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ALKYL-SUBSTITUTED AMINO-ARYL METAL OXIDES

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1 Claim. (Cl. 260—429)

This invention relates to the production of certain new chemical compounds or compositions which may be generally designated as nuclear alkyl substituted amino-aryl metal oxides or nuclear alkyl substituted amino-aryl metal hydroxylates or phenolates, the term "amino" being used in a broad generic sense to include both substituted and unsubstituted ($-NH_2$) groups (preferably a metal-substituted ($-NH_2$) group wherein an H is substituted by its equivalent weight of metal, such group being hereinafter referred to as a metal-amino group). 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 heavy alkyl-substituted or wax-substituted compounds or compositions which are soluble or miscible with mineral oil, and which remain substantially unreacted upon thereby.

Our preference for this preferred group is based upon the discovery that these oil-miscible wax-substituted amino-aryl metal oxides are of multi-functional 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 the pour point, improve the viscosity index (V. I.), and inhibit oxidation of the oil. By inhibiting oxidation these oil-miscible substituted amino-aryl metal oxides 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 they will act to depress the pour point and improve the viscosity index of the oil. Through a proper choice of metal substituent (lead, 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 further understood that the present invention is not concerned with mineral oil compositions containing these preferred oil-miscible amino-aryl metal hydroxylates, such oil compositions forming the subject matter of our copending application 317,122, filed February 3, 1940, patented April 4, 1942, U. S. Patent Number 2,280,039 to which reference is made for further details in the composition of these compounds.

It is also to be understood 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 example, these compounds or compositions may be used 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 metal-oxy 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.

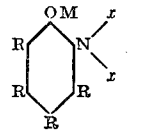
As has been previously pointed out, the compounds or compositions contemplated by this invention may be broadly designated as nuclear alkyl-substituted amino-aryl metal oxides or nuclear alkyl-substituted amino-aryl metal hydroxylates. All of the alkyl-amino-aryl metal oxides or alkyl-amino-phenolates contemplated by this invention are characterized by the presence of an aromatic nucleus in which at least one nuclear hydrogen is substituted with an hydroxyl group having its hydroxyl hydrogen replaced with its equivalent weight of metal, sometimes referred to herein as a metal-oxy group and in which an additional nuclear hydrogen is substituted with an ($-NH_2$) group or a substituted ($-NH_2$) group.

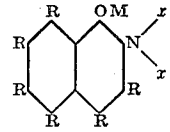
The compounds or compositions contemplated by this invention are further characterized by the fact that at least one replaceable hydrogen of the aromatic nucleus is substituted with an alkyl group and preferably with an aliphatic hy-

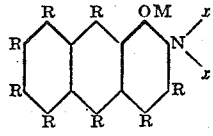
drocarbon radical or group characteristic of an aliphatic hydrocarbon of high molecular weight, which we may term a heavy alkyl group or a "wax" group. For obtaining the specially preferred group of compounds or compositions falling within this generally preferred class which are miscible with mineral oil and which possess the multifunctional oil-improving properties, we have found that this "heavy alkyl" substituent, in the substituent amino-aryl metal oxides 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 compositions described herein are referred to as "wax-substituted."

It will also be understood that when a mixture of aliphatic hydrocarbon compounds, such as petroleum wax, for example, is used as the source of the heavy alkyl substituent, the resulting composition will be an intimate mixture of compounds or alkyl-substituted amino-aryl metal oxides (alkyl-substituted amino-hydroxyaromatic compounds in which the hydroxyl hydrogen is substituted with metal), which compounds differ from each other with respect to the nature of the alkyl substituent. In other words, where alkylation of the aryl nucleus has been effected with a mixture of aliphatic hydrocarbons of at least twenty carbon atoms, the resulting product will likewise be a mixture of compounds, differing with respect to the alkyl substituent but having in common the characterizing nuclear group discussed above.

