

UNITED STATES PATENT OFFICE

2,270,183

DIALKYLPHENOL SULPHIDES

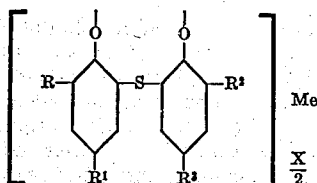
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No Drawing. Application March 13, 1941,
Serial No. 383,166

11 Claims. (Cl. 260-609)

This invention relates to 2,4-dialkylphenol sulphides and metal salts thereof.

The products of the present invention may be represented by the formula:



in which R, R¹, R² and R³ are alkyl radicals, Me is a heavy metal having a valence of at least 2 and X is the valence of Me. These products are of outstanding importance as corrosion inhibitors and sludge dispersers in lubricating oils. They have the important property that since the positions on the benzene ring ortho and para to the hydroxy group is occupied by alkyl radicals, there is no tendency toward linear polymerization with resultant sludge formation. When the alkyl radicals are of the length of five or more carbon atoms, extraordinary solubility of the salts in lubricating oils are obtained and the compounds withstand high temperature and oxygen to a marked degree. Sludge is dispersed even under extreme conditions and corrosion is not increased, and in many cases is reduced even with alloy bearings such as silver-cadmium, copper-lead, and the like, to extremely low figures. In this respect the compounds of the present invention are markedly superior to the mono-alkylated compounds, which although having some dispersing effect, tend to polymerize and form sludges. Also the mono-alkylated compounds do not have adequate solubility in the form of their metal salts.

The metal salts which are the most important species of the present invention may be of any heavy metal which is sufficiently basic to form salts with the weak acids. More particularly, salts of the heavy metals such as tin, zinc, and the like, are of importance as these compounds show maximum corrosion inhibiting effect. However, alkaline earth metal salts such as calcium and barium can also be prepared and in the case of the products of the present invention in which the alkyl chains have five or more carbon atoms, these salts are soluble in paraffin base hydrocarbons which is essential for use in lubricating oils.

While the present invention is not limited to any particular alkyl radicals, the 2,4-diamylphenol sulphides and their salts are particularly important because of the low price at which the

raw materials can be obtained for producing. Other alkyl substituents are, however, also important such as the hydrocarbon residues of waxes which may be partially chlorinated. In the case of such high molecular substituents it is preferable that only a single high molecular substituent be present in each ring and preferably in the ortho positions. Maximum high solubility is thereby obtained.

Another type of compound is the sulphide from 4-tertiary butyl-o-cresol which can also be cheaply prepared. The oil solubility of its salts in benzene hydrocarbons is, however, not quite so high and for use as a corrosion inhibitor in pure Pennsylvania lubricating oils, the products are therefore not quite so desirable as those containing higher molecular alkyl substituents.

While the present invention is not limited to any particular process of preparing the compounds, we have found that an excellent method is to react the corresponding 2,4-dialkylphenol with sulphur dichloride in solution in a suitable solvent such as carbon tetrachloride, ethylene chloride, trichlorethylene, and the like. The sulphide forms readily with good yield and salts can be prepared therefrom by direct action of the metal hydroxide or metal alcoholate in the case of strongly basic metals, or by double decomposition of the alkali metal salt with an alcoholic salt solution of the desired metal. Single metal salts can be prepared or mixed metal salts by using a mixture of the different metal compounds. In the case of mixed salts it is not certain whether each molecule of the disulphide unites with two different metals exclusively. It is probable, however, that at least a large portion of the product is of this form.

While in most cases it is desirable to use a single dialkylphenol, it is also possible to use a mixture of two different dialkyl phenols. In this case products obtained are usually mixed, associated with more or less of the two single compounds in question depending on the mixture of phenols used.

The invention will be described in greater detail in conjunction with the following specific examples. The parts are by weight.

EXAMPLE 1

2,4-diamylphenol monosulphide

468 parts of 2,4-diamylphenol was dissolved in about 180 parts of petroleum naphtha and 103 parts of sulphur dichloride, dissolved in about 50 parts of petroleum naphtha were added slowly with vigorous stirring. The temperature was

maintained at about 20–30° C. until all of the sulphur dichloride had been added and then heated under reflux for 45 minutes to complete the reaction and drive off the hydrogen chloride. The petroleum naphtha was then evaporated, and the viscous residue consisting of 2,4-diamylphenol monosulphide turned to a semi-crystalline mass after standing one or two weeks, having a melting point of 60–62° C. The product is readily soluble in organic solvents but insoluble in water.

