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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 mineral oil compositions of the lubricant type to which an agent has been added for the purpose of improving the oil in certain respects. It is the object of this invention to provide a novel class of mineral oil addition agents which will improve one or more important properties of a mineral oil fraction. It is a further object to provide improved mineral oil compositions containing such improving agents.

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 the "oiliness" characteristics and 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 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 lubrication 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 mineral oil-improving agents which are multifunctional in that a single ingredient may be added to the oil to effect improvement in one or more of the various properties enumerated above. More specifically, our invention contemplates as oil-improving agents the oil-miscible metal salts of alkyl-substituted hydroxyaromatic-aliphatic carboxylic acids in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal. We have

discovered that metal salts 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.

Our invention has as a further and more specific object the provision of a viscous mineral oil fraction which has been improved in one or more of the foregoing recited respects by having incorporated therein a minor proportion of an oil-miscible metal salt of an alkylated hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal.

The oil-improving agents contemplated by this invention may be considered as alkylated hydroxyaromatic compounds in which at least one nuclear hydrogen atom of the aromatic nucleus is replaced with an organic acid group such as a mono- or poly- basic aliphatic or cyclo-aliphatic acid group in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with their equivalent weight of metal. Compounds or compositions of this type are therefore characterized by the presence of an aromatic nucleus in which at least one nuclear hydrogen has been replaced with a metaloxy (OM) substituent and in which another nuclear hydrogen atom is replaced with an aliphatic acid salt residue (Z.COOM). (The terms "aliphatic carboxylic acid" and "alkyl carboxylic acid" as used herein are inclusive of aliphatic and cyclo-aliphatic acids.) This characterizing group may be represented by the formula:

I. T(OM)(Z.COOM')

in which T represents an aromatic nucleus; (OM) represents at least one hydroxyl group attached to T, the hydrogen thereof being replaced by a metal M; and (Z.COOM) represents at least one aliphatic or cyclo-aliphatic acid residue attached to the nucleus T, in which Z represents the aliphatic or cyclo-aliphatic radical attached to T and COOM' is at least one carboxyl group attached to Z, the hydrogen thereof being replaced with its equivalent weight of a metal M'.

The metal salts of hydroxyaromatic-aliphatic acids of the type corresponding to the group represented by the above formula which are otherwise unsubstituted are not in general miscible with mineral oil, particularly where the alkyl acid residue is derived from a low molecular weight acid. When the residue Z.COOM' is derived from a high molecular weight acid such as stearic acid, the salts may, with some difficulty, be blended with oil, but tend to cause gelation, which is undesirable. It is therefore important that the improving agents containing the above characterizing group have additional nuclear hydrogen replaced with substituents of an oil-solubilizing nature. In other words, it is important that the aryl nucleus T carry a substituent or substituents which will render the composition as a whole miscible with mineral oil fractions and will prevent gel formation therein. By the terms "oil-miscible" or "oil-soluble" as they are used herein we have reference to that property of remaining uniformly dispersed in the mineral oil fraction, either as a true solution or as a colloidal suspension without gelation during normal conditions of handling and use.

The improving agents contemplated by this invention are characterized by the presence of alkyl substituents directly or indirectly substituted in the aryl nucleus T, 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 T which will give other properties to the composition as a whole in addition to oil-miscibility. We have found, for example, that where this aryl nucleus is substituted with one or more aliphatic groups corresponding to certain aliphatic hydrocarbon compounds of relatively high molecular weight (such as aliphatic groups having at least twenty carbon atoms, 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 metal salts of hydroxyaromatic-aliphatic carboxylic acids having the characterizing group T(OM)(Z.COOM') described above, in which additional hydrogen on the aryl nucleus T 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, is substituted with aliphatic hydrocarbon radicals or groups, such aliphatic radicals or groups preferably being high molecular weight aliphatic derivatives or heavy alkyl groups.

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

II. R(T(OM)(Z.COOM')

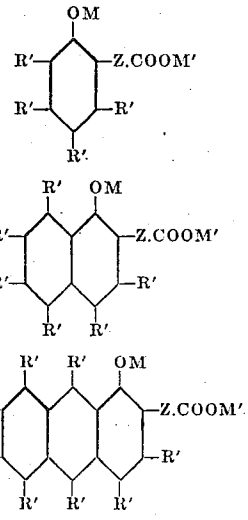
in which R represents at least one aliphatic hydrocarbon radical or group, such group or groups preferably corresponding to relatively high molecular weight aliphatic hydrocarbons and being attached to a mono- or poly- cyclic aromatic nucleus T, and in which (OM) and (Z.COOM') are as indicated above.

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 of the aryl nucleus T 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:

III. R(T(OM)(COOM')Y)

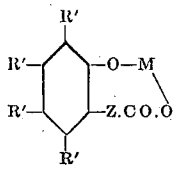
in which R, T, (OM) and (Z.COOM') have the same significance indicated above and in which Y represents residual hydrogen of the aryl nucleus T which may be replaced by a radical from the group consisting of: hydroxy, alkoxy, aroxy, aralkyl, aryl, alkaryl, halogen, nitro, amino and organic ester radicals or groups. In the case of a preferred multifunctional type of compound wherein R contains at least twenty carbon atoms, Y may also include alkyl radicals of less than twenty carbon atoms. 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, alkoxy, aroxy, aralkyl, aryl, alkaryl, halogen, nitro, amino and organic ester radicals or groups.

In the event the metal substituent is a polyvalent metal, it is probable that compounds of the type indicated above are in the nature of Chelate compounds, in which event a representative formula would be



but for purposes of description and illustration herein the former type of formula will be used, with the understanding that M and M' may represent different metals or the same mono- or poly-valent metals and with the further understanding that when M and M' represent the same polyvalent metal, a single atom of such metal may replace both the hydroxyl and the carboxyl hydrogens to form a Chelate ring.

