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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 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 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 multifunctional compound selected from that group or class of metal-organic compounds which may be designated as the oil-soluble or oil-miscible metal salts of alkyl-substituted aryl ether acids. More specifically our invention contemplates as oil-improving agents the oil-miscible metal salts of alkyl-substituted aroxy aliphatic acids and alkylated aroxy-aromatic acids in which the hydrogen of the carboxyl group or groups is substituted with metal. We have discovered that metal salts of alkylated aryl ether acids 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 aryl ether acid.

The oil-improving agents contemplated by this invention may be considered as alkylated hydroxyaromatic compounds in which the hydroxyl hydrogen is replaced with an organic acid group such as an aromatic acid group or an aliphatic acid group in which acid group the carboxyl hydrogen is substituted with its equivalent weight of metal. The compounds or products which are preferred, particularly from a standpoint of synthesis, may be considered as alkylated hydroxyaromatic compounds in which the hydroxyl hydrogen is replaced with an alkyl or aryl metal carboxylate group. Compounds or compositions of this type are characterized by the presence of an aromatic nucleus in which at least one nuclear hydrogen has been substituted with an ether acid or an oxy acid substituent, in which substituent the carboxyl hydrogen has been replaced with its equivalent weight of metal. This characterizing group may be represented by the formula: T (O.Z.COOM) in which T represents an aromatic nucleus; and (O.Z.COOM) represents at least one ether acid or oxy acid substituent in which Z represents an aromatic or aliphatic group having at least one carboxyl group, the hydrogen of which is replaced with its equivalent weight of a metal M.

The metal salts of aryl ether 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, and 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. 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 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 aryl ether acids having the characterizing group T(O·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, are 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:

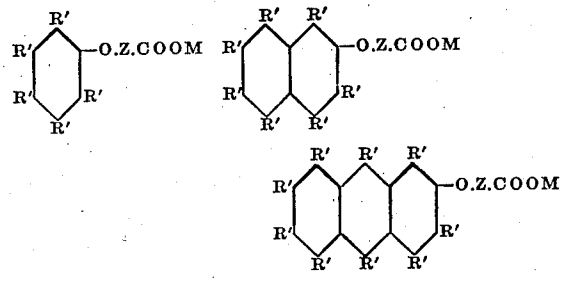
I. $R(T(O\cdot Z\cdot COOM))$

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 (O·Z·COOM) 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 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:

II. $R(T(O\cdot Z\cdot COOM)Y)$

in which R, T, and (O·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: 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 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 valences are attached to separate aromatic nuclear groups T.

Compounds of this type are included under the following general formula representation:

III. $R^v(T(O\cdot Z\cdot COOM)Y_b)_n$

in which T and (O·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 valance 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 and (O·Z·COOM); and n represents a whole number from one to four and indicates the total number of groups $(T(O\cdot Z\cdot COOM)Y_b)$ present in the molecule represented by the formula which are attached to the aliphatic group or groups represented by R^v through the 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 on 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 substituents, are included under the subgeneric formula representation:

IV. $R^{v'}(T(O\cdot Z\cdot COOM)Y_{b'}R_c)_{n'}$

in which T and (O·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 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 $R^{v'}$, (O·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 $R^{v'}$, (O·Z·COOM) and $Y_{b'}$; and n' represents a whole number from two to four and indicates the total number of the groups

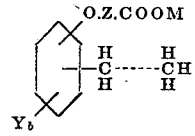
$(T(O\cdot Z\cdot COOM)Y_{b'}R_c)$

present in the molecule represented by the formula which are attached to the aliphatic group or groups represented by $R^{v'}$ through the valances 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 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 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 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 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:

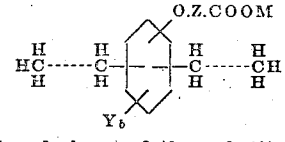
A.



In the above formula the chain represents the oil-solubilizing alkyl substituent (R^v), and Y_b and (O·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 one and in which there are two such monovalent R^v groups, may be represented by the following formula:

B.