In addition to the heavy alkyl substituent, the amino or substituted amino substituent and the metaloxy substituent, the characterizing aryl nucleus may have all or part of its replaceable hydrogen substituted with a radical selected from the group consisting of: aliphatic hydrocarbon groups having less than twenty carbon atoms, hydroxy, chlorine, alkoxy, aroxy, aralkyl, alkaryl, aryl, nitro, amino, keto, nitroso, diazo, azo, ether alcohol and ester radicals or groups. Typical compounds of the type contemplated herein having mono-, di-, and tri-cyclic nuclei are illustrated by the following formulae:







in which at least one of the R's represents an aliphatic hydrocarbon radical or group containing at least twenty carbon atoms and in which the remaining R's represent residual hydrogen which may be replaced with: aliphatic groups containing less than twenty carbon atoms, hydroxy, chlorine, alkoxy, aroxy, aralkyl, alkaryl, aryl, nitro, amino, keto, nitroso, diazo, azo, ether alcohol and ester radicals or groups and in which



represents an amino group in which x represents hydrogen which may be replaced with: alkyl, aralkyl, ester (acyl) and metal substituents.

In the preferred class of compounds or reaction products contemplated for use as oil-improving agents, it is important that the aryl nucleus of the amino-aryl metal hydroxylate be substituted with the heavy alkyl groups to an extent such that this heavy alkyl substituent comprise a sufficient proportion of the composition as a whole to render the same miscible with the mineral oil fraction in which it is to be used so as to form a solution or colloidal suspension which will remain stable under normal conditions of handling and use. It appears that there is a critical range of heavy alkyl- or "wax"-substitution of the compounds or compositions contemplated herein below which the wax-substituted amino hydroxylates will not satisfy the requirements for oil-miscibility. The critical range in the degree of heavy alkyl- or "wax"-substitution of the aryl nucleus in the compounds contemplated herein as oil-improving agents may vary with: (*a*) the mineral oil fraction in which the improving agent is to be used; (*b*) the character of the aryl nucleus (mono- or poly- cyclic and mono- or polyhydric); (*c*) mono- or poly-substitution of the aryl nucleus; and (*d*) other substituents on the nucleus which may be of positive or negative or neutral mineral oil-solubilizing activity.

In view of the foregoing variables it would be impracticable to attempt to give an expression and figure which would indicate accurately the proper ratio of amino-aryl hydroxide constituent to the "wax"-substituted amino-aryl hydroxide which would express a degree of aliphatic (wax) -substitution satisfying all cases taking these variables into account. In general, however, it may be said that in this preferred group of compounds the ratio by weight of amino-hydroxy-aromatic component in the product to the corresponding wax-substituted amino-hydroxyaromatic component therein should not be greater than about seventeen parts by weight of the former to about 100 parts by weight of the latter or about 17 per cent. when the amino-hydroxy-aromatic nucleus or component is expressed in terms of its chemically equivalent weight of phenol. This ratio, which may be termed the "phenolic ratio," does not take into account any other substituents in the nucleus than the heavy alkyl group or groups, the amino group and the hydroxy group; but since the heavy alkyl group is primarily relied upon in these preferred compositions, it is believed that the foregoing expression and limit will serve as a working guide for their preparation.

The general procedure for preparing the compounds contemplated herein involves nuclear alkylation of an aryl hydroxide or hydroxyaromatic compound preferably with heavy alkyl groups (of at least 20 carbon atoms), substitution of a residual nuclear hydrogen with an ($-NH_2$) group or a mono- or di-substituted ($-NH_2$) group and then the substitution of the hydroxyl hydrogen of the amino-aryl hydroxide compound thus obtained (and preferably also the substitution of a residual amino hydrogen in an ($-NH_2$) or a mono-substituted ($-NH_2$) group) with a metal.

It should be explained, however, that in the preparation, by the above general procedure, of our preferred type of compound, previously referred to above, wherein the amino group is a metal-amino group, we have found that the replacement of the hydroxyl hydrogen takes place before the replacement of the residual amino hydrogen. This is apparently due to the relatively greater acidity of the replaceable hydrogen of the hydroxyl group as compared to that of the (—NH_2) or mono-substituted (—NH_2) group. It will be obvious from this that either one or two additional equivalents of metal over and above that required to replaced the hydroxyl hydrogen of the hydroxyl group (or groups) must be used in order to form our preferred compound in which, as aleady explained, a nuclear hydrogen of the aromatic nucleus is replaced by a metal-amino group.

The above-mentioned substitution of nuclear hydrogen with an (—NH_2) group may be effected by nitration and subsequent reduction as shown by the following example which illustrates the general procedure to be followed in carrying out each of these two steps and which we have found to be generally applicable (with only slight changes which will be readily understood by those skilled in the art) in the preparation of the various compounds of the present invention.

