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MANUFACTURE OF THIOETHERS OF ALPHA-ANTHRAQUINONE

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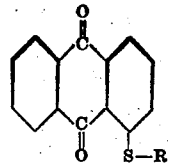
5 Claims. (Cl. 260—58)

This invention relates to the manufacture of thioethers of alpha-anthraquinone and it comprises methods of making such thioethers wherein an alkali metal salt of alpha-anthraquinone sulfonic acid is reacted with an alkali metal mercaptide, in an aqueous medium, the thioether so formed being isolated and recovered from the aqueous reaction mixture; and it also comprises the thioethers of alpha-anthraquinone so produced, particularly the alkyl thioethers of alpha-anthraquinone, these thioethers being useful as improvement agents for mineral lubricating oils and for other purposes; all as more fully hereinafter set forth and as claimed.

We have found that various organic thioethers are excellent improvement agents for mineral lubricating oils. Most of these thioethers are miscible with hydrocarbons and these, when incorporated with mineral lubricating oils, improve the lubricating qualities thereof. Thioethers of alpha-anthraquinone, particularly the alkyl thioethers thereof, are excellent improvement agents for this purpose. When small amounts are incorporated in mineral lubricating oils, the normal destructive action of mineral lubricating oil deterioration products on certain alloy bearing surfaces is mitigated or retarded. Also, the film strength of the lubricant is markedly improved. In our co-pending application Ser. No. 99,156 such methods of improving mineral lubricating oils and the improved lubricant so obtained with the aid of these thioethers are described and claimed.

The present application is directed to the thioether itself and methods of making the same. The thioethers made according to the present invention are particularly suitable for preparing the improved lubricants of our companion application.

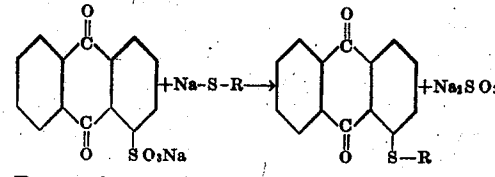
The thioethers made according to the present invention may be represented by the following formula:—



wherein "R" represents a hydrocarbon radical, advantageously an alkyl radical. As a class, these thioethers are soluble and miscible with mineral oils only in limited proportions. However, they are sufficiently soluble and miscible to permit incorporation with mineral oils of an amount of thioether sufficient to obtain the desired improvements.

In the present invention these thioethers are prepared from anthraquinone alpha sulfonic acid, that acid being first converted into a suitable salt for the reactions here employed. Alkali metal sulfonates of alpha anthraquinone are advantageous and the sodium salt of this sulfonic acid, being easily prepared, is ordinarily employed. Such salts of anthraquinone alpha sulfonic acid are reacted with metal mercaptides in aqueous solution to introduce a thioether group into the alpha position. Thus we may prepare various thioethers of alpha-anthraquinone by employing an appropriate mercaptan, the mercaptan being first converted into a suitable metal mercaptide. Again the alkali metal derivatives are advantageous, particularly the alkali metal alkyl sulfides. The sodium mercaptides being easily prepared and quite effective in these condensations, are ordinarily employed.

The reaction between the sodium salt of anthraquinone alpha sulfonic acid and sodium alkyl sulfide being typical, the following equation representing that reaction is illustrative of the condensation by which we obtain these thioethers of alpha anthraquinone:—



By employing other sodium hydrocarbon sulfides, various thioethers may be obtained in a similar manner. Thus the "R" in the structural formula given ante may represent various hydrocarbon radicals, such as acyclic, cyclic or heterocyclic, as well as simple aliphatic and aromatic compounds. By selecting various mercaptans we may obtain various thioethers having a wide range of properties. Thus by employing alkyl mercaptans we obtain alkyl thioethers of alpha-anthraquinone, which are particularly useful for improving mineral lubricating oils and making excellent lubricants. Likewise, the metal salts and derivatives employed may be selected and varied, according to the particular thioether being prepared, to facilitate the reaction and obtain high yields of the thioethers. However, as stated, the alkali metal salts and mercaptides, particularly those of sodium, are generally advantageous and are employed in the preparation

of most of our desired thioethers. With them the by-product sodium sulfite may be readily removed and separated from the thioether, for instance, by washing the thioether with water as more fully described post.

