

# UNITED STATES PATENT OFFICE

2,252,662

## METAL SALTS OF ALKYL SUBSTITUTED HYDROXYAROMATIC CARBOXYLIC ACIDS

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No Drawing. Application June 11, 1938,  
Serial No. 213,183

14 Claims. (Cl. 260—429)

This invention relates to the production of certain new chemical compounds or compositions which may be generally designated as the metal salts of wax-substituted hydroxy-aromatic carboxylic acids. Although the invention is broadly concerned with chemical compounds or compositions coming within the above designated general classification, it contemplates as a preferred group within such general classification those compounds or compositions which are soluble or miscible with mineral oil.

My invention is based upon the discovery that the oil-miscible metal salts of wax-substituted hydroxyaromatic carboxylic acids are of multifunctional activity when blended with viscous mineral oil fractions in that they effect improvement of several unrelated and related properties of the oil. For example, this preferred oil-miscible group of compounds or compositions coming within the general field of invention contemplated herein are effective, when blended in a minor proportion with mineral oil fractions of the lubricant type, to depress to pour point, improve the viscosity index (V. I.) and inhibit oxidation of the oil. By inhibiting oxidation these oil-miscible salts act to retard the formation of sludge and acidic products of oxidation. They also have a peptizing action on such sludge as may eventually be formed. Thus, any one of these preferred oil-miscible compounds or compositions may, for example, be used in internal combustion engine lubricants to retard or prevent the sticking of piston rings or prevent the corrosion of bearings, particularly those formed of alloy metals normally susceptible to corrosion, etc., and at the same time it will act to depress the pour point and improve the viscosity index of the oil. Through a proper choice of metal substituent (lead, copper, tin or zinc, for example) the load-carrying capacity or "lubricity" of the oil may also be improved.

It should be understood that the use of these preferred oil-miscible compounds or compositions is not confined to lubricating oils, but they may be employed in any mineral oil fractions where one or more of the improved properties recited above is desired. In this regard it is to be understood that the present invention is not concerned with mineral oil compositions to which these preferred oil soluble compounds have been added, such oil compositions forming the subject matter of my co-pending application Serial No. 206,682 filed May 7, 1938 (now Patent 2,197,832) to which reference is herein made for

further details in the composition of these compounds.

It is to be understood, however, that while my invention contemplates oil-miscible compounds or compositions of the type above referred to as a preferred class or group within the general field of invention, the invention is not limited to such oil-miscible compounds or compositions, since this whole class of new materials is possessed of valuable properties irrespective of oil-miscibility. For examples, these compounds or compositions may be used as such as oil-soluble resins for use in paints and varnishes or as intermediaries in the production of resins, resin-like materials, rubber substitutes, etc. Certain of the compounds or compositions are possessed of valuable pharmaceutical, insecticidal, or similar properties, such for example as those derived from the presence of a particular metal or residual hydroxyl group. Numerous other uses and applications of the compounds or compositions contemplated herein will be readily apparent to those skilled in the art from the following description of their compositions and preferred methods of synthesis.

As has been previously pointed out, the compounds or compositions contemplated by this invention may be broadly designated as metal salts of wax-substituted hydroxyaromatic carboxylic acids. All of the "salts" contemplated by this invention are characterized by the present of an aromatic nucleus in which at least one nuclear hydrogen is substituted with an hydroxyl group and another nuclear hydrogen is substituted with a carboxyl group wherein the carboxyl hydrogen is replaced with its equivalent weight of metal.

The compounds or compositions contemplated by this invention are further characterized by the fact that at least one hydrogen atom on the aromatic nucleus is substituted with an aliphatic hydrocarbon radical or group characteristic of an aliphatic hydrocarbon of high molecular weight which I may term a heavy alkyl group. For obtaining the preferred group of compounds or compositions which are miscible with mineral oil and which possess the multifunctional oil-improving properties, I have found that this "heavy alkyl" substituent in the salts under discussion must be derived from a predominantly straight chain aliphatic hydrocarbon of at least twenty carbon atoms such as characterize crystalline petroleum wax. As a matter of fact paraffin wax is considered to be a preferred source of the "heavy alkyl" substituent and it is for that reason that the compounds or com-

positions described herein are referred to as "wax"-substituted. It is to be understood, however, that the term "wax" as used herein, is applied in a broad sense and is intended to include any pure compound or mixture of compounds predominantly aliphatic in nature and containing at least twenty carbon atoms which is susceptible of attachment to an aromatic nucleus to provide a substituent which, in the proper proportions, will impart to the characterizing hydroxyl and carboxylate substituted aryl nucleus the multi-functional oil-improving properties referred to.