NITRATION OF T-AMYL PHENOL

Reaction mixture

t-Amyl phenol (hydroxy benzene)	mol	1
Benzol	litre	⅓
HNO_3 { 17.5% by weight H_2O / 1 part HNO_3—3 parts H_2O }	mols	2

Procedure

The tert. amyl phenol is dissolved in the benzol and the nitric acid solution added slowly at room temperature at such a rate that the temperature rises to 130–140° F. and is maintained there throughout the remainder of the addition. After addition of the nitric acid is complete, this temperature is maintained for ½ hour. The material is then water-washed until free of acid and the benzol removed by distillation.

REDUCTION OF T-AMYL NITROPHENOL

Reaction mixture

p-Tert. amyl nitrophenol	1 mol.
Tin metal	3 mols. (6 equivalents)
Conc. hydrochloric acid	1.5 litres

The amyl nitrophenol and the tin are mixed together, thereafter adding the HCl in 250 cc. portions with stirring over a period of one hour.

The reaction temperature is then raised to the boiling point and the mixture refluxed until all the tin has reacted and all the amyl nitrophenol has been reduced, which is indicated by its complete solution in the hot mixture.

The reaction mixture is then cooled, whereupon the amyl aminophenol hydrochloride precipitates as a solid compound. The precipitate is filtered off and redissolved in one liter of water and freed of tin chlorides by passing in H_2S gas. The tin sulfides are filtered off and while still hot, concentrated hydrochloric acid is added to the reaction mixture until a permanent cloudiness appears, whereupon the material is set aside to cool. The compound obtained as the hydrochloride is a white to light yellow crystalline product.

Due to the susceptibility of alkylated amino-hydroxyaromatic compounds to oxidation in the air it has been advisable to store them in the form of the hydrochloride. Where it is desired to obtain the corresponding basic compound free, the proper amount of the hydrochloride is added to a non-aqueous solvent and neutralized with ammonia gas. A concentrated blend of the free alkylated amino-hydroxyaromatic compound can be made in mineral oil in this manner.

The substitution of nuclear hydrogen with a mono- or di-substituted (—NH_2) group in accordance with the general procedure mentioned above, may be effected by reacting the compound formed by the reduction step illustrated in the above example with any suitable reactant such as an alkyl or aralkyl halide to form an alkyl- or aralkyl-amino group, or an inorganic acyl halide to form an inorganic acyl-amino group, or the acyl halide or anhydride of an organic acid to form an organic acyl-amino group, in accordance with known methods for making such substitutions in simple aryl amines except only as to minor variations and adaptations which will be obvious to those skilled in the art.

We have also found that this substitution of amino hydrogen in the nuclear alkylated amino-hydroxyaromatic compound may be effected by the use of either one or two equivalents of the above-mentioned reactants without corresponding substitutions of the hydroxyl hydrogen of the hydroxyaromatic compound, thus leaving the hydroxyl hydrogen free for later substitution with a metal.

Typical examples of aryl hydroxides or 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-benzylphenol, methyl-hydroxydiphenyl, guaiacol, alpha- and beta-naphthol, methyl alpha- and methyl betanaphthol, tolyl naphthol, xylyl naphthol, benzyl naphthol, anthranol, phenyl methyl naphthol, phenanthrol, monomethyl ether of catechol, methoxy phenol, phenoxy phenol, anisole, beta-naphthyl methyl ether, chlorphenol, and the like. Preference in general is to the monohydroxyphenols otherwise unsubstituted, particular preference being given to phenols and alpha- and beta-naphthol.

The alkylation of the aryl hydroxide may be accomplished in various ways, such as by a Friedel-Crafts synthesis, using a halogenated aliphatic hydrocarbon compound preferably of at least 20 carbon atoms or a mixture, such as chlorinated paraffin wax, predominantly comprised of such compounds. The alkylation may also be effected by reaction of the aryl hydroxide with an unsaturated aliphatic hydrocarbon or an alcohol in the presence of H_2SO_4 as a catalyst, the unsaturated hydrocarbon or the alcohol each being preferably of high molecular weight.

In some instances as where it is possible or convenient to obtain an aryl hydroxide starting compound already containing a nuclear alkyl group and where also it is not desired to prepare the preferred "wax"-substituted product or a compound containing a nuclear alkyl group or aliphatic radical of not less than twenty carbon atoms, the alkylation step may of course be omitted.

Substitution of the hydroxyl hydrogen (either alone or together with an amino hydrogen, which is preferred) with metal may be effected in various ways to be hereinafter detailed. For exam-

ple, the alkylated amino-aryl hydroxide may be reacted with elementary alkali metals in finely divided form, or it may be reacted with an alcoholate of the desired metal. Other procedures may also be employed, as will hereinafter appear.