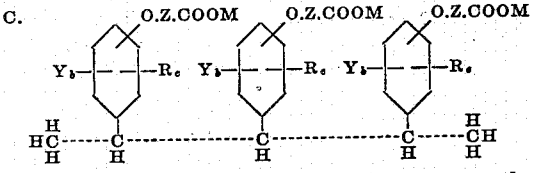


in which the chains and the substituent characters have the same significance defined above.

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:

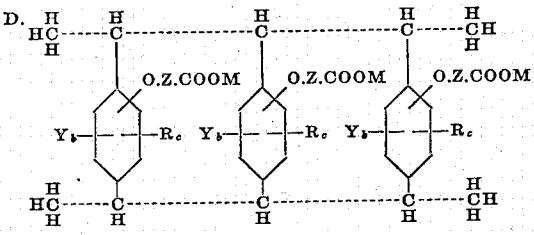
C.



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.

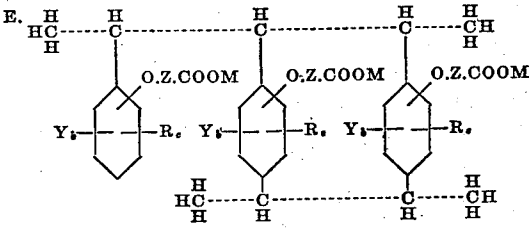
D.



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 used in the mineral oil compositions 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. 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 our 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 of the alkylated hydroxyaromatic compound from which the alkylated aryl ether acid 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 polycyclic); (*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; 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 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.

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 $(T(O{\cdot}Z{\cdot}COOM))_n$ to $R^v(T(O{\cdot}Z{\cdot}COOM))_n$ expressed as:

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

should not be greater than about .20 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 to about 0.6 by 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 twenty parts by weight of the former to about 100 parts by weight of the latter, or about twenty 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 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 multi-functional 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 a total of at least twenty-five carbon atoms for each aromatic nucleus T.

The ratio of twenty 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. For example, as will later apear, 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 sixteen per cent.

A further general guide for the synthesis of the prefered improving agents for viscous oils is to alkylate the aromatic nucleus so that 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. Our 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 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 contribute to solubility—and the properties of the agents may also be varied with the character of the metal substituent in the carboxyl group. In general, it appears that the oil-miscible 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 copper, lead, and zinc, may serve to increase the load-carrying capacity of lubricating oils.

Procedures whereby the oil-improving agents contemplated by this invention in which the oxyacid substituent is derived from a fatty acid can be prepared, may be broadly described as follows:

First the hydroxyl hydrogen in an alkylated hydroxyaromatic compound is substituted with an alkali metal to form an alkylated aryl alkali metal oxide:

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

The aryl metal oxide thus formed is then reacted with the alkali metal salt of a chlor (mono or poly basic) aliphatic acid to form the corresponding ether acid salt according to the following equation:

(b) $$R^v(T(OM^a)Y_b)_n + Cl{\cdot}Z'{\cdot}COOM^a \rightarrow R^v(T(O{\cdot}Z'{\cdot}COOM^a)Y_b)_n + M^aCl$$

in which $Cl{\cdot}Z'{\cdot}COOM^a$ represents the sodium salt of a chlor aliphatic acid, Z' in this case being an aliphatic group. This reaction may also be expressed as follows:

(b') $$R^v(T(OM^a)Y_b)_n + Cl(C_nH_{2n}){\cdot}COOM^a \rightarrow R^v(T(O{\cdot}(C_nH_{2n}){\cdot}COOM^a + M^aCl$$

Another desirable procedure for the formation of alkali metal salts of alkylated aryl ether acids in which the ether acid substituent is an aliphatic acid derivative consists in reacting an ester of the chlor aliphatic acid instead of the alkali salt of the aliphatic acid with the alkylated aryl metal oxide, followed by saponification of the product according to the following equations:

(c) $$R^v(T(OM^a)Y_b)_n + Cl{\cdot}Z'{\cdot}COOR'' \rightarrow R^v(T(O{\cdot}Z'{\cdot}COOR'')Y_b)_n + M^aCl$$

(c') $$R^v(T(O{\cdot}Z'{\cdot}COOR'')Y_b)_n + M^aOH \rightarrow R^v(T(O{\cdot}Z'{\cdot}COOM^a)Y_b)_n + R''{\cdot}OH$$

Alkali metal ether acid "salts" formed in the foregoing exemplary procedures may be obtained with the alkali metal salts of any chlor-aliphatic acid such as sodium, chlor-acetate, butyrate, heptylate, palmitate, stearate, etc. It is preferred that the reactions be carried out in the presence of a non-aqueous medium.

