in which: T represents an aromatic nucleus; (OM) represents at least one hydroxyl group in which the hydroxyl hydrogen is replaced with its equivalent weight of metal M, said group being attached to the nucleus T; R^v represents at least one aliphatic group having a valence v of one to four and attached by one valence only to at least one nucleus T; Y represents a monovalent radical selected from the group consisting of residual hydrogen, and chlorine, alkoxy, aroxy, aralkyl, aryl, nitro, and amino radicals; b represents the number of Y's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied by R^v or (OM); and n is a whole number from one to four; the total number of carbon atoms in all of the aliphatic groups taken together in said metalorganic compound being not less than about thirty for each nucleus T.

29. A composition of matter comprising a mineral oil fraction and in admixture therewith a minor proportion of an oil-miscible metalorganic compound having the general formula

$$R^v(T(OM)Y_b)_n$$

in which: T represents an aromatic nucleus; (OM) represents at least one hydroxyl group in which the hydroxyl hydrogen is replaced with its equivalent weight of metal M, said group being attached to the nucleus T; R^v represents at least one aliphatic group having a valence v of one to four, and attached by one valence only to at least one nucleus T; Y represents a monovalent radical selected from the group consisting of residual hydrogen, and chlorine, alkoxy, aroxy, aralkyl, alkaryl, aryl, nitro, and amino radicals; b represents the number of Y's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied by R^v or (OM); and n is a whole number from one to four; the equivalent ratio of T(OH) to

$$R^v(T(OH))_n$$

in said metalorganic compound being not greater than the chemical equivalent of seventeen per cent phenol.

30. A composition of matter comprising a mineral oil fraction and in admixture therewith a minor proportion of an oil-miscible metalorganic compound having the general formula

$$R^{v'}(T(OM)Y_{b'}R_c)_n$$

in which: T represents an aromatic nucleus; (OM) represents at least one hydroxyl group in which the hydroxyl hydrogen is replaced with its equivalent weight of metal M, said group being attached to the nucleus T; $R^{v'}$ represents at least one polyvalent aliphatic hydrocarbon group of at least twenty carbon atoms having a valence v' of from two to four; $Y_{b'}$ represents a monovalent radical selected from the group consisting of residual hydrogen, chlorine, alkoxy, aroxy, alkaryl, aralkyl, aryl, nitro, and amino radicals; b' represents the number of $Y_{b'}$'s and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied by $R^{v'}$, (OM), and R_c; R_c represents monovalent aliphatic radicals; c represents the number of R_c's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied by $R^{v'}$, (OM), and Y_b; and n is a whole number from two to four.

ORLAND M. REIFF.

CERTIFICATE OF CORRECTION.

Patent No. 2,197,833. April 23, 1940.

ORLAND M. REIFF.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 70, for "R's" read --Rs--; page 6, second column, line 72, for "((T(OH))n)" read --((T(OH))$_n$)--; page 7, first column, line 52, after "ARYL" insert --METAL--; line 73, for "abut" read --about--; and second column, line 31-32, for "dry-out" read --drying--; page 9, second column, line 59, "0" under the heading "14 days" should be on the line above, opposite "Wax sodium phenate"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of August, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

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