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

Some of the rare earth metals are given in the above; other rare earth metals suitable for the formation of amino-phenol salts are those now commercially available as the cerium and yttrium groups, namely, a mixture of praesodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and lutecium.

In the substitution of a metal for the hydroxyl hydrogen (and also for an amino hydrogen if desired), in accordance with the general procedure mentioned above, the metals are reacted in most instances in the form of metal alcoholates such as metal butylates, the alcohol being regenerated in the reaction. In the case of alkali metal alcoholates, these may conveniently be prepared by reacting the desired alkali metal with a suitable alcohol. In the case of the alcoholates of the other metals these may most conveniently be prepared from the alcohol-soluble salts (such as alcohol-soluble chlorides or alcohol-soluble acetates and the like) by double decomposition with an alkali metal alcoholate, preferably sodium or potassium alcoholate. The formation of the alkali-metal alcoholate and the double decomposition may be carried out in separate steps or simultaneously in the same reaction mixture as illustrated by the following example:

SUBSTITUTION OF THE HYDROXYL HYDROGEN OF TERTIARY C—AMYL AMINOPHENOL WITH METAL

Reaction mixture

Amyl aminophenol hydrochloride	1 mol
Sodium metal	2 mol. (i. e., 2 equivalents)
N-butyl alcohol	500 cc.
Stannous chloride (anhy.)	½ mol. (1 equiv.)

The sodium is added to the butyl alcohol at reflux temperature to form sodium butylate, to which is added the anhydrous stannous chloride dissolved in butyl alcohol. To this mixture is then added the solid amyl aminophenol hydrochloride. In the reaction, one equivalent of sodium is required to neutralize the hydrochloride, thereby releasing the free aminophenol which then reacts with the stannous butylate formed by double decomposition.

As an alternative procedure, which is more convenient to carry out, the aminophenol hydrochloride can be added to the stannous chloride dissolved in alcohol, followed by the gradual addition of the metallic sodium or sodium butylate.

In either method of mixing the reactants, the reaction temperature is then raised to 175–200° C. allowing the alcohol to distill, holding the temperature in this range about one hour to complete the reaction.

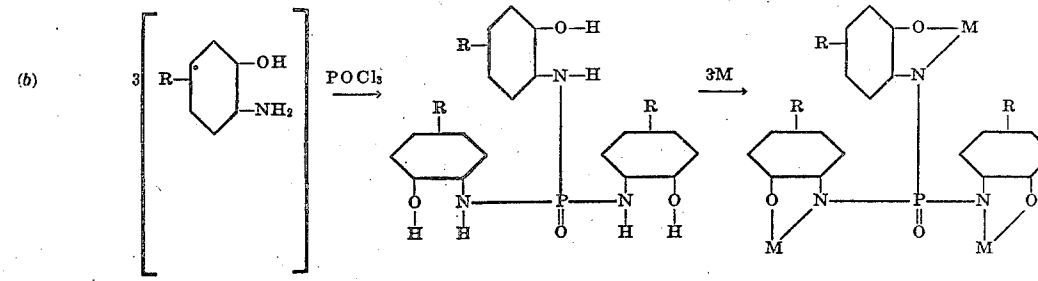
Upon cooling, 1 part of benzol is added to the mixture, which can be filtered to remove the reaction salts and the solvent removed to give the finished product. It is usually desirable to prepare a concentrated blend of the product containing about one part of the metal phenolate to 3 parts of a mineral oil, in which case the mineral oil is added during the process of formation of the metal phenolate and allowed to remain in the finished product.

SUBSTITUTION OF AMINO HYDROGEN WITH METAL

For the substitution of an amino hydrogen with metal in addition to the substitution of the hydroxyl hydrogen in the above example it is only necessary, except as to obvious minor variations, to employ an additional equivalent of metallic sodium and an additional equivalent of stannous chloride as previously explained.

Some of the metal phenolates are more stable than others to water-washing. Aminophenol phenolates of tin, cobalt and nickel have been found to decompose to some extent, losing about one equivalent of metal upon water-washing. The phenolates of chromium and titanium have been found to be completely stable upon water-washing.