In addition to the so called heavy alkyl group or groups, a part or all of the nuclear hydrogen on the hydroxyl and carboxylate substituted aryl nucleus may be replaced with: aliphatic groups containing less than twenty carbon atoms, hydroxy, alkoxy, aroxy, alkaryl, aralkyl, aryl, chlorine, nitro, and amino radicals or groups.

As aforesaid, it is important that the metal salts of wax-substituted hydroxyaromatic carboxylic acids preferred for use as oil improving agents have nuclear hydrogen in the aromatic nucleus substituted with aliphatic hydrocarbon material containing at least twenty carbon atoms, such as is derived from petroleum wax, to an extent such that this heavy alkyl substituent comprises a sufficient proportion of the composition as a whole to render the same miscible with the mineral oil fraction in which it is used. For obtaining a compound or product having the desired oil miscibility, it appears that the aryl hydroxide or hydroxyaromatic constituent should not exceed a certain percentage of the "wax" or "heavy alkyl" substituted composition as a whole.

The critical range in the degree of wax-substitution of the aryl nucleus for obtaining these preferred oil miscible compounds may vary with: (a) the mineral oil fraction in which the improving agent is to be used; (b) the character of the aromatic nucleus (mono or poly cyclic); (c) the hydroxyl content of the aryl nucleus (mono or poly hydric); (d) mono or poly substitution of the aryl nucleus; and (e) other substituents on the aryl nucleus which may be of positive or negative or of neutral mineral oil solubilizing activity. In general it may be said that a polycyclic nucleus appears to require a higher degree of wax-substitution than a monocyclic nucleus and that a polyhydric nucleus requires a higher degree of wax-substitution than a mono hydric nucleus.

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 that would satisfy all cases taking these variables into account. In general, however, it may be said that for these preferred compounds, the ratio by weight of hydroxyaromatic component in the product to the corresponding wax-substituted 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 percent, 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 this ratio does not take into account any other substituents which may be in

the nucleus of the ultimate product than the wax or heavy alkyl substituents (having at least twenty carbon atoms) and the hydroxyl group; but since the heavy alkyl substituent is primarily relied upon in these preferred compounds or compositions, it is believed that the foregoing ratio will serve as a working guide for the preparation of compounds contemplated for use as multifunctional oil addition agents. The ratio of twenty percent, which I may term the "phenolic ratio," represents what I consider a maximum figure for obtaining these preferred oil miscible products, and in general it will be found that this figure will be lower, the actual ratio, of course, being dependent upon the variable factors enumerated above.

It will be understood that the products contemplated by this invention may be pure compounds satisfying the general requirements outlined above with any one of the various mono or poly cyclic aromatic hydrocarbons forming the characterizing nucleus and with or without the various other enumerated substituents, the only requisites being that at least one nuclear hydrogen be substituted with a hydroxyl group, at least one nuclear hydrogen be substituted with a metal carboxylate (COOM, where M is metal) group, and at least one nuclear hydrogen be substituted with an aliphatic radical or group containing at least twenty carbon atoms, such as a radical or group predominantly characterizing paraffin wax. However in manufacturing the preferred composition of the present invention by the preferred method of procedure, the final product obtained is normally or usually a mixture of different compounds which differ in the character of the heavy alkyl substituents, the number of such substituents on a single nucleus and the number of nuclei which may be attached to a single alkyl group. For a more detailed description of the compounds constituting such a mixture reference is made to my aforementioned Patent 2,197,832.

