

UNITED STATES PATENT OFFICE

2,493,986

HEAVY METAL SALTS OF ALKYL PHENOL SULFIDES AND METHOD OF MAKING SAME

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No Drawing. Original application December 30, 1939, Serial No. 311,838. Divided and this application October 18, 1944, Serial No. 559,258

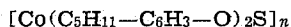
15 Claims. (Cl. 260—439)

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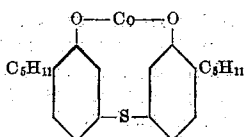
This invention relates to a novel type of metal compounds and methods of preparing same.

This is a division of our copending application Serial No. 311,838, filed December 30, 1939, now issued as Patent Number 2,362,293, granted November 7, 1944.

This invention relates to a class of metal compounds of which the cobalt salt of tertiary amyl phenol thioether is representative. This compound, which might also be called a cobalt tertiary amyl phenol sulfide, or a sulfide of cobalt tertiary amyl phenolate, is believed to have the formula:



where n is one or more. If the various groups attached to the aromatic nucleus are so positioned that the amyl group is in an ortho position to the oxygen, and the sulfur linkage is in a meta position to the oxygen, this compound probably has the following graphic formula in its simplest form:



Obviously, with both the cobalt and the phenol divalent, quite large complexes can theoretically be built up. It should be understood that the position of the various substituents around the aromatic nucleus may be varied without departing from the scope of the invention.

A similar disulfide compound may be used in which the group $-\text{S}-$ in the above graphic formula is replaced by the group



or if preferred by the group $-\text{S}-\text{S}-$, or even higher polysulfides may be used.

These various compounds can be produced by preparing the corresponding alkyl phenol sulfides or disulfides, which per se are known, and converting these into the corresponding sodium or potassium salts thereof, as by treatment with sodium or potassium hydroxide, and then converting the resultant derivative of the alkali metal into the corresponding derivative of cobalt by any suitable means, such as by double decomposition with a suitable corresponding cobalt compound, such as the chloride, nitrate, etc.

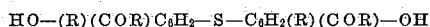
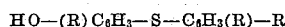
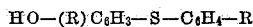
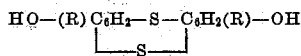
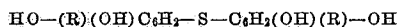
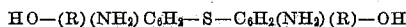
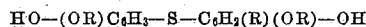
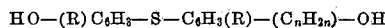
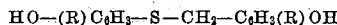
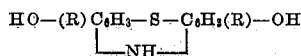
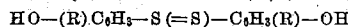
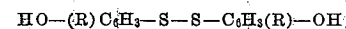
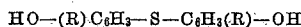
The invention may be described more broadly as comprising a product having an alkyl substituted aryl metal oxide in which the oxygen of

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the metal oxide group is directly attached to the aryl nucleus, in which at least two alkylated aryl nuclei are interconnected by at least one atom of an element of the sulfur family, in which the metal is a metal of group VIII, series 4, of the Mendeleeff periodic table, and in which the alkyl radicals each contain at least 4 carbon atoms.

The aryl nuclei may have attached other substituents for the hydrogen atoms and such substituents may be organic, inorganic, or both, for example, alkyl radicals and groups containing one or more of the non-metallic elements belonging to groups V, VI, and VII of the periodic system (Mendeleeff): nitrogen, phosphorus, oxygen, sulfur, and halogens, as in amino, nitro, phosphite, phosphate, hydroxy, alkoxy, sulfide, thioether, mercapto, chloro groupings, and the like.

Somewhat more specifically, the cobalt, nickel or iron derivatives may be used of the following type of phenolic compounds:



The configurations of the compounds are not limited to those shown in the illustrated structures, for the substituents may be in ortho, para, or meta relations to one another. Also, the substituents in any aromatic nucleus may be alike or different.

The aromatic nucleus may be polycyclic as in naphthalene, phenanthrene, diphenyl, etc. Where oxygen occurs, it may be replaced by sulfur, selenium or tellurium.