Relative to this alkyl carboxylate substituent we have found that it is advantageous to have the carboxylate group in a hydrocarbon substituent or side chain attached to the characterizing aromatic nucleus for the reason that compounds of this type are more stable against the formation of emulsions than are compounds of the type in which the carboxyl group is directly attached to the aromatic nucleus. Furthermore, aromatic-aliphatic carboxylate compounds of the type contemplated herein are characterized by the fact that the metal substituent is less susceptible to removal by water-washing, which permits more complete purification of the compound and removal of reaction products, such as inorganic salts, which might be found objectionable in mineral oil compositions compounded for certain uses.

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 our 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 valence bonds are attached to separate aromatic nuclear groups T. Compounds of this type are included under the following general formula representation:

IV. $R^v(T(OM)(COOM')Y_b)_n$

in which T, (OM) and (Z.COOM') 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 bond 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_b's and is equal to zero or a whole number corresponding to the valence bonds on the nucleus T not satisfied with R^v, (OM) and (Z.COOM'); and n represents a whole number from one to four and indicates the total number of groups $(T(OM)(COOM')Y_b)$ present in the molecule represented by the formula which are attached to the aliphatic group or groups represented by R^v through the valence bonds v.

In the foregoing general formula representation IV 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 2, 3 or 4); 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 IV is inclusive of compounds having aliphatic groups or radicals of different valences (from 1 to 4) in the same molecule. Also, it will be observed that since n may be any whole number from 1 to 4, the number of aromatic nuclei T in the molecule may likewise vary from 1 to 4. It will be seen, therefore, that the relationship between n and v in Formula IV, in its broadest aspect is such that when n is equal to 1, v is equal to 1; and when n is greater than 1, 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 on from the description of their synthesis, these materials represented by general Formula IV 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 hydroxyaromatic starting material as low molecular weight aliphatic groups, such as methyl, ethyl, propyl groups, etc. Compounds of this last-mentioned type in which R^v is a heavy alkyl group having at least twenty carbon atoms and in which the hydroxyaromatic starting material carries a low molecular weight alkyl group are characterized by the fact that they possess the property of improving viscosity index and inhibiting oxidation of a viscous mineral oil fraction but are not materially effective as pour point depressants, as contrasted with compounds in which all of the alkyl substituent is comprised of heavy alkyl groups, which compounds are highly effective pour point depressants in addi-

tion to being V. I. improvers and inhibitors of oxidation.

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

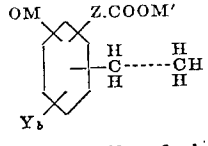
V. $R^{v'}(T(OM)(COOM')Y_bR_c)_{n'}$

in which T, (OM) and (Z.COOM') have the same significance as indicated above; $R^{v'}$ represents at least one polyvalent aliphatic radical or group having a valence v' of 2, 3 or 4 and preferably containing at least twenty carbon atoms; $Y_{b'}$ indicates the same group of substituents as described above for Y_b; R_c represents monovalent aliphatic radicals or groups and may include radicals containing less than twenty carbon atoms; 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), (Z.COOM') and R_c; c indicates the number of R_c's and is equal to zero or a whole number corresponding to the valence bonds on the nucleus T not satisfied with $R^{v'}$, (OM), (Z.COOM') and $Y_{b'}$; and n' represents a whole number from two to four and indicates the total number of the groups $(T(OM)(Z.COOM')Y_bR_c)$ 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 IV and V 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 bond 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 IV is always equal to 1 when n equals 1. 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 valence bonds 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 IV in which v and n is each to 1 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:

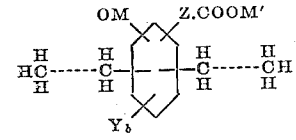
A.



In the above formula the chain represents the oil-solubilizing alkyl substituent (R^v), and Y_b, OM and Z.COOM' 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 1 and in which there are two such monovalent R^v groups, may be represented by the following formula:

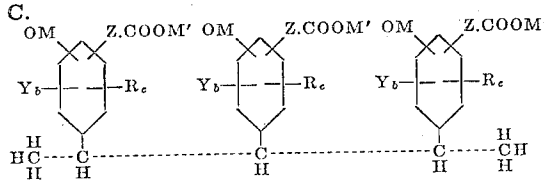
B.



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

Compounds of the type satisfying the general Formula IV and the subgeneric Formula V in which R^v (or $R^{v'}$) is polyvalent and v (or v') and n (or n') are more than 1 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:

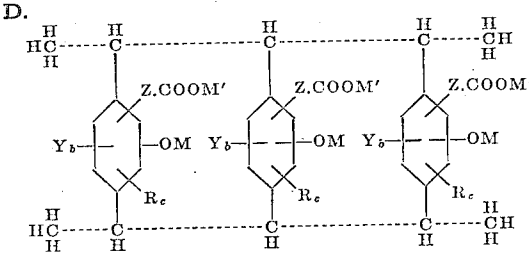
C.



In the above Formula C, R_c is a monovalent alkyl group as defined above under Formula V.

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.

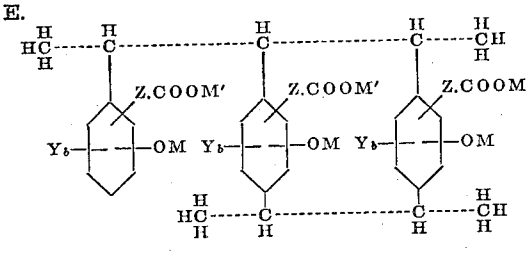
D.