The preferred procedure for making the metal salts of wax-substituted hydroxyaromatic carboxylic acids contemplated herein involves the steps of first preparing a "wax" substituted aryl hydroxide, then substituting the hydroxyl hydrogen therein with an alkali or alkaline earth metal to form a wax substituted or "heavy alkyl" substituted aryl metal hydroxylate of the corresponding alkali or alkaline earth metal. This may be accomplished by stirring with the finely divided alkali metal or reacting with an alcoholate of the alkali or alkaline earth metal. The alkali or alkaline earth metal hydroxylate thus obtained is then carboxylated to form the alkali or alkaline earth metal salt of the wax-substituted hydroxyaromatic carboxylic acid. The alkali and alkaline earth metal salts thus obtained constitute part of the compounds or compositions contemplated herein. They may also be used as intermediate products for forming the salts of the other metals by a process of double decomposition with an alcohol-soluble inorganic or fatty acid salt.

In this double decomposition reaction, the details of which will be hereinafter described, some of the metal may replace a nuclear hydrogen in the aromatic ring; but if such compounds form, they are in the minority and, in any event, are not considered harmful to the product.

The metal substituents in the carboxyl group of the improving agents described herein may be broadly classified as the metals belonging to

the silver, copper, tin, aluminum, iron, alkali and alkaline earth analytical groups, which include: silver, mercury, lead, and thallium; bismuth, copper, and cadmium; arsenic, antimony, and tin; iron, cobalt, nickel, and manganese; barium, calcium, strontium, and magnesium; and sodium, potassium, and lithium, respectively. Other desirable metals include: titanium, cerium, thorium, vanadium, molybdenum, tungsten, uranium, and platinum.

The starting material for the hydroxyaromatic constituent in the alkylation reaction to obtain wax-substituted hydroxyaromatic products of the type used in the foregoing procedure wherein the nucleus is otherwise unsubstituted, may be a mono or poly cyclic hydroxyaromatic compound otherwise unsubstituted; 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 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: alkyl groups containing less than twenty carbon atoms, chlorine, hydroxy, alkoxy, aroxy, aryl, alkaryl, and aralkyl groups.

Examples of the hydroxyaromatic compounds or aryl hydroxides which may be used as the 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, xylol naphthol, benzyl naphthol, anthranol, phenyl methyl naphthol, phenanthrol, monomethyl ether of catechol, diphenyl ether, 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 with aliphatic hydrocarbon groups containing at least twenty carbon atoms may be accomplished in various ways, such as by a Friedel-Crafts synthesis using a halogenated high molecular weight aliphatic hydrocarbon, such as chlorinated wax, or by reaction with unsaturated high molecular weight aliphatic compounds or higher alcohols in the presence of  $H_2SO_4$  as a catalyst.

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

In this reaction an appropriate halogenated high molecular weight aliphatic compound or material such as mono or poly chlorine-substituted aliphatic compound or material containing at least twenty carbon atoms, for example, chlorinated petroleum wax, 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 satisfying the above requisites may be used. However, as will be readily understood by those skilled in the art, since it is usually very difficult to prepare or obtain high molecular weight aliphatic hydrocarbons in a pure or substantially pure state and since it is equally difficult to prepare the chlorine (or other halogen) substitution products of such hydrocarbons in a pure or substantially pure state, I prefer to employ a mixture of such hydrocarbons, such as a suitable petroleum fraction (special preference being given to petroleum wax of melting point not substantially less than about  $120^\circ F.$ ), as the starting material, converting it into a mixture of different chlorine (or other halide) substitution products by any suitable method for use in the alkylation step. It will be understood, of course, that when such a mixture of high molecular weight aliphatic hydrocarbons is employed in the alkylation reaction, the resulting alkylated product and the metal salt ultimately derived therefrom will also be a mixture of compounds, the individual compounds thereof differing from each other with respect to the nature of the alkyl substituent. Thus, the ultimate product obtained from a wax-substituted phenol, which may be termed the salt of a wax-substituted hydroxy-aromatic carboxylic acid, where alkylation was effected with a halogenated petroleum wax, such as paraffin wax, will be a mixture of alkylated aromatic compounds differing in composition as the aliphatic constituents of the wax differ in composition. In other words, the alkyl substituents on the various alkylated hydroxyaromatic carboxylates of a mixture obtained from paraffin wax are predominantly radicals of at least twenty carbon atoms corresponding substantially to the different aliphatic hydrocarbons contained in paraffin wax.

