

UNITED STATES PATENT OFFICE

2,472,504

ORGANOMETALLIC COMPOUND

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No Drawing. Original application December 30, 1939, Serial No. 311,835. Divided and this application October 18, 1944, Serial No. 559,256

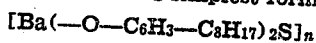
1 Claim. (Cl. 260-609)

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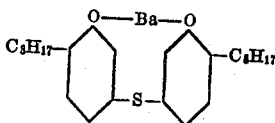
This invention relates to a novel type of metal compound and particularly to barium salts of alkylated phenol sulfides and the like.

This is a division of my copending application Serial No. 311,835, filed December 30, 1939, now issued as Patent Number 2,362,291, granted November 7, 1944.

The invention relates particularly to the preparation of a barium salt of diisobutyl phenol thioether, which might also be called a sulfide of barium tert.-octyl phenolate. It is believed to have the formula shown in its simplest form as



where n is one or more. If the various groups attached to the aromatic nucleus are so positioned that the tert.-octyl group is in an ortho position to the oxygen, and the sulfur linkage is in a meta position to the oxygen, this compound, although it might have other possibilities, probably has the following basic formula:



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. Furthermore, since both the barium and the organic molecule are divalent, it is apparent that, in combination, these agents may build up quite large molecules.

A similar disulfide compound may be prepared in which the group —S— in the above graphic formula is replaced by the group



or if preferred by the group —S—S— , and even higher polysulfides may be prepared.

These various compounds can be produced by preparing the corresponding alkyl phenol sulfides or disulfides, which per se are known, and converting these directly into the barium salts thereof, as by heating with barium hydroxide in a suitable diluent.

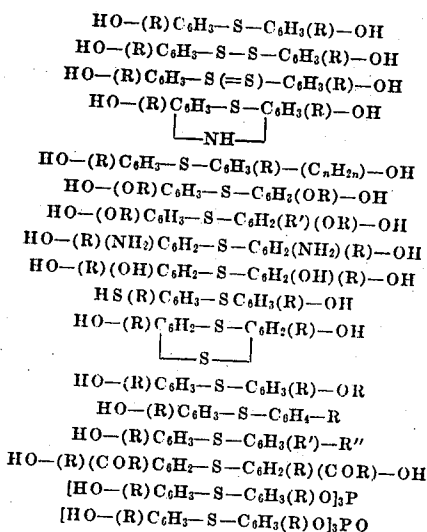
The new class of compounds described in the present specification have been found to be useful as addition agents for petroleum oils, particularly oils of the lubricating oil range, wherein they exhibit oxidation-inhibiting and corrosion-resisting properties.

The invention may be described more broadly as comprising an alkyl substituted aryl barium

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oxide in which the oxygen of the barium 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. This compound may contain one or more substituents in the aryl nucleus other than the alkyl radicals, and such substituents may be organic, inorganic, or both. For example, the substituents may be nitrogen, phosphorus, oxygen, sulfur or halogens, as in amino, nitro, phosphite, phosphate, hydroxy, alkoxy, sulfide, thioether, mercapto, chloro groups, and the like, or they may be organic radicals containing one or more of the inorganic groups.

Below are listed illustrative types of compounds whose barium salts fall within the scope of the present invention:



In the above formulas R, R' and R'' represent alkyl groups having at least four carbon atoms.

These preferred compounds may also contain sulfur in other positions or groups at the same time as in the places shown in the formulas.

The new compounds of the present invention may be described as oil miscible condensation products having an alkyl substituted aryl barium oxide in which the oxygen of the barium 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 sulfur, selenium or tellurium, the alkyl radicals each containing at least four carbon atoms. The aryl

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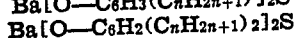
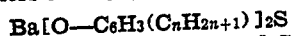
nucleus may also contain substituent atoms or groups such as halogen, nitro, nitroso, amino, hydroxy, carboxy, alkoxy, aroxy, mercapto, and the like. The alkyl substituents contain at least four carbon atoms but may contain many more, such as 8, 10, 16, 18, etc.

The configurations of the compounds are not limited to certain positions for the substituent groups, for these 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.

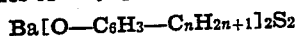
Specific examples of compounds falling into the classes mentioned, having at least one alkyl radical as a substituent are formulated as follows:

I. Thioethers of alkyl phenolates



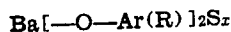
e. g. thioether of salts of tert.-octyl phenol, thioether of salts of tertiary amyl cresol.

