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PURIFICATION OF ALKYL PHENOLS

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This invention relates to the purification of alkyl phenols by removing nitrogen compounds from them by a solvent extraction process, and is a continuation-in-part of our co-pending application Serial No. 354,398, filed August 27, 1940.

The term "alkyl phenols," as used herein, refers to mixtures of acid-reacting hydroxy aromatic compounds consisting predominantly of alkyl phenols, such as may be obtained by extracting cracked mineral oils or coal tar distillates with strong aqueous caustic alkali solutions. These mixtures usually contain nitrogen compounds of a composition not definitely known but apparently comprising lactams, at least a portion of which have slight if any basic properties and which cannot therefore be removed by washing the alkyl phenols with solutions of strong acids. Neither can these nitrogen compounds be removed by washing a solution of the phenols in aqueous caustic alkali with a water-immiscible solvent, such as a hydrocarbon liquid. In addition, alkyl phenol mixtures ordinarily also contain small quantities of basic nitrogen compounds which can more or less readily be removed by acid treatment.

Alkyl phenols have a number of important applications, such as in the flotation of ores, manufacture of resins, cyclic alcohols, ketones and the like; or as anti-oxidants, disinfectants, selective solvents, etc. The presence of impurities such as nitrogen compounds frequently impairs the usefulness of the alkyl phenols for these purposes.

It is therefore the object of this invention to remove from alkyl phenols nitrogen compounds which resist removal by means heretofore known, thereby rendering the former more suitable for the uses to which they are put.

To simplify the language of the specification, hereafter nitrogen compounds which are insufficiently basic to be removed by acid washes are called "non-basic" to distinguish them from the nitrogen bases which are removable by scrubbing with acids.

The availability for removal of the non-basic nitrogen compounds seems to depend on their release from a complex with the alkyl phenols by the formation of another more stable complex.

Our co-pending application Serial No. 354,398 covers a process for removing these non-basic nitrogen compounds from alkyl phenols by adding a basic nitrogen compound which causes the non-basic nitrogen compounds to become soluble in water so that they may be removed by water and/or acid washing. These added basic nitrogen compounds react with the alkyl phenols to form another more stable complex which displaces the non-basic compounds from their complex with the alkyl phenols. In this way the non-basic nitrogen compounds are released and become water-soluble so that they may be easily removed.

The non-basic nitrogen compounds appear to be of the lactam type and we have found that compounds other than nitrogen bases may also be used to effect this release, provided these other compounds form complexes which are more stable than those formed by ordinary relatively simple lactams. Lactams, being amides, are known to form complexes with alkyl phenols. (See: Kremann and Wenzing, Monatshefte für Chemie, 38, 480 (1917).)

Among the compounds known to form such complexes are nitrogen bases and the lower fatty acids or alkanoic acids, hereinafter referred to as "agents." Preferably these compounds contain from one to four carbon atoms per molecule. Some specific agents are formic, acetic, propionic, butyric, etc., acids. Thus, it has been found that the addition of these agents is capable of extracting considerable portions of non-basic nitrogen compounds not removable by strong mineral acids.

In order to facilitate this treatment, a diluent is ordinarily added to the alkyl phenol mixture to be treated for the purpose of rendering it less viscous, thus helping phase separation. The diluent used for this purpose may be any substantially neutral, non-viscous solvent for alkyl phenols which has a boiling temperature sufficiently different from the alkyl phenols to permit its separation by fractional distillation and which does not react with the complex-forming agent or with the alkyl phenols under the conditions of the treatment. Preferably the diluent comprises one having a preferential solvent power for alkyl phenols, such as ethers of 4–8 carbon atoms, e. g. diethyl ether, di-isopropyl ether, dioxane, etc.; ketones as acetone, methyl ethyl ketone, methyl propyl ketone, diethyl ketone, ethyl propyl ketone, etc. However, other solvents capable of dissolving the alkyl phenols may be used, such as light hydrocarbon liquids, e. g. light gasoline, pentanes, hexanes, heptanes, octanes, benzene, toluene, xylenes; or oxygenated hydrocarbons such as simple alcohols of 3 or more carbon atoms; or chlorinated hydrocarbons such as dichlorethane, chlorpropane, carbon tetrachloride, hexachlorethane and the like. Suitable amounts of diluent may vary from about 25 to 500 volume percent.

In carrying out the present invention an amount of complex-forming agents at least sufficient to displace the non-basic nitrogen compounds from their complexes with the alkyl phenols is admixed with the alkyl phenols or their solution in a diluent. The resulting mixture is then contacted with an amount of water sufficient to form two layers, an alkyl phenol layer containing the agent and an aqueous layer containing the non-basic nitrogen compounds and a portion of the agent. These layers are then separated.

The amount of agent used to carry out the treatment may conveniently range from about 50 to 500 mol % of the alkyl phenols, and the amount of water should be at least sufficient to dissolve a substantial portion of the released non-basic nitrogen compounds. In general, the larger the amount of water, the more non-basic nitrogen compounds are removed. Only economical considerations impose an upper limit on these amounts. Thus, excessive quantities of water are expensive to handle and may cause losses of alkyl phenols.

The separated alkyl phenol layer may further be contacted with quantities of more agents and water under conditions to form two layers which are separated; or else this layer may, if desired, merely be washed with water once or several times to remove as much as possible of the non-basic nitrogen compounds.