In the event it is desired to obtain a wax-substituted hydroxyaromatic metal carboxylate of the class described which contains an alkoxy group as a substituent in the aryl nucleus, 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 of carbon chain length of twenty or more carbon atoms (such as eicosylene, cerotene, melene, etc.) or a higher alcohol of chain length of twenty or more carbon atoms (such as ceryl alcohol, myricyl 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 higher alcohols or high molecular weight 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 one OH group followed by treating with the desired alkyl halide, whereby the substitution to provide the alkoxy group is effected.

When it is desired to obtain a nitro or amino group as a substituent in the aryl nucleus, the hydroxyaromatic compounds are alkylated or wax-substituted 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.

The following description illustrates a preferred procedure which may be followed in synthesizing the metal salts of wax-substituted hydroxyaromatic carboxylic acids contemplated by this invention. The compounds or products obtained from the synthesis described below fall into that class or group of compositions hereinabove referred to as "preferred" because of their oil-solubility or their multi-functional activity when blended with mineral oil fractions. As will be apparent to those skilled in the art, compounds or compositions having a combined phenolic content in excess of that necessary for oil-miscibility may be readily obtained by using a chlorinated wax having a chlorine content substantially higher than that given in the example below or by changing the ratio of the reactants (chlorwax and phenolic compound).

PREPARATION OF METAL SALTS OF WAX-SUBSTITUTED PHENOL CARBOXYLIC ACID

(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 a 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<sub>6</sub>H<sub>5</sub>OH) 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 about 350° F. To control the evolution of HCl gas the temperature of the mixture is preferably raised from 250° F. to 350° F. at a rate of approximately one degree per minute, the whole heating operation occupying approximately two hours from the time of adding the aluminum chloride. If the emission of HCl gas has not ceased when the final temperature is reached, the mixture may be held at 350° F. for a short time to allow completion of the reaction. But to avoid possible cracking of the wax, the mixture should not be heated appreciably above 350° F., nor should it be held at that temperature for any extended length of time.

It is important to the formation of a preferred oil-miscible product that all unreacted or non-alkylated hydroxyaromatic material (phenol) remaining after the alkylation reaction be removed. Such removal can be effected generally by water-washing, but it is preferably 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.

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 chlorwax) 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 compounds to designate (A) the number of atomic proportions of chlorine in chloraliphatic material (chlorwax) reacted with one mole of hydroxyaromatic compound in the Friedel-Crafts reaction, and (B) the chlorine content of the chloraliphatic material (chlorwax). In the above example A=3 and B=20. This same designation will also apply to the salts of the carboxylic acids derived from these alkylated hydroxyaromatic compounds.

Wax-phenol (3-20) as obtained by the above procedure had a phenol content or a "phenolic ratio" of about sixteen per cent. My research indicates that this phenolic ratio of sixteen per cent may be considered as representing about the maximum for satisfactory miscibility in viscous oils of the metal salts of "alkylated hydroxyaromatic carboxylic acid" in which the alkyl substituent is derived from petroleum wax and the hydroxyaromatic constituent is derived from phenol (C<sub>6</sub>H<sub>5</sub>OH). 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 thirteen per cent.

(2) Formation of wax-substituted alkali or alkaline earth metal phenate

As an example of this step in the preparation of my 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 preparing a wax-substituted alkali metal phenate according to the above procedure were:

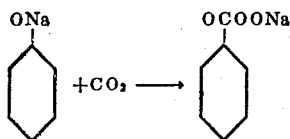
	Grams
Wax-phenol (13.2% combined phenol content) -----	500
Sodium or equivalent amount of potassium...	16

Wax-substituted phenates of the alkali and alkaline earth metals may also be prepared by reacting a wax-phenol with the desired alcoholate or alkyl metal oxide of an alkali or alkaline earth metal. For this purpose anhydrous methyl and ethyl alcohols are usually most suitable for use in preparing the alkyl metal oxides. As an example, 500 grams of wax-phenol (3-16) of 13.2 per cent combined phenol content was reacted with sixteen grams of sodium in the form of the ethyl sodium oxide by heating the mixture to about 300° F. during a one-hour period and allowing the alcohol released in the reaction to distill off, thereby obtaining the wax-substituted sodium phenate as the final product.