The metal phenolates are formed in anhydrous medium, but can be water-washed in the removal of reaction salts in the purification of the compounds. When one hydrogen equivalent of an acyl chloride (preferably an inorganic acyl chloride corresponding to the acid of a non-metallic or more acidic type of metalloid element such as phosphorus) is used in the formation of the N-ester (or N-acyl) product, followed by introduction of two hydrogen equivalents of a divalent metal substituent in accordance with the procedure described above, metal substitution of OH and also N-substitution with both metal and an acyl group results with probable formation of a metal chelate or metal ring type compound as indicated by the following generalized equation:



and wherein the ring nucleus represent mono or polycyclic aromatic nuclei where M indicates a divalent metal atom. The broad class of metal-chelate compounds is described by Diehl in Chemical Review, vol. 31, page 39 (1937).

Examples of acyl chlorides of the inorganic acids of non-metallic or acidic metalloid ele-

ments that may be used in the N-esterification (acylation) reaction shown above are the following: $POCl_3$, BCl_3, $SiCl_4$, PCl_3, SCl_2, $SeCl_2$, $TeCl_2$, as well as the corresponding bromides and iodides.

Representative examples of the organic acid anhydrides or acyl halides which may be used for this purpose are the anhydrides and acyl halides of the following organic acids:

(1) Saturated aliphatic mono carboxylic acids ranging from acetic to montanic acid.

(2) Unsaturated aliphatic monocarboxylic acids such as acrylic, oleic, elaidic, crotonic, etc.

(3) Saturated aliphatic polycarboxylic acids such as succinic oxalic, adipic, sebacic, etc.

(4) Unsaturated aliphatic polycarboxylic acids such as maleic and fumaric acids.

(5) Substituted mono and polycarboxylic aliphatic acids containing halogen, hydroxyl, amino, ether or keto groups such as chloracetic acid, hydroxystearic acid, tartaric acid, glycollic acid, octyloxyacetic acid and pyroracomic acid.

(6) Aromatic monocarboxylic acids such as benzoic and naphthoic acids.

(7) Aromatic polycarboxylic acids such as phthalic acid.

(8) Alkylene-substituted aromatic monocarboxylic acids such as cinnamic acid.

(9) Aryl substituted mono and polycarboxylic aliphatic acids with carboxyl in the side chain such as phenylstearic, naphthyl stearic and naphthyl polystearic acids.

(10) Substituted aromatic mono and polycarboxylic acids containing halogen, hydroxyl, amino, alkyl, aryl, aralkyl, keto, nitro, or alkoxy in the nucleus, such as chlorbenzoic, salcylic, anthiranilic, toluic, phenyl-benzoic, benzoylbenzoic, nitrobenzoic and anisic acids.

(11) Non benzenoid cyclic mono and polycarboxylic acids such as abietic and camphoric acids, and heterocyclic carboxylic acids such as furoic acid.

Of the above organic acylating agents, those corresponding to the saturated aliphatic and aromatic acids are preferred. In most cases, compounds of higher V. I. can be prepared by use of the dibasic acid chlorides because of the formation of more resinous products thereby.

It will be understood, of course, that the metal chelate type of compounds described above is not limited to divalent metals but may include metals of a valence of one (such as silver), two, three, four, and five, and probably also six and seven. In the case of monovalent metals, secondary valences come into play in forming the metal-containing ring, such secondary valence forming the linkage or bond between the metal and the nitrogen of the amino group. Such secondary valences also may come into play in forming certain types of metal-chelate compounds in which the metal is poly-valent as will be readily understood by those skilled in the art. The structural formulae and methods of formation of these secondary metal-valence compounds as well as those involving only primary valences will also be readily understood by those skilled in the art from the illustrative general equation and general formulae given above. All the foregoing types of metal-containing compounds, including the non-chelate as well as chelate types, are contemplated by the present invention particularly as oil-improving agents.

If it is desired to obtain an alkylated amino-aryl hydroxylate containing an alkoxy group as an additional substituent on 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 chain length of at least twenty carbons (such as eicosylene, cerotene, melene, etc.) or a higher alcohol (such as myricyl alcohol, ceryl 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 hydroxy with a low molecular weight alkyl group. In carrying out this latter procedure, the alkylated polyhydric phenol is treated with an alkali alcoholate to introduce alkali metal into one OH group, followed by treating with the desired alkyl halide, whereby the substitution is effected.