The ether acid salts in which the ether acid or oxyacid substituents is derived from an aliphatic acid are considered preferred from the standpoint of synthesis, but it is to be understood that similar salts may be obtained in which the group $\cdot Z\cdot COOM$ in the ether acid substituent $(O{\cdot}Z{\cdot}COOM)$ represents the residue of an aromatic acid salt. Alkali salts of diaryl ether

acids of this character can be synthesized by reacting an alkyl-substituted aryl alkali metal oxide with a brom-aryl alkali carboxylate in the presence of a small percentage of powdered copper as a catalyst, the reaction mixture being heated to about 400° F. This reaction may be represented by the following equation:

$$(b'')\quad R^v(T(OM^a)Y_b)_n + Br.Z''.COOM^a \xrightarrow{Cu} R^v(T(O.Z''.COOM^a)Y_b)_n + M^aBr$$

in which $Br\cdot Z''\cdot COOM^a$ indicates a brom-aromatic alkali carboxylate, such, for example, as brom-sodium benzoate.

These alkali metal ether acid salts of both the aryl-alkyl carboxy and the diaryl-carboxy type, when purified, constitute one group of metal salts contemplated by this invention. Corresponding "salts" of polyvalent metals may be formed by a double decomposition of the alkali metal salt in the presence of a suitable solvent as follows:

$$(d)\quad R^v(T(O\cdot Z\cdot COOM^a)\cdot Y_b)_n + MX \rightarrow R^v(T(O\cdot Z\cdot COOM)Y_b)_n + M^aX$$

in which MX indicates a salt of the metal M which is soluble in a solvent for the ether acid salt in which the corresponding alkali metal salt M^aX is insoluble.

Metal salts of alkylated aryl ether acids can also be formed by first neutralizing the alkali metal salt with mineral acid to form the ether acid, followed by water washing to purify the product, and then reacting the anhydrous acid with the alcoholate of the desired metal according to the following equation:

$$(e)\quad R^v(T(O\cdot Z\cdot COOH)Y_b)_n + Alk(OM) \rightarrow R^v(T(O\cdot Z\cdot COOM)\cdot Y_b)_n + Alk(OH)$$

in which Alk(OM) indicates an alcoholate of the metal M.

The details of the foregoing procedures will be discussed hereinafter with specific examples.

The metal substituents in the ether acid group attached to the aroxy nucleus 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 reactions described and illustrated above, have 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 hydroxy-aromatic 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 addition 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, alpha and beta naphthol, alpha and beta methyl naphthol, tolyl naphthol, xylyl naphthol, benzyl naphthol, 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.

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.

We 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 for 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 polychlorine-substituted aliphatic compound or material is reacted with the desired hydroxyaromatic compound in the presence of a catalytic amount of aluminum chloride. Pure or substantially pure mono- or 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, we prefer to employ a mixture of such hydrocarbons, such as a suitable petroleum fraction, as the starting material for our 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 350 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 trichloraliphatic 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 we consider it preferable that the number of valence bonds *v* (in R^v of Formulae II, 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 aliphatic substituent is 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 $R^v(T(O\cdot Z\cdot COOM)Y_b)_n$ (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 *n* and *v* in the formula $R^v(T(OH)Y_b)_n$ and the final alkylated aryl ether acid salt derived therefrom according to the reactions of equations *b*, *b''*, *d*, etc., above will likewise be a mixture of compounds corresponding to different values of *n* and *v* in 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, 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 dichloraliphatic hydrocarbon. Such a product will, of course, contain some mono- and trichlor 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 we 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 $R^v(T(O\cdot Z\cdot COOM)Y_b)_n$ 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 hydroxyl hydrogen 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 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 hydroxy aromatic 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 PHENYL ETHER ACID SALTS