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 2 and 4 will be readily understood from the exemplary Formulae C and D.

Another possible molecular structure of compounds coming under general Formula IV 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 significances 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 or multifunctional-imparting aliphatic groups for obtaining the desired properties in the product and is, of course, limited by the number of valence bonds 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 the nuclear hydrogen atoms available for replacement on several interrelated nuclei may all be substituted with polyvalent aliphatic substituents.

It will be understood that the oil-improving agents used in the mineral oil compositions contemplated by this invention may be pure compounds satisfying the general Formula IV 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. 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 IV and V 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 our research that there is a more or less 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 or oil-miscibility and multifunctional activity. Expressing this in another way, it appears that the hydroxyaromatic constituent of the alkylated hydroxyaromatic compound from which the alkylated metal-oxy-aromatic-aliphatic carboxylate metal salt 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 ranges within which operative and 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 final product is obtained (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 nucleus; (*f*) other substituents on the nucleus T, which may be of positive or negative or of neutral solubilizing activity; and (*g*) the character of the aliphatic group in the aliphatic acid residue (Z) carrying the COOM′ group or groups.

In general it may be said that a polycyclic nucleus appears to require a higher degree of alkylation than a monocyclic 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. Also, the condensation product containing a high molecular weight aliphatic acid residue such as an hydroxy-aryl stearic acid does not require for mere oil-solubility as extensive alkylation as the derivative containing a low molecular weight aliphatic acid group such, for example, as acetic acid.

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, our research indicates that for a product having pour-depressing and V. I.-improving properties in addition to other valuable properties the ratio of $(T(OM)(Z.COOM)_n$ to $R^v(T(OM)(COOM'))_n$ expressed as:

$$\text{VI.} \qquad \frac{(T(OH))_n}{R^v(T(OH))_n}$$

should not be greater than about .15 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 we have found that this ratio may be raised. For example, salts of the type contemplated herein which satisfy the requisites of oil-miscibility without gelation can be prepared from phenol-stearic acid having alkyl substituents as low as amyl or tertiary butyl. 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 15 parts by weight of the former to about 100 parts by weight of the latter, or about 15 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 VI does not take into account any other substituent in the nucleus than the aliphatic substituents and the hydroxyl group or groups; 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

IV should, for the preferred multifunctional materials contemplated herein, contain a total of at least twenty-five carbon atoms for each aromatic nucleus T.

The ratio of 15 per cent, which we may term the "phenolic ratio," represents what we consider a maximum figure for the preferred products contemplated herein, and in general it will be found that for these preferred multifunctional products this figure will be lower, the actual ratio, of course, being dependent upon the variable factors enumerated above.

A further general guide for the synthesis of the preferred improving agents for viscous oils is to alkylate the aromatic nucleus so that it is poly-substituted with aliphatic hydrocarbon radicals or groups preferably of relatively high molecular weight: that is, groups having at least twenty carbon atoms.

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. Our research indicates that compounds satisfying the requisites of general Formula IV 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 compounds of similar characteristics such as ester wax, for example, giving products which effect a marked improvement in viscosity index, pour point, inhibition of oxidation, retardation of lacquer formation or ring-sticking, etc. The effectiveness may also be varied with other substituents in the aryl nucleus, as has been previously indicated. Low molecular weight alkyl groups or halogen, as nuclear substituents, tend to modify the properties of the compounds by reducing the pour point-depressing action without disturbing their effectiveness as V. I.-improvers and antioxidants. The properties of the agents may also be varied with the character of the metal substituent in the hydroxyl and the carboxyl groups. In general it appears that the oil-miscible heavy alkyl-substituted salt of any metal satisfying the requisites of Formula IV above will provide a multifunctional oil-improving agent in that they improve the V. I. and function as inhibitors. Certain of the metals, such, for example, as copper, lead, and zinc, may serve to increase the load-carrying capacity of lubricating oils.

The general procedure followed in synthesizing the oil-improving agents contemplated herein involves substituting a nuclear hydrogen atom on an alkylated hydroxyaromatic compound with an aliphatic or cyclo-aliphatic carboxylic acid group and then substituting the hydroxyl hydrogen and the carboxyl hydrogen with metal. In the event one of the preferred multifunctional products is desired, the alkylated hydroxyaromatic compound is obtained by condensing a substituted or unsubstituted mono- or polycyclic hydroxyaromatic compound with a high molecular weight aliphatic compound containing at least twenty carbon atoms.

The alkylation procedure last-mentioned above may be carried out in various ways, as by the use of a halogenated high molecular weight hydrocarbon or mixture of such halogenated hydrocarbons such as chlorinated petroleum wax, effecting the condensation in the presence of a Friedel-Crafts catalyst. This alkylation may also be carried out by using high molecular weight unsaturated aliphatic hydrocarbons (such as eicosylene, cerotene, melene, polymerized isobutylene, etc.) or high molecular weight alcohols (such as myricyl alcohol, ceryl alcohol, etc.) using H_2SO_4 or anhydrous aluminum chloride as a catalyst. The Friedel-Crafts synthesis is preferred because it affords a convenient means of controlling the "degree of alkylation," and as a source of the alkyl substituent preference is given to mixed high molecular weight hydrocarbons 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 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., which is predominantly comprised of aliphatic hydrocarbons having a molecular weight of at least 350 and containing at least twenty carbon atoms.