When it is desired to obtain a compound of the present invention containing a keto group as an additional substituent on the aryl nucleus, the hydroxyaromatic starting material is first alkylated and then reacted with an aliphatic or aromatic acid anhydride in the presence of aluminum chloride as catalyst to effect the substitution before nitrating the compound. This substitution may also be carried out by reacting the alkylated hydroxyaromatic compound with an aliphatic or aromatic acid chloride, whereby the ester group is formed, followed by rearrangement of the acyl group to the nucleus. To cause this rearrangement, sufficient $AlCl_3$ must be used as catalyst.

Nuclear substituents such as nitroso, diazo, azo, ester, alkoxy, and ether-alcohol groups may be introduced after the nitration and reduction reaction by methods well-known to those skilled in the art.

A nuclear nitro group may be introduced by dinitrating the alkylated hydroxyaromatic compound, followed by selective reduction of only one nitro group, such as can be carried out by the ammonium sulfide method of reduction.

The following description illustrates certain preferred procedures which may be followed in synthesizing the wax-substituted amino-aryl metal oxides or hydroxylates contemplated by this invention. The compounds or products obtained from the procedures described below fall into that class or group of compositions hereinabove referred to as "preferred" because of their oil-solubility and their multifunctional activity when blended with mineral oil fractions. As will be apparent to those skilled in the art, compounds or compositions having a combined phenol 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 (PHENATES) OF NUCLEAR WAX-SUBSTITUTED AMINO- AND SUBSTITUTED AMINO-HYDROXYAROMATIC COMPOUNDS

(1) *Alkylation of phenol with petroleum wax*

A paraffin wax melting at approximately 120° F. and predominantly comprised of compounds having at least twenty carbon atoms in their molecules is melted and heated to about 200° F., after which chlorine is bubbled therethrough until the wax has absorbed about sixteen per cent

of chlorine, such product having an average composition between a monochlor wax and a dichlor wax. Preferably the chlorination is continued until about one-sixth the weight of the "chlorwax" formed is chlorine. A quantity of chlorwax thus obtained, containing three atomic proportions of chlorine, is heated to a temperature varying from just above its melting point to not over 150° F., and one mole of phenol (C_6H_5OH) is admixed therewith. The mixture is heated to about 150° F., and a quantity of anhydrous aluminum chloride corresponding to 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.

In forming the oil-miscible compounds or compositions it is important that all unreacted or non-alkylated hydroxyaromatic material (phenol) remaining after the alkylation reaction be removed. Such removal can be effected generally by water-washing, but it is preferable to treat the water-washed product with superheated 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 (sixteen per cent chlorine in the chlorwax) is reacted with one mole of phenol, may, for brevity herein, be designated as "wax-phenol (3—16)." Parenthetical expressions of this type (A—B) will be used hereinafter in connection with the alkylated hydroxyaromatic compounds to designate (A) the number of atomic proportions of chlorine in chloraliphatic material (chlorwax) reacted with one mole of hydroxyaromatic compound in the Friedel-Crafts reaction, and (B) the chlorine content of the chloraliphatic material. In the above example A=3 and B=16. This same designation will also apply to the heavy alkyl-substituted aryl metal oxides or wax-aryl metal phenolates derived from these alkylated hydroxyaromatic compounds.

Wax-phenol (3—16) as obtained by the above procedure had a phenol content or a "phenolic ratio" of about thirteen per cent. Our research indicates that this phenolic ratio of thirteen per cent may be considered as representing about the maximum for satisfactory miscibility in viscous oils of the alkyl-substituted aminoaryl metal oxides in which the alkyl substituent is derived from petroleum wax and the hydroxyaromatic constituent is derived from phenol (C_6H_5OH). Compounds or compositions of the type derived from phenol may be termed wax-substituted metal amino-phenolates or wax-substituted amino-phenyl metal oxides.

(2) *Introduction of amino and substituted amino groups into wax-substituted hydroxyaromatic compounds*

(*a*) INTRODUCTION OF (—NH_2) GROUPS

The introduction of an amino group into a wax-substituted hydroxyaromatic compound may be carried out by nitration followed by reduction in accordance with the previously described examples (with only slight variations) which illustrate these two steps in the conversion of tertiary amyl phenol into the corresponding tertiary amyl aminophenol. These variations consist mainly in the use of a suitable solvent or diluent for the wax-substituted compound and other minor variations such as the use of zinc dust as reducing agent which will be readily understood, by those skilled in the art, from the following example:

NITRATION AND REDUCTION OF WAX-SUBSTITUTED HYDROXYAROMATIC COMPOUND

Reaction mixture

100 g. of wax phenol (3—16, 13.7% combined phenol) (1 equiv.)
100 c. c. of Stoddard solvent
25 g. of $NaNO_3$ (2 equivalents)
60 cc. of water
31 g. of conc. H_2SO_4

Procedure

The sodium nitrate is dissolved in water and acidified with the conc. H_2SO_4, cooling to 120° F. and adding thereto the wax phenol dissolved in the Stoddard solvent. The temperature is allowed to rise to 140–160° F. during a one-hour period and then raised to 200° F. to complete the reaction. The mixture is cooled and all traces of acid removed by water-washing, thereafter removing the Stoddard solvent diluent to obtain the nitrated product.

The reduction of the nitro group of this nitrated product may be carried out as already stated in accordance with the previously described example of the reduction method showing the reduction of t-amyl nitro phenol, with use of a solvent and other variations similar to those indicated in the above nitration of wax-phenol.

INTRODUCTION OF SUBSTITUTED AMINO GROUPS INTO NUCLEAR WAX-SUBSTITUTED HYDROXYAROMATIC COMPOUNDS

After introduction of an unsubstituted amino group (—NH_2) into the nuclear wax-substituted hydroxyaromatic compounds by nitration and reduction as illustrated above the unsubstituted amino group may be N-substituted with alkyl, aralkyl or acyl (ester) groups as previously described.

(3) *Formation of metal salts (phenolates) of metal-free nuclear wax-substituted amino- and substituted amino-hydroxyaromatic compounds*

The substitution of the hydroxy hydrogen of the nuclear wax-substituted amino- or substituted amino hydroxyaromatic compound or product with its equivalent weight of metal may be effected in various ways of which the following is an example.

Example A

Wax-substituted amino-aryl oxides of the alkali and alkali earth metals and metals from the silver, copper, aluminum, tin and iron analytical groups can be readily prepared by the reaction of the wax-amino hydroxyaromatic compound with the desired alkyl metal oxide (metal alcoholate). The reaction mixture is heated to about 400° F. during a one-hour period, allowing the alcohol released to distill off, thereby obtaining nuclear wax-substituted amino-aryl metal oxide as the finished product. Anhydrous methyl, ethyl and butyl alcohols are considered preferable for preparing the alcoholates for use in this reaction. Illustrative reacting proportions are:

(*a*) 500 parts by weight wax-amino phenol (13.2% combined phenol)
16 parts by weight of sodium in the form of alkyl solution oxide; or equivalent amount of other alkali alcoholates.

(*b*) 500 parts by weight of wax-phenol (13.2% combined phenol).
14 parts by weight of calcium in form of alkyl calcium oxide or equivalent amount of other alkaline earth metal alcoholate.

In forming the wax-substituted amino-aryl metal oxides of the metals other than alkali metals through the use of alcoholates of such metals, the preferred procedure is to first form the alkyl oxides (alcoholates) of such metals by double decomposition of alkyl sodium oxide with an alcohol-soluble salt (such as a chloride acetate, or the like) of the desired metal. The wax-substituted amino hydroxyaromatic compound is then added to the alkyl metal oxide mixture without separating the pure alkyl oxide of the desired metal from the alkali salt, and the mixture is heated during one hour at 400° F., allowing the alcohol to distill off to complete the formation of the nuclear wax-substituted amino aryl oxide of the desired metal. The reaction product is then purified by diluting the mixture with a light mineral oil to aid the separation of the alkali salt, which is removed by settling, filtering or centrifuging, after which the diluent is distilled off to obtain the finished product.

By the use of an additional equivalent of metal in the above examples of reacting proportions, amino hydrogen may also be substituted to form compounds of the metal-phenolate-metal aminate type, as previously pointed out.

Additional examples

By the use of different metal salts and by varying the proportions of reactants, as will be understood from the above examples by those skilled in the art, the following additional oil-miscible wax-substituted compounds have been prepared and tested as oil-improving agents:

Cobaltous phenolate of wax aminophenol (3—16).

Cobaltous phenolate-cobaltous aminate of wax aminophenol (3—16).

Vanadyl phenolate-vanadyl aminate of wax aminophenol (3—16).

Stannous phenolate of wax aminophenol (3—16).

Stannous phenolate-stannous aminate of wax amino phenol (3—16).

Chromic phenolate-chromic aminate of wax aminophenol (3—16).