(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 sixteen per cent to twenty 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 one-fifth 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 about 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 around 300° F.–350° F. To control the evolution of HCl gas the temperature of the mixture is preferably raised from 250° F. to 300° F.–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 nonalkylated 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 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 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 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 (twenty per cent chlorine in the chlor wax) is reacted with one mole of phenol, may, for brevity herein, be designated as "wax-phenol (3–20)." Parenthetical expressions of this type (A—B) will be used hereinafter in connection with the alkylated hydroxyaromatic compound to designate (A) the number of atomic proportions of chlorine in chloraliphatic 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=20. This same designation will also apply to the aroxy metal salt carboxylate derivatives.

Wax-phenol (3–20) as obtained by the above procedure had a phenol content or a "phenolic ratio" of about sixteen per cent. Our research indicates that this phenolic ratio in the neighborhood of sixteen or seventeen per cent may be considered as representing about the maximum for satisfactory miscibility and multifunctional activity in viscous oils of the aroxy carboxylate metal salt derivatives of alkylated hydroxyaromatic compounds in which the alkyl substituent is derived from wax and the hydroxyaromatic constituent is derived from phenol (C_6H_5OH). Effective oil-improving agents can, however, be obtained from wax-phenol (3–16), in which the phenol content or phenolic ratio is in the neighborhood of twelve or thirteen per cent.

(2) Formation of Wax-Substituted Alkali or Alkaline Earth Metal Phenate

As an example of this step in the preparation of our oil-improving agents, wax-substituted sodium phenate can be prepared by the reaction of wax-phenol with metallic sodium in the presence of a non-oxidizing gas. The reaction mixture is heated at 500° F. during a two-hour period with rapid stirring to produce finely divided sodium and thereby accelerate the reaction. The proportions of reactants which were used in prepa-

ing a wax-substituted alkali metal phenate according to the above procedure were:

	Grams
Wax-phenol (13.2 per cent combined phenol content)	500
Sodium or equivalent amount of potassium	16

It will be understood, of course, that other reactions may be employed to effect the alkali metal substitution.

(3) Formation of Ether Acid Salts From Wax-Alkali Metal Phenate

(a) 24.7 grams of monochloracetic acid in 100 cc. of absolute ethyl alcohol was converted to sodium chloracetate by adding dropwise a standard alcohol solution of sodium hydroxide, maintaining the temperature of the reaction mixture below 100° F. This sodium chloracetate mixture was then added to a solution of 200 grams of wax-phenol (3–16) as the wax-sodium phenate, in 600 grams of mineral oil (Say. Vis. 244 sec. at 130° F.), and the reaction mixture was held at 150° F. during a two-hour period to form the wax-substituted phenoxy sodium acetate. By diluting the mixture sufficiently with Stoddard solvent or other appropriate diluent, the mixture can be centrifuged to remove reaction salts, thereafter removing the light diluent by distillation to obtain the pure product.

The wax-phenoxy acetic acid used in certain of the hereinafter described procedures can be obtained by neutralizing the reaction mixture, before purification, with hydrochloric acid. The free acid is purified by water-washing the product to remove reaction salts and drying to give a concentrated mineral oil blend of the finished product.

(b) 200 grams of wax-phenoxy-sodium acetate (3–16) in mineral oil solution was reacted with 17.68 grams of zinc chloride by adding dropwise an alcoholic solution of zinc chloride to the sodium ether acid salt (wax-phenoxy sodium acetate) and holding the temperature of the reaction mixture at a temperature of 175° F. during a two-hour period to complete the reaction. The mixture may be diluted with Stoddard solvent or other suitable diluent and the wax-phenoxy-zinc acetate (3–16) obtained can be purified by water-washing and distilling to remove the diluent.