In order to reduce possible losses of alkyl phenols by dissolution in the wash water, an inorganic salt such as sodium chloride, sodium sulfate, calcium chloride, etc., may be dissolved in it in amounts just sufficient to salt out the alkyl phenols.

Any convenient method for effecting the washing may be employed. Thus, ordinary mixing and settling in one or several stages may be used; or the liquids may be contacted in a countercurrent column which, if desired, may embody the backwash principle, etc.

The removal of the complex-forming agents from the purified alkyl phenol layer may be achieved in several ways which depend upon the properties of these compounds themselves. Usually, water-washing will remove a sufficient portion. However, if desired, distillation with steam may be employed, particularly in cases where they have relatively low boiling temperatures substantially below the boiling temperatures of the alkyl phenols, or when using salts for complex formation the alkyl phenols may be taken overhead.

The nitrogen bases originally associated with the alkyl phenols may simultaneously be removed with the complex-forming agent, thus contaminating said agent. If for some reason this should be undesirable the alkyl phenol mixture may be given a wash with an aqueous solution of strong mineral acid prior to the treatment of this invention. In this manner the nitrogen bases naturally associated with the alkyl phenols are pre-removed.

While the nitrogen bases naturally contained in the alkyl phenols help displace the non-basic nitrogen compounds from their complexes, the quantities of the former are normally far too small to have any material effect. Therefore, in many instances the advantages gained by their pre-removal may be greater than any advantage which may result from their presence during the treatment.

The aqueous layer or layers resulting from the water washes which contain the non-basic nitrogen compounds, and frequently in addition varying amounts of nitrogen bases, as well as alkyl phenols, may be further treated in different ways, depending upon their exact compositions. Frequently, they are merely discarded; or else they may be subjected to fractional distillation, neutralization, acidification, or other conventional means normally employed to separate mixtures of different components having different properties.

Example

An alkyl phenol mixture was obtained by extracting a cracked petroleum distillate with strong caustic soda, steaming the resultant solution, and springing it with carbon dioxide. A high boiling fraction of alkyl phenols so obtained contained 1.95% by weight nitrogen. 100 grams of this material were dissolved in 200 cc. of diisopropyl ether, and the resultant solution was extracted with 200 cc. of aectic acid dissolved in 500 cc. of water whereby two liquid phases are formed, an alkyl phenol phase and an aqueous phase, each containing dissolved part of the acetic acid. The two phases thus produced were separated, and analyzed for their nitrogen content. The lower aqueous phase contained 1.12 grams of nitrogen and the upper phase contained .83 gram of nitrogen. This represents a reduction of the nitrogen content of alkyl phenols from 1.95 to .83 by a single-stage extraction (which is comparable to the results shown in our co-pending application Serial No. 354,398 mentioned above).

We claim as our invention:

1. In a process for purifying alkyl phenols containing non-basic nitrogen compounds naturally associated with petroleum and coal tar alkyl phenols, which compounds are not removable from said alkyl phenols by strong mineral acid washes, the steps comprising contacting said alkyl phenols with at least 50 mol percent of an alkanoic acid having from one to four carbon atoms and with water to produce two liquid layers, one an alkyl phenol layer and the other an aqueous layer containing said non-basic nitrogen compounds, and separating said layers.

2. The process of claim 1 wherein said alkanoic acid has a boiling temperature lower than the boiling temperature of the alkyl phenols.

3. The process of claim 1 wherein the amount of said alkanoic acid is from 50 to 500 mol percent of the alkyl phenols.

4. The process of claim 1 wherein said alkanoic acid is acetic acid.

5. The process of claim 1 wherein said water contains an inorganic salt to salt out dissolved alkyl phenols.

6. In the process of purifying alkyl phenols containing non-basic nitrogen compounds naturally associated with petroleum and coal tar alkyl phenols, which compounds are not removable from said alkyl phenols by strong mineral acid washes, the steps comprising contacting said alkyl phenols with water in the presence of an alkanoic acid having from one to four carbon atoms, said alkanoic acid being dissolved in said alkyl phenols and being present in an amount at least 50 mol percent of said alkyl phenols, whereby two liquid layers are formed, an alkyl phenol layer containing at least a substantial portion of said alkanoic acid, and an aqueous layer containing at least a portion of said non-basic nitrogen compounds, separating the layers, and removing the alkanoic acid from the alkyl phenol layer.

7. In the process of purifying alkyl phenols con-

taining non-basic nitrogen compounds naturally associated with petroleum and coal tar alkyl phenols, which compounds are not removable from said alkyl phenols by strong mineral acid washes, the improvement comprising contacting said alkyl phenols with water in the presence of a neutral solvent for said alkyl phenols, inert towards the conditions of the process, and of an alkanoic acid having from one to four carbon atoms, said alkanoic acid being dissolved in said alkyl phenols and being present in an amount at least 50 mol percent of said alkyl phenols, whereby two liquid layers are formed, an alkyl phenol layer containing at least a substantial portion of said alkanoic acid and said solvent, and an aqueous layer containing at least a portion of said non-basic nitrogen compounds, separating the layers, and removing said dissolved alkanoic acid and solvent from the alkyl phenol layer.

8. The process of claim 7 wherein the solvent is an ether.

9. The process of claim 7 wherein the amount of said solvent is from 25% to 500% by volume of said alkyl phenols.

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