Examples of hydroxyaromatic or oxyaromatic compounds which may be used in the alkylation reaction are: phenol, resorcinol, hydroquinone, catechol, cresol, xylenol, hydroxy-diphenyl, benzylphenol, phenyl-ethyl-phenol, phenol resins, methyl-hydroxydiphenyl, alpha and beta naphthol, xylyl naphthol, benzyl phenol, anthranol, phenyl-methyl naphthol, phenanthrol, 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. Mixed alkyl-aryl and aralkyl-aryl ethers such as anisole and beta-naphthyl-methyl ether are given as examples because the Friedel-Crafts reaction with these ethers is accompanied by some rearrangement, yielding free hydroxyl groups.

The substitution of the alkyl acid residue for a nuclear hydrogen atom in the alkylated hydroxyaromatic compound or product may be effected (*a*) by condensation of the alkylated hydroxyaromatic compounds with unsaturated aliphatic acids such as oleic acid, using a so-called kationoid catalyst; (*b*) by condensation of the alkylated hydroxyaromatic compounds with halogenated aliphatic or cyclo-aliphatic acids such as chloracetic, chlorstearic and chlornaphthenic acids with a Friedel-Crafts reaction, aluminum chloride being a preferred catalyst; and (*c*) by rearrangement of aryl ether aliphatic acids in the presence of kationoid catalysts such as HCl gas. The preferred procedure consists in condensing the unsaturated acids with the alkylated hydroxyaromatic compounds in the presence of anhydrous $AlCl_3$. Acids which may be used in this preferred procedure are typified by oleic, elaidic, maleic, acrylic, erucic, and sorbic acids. Procedure (*c*) above gives a wider latitude of aliphatic acid substituents to choose from; typical chlor-acids which may be used in this procedure being chloracetic acid, chlorbutyric acid, chlorcaprylic acid, chlorpalmitic acid, chlorstearic acid, etc.

The metal-phenate, metal-carboxylate salts derived from complex acids of the type obtained according to the foregoing general procedures may be prepared (*a*) by reacting the alkylated hydroxyaryl-aliphatic acid with an alcoholate of the desired metal in an amount equivalent to the combined hydroxyl and carboxyl content, (*b*) by formation first of the alkylated hydroxyaro-

matic carboxylate salt, followed by reaction with an alcoholate of the desired metal to replace the hydroxyl hydrogen, and (c) by reaction of the alkyl-substituted hydroxyaryl-aliphatic acid with an alkali (sodium) alcoholate in an amount sufficient to neutralize both the hydroxyl and carboxyl hydrogens, followed by double decomposition with an equivalent amount of an alcohol-soluble anhydrous salt of the desired metal.

The metals contemplated herein may be broadly classified as metals of groups one to eight, inclusive, of the periodic system, which are capable of forming carboxylate salts. These metals comprise the following: the alkali metals: lithium, sodium, potassium, rubidium and caesium; the alkaline earth group: beryllium, magnesium, calcium, strontium and barium; the metals zinc, cadmium, mercury, scandium; the metals 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, iridium and platinum.

Some of the rare earth metals are given in the foregoing. Other rare earth metals suitable for the formation of the phenate-carboxylate metal salts of hydroxyaromatic-aliphatic acids are those now commercially available as the cerium and yttrium group: namely, a mixture of praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thallium and lutecium.

As stated above, the Friedel-Crafts reaction for alkylating the hydroxyaromatic compound 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 IV) 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 monochlor-aliphatic hydrocarbon containing, say, three atomic proportions of chlorine is reacted with one molecular proportion of hydroxyaromatic compound, the resulting alyklated product, $R^v(T(OH)Y_b)_n$, is one in which v and n are equal to 1 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 3 atomic proportions of chlorine is reacted with 1 molecular proportion of hydroxyaromatic compound, the product would be one in which v and n of general Formula IV are each equal to 3, 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 we consider it preferable that the number of valence bonds "v" (in R^v of Formulae IV, etc.) be maintained within the range of from 1 to 4 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 aliphatic substituent is a heavy alkyl group such as a wax derivative and the agent is to be used for multifunctional activity in viscous oils, is not obtained with materials predominantly comprised of a compound or compounds

$$R^v(T(OM)(Z.COOM')Y_b)_n$$

(Formula IV) in which v and n are greater than 4. 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-chlor-aliphatic 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 alkylated metal-oxyaromatic aliphatic acid salt derived therefrom according to the reactions described above will likewise be a mixture of compounds corresponding to different values of n and v in general Formula IV. 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 IV or in mixtures thereof, we 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

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

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 (in the case of a high molecular weight aliphatic hydrocarbon) 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 mol 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.

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

Further details in the procedures which may be followed in synthesizing the preferred multifunctional oil-improving agents contemplated herein will appear from the following examples describing the preparation of the metal-phenate, metal-carboxylate salts of wax-hydroxyphenyl-stearic acids:

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 from 16 per cent to 20 per cent of chlorine, such product having an average composition between a monochlor-wax and a dichlor-wax or corresponding roughly to a dichlor-wax. Preferably the chlorination is continued until about ⅙ the weight of the "chlor-wax" formed is chlorine. A quantity of chlor-wax thus obtained, containing 3 atomic proportions of chlorine, is heated to a temperature varying from just above its melting point to not over 150° F., and 1 mol 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 about 3 per cent of the weight of the chlor-wax 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 (to control the evolution of HCl gas) to a temperature of from 250° F. to 300° F.–350° F. 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.

Removal of non-alkylated material (phenol) 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 drying 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 1 to 4; 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 1 to 4 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 3 atomic proportions of chlorine (16 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 metaloxyaromatic-aliphatic-metal carboxylate derivatives.