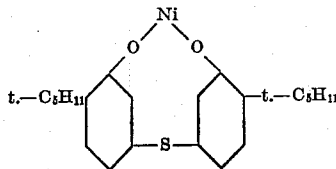
In the case where the metal is trivalent such as ferric iron, one, two, or all three of the valences of the metal may be connected to a

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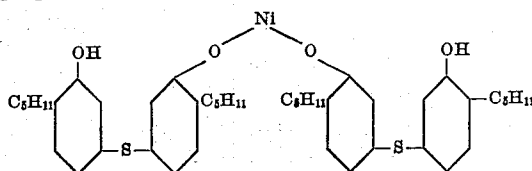
phenolic oxygen. For instance, in case of a tri-valent metal the thioethers of alkyl phenolate may have a formula such as the following:



As these substituted phenolates are generally made by reacting the corresponding phenols with a metal oxide or hydroxide (either the one desired, or the sodium or potassium compound to be converted into the one desired), the amount of metal in the phenolate product will depend on the proportions of reactant used, and if products having different proportions are possible, the products will usually consist of a mixture, which may be used as such or may be separated into several constituents. For instance, as will be seen from the experimental data given later, nickel derivatives of tertiary amyl phenol thioethers have been prepared which contain 3 different proportions of nickel. It is probable that the normal compound containing 1 nickel atom per thioether molecule, which should contain 18% NiO, should have the following graphic formula:



On the other hand, if only enough metal is reacted with the phenolic compound to combine with one of the hydroxyl groups it is likely that the resultant product will have the following graphic formula:

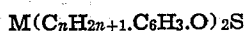


Finally, by using an excess of the metal, in using the cobalt or like salt for the double decomposition it is possible to make compounds containing even more metal than 1 atom per dihydroxy thioether molecule.

As seen from the above description, the metal compound preferably has the general formula:



where M is a metal selected from the group consisting of cobalt, nickel and iron, R represents one or more alkyl groups having enough carbon atoms (preferably a total of at least 10) to insure solubility of the total compounds in mineral oil, Ar is an aromatic nucleus, preferably a benzene nucleus, x is 1 or 2, and n is the valency of the metal. More particularly, compounds having the following general formula are preferred:



where M is cobalt, nickel or iron, n is at least 4, and preferably 5 or more, and where the group C_nH_{2n+1} is preferably a branched chain alkyl group.

For the objects stated, the metal phenolates have been preferably prepared from phenolic compounds readily obtainable by alkylation of the simple phenols or by extraction from high boiling petroleum oils.

Suitable synthetic alkyl phenols for preparing the desired phenol sulfides are principally of the

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secondary and tertiary types, because alkylation of a simple phenol occurs more readily with branched aliphatic reactants. Commonly, the alkylation reaction involves a condensation of olefins with the simple phenols, the reaction being catalyzed by anhydrous metal halides, sulfuric acid, phosphoric acid, or certain activated clays. As olefinic reactants, refinery gases containing propylene, butylenes, amylenes, etc., are economically useful, although individual olefins, e. g., isobutylene, iso-amylene, diisobutylene, triisobutylene, etc., or olefin-containing mixtures from other sources may be used. The reaction temperature is usually controlled to avoid side reactions. In employing sulfuric acid, a liquid phase reaction at relatively low temperatures is preferred; with phosphoric acid the reaction may be carried out in the vapor phase.

As starting materials for conversion into the metal phenol sulfides, the phenols may contain one or more substituents which provide a desired number of saturated carbon atoms in groups having the form of straight chains, branched chains, or even rings. Monoalkyl or polyalkyl phenols are synthesized conveniently by alkylating a phenol with branched chain olefin polymers, such as diisobutylene, di-tert-amylene, or other suitable agents, such as alcohols, alkyl sulfates, alkyl phosphates, or alkyl halides, thereby forming carbon-to-carbon bonds between the aromatic nuclei and the alkyl groups.

Petroleum phenols which qualify for the present purpose are considered to contain polymethylene or cycloalkyl side chains, as evidenced by their hydrogen and carbon analysis. The petroleum phenols are obtained by extraction of various stocks, chiefly from cracking process heating oil stocks, with caustic soda, and acidification of the alkaline extract with a weak mineral acid, followed by a non-destructive distillation if desired.

By using the described methods or any other well known method for preparing alkyl phenols, the following alkylated phenols may be procured for preparing the phenol sulfides, e. g., tert-amyl phenol, iso-hexyl phenol, tert-octyl phenol, di-tert-butyl phenol, di-tert-amyl phenol, di-normal amyl phenol, etc.