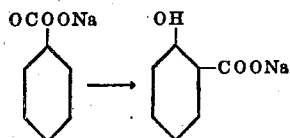
(3) Carboxylation to form alkali or alkaline earth metal salt of wax-phenol carboxylic acid

A product of the foregoing step, such as the wax-substituted sodium phenate, is heated to a

temperature of about 350° F. with stirring and CO<sub>2</sub> is introduced at a rate sufficient to maintain this temperature. The pressure is gradually raised to about 500 pounds per square inch to complete the reaction at this temperature during a two-hour period. The reaction may be illustrated with unsubstituted sodium phenate by the following equations:



By rearrangement the carboxy group is transferred to the ring, giving the sodium salt of the phenol carboxylic acid:



Other carboxylating reactions may be used in this step of the process, such as the reaction of the alkali metal wax-phenate with carbonyl chloride or carbon tetrachloride; but since the salt formed in the presence of CO<sub>2</sub> is obtained in high yield and in a pure state, this is the preferred carboxylation procedure. Although pressures in the neighborhood of 500 pounds per square inch are mentioned above in the description of the preferred carboxylation procedure, it may under certain circumstances be more desirable to use lower pressures or even to effect the carboxylation at atmospheric pressure.

Because of the high viscosity of the mixture it is advantageous to dilute the wax-substituted phenol initially with one or two parts of mineral oil. When a diluent has been used, the mixture can be stirred more readily, making it suitable to introduce the CO<sub>2</sub> at a lower temperature. By introducing the CO<sub>2</sub> under pressure at room temperature and gradually raising the mixture to 350° F. the temperature can be more readily controlled. When CO<sub>2</sub> is introduced under pressure at 350° F., rapid changes in viscosity occur, making it more difficult to control the temperature of the reaction mixture.

The product of this step, where the starting material was wax-substituted sodium phenate, is the sodium salt of wax-substituted phenol carboxylic acid.

#### (4) Formation of the salts of other metals

With an alkali or alkaline earth metal salt, such as the sodium salt of the foregoing step, as the starting material, the corresponding salts of the other metals can be prepared by double decomposition of the first-mentioned salt with an alcohol-soluble inorganic or fatty acid salt of the desired metal. The use of alcohol as a solvent for the salt is desirable to insure proper solution and reaction, the reaction being conveniently carried out by heating the mixture at 175° F. during a two-hour period.

The reaction product of this double decomposition can be purified by diluting the mixture with a light mineral oil and settling out the insoluble reaction salts, followed by removal of the diluent by distillation to obtain the finished product. Another procedure of purification is to water-wash the reaction mixture to remove the reaction salts, breaking any emulsion that may

be formed in the water-washing operation by the use of an alcohol such as amyl alcohol.

The reaction mixture employed in this double decomposition reaction may, for example, consist of one mole of the sodium salt of wax-substituted phenol carboxylic acid and one mole equivalent of the inorganic or fatty acid salt of the desired metal in alcohol solution. One part by volume of Stoddard solvent may be employed as a diluent for the mixture.

In the formation of polyvalent metal salts of wax phenolic acids by carrying out the double decomposition in non-aqueous medium, alcohol-soluble inorganic or fatty acid salts are required. The reaction may also be carried out in aqueous medium, in which case a water-soluble inorganic salt of a polyvalent metal is used.