EXAMPLE 2

2,4-diamylphenol disulphide

The process of Example 1 was repeated except that equimolecular parts of the sulphur monochloride was substituted for the dichloride used above. The disulphide of 2,4-diamylphenol was obtained.

EXAMPLE 3

2-methyl-4-tert. butylphenol monosulphide

328 parts of p-tert. butyl-o-cresol dissolved in 180 parts of petroleum naphtha, was reacted with 103 parts of sulphur dichloride dissolved in 50 parts of petroleum naphtha. Low temperatures of about 20–30° C. were maintained and the reactants added with vigorous stirring, thereafter completing the reaction under reflux for about an hour. After evaporation of the petroleum naphtha the product was obtained in the form of a rich brown colored viscous material melting at around 70° C. It was readily soluble in the usual organic solvents such as alcohol, ether and chloroform, and soluble in petroleum naphthas and lubricating oil, but substantially insoluble in water.

EXAMPLE 4

Barium salt of 2,4-diamylphenol sulphide

30 parts of 2,4-diamylphenol monosulphide was dissolved in about 50 parts of absolute alcohol and 50 parts of a petroleum naphtha containing about 70% aromatic hydrocarbons. With stirring 17.1 parts of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was added and the mixture warmed to effect solution and later to expel the water along with the solvents. Additional petroleum naphtha may be added and evaporation repeated to remove the last traces of water. Traces of the solvent are removed by warming in vacuo. The barium salt of the 2,4-diamylphenol monosulphide was obtained as a very viscous product which turned a dark dull colored green on exposure to the atmosphere.

EXAMPLE 5

Stannous salt of 2,4-diamylphenol sulphide

30 parts of 2,4-diamylphenol monosulphide was dissolved in about 70 parts of anhydrous alcohol and about 22 parts of benzene. 6.5 parts of solid sodium methylate was added and the mixture warmed until clear. 11.4 parts of anhydrous stannous chloride dissolved in 65 parts of absolute alcohol was added with stirring. The resulting mixture was warmed and part of the alcohol evaporated, adding benzene to replace it. After allowing to cool down gradually and stand for several hours, sodium chloride was removed by filtration. The stannous 2,4-diamylphenol monosulphide salt was obtained as a brown viscous material by evaporating the solvent.

EXAMPLE 6

Zinc salt of 2,4-diamylphenol sulphide

30 parts of 2,4-diamylphenol monosulphide was

dissolved in about 70 parts of anhydrous alcohol and about 22 parts of benzene. 6.5 parts of solid sodium methylate was added and the mixture warmed until clear. Thereupon 8.2 parts of zinc chloride dissolved in 65 parts of absolute alcohol was added with constant stirring. The resulting mixture was warmed to evaporate part of the alcohol, benzene being added from time to time to replace the alcohol lost through evaporation. After standing for several hours, sodium chloride was filtered off, and the zinc salt of 2,4-diamylphenol monosulphide was recovered by evaporation of the solvent.

EXAMPLE 7

Aluminum salt of 2,4-diamylphenol sulphide

30 parts of 2,4-diamylphenol monosulphide and 10 parts of aluminum butylate were reacted together following the procedure of Example 4, yielding the aluminum salt of 2,4-diamylphenol sulphide.

EXAMPLE 8

Stannous salt of 2,4-diamylphenol disulphide

30 parts of 2,4-diamylphenol disulphide was dissolved in 40 parts of absolute alcohol, 6.1 parts of sodium methylate was added, and the mixture warmed until reaction was complete. 10.7 parts of anhydrous stannous chloride in 50 parts of absolute alcohol were then added with stirring. After cooling and filtering off sodium chloride, the tin salt of 2,4-diamylphenol disulphide was obtained.

EXAMPLE 9

Barium salt of p-tert.-butyl-o-cresol monosulphide

p-tert.-Butyl-o-cresol monosulphide (30 parts by weight) was dissolved in 50 parts of absolute alcohol and 60 parts of aromatic petroleum naphtha. Finely ground barium hydrate (21 parts by weight) was then added and the mixture warmed with stirring until homogeneous. Heating was continued to evaporate the water along with part of the solvent. Additional petroleum naphtha was added from time to time to make up for that lost by evaporation. Finally, all the solvents are removed by evaporation leaving the barium salt as a yellow solid.