Inorganic substituents are introduced into alkyl phenols by well known methods. For example, an alkyl phenol, e. g., tert-amyl phenol, is reacted with sulfur mono-chloride, S_2Cl_2 , in about 1:1/2 mole ratio and preferably in a solvent such as dichloro-ethane, to produce the alkyl phenol disulfide. Using substantially the same procedure but substituting sulfur dichloride, SCl_2 , for the mono-chloride, the alkyl phenols are given a thioether linkage substituent. Alkyl chlorophenols are obtained by chlorination, preferably controlled to replace nuclear hydrogen by a chloro group. This may be accomplished by chlorinating the phenol before alkylation. In such a manner, for example, 2-chlor-4-tert-amyl phenol can be produced. Nitro substituents are introduced readily into the aromatic nucleus by direct nitration, and nitro substituents can be reduced to amino groups. It is to be understood, however, that the preparation of substituted phenolic compounds which have been described does not form part of this invention and that any of the well known methods for their production may be used.

The following experimental data illustrate the preparation of some cobalt and nickel derivatives of the substituted phenolic compounds according to this invention.

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Example 1.—Cobalt salt of tertiary amyl phenol sulfide.

7.7 grams ($\frac{1}{2}$ mole) of sodium were dissolved in 150 ccs. of absolute ethyl alcohol. 60 grams ($\frac{1}{2}$ mole) of tertiary amyl phenol sulfide, dissolved in 100 ccs. of absolute ethyl alcohol, were added. 23 grams (21.7 equals $\frac{1}{2}$ mole) of cobalt chloride, CoCl_2 (anhydrous) were dissolved in 250 ccs. of absolute ethyl alcohol and added to the above mixture with agitation. The solution turned brown. The alcohol was stripped off and the brown residue was agitated with 54 naphtha,¹ in which the cobalt salt of tertiary amyl phenol sulfide dissolved very readily, the sodium chloride resulting from the double decomposition remaining insoluble. The solution was filtered free of sodium chloride and then distilled to strip off the naphtha. 70 grams of a dark chocolate colored product were obtained. This product, which was cobalt tertiary amyl phenol sulfide, dissolved readily in a naphthenic base lubricating oil having a Saybolt viscosity of about 55 seconds at 210° F., such as is suitable for use as a crankcase lubricant for Diesel engines. Analysis indicated that this cobalt salt contained 17.65% of Co_3O_4 (theoretical 19.36%).

Example 2.—Nickel salt of tertiary amyl phenol sulfide

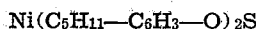
Some tertiary amyl phenol sulfide was converted into the corresponding sodium salt by treating with a solution of sodium in absolute ethyl alcohol, using $\frac{1}{2}$ mole of sodium and $\frac{1}{2}$ mole of the tertiary amyl phenol sulfide. 21.6 grams ($\frac{1}{2}$ mole) of nickel chloride, NiCl_2 , were suspended in 200 ccs. of absolute alcohol, and the resulting suspension was added to the alcohol solution of the sodium tertiary amyl phenol sulfide. The mixture was refluxed for 4 hours and gradually turned a dark green color. After refluxing for 24 hours more the solution was filtered free from insoluble materials (mostly sodium chloride and some unreacted nickel chloride), and the alcohol was stripped off the filtrate yielding 67 grams of a green solid which was readily soluble in the naphthenic oil base stock referred to in Example 1. Analysis of the product indicated a content of 6.40% of nickel oxide expressed as NiO . Based on the formula $\text{Ni}(\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_3-\text{O})_2\text{S}$ the reaction do not go to completion because the calculated content of NiO should be 18.0%.

This experiment was repeated using absolute methyl alcohol instead of ethyl alcohol as the solvent for the nickel chloride, a better reaction took place, and this time a green solid product was obtained which was found to have a content of 21.6% nickel oxide (NiO), which is slightly above the theoretical amount calculated for the formula given above. This product is also soluble in the naphthenic oil referred to.