#### METAL SALTS OF WAX-SUBSTITUTED NAPHTHOL CARBOXYLIC ACID

In addition to the salts just discussed above I have, by following the same procedure, prepared metal salts of wax-substituted naphtholic acid. A wax-naphthol (3-14) was obtained from the alkylation reaction. This product and the corresponding salts obtained therefrom had a combined naphthol content of sixteen per cent and an equivalent phenol content or "phenolic ratio" of 9.7 per cent.

The "salts" obtained by the exemplary procedures described above are, as the result of their relatively low "phenolic ratio" or combined phenol content, all oil-miscible or oil-soluble products. Although products of this type are designated herein as preferred, because of their multifunctional oil-improving properties, it is again emphasized that the invention is not limited to metal salts of wax-substituted hydroxy-aromatic acids which are oil-soluble but is inclusive of this entire field of products irrespective of oil-solubility. As has been previously stated, this entire class of compounds or compositions possesses valuable properties outside of the petroleum industry as intermediaries in the production of resins. Furthermore, as the phenol content is increased beyond the limits necessary for mineral oil-miscibility, the products lose their waxy characteristics and become rubber-like in character and show definite promise as rubber substitutes without any substantial amount of additional treatment.

Compounds or compositions of both the oil-miscible and non-miscible types have been prepared, and of the oil-miscible products synthesized all have been tested as additive agents for viscous mineral oils and have been found to be of multifunctional activity, improving the pour point and viscosity index and inhibiting oxidation of viscous mineral oil fractions. The following list is illustrative of the various oil-miscible metal salts of wax-substituted hydroxy-aromatic acids, which I have prepared and tested to demonstrate their value as additive agents for viscous mineral oils.

#### Table

Cupric salt of wax phenol carboxylic acid (3-16)
Aluminum salt of wax phenol carboxylic acid (3-16)
Zinc salt of wax phenol carboxylic acid (3-16)
Chromic salt of wax phenol carboxylic acid (3-16)
Ferric salt of wax phenol carboxylic acid (3-16)
Cobaltous salt of wax phenol carboxylic acid (3-16)

Nickelous salt of wax phenol carboxylic acid (3-16)  
 Manganous salt of wax phenol carboxylic acid (3-16)  
 Calcium salt of wax phenol carboxylic acid (3-16)  
 Magnesium salt of wax phenol carboxylic acid (3-16)  
 Potassium salt of wax phenol carboxylic acid (3-16)  
 Sodium salt of wax phenol carboxylic acid (2-16)  
 Sodium salt of wax phenol carboxylic acid (3-20)  
 Stannous salt of wax phenol carboxylic acid (3-20)  
 Zinc salt of wax phenol carboxylic acid (3-20)  
 Aluminum salt of wax phenol carboxylic acid (3-20)  
 Sodium salt of wax phenol carboxylic acid (3-18)  
 Sodium salt of wax phenol carboxylic acid (4-20)  
 Sodium salt of wax-beta naphtholic acid (3-18)  
 Sodium salt of wax-alpha naphtholic acid (3-18)

I claim:

1. A metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid in which the alkyl substituent contains at least twenty carbon atoms and is attached to the aryl nucleus.

2. A metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid in which the alkyl substituent contains at least twenty carbon atoms and is attached to the aryl nucleus, said composition being miscible with mineral oil and possessing the property of improving the pour point and viscosity index and inhibiting oxidation of a viscous mineral oil fraction when admixed therewith.

3. A metal salt of an alkyl-substituted phenol carboxylic acid in which the alkyl substituent contains at least twenty carbon atoms and is attached to the aryl nucleus.

4. A metal salt of an alkyl-substituted phenol carboxylic acid in which the alkyl substituent contains at least twenty carbon atoms and is attached to the aryl nucleus, said composition being miscible with mineral oil and possessing the property of improving the pour point and viscosity index and inhibiting oxidation of a viscous mineral oil fraction when admixed therewith.

5. A metal salt of an alkyl-substituted naphthol carboxylic acid in which the alkyl substituent contains at least twenty carbon atoms and is attached to the aryl nucleus.

6. A metal salt of an alkyl-substituted naphthol carboxylic acid in which the alkyl substituent contains at least twenty carbon atoms and is attached to the aryl nucleus, said composition being miscible with mineral oil and possessing the property of improving the pour point and viscosity index and inhibiting oxidation of a viscous mineral oil fraction when admixed therewith.