(c) Cobaltous ethylate was formed by adding an alcoholic solution of 16.7 grams anhydrous cobaltous chloride to sodium ethylate (5.97 gm. Na content.) Without purification, the cobaltous ethylate was added to a mineral oil blend containing 200 grams of wax-phenoxy-acetic acid (3–16) and the reaction mixture was heated to 350° F. and held at that temperature for a two-hour period during which the alcohol distilled off with completion of the reaction. The wax-phenoxy cobaltous acetate thus formed can be purified by settling and centrifuging or water-washing to remove reaction salts.

(d) The same general procedures described above have been used in preparing wax-phenoxy-acetates from wax-phenol (3–19) having a combined phenol content or phenolic ratio of 15.7 per cent. Here the proportions of reactants for making the wax-sodium phenate were 200 grams of wax-phenol (15.7 per cent combined phenol) in 800 grams of mineral oil and eight grams of sodium as the sodium ethylate. 200 grams of wax-phenoxy acetic acid prepared from the wax phenate obtained above was reacted with 76.8 grams of sodium as sodium ethylate to form the wax-phenoxy-sodium acetate (3–19).

Wax-substituted aryl ether acid salts of the general character described above can be prepared from other wax-substituted hydroxyaromatic compounds, either mono- or poly-cyclic and substituted or unsubstituted, such, for example, as wax-naphthol (3–19) having a combined naphthol content of sixteen per cent and equivalent phenol content or "phenolic ratio" of 9.7 per cent. They may also be obtained with other alkyl substituents than petroleum wax, although, as indicated above, alkylated hydrocarbons of the wax type (having at least twenty carbon atoms) are preferred because of the multifunctional activity of their products. It is also emphasized that the invention is not limited to products obtained from acetic acid as a source for the ether acid substituent but that any chloraliphatic acid (as the alkali salt thereof) may be used to obtain various alkyl chains or groups in the ether acid or oxy-acid substituent. Also, as we have previously pointed out, the wax-phenoxy-aromatic carboxylate types of salts are contemplated herein. Such compounds can best be prepared from a wax-alkali phenate and brom-aromatic acid, the reaction being carried out at elevated temperature in the presence of powdered copper as a catalyst.

Wax-aryl ether acid salts of the type described above are highly viscous rubber-like products, which with the phenolic ratio properly controlled are readily soluble in mineral oils. Their color is such that they can be readily blended with light-colored mineral oil fractions without substantial darkening of the oil, which makes them particularly desirable for use in this connection.

As will appear from the foregoing description, the oil-improving agents contemplated by this invention are characterized by the general Formula III ($R^v(T(O.Z.COOM)Y_b)_n$) described hereinabove. Such compounds or products may also be broadly characterized as oil-miscible metal salts of alkylated aroxy-carboxylic acids in which part of the hydrogen in the aroxy nucleus is replaced with a mineral oil-solubilizing substituent. Compounds of this general type may be further characterized as oil-miscible metal salts of alkylated or alkyl-substituted aryl ether acids in which the carboxyl hydrogen has been substituted with its equivalent weight of metal; also as alkylated hydroxyaromatic compounds in which the hydroxyl hydrogen has been substituted with an organic acid salt radical or group, 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, and that an "organic acid salt radical or group" is an aliphatic, alicyclic, or aromatic carboxylic acid residue having one carbon valence available for attachment to the oxygen of a hydroxyaromatic compound to form an aryl ether linkage.

To demonstrate the effectiveness of compounds or products of the type described above in the mineral oil compositions contemplated by this invention, we have conducted several comparative tests, the results of which are listed below, with representative mineral oils alone and with the same oils blended with the improving agents contemplated by this invention.

POUR POINT DEPRESSION

The metal salts of wax-substituted aroxy-carboxylic acids are effective pour point depressants,

as indicated by the results tabulated below. These results were obtained from blends of mineral lubricating oil having a Saybolt Universal viscosity of 244 seconds at 130° F. and containing wax-substituted metal salts of the phenyl-ether type derived from wax-phenol and prepared according to the procedures outlined above. The pour point of the oil alone was +20° F., and as is clearly indicated by Table I below, the wax-aryl ether acid salts which are the preferred type of improving agents contemplated by this invention are effective in very small amounts to reduce the pour point as much as 40° F.