In another experiment using methyl alcohol, 60 grams ($\frac{1}{2}$ mole) of tertiary amyl phenol sulfide were dissolved in 100 ccs. of absolute methyl alcohol and added to a solution of 7.7 grams ($\frac{1}{2}$ gram-atom) of sodium dissolved in 150 ccs. of methyl alcohol. 28 grams (21.6 grams equal $\frac{1}{2}$ mole) of anhydrous nickel chloride (NiCl_2) were dissolved in 300 ccs. of absolute methyl alcohol by refluxing, and after cooling this solution was added to the alcohol solution of sodium tertiary amyl phenol sulfide prepared first. A precipitate formed and another 60 cc. of alcohol were added

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and the mixture was permitted to stand over night. After recovering the precipitate, dissolving it in 54 naphtha, filtering off the residual sodium chloride and evaporation of the naphtha, a yellow-colored product was obtained which had a nickel oxide content of 17.9% NiO , which corresponds closely with the theoretical 18.0% for the compounds having the formula



This product is also soluble in the naphthenic oil referred to.

Example 3.—Nickel methoxo salt of tertiary amyl phenol sulfide

15.5 grams ($\frac{2}{3}$ gram-atom) of sodium were dissolved in 300 cc. of absolute methyl alcohol. 60 grams ($\frac{1}{2}$ mole) of tertiary amyl phenol sulfide dissolved in 100 cc. of methyl alcohol were added. 44 grams (23.2 grams equal $\frac{1}{2}$ mole) of anhydrous nickel chloride (NiCl_2) were dissolved in 400 cc. of trimethyl alcohol by refluxing. The nickel chloride solution was added to the above with agitation. A precipitate formed, and after standing for several hours the solution was filtered off, the precipitate being air-dried and the alcohol being stripped off from the filtrate. 30 grams of green solid were obtained from the filtrate and 114 grams of light-green solid from the precipitate. The two solids were combined and warmed with 54 naphtha, cooled and then filtered after standing over night. The naphtha was stripped off from the solution and a yield of 91 grams of an oil-soluble green solid was obtained which had a content of 27.45% of nickel oxide (NiO), which corresponds closely to the theoretical 27.90% calculated for the formula $(\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_3-\text{O}-\text{Ni}-\text{O}-\text{CH}_3)_2\text{S}$, the nickel methoxo salt of tertiary amyl phenol sulfide.

Example 4.—Nickel salt of tertiary amyl phenol disulfide

7.7 grams ($\frac{1}{2}$ gram-atom) of sodium were dissolved in 150 cc. of pure methyl alcohol. 65 grams ($\frac{1}{2}$ mole) of tertiary amyl phenol disulfide (obtained by treating tertiary amyl phenol with sulfur monochloride (S_2Cl_2)) dissolved in 100 cc. of methyl alcohol, were added to the first solution to form the sodium salt of tertiary amyl phenol disulfide. 25 grams (21.6 grams equal $\frac{1}{2}$ mole) of nickel chloride (NiCl_2) were dissolved in methyl alcohol by refluxing and the resulting solution was slowly added to the solution of sodium tertiary amyl phenol disulfide with agitation. After standing, the precipitate which formed was filtered off and dried. The yield equalled 68 grams.

The filtrate was stripped free of alcohol, leaving a residue of 39 grams. These two residues were combined and refluxed with 54 naphtha for a few minutes, cooled, settled for a day and the supernatant liquid was drawn off and stripped free of naphtha, leaving a residue of 75 grams of greenish-yellow solid which dissolved readily in the naphthenic oil referred to in Example 1 on heating. This product contained 15.49% of nickel oxide (NiO), which corresponds fairly well with the theoretical 16.72% calculated for the formula $\text{Ni}(\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_3-\text{O})_2\text{SS}$, the nickel salt of tertiary amyl phenol disulfide.

Example 5.—Cobalt salt of tertiary amyl phenol sulfide

This is the laboratory method of preparation which was subsequently adopted for the commer-

¹ A light solvent naphtha having a boiling range of 160–240° F.

cial manufacture of cobalt tertiary amyl phenol sulfide.