One advantageous starting material is the ethyl mercaptan; either the chemically pure or the technical grade may be used. In lieu of the ethyl compound, other alkyl mercaptans such as propyl or butyl mercaptans may be likewise employed. Also mixtures of two or more mercaptans may be employed, for instance, the commercial amyl mercaptan which contains both the normal and isomeric amyl compounds. The commercial amyl mercaptans having the following properties are advantageous in producing thioethers of anthraquinone useful as improvement agents for mineral oils:—

Inspection	Commercial amyl mercaptan	Ethyl mercaptan
Gravity ° A. P. I.	36.5	37.1
Specific gravity: 60°/60° F.	0.842	0.839
Sulfur percent	30.5	51.6
Boiling range ° F.	220–260	96.8–98.6

In the above table the properties of ethyl mercaptan are given for purposes of comparison with the properties of commercial amyl mercaptan.

Any of these organic mercaptans may be readily converted into alkali metal mercaptides for the present purposes. The thioether being formed from the mercaptide in an aqueous medium, the alkyl mercaptan is added to an aqueous caustic soda solution and the mixture is heated, if necessary, until the mercaptide is obtained. The solution of alkali metal mercaptide so prepared may contain a small amount of mercaptan. While we ordinarily employ the described procedure, the sodium alkyl mercaptide, when available as such, may be directly dissolved in water.

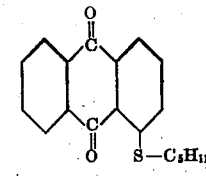
While any of the alkali metal sulfonates of alpha anthraquinone may be used it is advantageous to employ the sodium salt. The sodium salt is readily soluble in water and ordinarily we separately prepare an aqueous solution of the alkali metal sulfonate and then admix this solution with the solution of the mercaptide.

In forming the thioether we find it is advantageous to employ a slight excess of the mercaptide or mercaptan over that theoretically necessary to react with the alkali metal sulfonate. In this way substantially all of the anthraquinone compound is converted into the thioether, the presence of the mercaptide in slight excess causing a substantially complete precipitation of the thioether. Thus a high yield of anthraquinone thioether is obtained from the initial anthraquinone compound. However, during the mixing of the two solutions and during the early part of the reaction, we have found it advantageous to have the alkali metal sulfonate present in excess as the reaction is more easily controlled and a uniform reaction more readily obtained under such conditions. To obtain the desired conditions at each stage, we first heat the solution of the alkali metal sulfonate to about boiling temperature and then slowly add the alkali mercaptide solution; it being added at such a rate that no substantial excess of mercaptide is present until after the main reaction is substantially complete. During this addition of the mercaptide solution the mixture is maintained at boiling temperature under reflux. When all the mercaptide solution has been added there is a slight excess of mercaptide over that necessary to form the thioether. This mixture is then further boiled under reflux to complete the reaction; this additional heating being continued until substantially all the thioether has been precipitated, ordinarily five to ten hours of heating being sufficient to complete the reaction. At the end of the reaction the refluxing is discontinued and any mercaptan present is distilled off and recovered. Sometimes it is advantageous to add a small amount of free mercaptan before the final heating to complete the reaction, the mercaptan being added for instance in the proportion of one to two percent by weight.

The thioether is then separated and recovered. It may be separated from the aqueous liquid by decantation, filtration or other suitable method, depending upon whether the particular thioether is a liquid or solid material. The separated thioethers may be further purified if desired. Being insoluble in water, they may be washed with water and then dried. The solid thioethers may be drained and dried in a current of warm air. The wet liquid thioethers may be warmed and a current of air blown through the heated liquid to remove the residual moisture.

In this way, thioethers, either liquid or solid at room temperature and having a wide range of properties, may be obtained according to this invention.

