Patented Feb. 8, 1949 2,461,335

UNITED STATES PATENT OFFICE

2,461,335

ORGANOMETALLIC COMPOUND

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No Drawing. Original application December 16, 1938, Serial No. 246,073. Divided and this application October 18, 1944, Serial No. 559,254

9 Claims. (Cl. 260—608)

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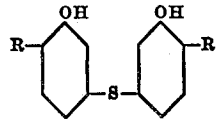
This invention relates to a novel type of metal compound and methods of preparing the same.

This is a division of my co-pending application Serial No. 246,073, filed December 16, 1938, now issued as Patent Number 2,362,289, granted November 7, 1944.

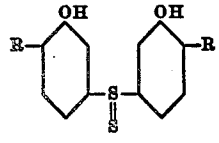
The new compounds of the present invention may be broadly described as compounds having an alkyl substituted aryl calcium oxide in which the oxygen of the calcium oxide group is directly attached to the aryl nucleus and in which at least two alkylated aryl nuclei are interconnected by at least one atom of an element of the sulfur family, the alkyl radicals each containing at least four carbon atoms. The aryl nuclei may contain additional substituents, such as halogens or nitro, nitroso, amino, hydroxy, carboxy, alkoxy, aroxy, mercapto groups, and the like.

Metal salts of alkyl phenol sulfides and polymers thereof have been found particularly effective improving agents for lubricating oils. These alkyl phenol sulfides include the following classes:

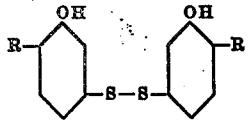
1. Alkyl phenol thioethers



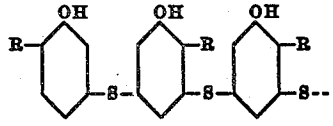
2. Alkyl phenol disulfides



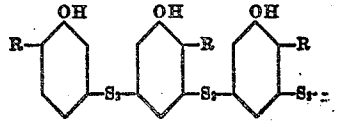
and



3. Polymers of alkyl phenol sulfides

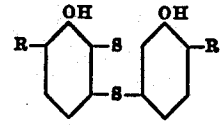


and

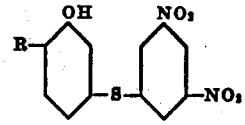


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4.



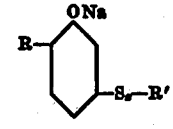
5. Dinitro phenyl alkyl phenol sulfide



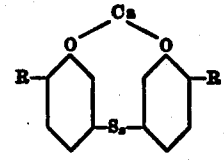
In all the above Formulae 1 to 5, R represents an alkyl group containing preferably about 4 to 8 carbon atoms. The sulfur atom represented by S in the above formulas may be substituted by selenium or tellurium.

This invention relates to calcium derivatives of all such compounds, in which the hydrogen of one or more of the hydroxyl groups is replaced by calcium. The metal may be connected to two hydroxyl groups of the same molecule or it may join two different molecules, which may be similar or different, at least one of the molecules being a phenol sulfide. Illustrative salts are represented by the following formulae:

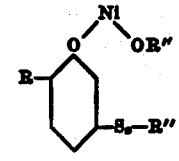
6.



7.



8.



The groups R, S_x, R' and R'' in the above formulae are the same as those described above. OR'' is preferably the same group as the other organic group attached to the nickel.

Illustrative compounds and suitable methods for their preparation are as follows:

Example I

1 mole of tertiary amyl phenol thioether (prepared by the method described in the French Patent 824,600) is dissolved in about 1½ times its volume of absolute ethyl alcohol. This solution is then added to a solution of sodium ethoxide, prepared by dissolving 2 moles of metallic sodium in an excess of absolute ethyl alcohol. The sodium salt of the phenol, described as the thioether of tertiary amyl sodium phenolate, is thereby formed and remains in solution in the excess ethyl alcohol.

It may be recovered by evaporation of the alcohol, or the solution may be added directly to a lubricating oil, in which case the alcohol may be removed by evaporation in case a lubricant having a high flash point is desired.

Other metal salts may be prepared from the sodium salt by a simple double decomposition reaction which is illustrated in the following example:

Example II

A slight excess over the calculated amount of the anhydrous halide (chloride or bromide) of calcium, such as calcium chloride, is dissolved in absolute ethyl alcohol, and the resulting solution is added with stirring to the alcoholic solution of the thioether of tertiary amyl sodium phenolate described in the preceding example. The thioether of tertiary amyl calcium phenolate (calcium salt of dialkyl dihydroxy diphenyl sulfide) is thus formed along with sodium chloride, which is insoluble in the absolute alcohol and precipitates therefrom. The mixture is then filtered to remove the precipitated sodium chloride and the alcohol removed by evaporation of the filtrate, the last stage of the evaporation being conducted under vacuum. If it is found that the sodium chloride is not completely removed, due to the presence of traces of water or other reason, the product may be further treated to remove the sodium chloride by any suitable means. For example, the dried product may be dissolved in petroleum naphtha in the absence of water. The sodium chloride remains undissolved and is separated from the naphtha solution by filtration.

In some cases it will be found that some of the metal salt of the phenol thioether precipitates along with the sodium chloride. It may be recovered by extracting the dried precipitate with 54° Bé. naphtha. The desired product is then obtained in concentrated form by evaporation of the naphtha.