71.6 grams of tertiary amyl phenol sulfide were dissolved in 300 cc. of 98% isopropyl alcohol by warming and agitating. 16 grams of flake caustic soda were added and the mixture warmed to about 150° F. and agitated until the caustic soda was completely reacted to give a yellowish-brown solution of sodium tertiary amyl phenol sulfide in the alcohol. A solution of 27.6 grams of cobalt chloride hexahydrate in 150 cc. of isopropyl alcohol, prepared by warming the alcohol to about 125° F. and stirring, was then added, with stirring, to the alcoholic sodium tertiary amyl phenol sulfide solution, producing a brownish paste of cobalt tertiary amyl phenol sulfide suspended in alcohol. 320 grams of a Coastal naphthenic lubricating oil base stock having a viscosity of about 55 seconds Saybolt at 210° F. (a sufficient quantity to give a 20% solution of the cobalt salt) was then added and the alcohol was removed by stripping in vacuum. In order to assist in removing the last portion of the solvent, the product was blown with air. The finished product was filtered through paper and the filtered 20% concentrate of cobalt tertiary amyl phenol sulfide in the naphthenic lubricating oil base stock was found upon analysis to contain 3.42% of cobalt oxide (Co_3O_4) (which checks satisfactorily with the theoretical amount of 3.33%).

Corresponding cobalt, nickel or iron salts of other alkyl phenol sulfides may be prepared, for instance, by substituting polysulfide or polymers, such as the dimers, trimers, and tetramers of the alkyl phenol thio-ethers used in the above examples. Also, the corresponding metal salts of the corresponding selenides and tellurides may be prepared, although the sulfur compounds are preferred.

The various products obtained may be purified, if desired, by fractional crystallization, extraction, precipitation with selective solvents, etc. Also, impurities may be removed by treatment with suitable adsorptive agents such as clay.

The new compounds of the present invention are useful as additives for mineral lubricating oils, in which they are particularly effective in inhibiting oxidation and the formation of sludge under the high temperature conditions of service in internal combustion engines.

This invention is not to be limited to any of the specific examples presented herein, which were given solely for the purpose of illustration, but only by the following claims in which it is desired to claim all novelty inherent in the invention as far as the prior art permits.

We claim:

1. An oil miscible condensation product consisting of an alkyl substituted aryl metal oxide in which the oxygen of the metal oxide group is directly attached to the aryl nucleus, in which at least two alkylated aryl nuclei are interconnected by at least one atom of an element of the sulfur family in which said metal is a metal of group VIII, series 4, of the Mendeleeff Periodic Table, all of the valences of said metal being satisfied by an aryl oxide group as defined above, and in which the alkyl radicals each contain at least four carbon atoms.

2. Compound according to claim 1 in which said metal is cobalt.

3. Compound according to claim 1 in which said metal is nickel.

4. A metal salt of an alkyl phenol sulfide where-

in the metal is a metal of group VIII, series 4, of the Mendeleeff Periodic Table, all of the valences of the metal being satisfied by an alkyl phenol sulfide radical, and wherein each of the alkyl radicals contains at least four carbon atoms.

5. A neutral cobalt salt of an alkyl phenol sulfide in which each alkyl group contains at least 4 carbon atoms.

6. A neutral nickel salt of an alkyl phenol sulfide in which each alkyl group contains at least 4 carbon atoms.

7. A metal salt of a tertiary amyl phenol sulfide wherein the metal is a metal of group VIII, series 4, of the Mendeleeff Periodic Table, all of the valences of said metal being satisfied by a tertiary amyl phenol sulfide radical, and wherein each of the alkyl radicals contains at least four carbon atoms.

8. A neutral cobalt salt of a tertiary amyl phenol sulfide.

9. A neutral nickel salt of a tertiary amyl phenol sulfide.

10. A metal salt of an oil-soluble alkyl substituted phenol sulfide, each aliphatic radical containing at least four aliphatic carbon atoms, the metal being of group VIII, series 4, of the Mendeleeff Periodic Table, all of the valences of said metal being satisfied by an alkyl phenol sulfide radical.

11. The method of preparing a cobalt salt of an alkyl phenol sulfide which comprises reacting an alkali metal salt of an alkyl phenol sulfide with a cobalt halide.

12. A method according to claim 11 in which the cobalt salt is cobalt chloride.

13. A method according to claim 11 in which the alkali metal salt is a salt of di-tert.-amyl phenol sulfide and in which the cobalt salt is cobalt chloride.

14. A method of preparing a nickel salt of an alkyl phenol sulfide which comprises reacting an alkali metal salt of an alkyl phenol sulfide with a nickel halide.

15. A method of preparing a nickel salt of di-tert.-amyl phenol sulfide which comprises reacting the sodium salt of di-tert.-amyl phenol sulfide with nickel chloride.

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