2. Formation of Wax-Substituted Hydroxyphenyl Stearic Acid

(a) Condensation of unsaturated aliphatic acids with wax-phenol

One molecular proportion of wax-phenol (3–16) prepared according to the foregoing procedure was admixed with one molecular proportion of oleic acid. The mixture was heated to a temperature of about 150° F. and one molecular proportion of $AlCl_3$ was gradually added thereto with stirring to control the evolution of HCl. After addition of the aluminum chloride the temperature of the reaction mixture was raised to about 250° F. and held at that temperature during a two-hour period to complete the reaction.

The reaction mixture was then treated with water and kept acid with hydrochloric acid to remove all traces of aluminum, being repeatedly washed until the aqueous extract did not contain $Al(OH)_3$ when made ammoniacal, followed by washing with water until free of HCl. The operation of water-washing was facilitated by the use of a diluent such as benzol or Stoddard Solvent, the solvent thereafter being distilled, whereby any entrained water was removed. The reaction product was then steam-treated with superheated steam at a temperature of about 200° C. to remove any unreacted aliphatic acid. The operation of steam-treating is facilitated by use of a stirrer, whereby better contacting with steam is obtained and run-back of condensed water is eliminated. Steam was passed through

the mixture at about 200° C. until the distillate showed a negligible neutralization number, indicating that any unreacted aliphatic acid was removed. When the steam-treat was finished, which generally requires about 10 hours, the steam vapors were removed by blowing with a non-oxidizing gas such as nitrogen, thereby yielding an anhydrous product, wax-hydroxyphenyl-stearic acid, in which the stearic acid group was attached to the phenyl nucleus at an intermediate point on the chain.

By the use of a polycarboxylic acid such as maleic acid, at least dicarboxylation results, forming hydroxyphenyl-succinic acid. By using wax-naphthol the corresponding wax-naphthol-aliphatic acid is obtained.

(b) Condensation of halogenated aliphatic acids with wax-phenol

In this procedure one mol of wax-phenol (3–16) was condensed with one mol of chlorstearic acid in the presence of one mol of $AlCl_3$ following the same procedure for reaction and purification described above. The product here was wax-hydroxyphenyl-alpha-stearic acid, since the condensation took place at the alpha carbon atom of the stearic acid group.

In both of the procedures (*a*) and (*b*) described above the isolated or purified wax-hydroxy-aromatic compound may be used. However, it is preferred to react the alkylated or wax-substituted phenol with the aliphatic acid without removing the aluminum or $AlCl_3$ therefrom following the Friedel-Crafts condensation.

3. Formation of the Metal Salts

Because of the tendency of alkali metal salts to emulsify, it is advantageous to prepare such salts in non-aqueous medium. The acid is treated with an alkali alcoholate (prepared from amyl or lower alcohol) or with a solution of alkali hydroxide in alcohol in an amount sufficient to neutralize the hydroxyl and the carboxyl group. The reaction mixture is heated at about 300° F. for an hour, allowing the alcohol to distill to obtain the finished product. If the alkali hydroxide is used instead of the metal alcoholate, the water of reaction is removed along with the alcohol.

The salts or derivatives of metals other than the alkali metals are preferably prepared by first neutralizing the hydroxyl and carboxyl hydrogens with an alkali metal such as sodium according to the procedure described above and then effecting a double decomposition with an equivalent amount of an alcohol-soluble anhydrous salt of the desired metal. For example, the sodium salt may be prepared according to the foregoing procedure, after which it is reacted with an alcohol solution of cobaltous chloride having a cobalt content equivalent to the sodium in the original salt. The reaction mixture is heated to a temperature of about 350° and held at that temperature for about 2 hours, during which time the alcohol distills off with completion of the reaction. The cobalt salt of the wax-hydroxyphenyl stearic acid thus formed is purified by settling and centrifuging or water-washing to remove reaction salts.

We have found that salts of the type contemplated herein in which the carboxyl group is in an aliphatic or cycloaliphatic substituent are superior to similar wax-aromatic acid salts in which the carboxyl group is attached to the nucleus in that the reaction salts formed in their synthesis may be more easily removed and further in that they have less tendency to emulsify.

Salts of wax-substituted hydroxyaromatic carboxylic acids can be prepared from other mono- or poly-cyclic and mono- or poly-hydric hydroxy-aromatic compounds and other aliphatic or cycloaliphatic acids by following the general procedure described. Salts of wax-substituted naphthol-stearic acid, for example, represent another group of desirable oil-improving agents within the general class contemplated herein. Similar salts may also be obtained with other alkyl substituents than those derived from petroleum wax, although, as indicated above, aliphatic hydrocarbons of the so-called "petroleum wax" or "wax" type (having at least 20 carbon atoms) are preferred because of the multifunctional activity of the resulting products.

To demonstrate the effectiveness of compounds or products of the type herein described as mineral oil-improving agents, 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 typical improving agents of the type contemplated herein.

POUR POINT-DEPRESSION

The metal salts of wax-substituted hydroxy-aromatic aliphatic acids of the type contemplated herein, in which both the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal, are, except in certain instances where the aryl nucleus carries another substituent such as a low alkyl group, effective pour point-depressants, as indicated by representative compounds in Table I below. The results in this table were obtained from blends of mineral lubricating oil having a Saybolt viscosity of 67 seconds at 210° F. and an A. S. T. M. pour test of +20° F.