The alkaline earth and heavy metal salts of 2,4-diamylphenol monosulphide described in the foregoing Examples 4–7 are very soluble in mineral oils. A concentrate containing as much as 50% can be prepared in the highly paraffinic lubricating oils of the Pennsylvania type. The barium salt of 2-methyl-4-tert.-butylphenol monosulphide described in Example 9 was relatively less soluble in lubricating oil than the corresponding barium salt of 2,4-diamylphenol monosulphide.

EXAMPLE 10

2-dodecyl-4-tert. amylphenol monosulphide

Eighty parts of p-tertiary amylphenol monosulphide prepared by reacting p-tertiary amylphenol with sulphur dichloride, was warmed on a steam bath with 91.5 parts of crude dodecyl chloride obtained by chlorinating kerosene to the mono-chlorinated stage, and 20 parts of aluminum chloride. Vigorous stirring was maintained and the reaction continued for 2–3 hours until hydrogen chloride ceased to evolve. After reaction was complete the aluminum chloride was removed from the reaction product by washing first with warm dilute hydrochloric acid and

finally by washing in naphtha solution with water. After evaporating the naphtha solution the 2-dodecyl-4-tertiary amyphenol monosulphide was obtained in the form of a dark brown liquid.

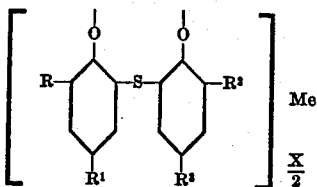
EXAMPLE 11

Barium salt of 2-dodecyl-4-tert. amyphenol monosulphide

Forty parts of 2-dodecyl-4-tertiary amyphenol monosulphide prepared as described in Example 10 was dissolved in 50 parts of absolute alcohol and 60 parts of toluene. Sixteen parts of finely divided barium hydrate was added and the mixture stirred with warming until it became homogeneous. On evaporation of the solvent the barium salt of 2-dodecyl-4-tertiary amyphenol monosulphide was precipitated as a semi-solid brown mass.

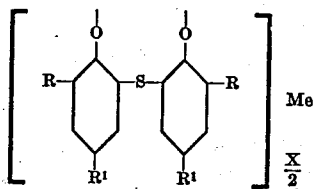
We claim:

1. 2,4-dialkylphenol sulphides having the following formula:



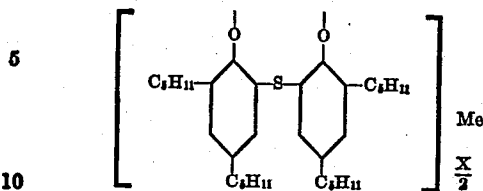
in which R, R¹, R² and R³ are alkyl radicals, Me is a heavy metal having a valence of at least 2 and X is the valence of Me.

2. 2,4-dialkylphenol sulphides having the following formula:



in which R and R¹ are alkyl radicals, Me is a heavy metal having a valence of at least 2 and X is the valence of Me.

3. Diamylphenol sulphides having the following formula:



in which Me is a heavy metal having a valence of at least 2 and X is the valence of Me.

4. The compounds according to claim 1 in which Me is tin.

5. The compounds according to claim 3 in which Me is tin.

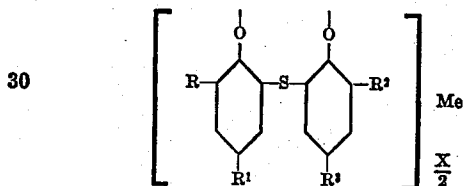
6. The compounds according to claim 1 in which Me is zinc.

7. The compounds according to claim 3 in which Me is zinc.

8. The compounds according to claim 1 in which Me is barium.

9. The compounds according to claim 3 in which Me is barium.

10. A method of preparing a 2,4-dialkylphenol sulphide of the formula:



in which R, R¹, R² and R³ are alkyl radicals, Me is a heavy metal having a valence of at least 2 and X is the valence of Me which comprises the steps of mixing sulphur dichloride with a 2,4-dialkylphenol, heating the mixture to expel HCl and complete the sulphide formation, adding a heavy metal hydroxide and continuing the heating to complete the salt formation.

11. A method of preparing a heavy metal salt of 2,4-diamylphenol monosulphide which comprises the steps of mixing 2,4-diamylphenol with sulphur dichloride, heating the mixture to expel HCl and complete the sulphide formation, adding a heavy metal hydroxide and continuing the heating to complete the salt formation.

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