

UNITED STATES PATENT OFFICE

2,279,711

DESULPHURIZATION OF ALKYL PHENOLS

Daniel B. Luten, Jr., and Aldo De Benedictis,
Berkeley, Calif., assignors to Shell Development
Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application May 7, 1940,
Serial No. 333,834

8 Claims. (Cl. 260—627)

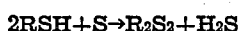
This invention relates to the desulphurization of alkyl phenols by treating the same preferably in the liquid state at moderately elevated temperature with sulphur.

The term alkyl phenols as employed herein refers to mixtures of acid-reacting hydroxy aromatic compounds consisting essentially of hydroxy alkyl-substituted benzenes and containing varying amounts of phenols and impurities such as sulphur and nitrogen compounds. The alkyl phenols, frequently spoken of in the trade as "acid oils" and "cresylic acid," are obtained in the extraction of cracked mineral oils or coal tar distillates with aqueous alkali metal hydroxide solutions and subsequent acidification of the alkaline extracts so obtained.

The applications for the alkyl phenols are numerous. For instance, the alkyl phenols are employed in ore flotation processes; also in the synthesis of many chemicals, such as resins, cyclic alcohols, ketones and acids. They are also commonly used as anti-oxidants, disinfectants, insecticides, selective solvents, etc. The presence of certain impurities, in particular organic sulphur compounds, very frequently decreases the usefulness of the alkyl phenols.

The purpose of this invention is to provide a method for desulphurization of alkyl phenols, whereby the sulphur content is decreased sufficiently so that it does not restrict the usefulness of the alkyl phenols unduly. Another purpose is to provide a process which is economical, simple and easy to carry out.

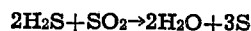
We have found that alkyl phenols containing aromatic mercaptans may be treated with sulphur to produce higher boiling disulphide which then can be readily separated from the treated alkyl phenols by fractional distillation thereby recovering the alkyl phenols with a greatly reduced sulphur content. Our invention comprises treating alkyl phenols containing aromatic mercaptans with sulphur until a major portion of and preferably substantially all of said mercaptans have been converted to the higher boiling disulphides, and recovering the alkyl phenols from the treated mixture by fractional distillation. In the reaction between the free sulphur and mercaptans, free sulphur is consumed probably in accordance with the equation:



Time and temperature of the sulphur treatment are preferably 2 to 10 hours at 60° to 200° C. In the fractional distillation the higher boiling fractions, i. e., the still bottoms, normally

accumulate the major portion of sulphurous components. Moreover a relatively low-boiling first cut frequently has a high content of sulphur compounds comprising hydrogen sulphide. Consequently it may be desirable to divide the distillate into three or more fractions, a small fore-cut, a large heart-cut, and a relatively small high-boiling residue or bottoms. By separately collecting the heart-cut, which may amount to about 75 to 95% of the still charge, purified alkyl phenols are obtained of very low sulphur content.

The treating agent in our process is sulphur, preferably elementary sulphur. Both pure and crude forms of sulphur may be used, provided impurities which may be present do not adversely affect the conversion of the mercaptans to disulphides. The sulphur may be introduced in any physical shape, granulated or pulverized sulphur usually being most satisfactory. Instead of admixing free sulphur, we may employ sulphur yielding compounds such as inorganic polysulphides, which liberate elemental sulphur under the conditions of the treatment. Or else we may introduce into the alkyl phenols two or more compounds which when reacting with each other form free sulphur. Thus we may introduce H_2S and SO_2 which react according to the equation:



The principal factors in the conversion of the aromatic mercaptans to disulphides are time of treatment, temperature and amount of treating agent.

As already stated, generally a time of treatment between about 2 to 10 hours is sufficient for our purposes, although the treatment may be conducted for periods of time outside these limits. Usually periods less than 2 hours are insufficient for the conversion, while periods greatly in excess of 10 hours are of little additional advantage, and merely increase the cost of the treatment.

Suitable reaction temperatures lie between about 60° to 290° C., and preferably between about 80° to 150° C. At temperatures below this limit the conversion of mercaptans to disulphides proceeds too slowly. Above 200° C. side reactions involving the destruction of the alkyl phenols as by dehydration, sulphurization, etc., become extensive, and consequently treating temperatures should not exceed this limit.

Amounts of sulphur for satisfactory conversion of the mercaptans to disulphides should be at least about 10% and preferably not less than

25% in excess of the stoichiometric quantity required in the reaction. Smaller amounts of sulphur tend to result in inadequate conversion. Generally we prefer to mix with the alkyl phenols twice or several times the stoichiometric quantity calculated from the probable reaction shown earlier. Preferably the conversion reaction is operated in the liquid phase. Vapor phase operation introduces the possibility of cracking, difficulty of proper contact with the sulphur, and necessity of large and cumbersome equipment, etc.