7. A product obtained by condensing an aryl hydroxide with chlorinated paraffin wax in proportions such that the aryl hydroxide constituent in the resulting wax-substituted aryl hydroxide product comprises a substantially smaller proportion of said product than the wax substituent; substituting the hydroxyl hydrogen of said wax-substituted aryl hydroxide product with an alkali metal; and carboxylating the metal-substituted product.

8. A product obtained by condensing an aryl

hydroxide with chlorinated paraffin wax in proportions such that the aryl hydroxide constituent in the resulting wax-substituted aryl hydroxide product comprises a substantially smaller proportion of said product than the wax substituent; substituting the hydroxyl hydrogen of said wax-substituted aryl hydroxide product with an alkali metal; carboxylating the metal-substituted product to form an alkali metal carboxylate; and replacing said alkali metal of said carboxylate with another metal by double decomposition with a salt of said other metal.

9. A product obtained by condensing phenol with chlorinated paraffin wax in proportions such that the wax-phenol formed has a combined phenol content not to exceed twenty per cent; replacing the hydroxyl hydrogen of the phenol with a metal to form a wax-substituted metal phenate; and then carboxylating said wax-substituted metal phenate.

10. A product obtained by condensing phenol with chlorinated paraffin wax in proportions such that the wax-phenol formed has a combined phenol content not to exceed twenty per cent; replacing the hydroxyl hydrogen of the phenol with an alkali metal to form a wax-substituted alkali metal phenate; then carboxylating said wax-substituted alkali metal phenate; and finally replacing the alkali metal with another metal by a double decomposition between said wax-alkali metal phenate and a salt of said other metal.

11. The method of preparing a metal salt of a paraffin wax-substituted hydroxyaromatic acid which comprises: condensing a chlorinated paraffin wax with an aryl hydroxide in the presence of aluminum chloride to form a wax-substituted aryl hydroxide; heating the wax-substituted aryl hydroxide and reacting same with an alcoholate of a metal selected from the group consisting of alkali and alkaline earth metals, to form the wax-substituted aryl hydroxylate of said metal; and finally carboxylating the product of the preceding step by passing carbon dioxide gas into the reaction product in sufficient quantity to substantially convert the wax-substituted aryl metal hydroxylate into the metal salt of the corresponding wax-substituted aryl-hydroxyl-carboxylic acid.

12. As a composition of matter, an intimate mixture of the metal salts of alkyl substituted hydroxyaromatic carboxylic acids, the said acids differing from each other with respect to the nature of the alkyl substituents and the salts having the carboxyl hydrogen substituted with the same metal, the alkyl substituents comprising essentially aliphatic hydrocarbon groups having a composition corresponding substantially to the different aliphatic hydrocarbons contained in paraffin wax.

13. As a composition of matter, an intimate mixture of the metal salts of alkyl substituted hydroxyaromatic carboxylic acids, the said acids differing from each other with respect to the nature of the alkyl substituents and the salts having the carboxyl hydrogen substituted with the same metal, the alkyl substituents comprising essentially aliphatic hydrocarbon groups having a composition corresponding substantially to the different aliphatic hydrocarbons contained in paraffin wax, the said alkyl substituent comprising a sufficient proportion of said composition to render the same miscible with mineral oil, said composition possessing the property of improving the pour point, improving the viscosity

index and inhibiting oxidation of a viscous mineral oil fraction when admixed therewith.

14. As a composition of matter, an intimate mixture of the metal salts of alkyl substituted hydroxyaromatic carboxylic acids, the said acids differing from each other with respect to the nature of the alkyl substituents and the salts having the carboxyl hydrogen substituted with the same metal, the alkyl substituents compris-

ing essentially aliphatic hydrocarbon groups having a composition corresponding substantially to the different aliphatic hydrocarbons contained in paraffin wax, the metal substituent in the carboxyl group being selected from the group consisting of copper, tin, zinc, chromium, manganese, iron, and cobalt.

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