Table I

Depressant blended with motor oil of Saybolt viscosity of 244 sec. at 130° F.	A. S. T. M. pour tests on oil and oil blends		
	0%	¼%	½%
	°F.	°F.	°F.
Wax-phenoxy-zinc acetate (3–16)	+20	−20	−10
Wax-phenoxy-cobaltous acetate (3–16)	+20	−20	−15
Wax-phenoxy-sodium acetate (3–19)	+20	−25	−10
Wax-phenoxy-cobaltous acetate (3–19)	+20	−15	−10
Wax-phenoxy-cobaltous benzoate (3–16)	+20	−20	−15

V. I. IMPROVEMENT

Another property of the mineral oil compositions contemplated by this invention which has been investigated and found to have been improved by metal salts of certain of the alkylated aryl-ether acids is the viscosity index. The effectiveness of the wax-aryl ether acid salts as V. I. improvers is demonstrated by the data in Table II below. In obtaining this data the viscosity index 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.	Saybolt viscosity		
		100° F.	210° F.	V. I.
	Per cent			
None	0	141.4	41.9	81.6
Wax-phenoxy-sodium acetate	2	173.1	44.5	94.5
Wax-phenoxy-cobaltous acetate	2	174.9	44.7	96
Wax-phenoxy-cobaltous benzoate	2	164.1	43.9	94.3

OPERATION TEST

In addition to the foregoing tests we have also made tests of an oil and an oil blend containing a representative improving agent of the type contemplated by this invention 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 twenty-eight hours, with the cooling medium held at a temperature of about 390° F., at a speed of 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 oil used in this test was a lubricating oil stock of 120 seconds Saybolt Universal viscosity at 210° F., and 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 acidity or neutralization number (N. N.) of the oil at the end of the test. The "oil" indicated as "A" in Table III below is the unblended oil, and oil "B" is the same oil containing ½% of wax-phenoxy-cobaltous acetate. The results of this test indicate a substantial inhibition against the deleterious effects of oxidation.

Table III

Oil	Ring condition								Carbon deposit	N. N.
	Degrees stuck					Percent slots filled				
	1	2	3	4	5	3	4	5		
A	180	360	360	360	360	50	50	0	17.25	1.7
B	0	0	0	0	0	0	0	0	6.63	0.4

Table IV below shows the effectiveness of amyl phenoxy cobaltous acetate as an inhibitor. The oil indicated as "A" was blended with one-third per cent of this inhibitor to give oil "B."

Table IV

Oil	Ring condition								Carbon deposit	N. N.
	Degrees stuck					Percent slots filled				
	1	2	3	4	5	3	4	5		
A	270	60	360	90	0	20	10	5	9.69	2.5
B	0	0	0	0	0	0	0	0	3.87	0.5

From the foregoing results it will be apparent that metal salts of alkylated aryl ether 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 aryl-ether acid 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, and 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 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 aryl ether 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 aryl-ether 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 viscous mineral oil fraction having admixed therewith a minor proportion of an oil-miscible metal salt of an aryl ether acid in which part of the hydrogen on the aryl nucleus has been substituted with predominantly aliphatic organic material, said last-mentioned substituent comprising a sufficient proportion of the aryl ether acid salt to render said salt miscible with said oil under normal conditions of handling and use.

2. An improved mineral oil composition comprising a mineral oil having admixed therewith in minor proportion: an oil-miscible metal salt of a wax-substituted aroxy-aliphatic carboxylic acid.

3. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith in minor proportion: an oil-miscible metal salt of an alkyl-substituted aryl ether-carboxylic acid.

4. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith in minor proportion: an oil-miscible metal salt of an alkyl-substituted aryl-ether carboxylic acid in which the alkyl substituent is derived from an aliphatic hydrocarbon having at least twenty carbon atoms.

5. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith in minor proportion: an oil-miscible metal salt of an alkyl-substituted aryl-ether carboxylic acid in which the alkyl substituent is derived from petroleum wax.

6. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith in minor proportion: an oil-miscible metal salt of an alkyl-substituted aryl-ether carboxylic acid in which the alkyl substituent is a high molecular weight aliphatic hydrocarbon group and in which the aryl nucleus is poly-substituted with said alkyl substituent.

7. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith a minor proportion of an oil-miscible metal salt of an alkyl-substituted phenoxy-aliphatic carboxylic acid.

8. An improved mineral oil composition comprising a viscous mineral oil fraction having admixed therewith a minor proportion of an oil-miscible metal salt of any alkyl-substituted naphthoxy-aliphatic carboxylic acid.

9. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of a wax-substituted phenoxy-aliphatic carboxylic acid.

10. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of a wax-substituted naphthoxy-aliphatic carboxylic acid.

11. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil-miscible metal salt of a wax-substituted phenoxy-aliphatic carboxylic acid in which the metal substituent is selected from the group consisting of sodium, zinc, and cobalt.

12. 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 aryl-ether carboxylic acid.

13. 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 aryl-ether carboxylic acid in which said alkyl substituent is derived from petroleum wax.

14. 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: $R^v(T(O\cdot Z\cdot COOM)Y_b)_n$ in which: T represents an aromatic nucleus; (O·Z·COOM) represents at least one ether acid salt substituent attached to T and wherein O represents oxygen, Z represents an aliphatic or an aromatic group and COOM represents at least one carboxyl group, the hydrogen thereof being replaced by its equivalent weight of a metal M; R^v represents at least one aliphatic group having a valence v of from one to four, and attached by one valence only to at least one nucleus T; Y_b represents a monovalent radical attached to T and 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_b's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied with R^v and (O·Z·COOM); and n is a whole number from one to four, the substituent R^v comprising a sufficient proportion of the metalorganic compound as a whole to render the same miscible with said mineral oil under normal conditions of handling and use.

15. 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: $R^v(T(O\cdot Z\cdot COOM)Y_b)_n$ in which: T represents an aromatic nucleus; (O·Z·COOM) represents at least one ether acid salt substituent attached to T and wherein O represents oxygen, Z represents an aliphatic or an aromatic group and COOM represents at least one carboxyl group the hydrogen thereof being replaced by its equivalent weight of a metal M; 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_b represents a monovalent radical attached to T and 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_b's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied with R^v and (O·Z·COOM); 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 twenty-five for each nucleus T.

16. 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: $R^v(T(O\cdot Z\cdot COOM)Y_b)_n$ in which: T represents an aromatic nucleus; (O·Z·COOM) represents at least one ether acid salt substituent attached to T and wherein O represents oxygen, Z represents an aliphatic or an aromatic group and COOM represents at least one carboxyl group the hydrogen thereof being replaced by its equivalent weight of a metal M; R^v represents at least one aliphatic group having a valence v of one to four and attached by one valence bond only to at least one nucleus T; Y_b represents a monovalent radical attached to T and 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_b's and is equal to zero or a whole number corresponding to the valences on the nucleus T not satisfied with R^v and (O·Z·COOM); and n is a whole number from one to four, the ratio of $(T(O\cdot Z\cdot COOM))_n$ to $R^v(T(O\cdot Z\cdot COOM))_n$ in said metalorganic compound expressed as

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

being not greater than the chemical equivalent of twenty per cent phenol.

17. 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: $R^{v'}(T(O\cdot Z\cdot COOM)Y_{b'}R_c)_{n'}$ in which T represents an aromatic nucleus; (O·Z·COOM) represents at least one ether acid salt substituent attached to T and wherein O represents oxygen, Z represents an aliphatic or an aromatic group and COOM represents at least one carboxyl group, the hydrogen of which 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 attached to T and 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 $R^{v'}$, (O·Z·COOM) or 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 with $R^{v'}$, (O·Z·COOM) and $Y_{b'}$; and n is a whole number from two to four.

ORLAND M. REIFF.
FERDINAND P. OTTO.

CERTIFICATE OF CORRECTION.

Patent No. 2,198,292. April 23, 1940.

ORLAND M. REIFF, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 10, first column, line 20, in the right-hand column in the heading of Table 1, for "1/2 %" read --1/8 %--; 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 18th day of March, A. D. 1941.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

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