As stated ante, alpha anthraquinone thioethers containing alkyl groups, such as the various amyl groups, may be readily obtained by the method of the present invention. All the amyl compounds have advantageous properties. Of these the normal-amyl thioether of alpha anthraquinone is typical; this amyl compound has the following formula:—

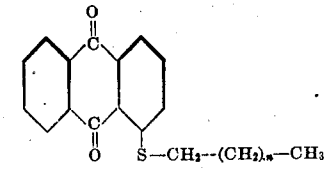


The thioethers obtained from the commercial amyl mercaptans often contain all the possible isomers and, being mixed thioethers, are advantageous for certain purposes such as improving the qualities of mineral oils. There are some specific advantages in both normal-amyl and iso-amyl compositions. The same is true of thioethers derived from butyls and propyls; each having specific advantages in certain relationships.

Other alkyl thioethers which may be obtained by the present method are as follows:—

Alpha-anthraquinone-ethyl-thioether
Alpha-anthraquinone-butyl-thioether
Alpha-anthraquinone-propyl-thioether

These specific thioethers, especially advantageous for improving petroleum oils and mineral oil lubricants, as a sub-class may be represented by the following formula:—



wherein "*n*" is 0 to 3. However, in the broad practice of this invention, other thioethers of al-

pha anthraquinone may be prepared as stated ante.

These thioethers are quite stable even at the elevated operating temperatures often encountered in the lubrication of alloy bearings. Also, they are substantially neutral in reaction. The properties of some of the alkyl thioethers, ordinarily employed in the present invention, are as follows:—

Alkyl-thioether of alpha-anthraquinone	Melting point ° C.	Percent theoret.	Sulfur empiric.	Color
Ethyl	180–185	11.62	11.40	Orange
Propyl	147–150	11.40	11.27	Orange
Butyl	108–110	10.82	10.40	Golden-yellow
Commercial amyl (mixture of n-amyl and iso-amyl).	Oil at normal temp.	---------	10.33	Golden-yellow

The above compounds are insoluble in water, slightly soluble in ethyl alcohol, and soluble in benzene. When crystallized as pure compositions from benzene they yield golden-yellow to red colored crystals.

The amyl thioether, being liquid, has excellent blending qualities and is readily soluble in mineral oils at the usual blending temperatures, for instance from 120° to 280° F. By employing different thioethers of alpha anthraquinone containing as the ether group any radical from either the aliphatic or aromatic series of hydrocarbons we can obtain products of various properties, this being advantageous for particular embodiments of the present invention. These various products may be produced by selecting the proper mercaptan as the starting material.

Example 1.—An aqueous solution of sodium anthraquinone alpha sulfonate is prepared by dissolving 320 pounds of said sodium sulfonate in 5000 pounds of hot water, advantageously boiling water. If necessary the solution may be filtered to remove any solid or undissolved material. Ordinarily this filtration is not necessary as the usual commercial grades of this sodium salt are comparatively pure and no solid nor undissolved matter remains suspended in solution.

Separately there is prepared an aqueous solution of sodium alkyl mercaptide by adding 64 pounds of ethyl mercaptan to 800 pounds of 5.0% aqueous caustic soda solution, the mixture being stirred and maintained at room temperature until the reaction is substantially complete. With the proportions given, the solution of mercaptide also contains a small amount of ethyl mercaptan.

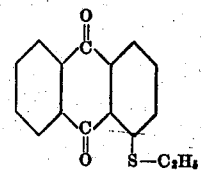
The aqueous solution of sodium sulfonate, as prepared above, is heated to boiling and then the aqueous mercaptide solution is gradually added while continuing the boiling; about one hour being required to so mix the amounts of the two aqueous solutions given ante. During this time the mixture is heated under reflux. After all the mercaptide solution is added, the mixture is further boiled under reflux for a period of five hours or more until the reaction is complete and substantially all the alpha anthraquinone ethyl thioether has been precipitated.

The mixture is then cooled and permitted to stand for about ten hours to permit complete settling of the precipitated thioether; the thioether settling to the bottom of the reaction vessel as a solid material. After thorough settling, the aqueous sodium sulfite liquor is removed by decantation. The crystalline mass of thioether so obtained is then washed with two volumes of water to free it from residual sodium sulfite. The washed crystals are then air dried.