Table I

Improving agent	A. S. T. M. pour tests on oil blends containing improving agents			
	0%	¼%	⅛%	1%
	Deg.	*Deg.*	*Deg.*	*Deg.*
Cobaltous phenate-cobaltous carboxylate salt of wax-hydroxyphenyl-stearic acid (3–16)	+20	−20	−10	------
Vanadyl phenate-vanadyl carboxylate salt of wax-hydroxyphenyl-stearic acid (3–14)	+20	−25	+10	------
Cobaltous phenate-cobaltous carboxylate salt of wax-naphthol-stearic acid (3–14)	+20	0	+20	------
Cobaltous phenate-cobaltous carboxylate salt of wax-cresol-stearic acid (2–16)	+20	------	------	+25
Titanium phenate-titanium carboxylate salt of wax-hydroxyphenyl-stearic acid (3–14)	+20	−10	+10	------
Stannous phenate-stannous carboxylate salt of wax-hydroxyphenyl-stearic acid (3–14)	+20	−15	+5	------

V. I. IMPROVEMENT

As was previously pointed out, certain substituents such as low alkyls in the wax-substituted aryl nucleus tend to reduce materially the pour-depressing action of the improving agents herein without disturbing the property of these compounds to improve the viscosity index. The effect on the pour-depressing action is indicated by the cresol derivative in the above table, and the effectiveness of these compounds to improve the viscosity index is indicated in Table II below. The viscosity index (V. I.) data was obtained in the conventional manner from the Saybolt viscosity of the oil and the oil blends at 100° F. and

210° F. The oil used was a viscous mineral oil of the lubricant type.

Table II

Improving agent used	Wt. conc.	100°	210°	V. I.
	Per cent			
None		142.3	41.8	76.1
Cobaltous phenate-cobaltous carboxylate salt of wax-hydroxyphenyl-stearic acid (3-16)	1	148.9	42.6	86.2
Vanadyl phenate-vanadyl carboxylate salt of wax-hydroxyphenyl-stearic acid (3-14)	1	151.7	42.5	80.8
Cobaltous phenate-cobaltous carboxylate salt of wax-naphthol stearic acid (3-14)	1	158.1	43.4	91.9
None		141.2	41.8	78.3
Cobaltous phenate-cobaltous carboxylate salt of wax-hydroxyphenyl-stearic acid (3-14)	1	153.3	43.1	92.4
Cobaltous phenate-cobaltous carboxylate salt of wax-cresol stearic acid (2-16)	1	153.3	43.1	92.4
Cobaltous phenate-cobaltous carboxylate salt of wax-xylenol alpha-stearic acid (2-18)	1	151.6	42.7	85.2
Cobaltous phenate-cobaltous carboxylate salt of wax-chlor-hydroxyphenyl-stearic acid (2-16)	1	149.7	42.8	90.9
Cobaltous phenate-cobaltous carboxylate salt of wax-p-hydroxyphenyl-stearic acid (2-14)	1	155.2	42.9	84.5
Cobaltous phenate-cobaltous carboxylate salt of wax-amyl beta-naphthol-stearic acid (3-18)	1	156.7	43.3	91.8
Titanium phenate-titanium carboxylate salt of wax-hydroxyphenyl-stearic acid (3-14)	1	152.2	42.8	86.8
Stannous phenate-stannous carboxylate salt of wax-hydroxyphenyl-stearic acid (3-14)	1	152.3	42.7	84.1

OPERATION TEST

In addition to the foregoing tests we have also made tests on an oil and an oil blend containing a representative improving agent of the type contemplated herein to determine the comparative behavior of the unblended oil and the improved oil under actual operating conditions. The test was carried out in a single cylinder C. F. R. engine. The engine was operated continuously over a time interval of 28 hours, with the cooling medium held at a temperature of about 390° F., at a speed of 1200 R. P. M., which was equivalent to a road speed of about 25 miles per hour. The oil temperature was held at about 150° F. during the test.

The oil used in this test was a lubricating oil stock of 120 seconds Saybolt viscosity at 210° F. and the conditions observed 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, and (*c*) the amount of carbonaceous deposits in the oil. The "Oil" indicated as "A" in Table III below is the unblended oil; Oil "B" is the same oil containing ⅓ per cent of the cobaltous phenate-cobaltous carboxylate salt of wax-hydroxyphenyl alpha-stearic acid (3-16); Oil "C" is another sample of unblended oil; and Oil "D" is Oil "C" blended with ⅛ per cent of the vanadyl phenate-vanadyl carboxylate salt of wax-hydroxyphenyl-stearic acid (3-14).

Table III

Oil	Ring condition								Carbon deposits	N. N.
	Degrees stuck					Percent slots filled				
	1	2	3	4	5	3	4	5		
A	180	0	360	360	0	40	40	25	11.97	2.2
B	0	0	0	0	0	0	0	0	5.31	0.3
C	270	360	360	360	330	75	90	50	13.9	3.3
D	0	0	0	0	0	10	0	0	4.3	1.8

From the foregoing results it will be apparent that phenate-carboxylate metal salts of alkylated hydroxyaromatic aliphatic acids of the type contemplated by this invention are effective oil-improving agents and the preferred wax-substituted products are characterized by the fact that they have, through the presence of the wax-substituted aryl nucleus and the metal substituents, multifunctional activity. Although we do not wish to be bound in any regard by any theory as to the function which the metal substituents have, it is believed that such substituents act by promoting the preferential oxidation of the alkylated hydroxyaromatic-aliphatic acid salt molecule, thereby taking up active oxygen and acting as a direct antioxidant; also by acting as a peptizing agent on any sludge that is formed in the oxidation of the oil; and in the event an alkali or alkaline earth metal is present as the metal substituent, the salts act by neutralizing strong acids in the oil, particularly sulfur acids such as may be formed by oxidation. The improved properties obtained and the degree of improvement in a particular property may be varied with the metal substituents, the aryl constituents, the degree of alkylation of the aryl nucleus, and the aliphatic acid residue.

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 without tendency toward gelation—that is, one which will remain uniformly dispersed in the oil in sufficient amount to effect the desired improvement under normal conditions of storage and use.