II. Disulfides of alkyl phenolates

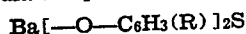


e. g. salts of tert. amyl phenol disulfide.

As suggested above, the barium compounds of this invention preferably have the general formula:



where x is 1 or 2, R represents one or more alkyl groups containing at least four carbon atoms each, having enough carbon atoms, preferably a total in the molecule of at least 10, to insure solubility of the compounds in mineral oil. More particularly still, compounds having the following general formula are preferred:



For the objects stated, the barium phenolates employed in the manufacture of the salts of phenol sulfides have been preferably prepared from phenolic compounds readily obtainable by synthetic alkylation of the simple phenols and cresols or by extraction from high boiling petroleum oils.

Suitable synthetic alkyl phenols for preparing the desired phenol sulfide salts are principally of the 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 barium salts of phenol sulfides, the phenols may contain one or more substituents which provide a desired number of carbon atoms in groups having the form of straight chains, branched chains, or even rings. Mono-alkyl or poly-alkyl phenols are synthesized conveniently by alkylating a phenol with branched chain olefin polymers, such as diisobutylene, triisobutylene, di-tert.-amylene, or

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other suitable agents, such as alcohols, alkyl sulfates, alkyl phosphates, or alkyl halides, thereby forming carbon-to-carbon bonds between the aromatic nucleus and the alkyl group.

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 phenolates: tert.-amyl phenols, iso-hexyl phenol, tert.-octyl phenol, di-tert.-butyl phenol, di-(tert.-octyl) phenol, etc.

Sulfur is 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 a 1:1/2 mol ratio and preferably in a solvent such as dichlorethane, 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.

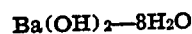
The invention will be better understood from a consideration of the following experimental data:

Example 1.—Barium salt of tertiary amyl phenol sulfide

7.7 grams (1/3 mole) of sodium were reacted with 150 ccs. of absolute methyl alcohol. 60 grams (1/3 mole) of tertiary amyl phenol sulfide in 100 ccs. of absolute methyl alcohol were added. 54.5 grams (49.5 grams = 1/2 mole) of anhydrous barium bromide dissolved in 300 ccs. of methyl alcohol were added with agitation. A copious yellow precipitate formed and was filtered off and air-dried. The filtrate was stripped free of methyl alcohol, leaving some more yellow solid. The two solid residues were combined and, after drying, were refluxed with light naphtha. A little naphtha was distilled off to remove some methyl alcohol still present, and then, after partially cooling, the salts were filtered off to leave sodium bromide as a filter residue. The naphtha was stripped from the filtrate, leaving a yield of 75 grams of the barium phenolate, a yellow product which dissolved very readily in naphthenic Diesel oil (viscosity of 55 secs. Saybolt at 210° F.) on heating. The product was found to contain 28.6% of BaO (theoretical 31.1%).

Example 2.—Barium tertiary octyl phenol sulfide

442 grams (1 mole) of tert.-octyl phenol sulfide (prepared by the reaction of sulfur dichloride with tert.-octyl phenol) were dissolved in 2316 grams of a 55 viscosity (Saybolt at 210° F.) naphthenic base oil. The solution was agitated and the temperature raised to 225° F. To the agitated solution 331 grams of barium hydroxide,



(the 331 grams of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ representing 1 mole of the hydroxide + 5% excess, to make allowance for impurities, particularly barium carbonate, in the hydroxide) were added gradually over a period of one and one-half hours, the rate of addition being governed by the rate of removal of water from the system. Towards the end of the reaction considerable foaming of the mixture

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occurred and the temperature was therefore raised to 275° F.-300° F. The product was stirred for an additional 15 minute period at 300° F., after complete removal of the water had been effected. The resulting 20% blend of barium tert-octyl phenol sulfide, a rather viscous light reddish-colored oil, was filtered through paper, using a filter aid. The filtering step was employed to remove small amounts of barium carbonate and unreacted barium oxide. The barium phenolates were thus obtained in oil solution in a form convenient for dilution to working strength.

Corresponding barium salts of other alkyl phenol sulfides may be prepared; for instance, by substituting polysulfides or polymers such as the dimers, trimers, and tetramers, of the alkyl phenol thioethers, disulfides, and the like, in place of the alkyl phenol thioethers used in the above examples. Also, the barium salts of the corresponding selenides and tellurides may be prepared, although the sulfur compounds are preferred for use as lubricating oil additives.

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 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 of the specific examples presented herein, which were given solely for the purpose of illustration, nor by any theory as to the mechanism of the

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operation of the invention, 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.

I claim:

The barium salt of a tertiary amyl phenol sulfide.

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