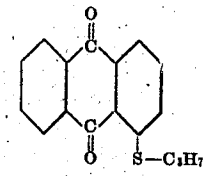
The alpha anthraquinone ethyl thioether dry crystals have the following properties:—

Melting point ° F.----------180–185
Sulfur per cent.----------11.40
Color.----------Orange

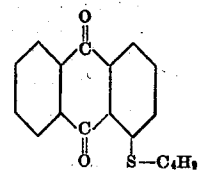
This thioether may be represented by the following formula:—



By employing a solution of sodium propyl mercaptide or of sodium butyl mercaptide, in lieu of the ethyl compound in the procedure of Example 1, there is obtained the corresponding butyl or propyl thioether of alpha anthraquinone. The thioethers so obtained have the following structural formulae:—



Anthraquinone alpha propyl thioether



Anthraquinone alpha butyl thioether

The above alpha anthraquinone thioethers have the following properties:—

Inspection	Alpha anthraquinone thioether	
	Propyl	Butyl
Melting point ° F.	147–150	108–110
Sulfur, percent.	11.27	10.40
Color.	Orange	Golden-yellow

Example 2.—An aqueous solution of sodium anthraquinone alpha sulfonate is prepared by dissolving 320 pounds of said sodium sulfonate in 5000 pounds of hot water, advantageously boiling water. If necessary the solution may be filtered to remove any solid or undissolved material. Ordinarily this filtration is not necessary as the usual commercial grades of this sodium salt are comparatively pure and no solid nor undissolved matter remains suspender in solution.

Separately there is prepared an aqueous solution of sodium amyl mercaptide by adding 106 pounds of commercial amyl mercaptan to 800 pounds of 5.0% aqueous caustic soda solution, the mixture being stirred and maintained at room temperature until the reaction is substantially complete. With the proportions given, the solution of mercaptide also contains a small amount of amyl mercaptan.

The aqueous solution of sodium sulfonate, as prepared above, is heated to boiling and then the aqueous mercaptide solution is gradually added

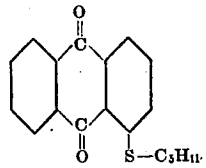
while continuing the boiling; about one hour being required to so mix the amounts of the two aqueous solutions given ante. After all the mercaptide solution is added, the mixture is further boiled under reflux for a period of five hours or more until the reaction is complete and substantially all the alpha anthraquinone amyl thioether has precipitated.

The mixture is then cooled and permitted to stand until it has stratified into an oily thioether layer and an aqueous liquid. The aqueous liquid is withdrawn and the oily thioether of anthraquinone is washed with water to free it from residual sodium sulfite. The wet oil is warmed to about 185° F., or slightly higher, and blown with a current of air until substantially dry.

The anthraquinone alpha amyl thioether so obtained has the following properties:—

Melting point ° F	Oil at ordinary temperatures
Sulfur, per cent	10.33
Color	Golden-yellow

Amyl thioether of alpha anthraquinone as prepared above may be represented by the following structural formula:—



What we claim is:—

1. In the manufacture of organic thioethers of anthraquinone from alpha-anthraquinone sulfonic acid, the improvement which comprises heating an aqueous solution of an alkali metal salt of alpha-anthraquinone sulfonic acid to boiling, gradually adding to the said boiling solution an aqueous solution of an alkali metal mercaptide, further boiling the reaction mixture until the reaction is substantially complete and recovering the organic thioether of alpha-anthraquinone so obtained.

2. In the manufacture of organic thioethers of anthraquinone from alpha-anthraquinone, the improvement which comprises preparing an aqueous solution of an alkali metal salt of alpha-anthraquinone sulfonic acid by dissolving said alkali metal salt in boiling water, separately preparing an aqueous solution of an alkali metal mercaptide by adding the mercaptan to an aqueous solution of caustic soda and stirring the mixture at room temperature until the formation of the mercaptide is substantially complete, then gradually adding the said solution of alkali metal mercaptide to the said boiling solution of alkali metal salt of alpha-anthraquinone sulfonic acid and further boiling the reaction mixture until the reaction is substantially complete and subsequently recovering the organic thioethers of alpha-anthraquinone from said reaction mixture.

3. The process of claim 2 wherein said sulfonate is sodium sulfonate.

4. The process of claim 2 wherein said mercaptide is sodium ethyl mercaptide.

5. The process of claim 2 wherein said mercaptide is sodium amyl mercaptide.

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