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 hydroxyaromatic-aliphatic acid salts of the type described herein may be used in amounts ranging from one-sixteenth per cent to ten per cent, and in general compositions of the desired improved properties may be obtained with these improving agents in amounts of from one-sixteenth per cent to two per cent.

It is to be understood that while we have described certain preferred procedures which may be followed in the preparation of the alkylated hydroxyaromatic-aliphatic acid salts used as improving agents in the mineral oil compositions contemplated by this invention and have referred to various representative constituents in these improving agents, 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.

We claim:

1. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which part of the hydrogen of the aromatic nucleus 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 metal salt of an hydroxyaromatic aliphatic carboxylic acid

in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which part of the hydrogen of the aromatic nucleus has been substituted with predominantly aliphatic material, said last-mentioned substituent comprising a sufficient proportion of said salt 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 metal salt of a hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal.

4. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which the alkyl substituent is attached to the aromatic nucleus and is derived from an aliphatic hydrocarbon having at least twenty carbon atoms.

5. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which the alkyl substituent is attached to the aromatic nucleus and is derived from petroleum wax.

6. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal, the alkyl substituent in said salt being a high molecular weight aliphatic hydrocarbon derivative and the aromatic nucleus being poly-substituted with said aliphatic derivative.

7. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal, the alkyl substituent in said salt being derived from an aliphatic hydrocarbon having at least twenty carbon atoms and the aromatic nucleus being poly-substituted with said aliphatic derivative.

8. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal, the alkyl substituent in said salt being a derivative of petroleum wax and the aromatic nucleus being poly-substituted with said wax derivative.

9. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted hydroxy-phenyl aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal.

10. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted naphthol-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal.

11. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted hydroxy-phenyl stearic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which the alkyl substituent is derived from petroleum wax.

12. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible salt of an alkyl-substituted naphthol-stearic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which the alkyl substituent is derived from petroleum wax.

13. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted hydroxy-phenyl stearic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which the alkyl substituent is derived from petroleum wax, the said phenyl nucleus being poly-substituted with said wax derivative.

14. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible salt of an alkyl-substituted naphthol-stearic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which the alkyl substituent is derived from petroleum wax the said naphthol nucleus being poly-substituted with said wax derivative.

15. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of a metal salt of an hydroxyaromatic condensation product comprising a hydroxyaromatic nucleus in which the hydroxyl hydrogen is replaced with metal and in which at least one nuclear hydrogen atom is substituted with an alkyl carboxylate radical selected from the group consisting of aliphatic and cyclo-aliphatic acid radicals wherein the carboxyl hydrogen is replaced with its equivalent weight of metal and in which at least one other nuclear hydrogen atom is substituted with an aliphatic hydrocarbon radical of at least twenty carbon atoms.

16. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of a metal salt of an hydroxyaromatic condensation product comprising a hydroxyaromatic nucleus in which the hydroxyl hydrogen is replaced with metal and in which at least one nuclear hydrogen atom is substituted with an alkyl carboxylate radical selected from the group consisting of aliphatic and cyclo-aliphatic acid radicals wherein the carboxyl hydrogen is replaced with its equivalent weight of metal and in which at least one other nuclear hydrogen atom is substituted with an aliphatic hydrocarbon radical derived from petroleum wax.

17. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of a metal salt of an hydroxyaromatic condensation product comprising a hydroxyaromatic nucleus in which the hydroxyl hydrogen is replaced with metal and in which at least one nuclear hydrogen atom is substituted with an alkyl carboxylate radical selected from the group consisting of aliphatic and cyclo-aliphatic acid radicals wherein the carboxyl hy-

drogen is replaced with its equivalent weight of metal and in which at least one other nuclear hydrogen atom is substituted with an aliphatic hydrocarbon radical of at least twenty carbon atoms and at least one other hydrogen atom of the characterizing aromatic nucleus being substituted with a radical selected from the group consisting of hydroxyl, aralkyl, aryl, alkaryl, halogen, nitro, amino and organic ester radicals and alkyl radicals containing less than twenty carbon atoms.

18. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of a metal salt of an hydroxyaromatic condensation product comprising a hydroxyaromatic nucleus in which the hydroxyl hydrogen is replaced with metal and in which at least one nuclear hydrogen atom is substituted with an alkyl carboxylate radical selected from the group consisting of aliphatic and cyclo-aliphatic acid radicals wherein the carboxyl hydrogen is replaced with its equivalent weight of metal and in which at least one other nuclear hydrogen atom is substituted with an aliphatic hydrocarbon radical derived from petroleum wax and at least one other hydrogen atom of the characterizing aromatic nucleus being substituted with a radical selected from the group consisting of hydroxy, alkoxy, aroxy, aralkyl, aryl, alkaryl, halogen, nitro, amino and organic ester radicals and alkyl radicals containing less than twenty carbon atoms.

19. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal, said metal substituents being selected from metals of groups one to eight of the periodic system.

20. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of a product of the type obtained by: chlorinating petroleum wax until about one-sixth of the reaction product is chlorine; reacting the chlorinated wax with a hydroxyaromatic compound in the proportion of one mol of the latter to an amount of the chlorinated wax containing from two to three atomic proportions of chlorine to form a wax-substituted hydroxyaromatic compound; substituting at least one nuclear hydrogen on the aromatic nucleus with an aliphatic acid group to form a wax-substituted hydroxyaromatic-aliphatic acid; and then substituting the hydroxyl hydrogen and the carboxyl hydrogen with metal.

21. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith a minor proportion, from about one-sixteenth to about ten per cent, of an oil-miscible metal salt of an alkyl-substituted hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal.