Following the conversion of the aromatic mercaptans to higher boiling disulphides, the treated mixture of alkyl phenols is fractionally distilled. The distillation should be carried out at the lowest practical temperature to avoid, or at least retard, decomposition of disulphides through reforming to volatile sulphur compounds boiling within the boiling-range of the alkyl phenols. Vacuum distillation is preferred, and the time during which the still charge is kept at the distilling temperature should be reduced to a minimum.

The first fraction coming over usually contains some low-boiling sulphur compounds, such as hydrogen sulphide. For this reason it is preferable to discard a first cut amounting to between 1 to 15% of the still charge. One or more middle fractions which are collected separately constitute the heart-cut of the distillate and make up the desulphurized alkyl phenols. They may amount to about 75 to 95% of the still charge. A distillation residue is obtained generally amounting to 2 to 10% of the charge, which contains most of the sulphurous materials and therefore is discarded.

Batchwise or continuous sulphur treatment and distillation methods may be employed.

If it is desired further to reduce the sulphur content of the resulting purified alkyl phenols, they may be treated by the method of De Simo, described in U. S. Patent 2,168,256. However, for most uses, the desulphurized phenols produced by our process will be highly satisfactory.

The conversion of the aromatic mercaptans to disulphides with sulphur does not normally require the presence of catalysts, although if desired sulphur-active catalysts such as PbS, NiS, etc., may be present.

The following examples serve to illustrate our process:

Example I

A quantity of 2 kilograms of alkyl phenols boiling from 220° to 240° C., and containing about 0.25% of mercaptan sulphur was treated with 30 grams of elementary sulphur at 100° C. for a period of 6.5 hours. At the end of this time the mercaptan content was 0.01%. After heating for another 7 hours, the sample was vacuum distilled. The first 71% of the distillate contained 0.027% total sulphur (lamp-acidimetric method, corrected) of which less than 0.001% was hydrogen sulphide and less than 0.0001% was mercaptan sulphur. The next 26% of distillate contained 0.10% total sulphur.

Example II

An amount of 135 parts of alkyl phenols boiling at 220° to 240° C. and containing 0.61% total sulphur including 0.22% as mercaptan sulphur, was treated with one part of elementary sulphur for about 5 hours at about 100° C. Following

this treatment the sample was fractionally distilled under vacuum. The sulphur distribution in the various fractions was as follows:

Fraction No.	Per cent of still charge	Per cent sulphur
1	26.2	0.09
2	51.3	0.06
3	19.1	0.21
Bottoms	3.6	23.3

We claim as our invention:

1. In a process for desulphurizing alkyl phenols containing aromatic mercaptans, the steps of treating said alkyl phenols in the liquid state with an amount of free sulphur at a temperature between 60° and 200° C. for a time sufficient to consume a portion of said free sulphur, and fractionally distilling the resulting product to produce a relatively small residue of high sulphur content and a large distillate fraction having a reduced sulphur content, said amount of free sulphur being at least 10% in excess of the stoichiometric amount required to react all of said mercaptans according to the equation:



2. The process of claim 1 in which the temperature is about 80 to 150° C.

3. The process of claim 1 in which the time of contact is between 2 to 10 hours.

4. The process of claim 1 in which the excess of free sulphur is at least 25%.

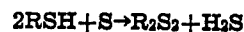
5. The process of claim 1 in which the distillate fraction amounts to 75 to 95% of the still charge.

6. The process of claim 1 in which the residue is less than 10% of the still charge.

7. In a process for desulphurizing alkyl phenols containing aromatic mercaptans, the steps of treating said alkyl phenols in the liquid state with an amount of free sulphur at a temperature between 60° and 200° C. for a time sufficient to consume a portion of said free sulphur, and fractionally distilling the resulting product to produce three fractions comprising a low-boiling first fraction, a second fraction, and a residual third fraction, said amount of free sulphur being at least 10% in excess of the stoichiometric amount required to react all of said mercaptans according to the equation:



8. In a process for desulphurizing alkyl phenols containing aromatic mercaptans, the steps of treating said alkyl phenols in the liquid state with an amount of free sulphur at a temperature between 60° and 200° C. for a time sufficient to consume a portion of said free sulphur, and fractionally distilling the resulting product to produce three fractions comprising a low-boiling first fraction amounting to 1 to 15% of the still charge, a second fraction amounting to 75-95% of the still charge, and a residual third fraction amounting to 2 to 10% of the still charge, said amount of free sulphur being at least 10% in excess of the stoichiometric amount required to react all of said mercaptans according to the equation:



DANIEL B. LUTEN, Jr.
ALDO DE BENEDICTIS.