Stannous phenolate-phosphorous amide of wax amino-phenol (3—16).

Stannous phenolate-silicon amide of wax aminophenol (3—16).

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

As has been previously pointed out, the alkyl substituent in these alkyl-substituted amino-aryl metal oxides of the present invention should preferably be of relatively high molecular weight. In order to obtain compounds which have, when incorporated in oil, pour depressant and viscosity index improving properties along with other improved properties, such as sludge inhibition, etc., we have found that the alkyl substituents should preferably be in the nature of petroleum wax or an aliphatic hydro-carbon of correspondingly high molecular weight, and for that reason the wax-substituted compounds are considered preferable for these purposes. Although the wax-substituted products are considered preferable for the reasons just stated, oil-miscible nuclear alkyl-substituted amino-aryl metal oxides may be prepared from nuclear alkylated hydroxyaromatic compounds in which the alkyl substituent is derived from Transil oil (a highly refined viscous paraffin base white oil having a Saybolt viscosity of eighty-two seconds at 100° F. and specific gravity of 0.8498) and from tertiary amyl-phenol.

As will appear from the foregoing description, these oil-improving agents which are comprised within the scope of this invention may be characterized as oil-miscible "alkylated or alkyl-substituted amino-aryl metal oxides" or "alkylated amino-hydroxy-aromatic compounds in which the hydroxyl hydrogen has been replaced with its equivalent weight of metal," it being understood that the term "alkyl" and "alkylated" are used in a broad sense to include polyatomic or polyvalent, as well as monovalent aliphatic radicals or groups and also that the term "amino," except where otherwise indicated, is inclusive of substituted amino groups.

While the preferred method of preparing the alkylated amino-hydroxyaromatic compounds in which the amino group is unsubstituted is the nitration and reduction of the corresponding alkylated compound as described above, other methods may be employed for this purpose as follows:

(1) By reduction of alkylated nitroso-hydroxy-aromatic compounds (isomeric with quinone monoximes) with the above reagents.

(2) By coupling alkylated hydroxyaromatic compounds with benzene diazonium chloride and subsequent reduction as above.

(3) By electrolytic reduction of alkylated nitro-aromatic compounds.

(4) By reduction of alkylated nitro-hydroxy-aromatic compounds with hydrogen in the presence of a catalyst.

For the formation of the alkylated polycyclic compounds such as amino-naphthols, procedure 2 above is the preferred method.

As will be noted, each of these me thods is carried out after alkylation of the aromatic starting material. In method 3, as is well known to those skilled in the art, the aromatic nitro com-

pound is first reduced to aryl hydroxyl amine which under the conditions undergoes molecular rearrangement into the corresponding aminohydroxyaromatic compound.

SOLUBILITY OF THE METAL SALTS (PHENOLATE-TYPE) OF ALKYLATED AMINO- AND SUBSTITUTED AMINO-PHENOLS IN MINERAL OILS

As previously explained the compounds of the present invention can be rendered soluble in mineral oils when prepared from amino-hydroxyaromatic compounds containing C-alkyl substituents of sufficient molecular weight. An isoamyl substituent or a wax radical has been found necessary to give the desired oil-solubility. Substituents such as C-alkoxy or organic ester groups or N-alkyl, aralkyl or ester groups have solubilizing value, but are not desirable without C-alkyl substituents being present.

C-alkyl substituents are preferred to N-alkyl substituents not only for oil-solubilizing value, but because of the readiness of preparation and the effectiveness of metal or acyl metalloid derivatives prepared therefrom as oil-improving agents.

The wax-substituted amino-aryl metal oxides or wax-substituted amino-aryl metal hydroxylates 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 wax-substituted amino-aryl metal oxides 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, for example, intermediaries in the production of resins. Furthermore, as the phenol content is increased beyond the limits necessary for mineral oil-miscibility, the products become rubber-like in character and show definite promise as rubber substitutes without any substantial amount of additional treatment.

It is to be understood that while we have described certain preferred procedures for synthesizing the products contemplated by this invention and have listed a number of illustrative products or compositions, the invention is not limited to the particular procedures or products described but includes within its scope such changes and modifications as fairly come within the spirit of the appended claim.

This application is a continuation in part of our copending application Serial Number 317,122 filed February 3, 1940, patented 1942, U. S. Patent No. 2,280,039.

We claim:

Stannous phenolate of paraffin-wax-substituted aminophenol.

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