Absolute methyl alcohol may also be used as solvent in place of the ethyl alcohol in the same processes described above.

Example III

Thioether phenolates of calcium may be prepared by a direct reaction of the phenol thioether and the oxide in the following manner: A mixture of 107 parts of tertiary amyl phenol thioether, 214 parts of xylol, 10.8 parts of water, and 16.8 parts of hydrated calcium oxide was heated to boiling under a reflux condenser provided with a trap for removing water from the reflux condensate. The refluxing was continued until all the water (16.5 parts) had been removed. There was thus obtained a xylol solution of the thioether of tertiary amyl calcium phenolate (calcium salt of diamyl dihydroxy diphenyl sulfide). The excess calcium oxide (or hydroxide) was insoluble in the xylol and was removed by filtration. The calcium salt of the tertiary amyl phenol thioether was then obtained by evaporation of the xylol from the filtrate.

Example IV

One part of anhydrous sodium hydroxide is suspended in 3 parts of 98% strength isopropyl alcohol. The theoretical amount of tertiary amyl phenol thioether for neutralization of the phenolic hydroxyl groups by the sodium hydroxide was then added. The resulting solution was then heated to boiling and two parts of the alcohol were distilled off. This rendered the distillation residue substantially anhydrous, since the distillate isopropyl alcohol is of 91% strength so long as water is present in the mixture being distilled. There was thus obtained a solution of the thioether of tertiary amyl sodium phenolate in absolute isopropyl alcohol.

Salts of calcium may be prepared by reacting the sodium salt with a calcium halide. For example, the theoretical amount of anhydrous calcium chloride is added to the distillation residue and the suspension heated under reflux until the calcium chloride has all reacted. The precipitated sodium chloride is then removed by filtration and the thioether of tertiary amyl calcium phenolate is obtained as a residue by evaporation of the isopropyl alcohol.

Example V

100 parts of benzene are added to 100 parts of 95% alcohol containing 25 parts of tertiary amyl phenol thioether and enough sodium hydroxide to neutralize the latter. The resulting solution is heated to boiling and water removed in the constant boiling mixture benzene-water-alcohol which distills over. Thereafter anhydrous calcium chloride is added to the distillation residue, which is an anhydrous solution in benzene and alcohol and the reaction is completed in the same manner as in Example IV.

A solution of calcium chloride in 95% ethyl alcohol may be used, instead of anhydrous calcium chloride, in which case the water present in the alcohol is removed by further azeotropic distillation. After removal of the water, the preparation of the thioether of tertiary amyl calcium phenolate is completed as described in Example IV.

Corresponding metal salts of alkyl phenol disulfides and polysulfides and of the polymers, such as the dimers, trimers, and tetramers of the alkyl phenol thioethers, disulfides, and polysulfides, may also be prepared by substituting the respective alkyl phenol sulfide for the alkyl phenol thioethers used in the above examples. Metal salts of the corresponding selenides and tellurides may also be prepared by similar methods.

The crude products may also, if desired, be subjected to further purification in addition to, or in combination with or in place of the distillations described above. Preparation of products of enhanced purity may be accomplished by fractional crystallization, by extraction or precipitation with selective solvents. Impurities may also be removed by treatment with suitable adsorptive agents, such as clay.

The new compounds of the present invention are particularly valuable as additives for lubricating oils, in which they inhibit oxidation and promote engine cleanliness when employed as

crankcase lubricants for internal combustion engines.

This invention is not to be limited to any specific examples presented herein, all of such being intended solely for purpose of illustration, but is limited only by the following claims in which it is desired to claim all novelty insofar as the prior art permits

I claim:

1. An oil miscible condensation product having an alkyl substituted aryl calcium oxide in which the oxygen of the calcium oxide group is directly attached to the aryl nucleus and in which at least two alkylated aryl nuclei are interconnected by at least one atom of an element of the sulfur family, the alkyl radicals each containing at least four carbon atoms.

2. As a new chemical compound, an alkyl substituted aryl calcium oxide having the structure —O—Ca—O—, in which each of the two atoms of oxygen is a nuclear attached oxygen of an alkyl phenol sulfide, the said alkyl groups containing at least four carbon atoms per molecule.

3. As a new chemical compound, a calcium salt of an alkylated phenol sulfide having the formula

$$R(OH)C_6H_3—S_x—C_6H_3(OH)R'$$

in which the groups R, R', OH and S_x are each connected to an aromatic nucleus (C_6H_3), R and R' represent alkyl groups (C_nH_{2n+1}), n being at least 4, and x is an integer, 1 or 2.

4. As a new chemical compound, a calcium salt of an alkyl phenol sulfide in which a plurality of phenol groups are attached to a single calcium atom and in which the alkyl groups each contain at least four carbon atoms.

5. The calcium salt of an alkyl phenol sulfide in which the alkyl radicals each contain at least four carbon atoms.

6. The calcium salt of a tertiary amyl phenol sulfide.

7. The calcium salt of an alkyl phenol sulfide in which each of the alkyl radicals contains between four and eight carbon atoms.

8. The method of preparing a calcium salt of an alkyl phenol sulfide which comprises reacting the sodium salt of an alkyl phenol sulfide with a calcium halide.

9. A process according to claim 8 in which the sodium salt is a salt of di-tert. amyl phenol sulfide.

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