22. 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 ten per cent, of an oil-miscible metal salt of an alkyl-substituted hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal, said alkyl substituent being derived from petroleum wax and attached to said hydroxyaromatic nucleus.

23. 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:

$$R^v(T(OM)(Z.COOM')Y_b)_n$$

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 M, said group being attached to the nucleus T; (Z.COOM') represents an aliphatic acid residue in which Z is an alkyl radical attached to the nucleus T and selected from the group consisting of aliphatic and cyclo-aliphatic radicals, and COOM' is at least one carboxyl group attached to the alkyl radical Z, the carboxyl hydrogen thereof being replaced by a metal M'; R^v represents at least one aliphatic group having a valence v of one to four and is attached by one valence bond only to at least one nucleus T; Y_b represents a monovalent radical selected from the group consisting of residual hydrogen, and hydroxy, alkoxy, aroxy, aralkyl, aryl, alkaryl, halogen, nitro, amino and organic ester radicals; b represents the number of Y_b's and is equal to zero or a whole number corresponding to the valence bonds on the nucleus T not satisfied by R^v, (OM) or (Z.COOM'); and n is a whole number from one to four; the substituent R^v comprising a sufficient proportion of the metalorganic compound to render same miscible with said oil under normal conditions of handling and use.

24. 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:

$$R^{v'}(T(OM)(Z.COOM')Y_bR_c)_n$$

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; (Z.COOM') represents an aliphatic acid residue wherein Z is an alkyl radical attached to the nucleus T and selected from the group consisting of aliphatic and cyclo-aliphatic radicals and COOM' represents at least one carboxyl group attached to the alkyl radical Z and wherein the carboxyl hydrogen is replaced with its equivalent weight of a metal M'; $R^{v'}$ 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 and chlorine, hydroxy, alkoxy, aroxy, aralkyl, aryl, alkaryl, halogen, nitro, amino and organic ester 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), (COOM') 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 coresponding to the valences on the nucleus T not satisfied by $R^{v'}$, (OM), (COOM') and Y_b; and n is a whole number from two to four.

25. An improving agent for mineral oils and the like comprising a metal salt of an alkyl-substituted hydroxyaromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which the alkyl substituent contains at least twenty carbon atoms and is attached to the aromatic nucleus.

26. An improving agent for mineral oils and the like comprising a metal salt of an hydroxy-aromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which at least one nuclear hydrogen atom of the aromatic nucleus is substituted with an aliphatic hydrocarbon group containing at least twenty carbon atoms.

27. An improving agent for mineral oils and the like comprising a metal salt of an hydroxy-aromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which at least one nuclear hydrogen atom of the aromatic nucleus is substituted with an aliphatic hydrocarbon group containing at least twenty carbon atoms, and at least one other nuclear hydrogen atom of the aromatic nucleus being substituted with a radical selected from the group consisting of hydroxy, alkoxy, aroxy, aralkyl, aryl, alkaryl, halogen, nitro, amino and organic ester radicals and aliphatic hydrocarbon radicals containing less than twenty carbon atoms.

28. An improving agent for mineral oils and the like comprising a metal salt of an hydroxy-aromatic-aliphatic carboxylic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal and in which at least one nuclear hydrogen atom of the aromatic nucleus is substituted with an aliphatic hydrocarbon group derived from petroleum wax.

29. An improving agent for mineral oils and the like comprising a metal salt of wax-substituted hydroxy-phenyl-stearic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal.

30. An improving agent for mineral oils and the like comprising a metal salt of wax-substituted naphthol-stearic acid in which the hydroxyl hydrogen and the carboxyl hydrogen are substituted with metal.

31. An improving agent for mineral oils and the like comprising a metalorganic compound having the general formula

$$R^v(T(OM)(Z.COOM')Y_b)_n$$

in which: T represents an aromatic nucleus; (OM) represents at least one hydroxyl group attached to the nucleus T, the hydroxyl hydrogen thereof being replaced with its equivalent weight of a metal M; (Z.COOM') represents an aliphatic acid residue in which Z is an alkyl radical attached to T and selected from the group consisting of aliphatic and cyclo-aliphatic hydrocarbon radicals, and COOM' represents at least one carboxyl group with the hydrogen replaced by an equivalent weight of metal M' and attached to the alkyl radical Z; R^v represents at least one aliphatic group having a valence v of one to four and is attached by one valence bond only to at least one nucleus T; Y_b represents a monovalent radical selected from the group consisting of residual hydrogen and chlorine, hydroxy, alkoxy, aroxy, aralkyl, aryl, alkaryl, halogen, nitro, amino and organic ester radicals; b represents the number of Y_b's and is equal to zero or a whole number corresponding to the valence bonds on the nucleus T not satisfied by R^v, (OM) or (Z.COOM'); and n is a whole number from one to four; the substituent R^v comprising a sufficient proportion of the metalorganic compound to render same miscible with a mineral oil fraction under normal conditions of handling and use.

32. An improving agent for mineral oils and the like comprising a metalorganic compound having the general formula:

$$R^v(T(OM)(Z.COOM')Y_bR_c)_n$$

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; (Z.COOM') represents an aliphatic acid residue wherein Z is an alkyl radical attached to the nucleus T and selected from the group consisting of aliphatic and cyclo-aliphatic radicals and COOM' represents at least one carboxyl group attached to the alkyl radical Z and wherein the carboxyl hydrogen is replaced with its equivalent weight of a metal M'; 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 and chlorine, hydroxy, alkoxy, aroxy, aralkyl, aryl, alkaryl, halogen, nitro, amino and organic ester 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), (COOM') 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), (COOM') and Y_b; and n is a whole number from two to four.

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