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PROCESS OF SEPARATING THIOPHENOLS FROM ALKYL PHENOLS

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This invention is a continuation-in-part of our application Serial No. 194,376, filed March 7, 1938, Patent No. 2,218,139 granted October 15, 1940, and relates to the refining of acid oils containing phenols and thiophenols, and more particularly is concerned with a method of separating thiophenols from phenols to produce relatively pure fractions of phenols and thiophenols, respectively.

The terms, phenols and thiophenols, as herein used refer to aromatic hydroxy and hydrosulfide compounds, respectively, which are normally contained in raw cracked mineral oil distillates or coal tar hydrocarbons. Mixtures of these aromatic compounds as obtained from hydrocarbon oils by extraction with caustic alkali are generally called "acid oils." As is known, acid oils comprise largely alkylated phenols and thiophenols, although the higher boiling fractions may contain varying amounts of polycyclic aromatic rings, such as naphthalene and other rings.

It is a purpose of this invention to produce from acid oils phenol fractions which are relatively free from thiophenols. It is another purpose to produce thiophenol fractions of high degrees of concentration, from which substantially pure thiophenols can be prepared. Another purpose is to separate acid oils into phenol and thiophenol fractions efficiently, at low cost, and without substantial loss of either component.

Acid oils are normally separated from cracked mineral oil distillates by extracting same with aqueous solutions of caustic alkali, in particular alkali metal hydroxides. The extracts so produced are alkali phenolate solutions which contain varying amounts of sulfur compounds, particularly salts of aromatic hydrosulfides. Depending upon their source, acid oils liberated from the phenolate solutions by acidification may contain up to 15% or 20% organic hydrosulfides, most of which are usually thiophenols. For instance, acid oils obtained from highly cracked mineral oil dstillates, particularly if derived from sour petroleum oils such as West Texas crude, may contain relatively large amounts of thiophenols, whereas coal tar phenols are usually substantially free therefrom.

Instead of liberating acid oils from alkali phenolate solutions by acidification it has been proposed to extract the latter with a solvent for phenols which is substantially insoluble in the phenolate solution; or with a mixture of insoluble and soluble or partly soluble solvents, if desired in the presence of an organic base soluble in the solvent. In this manner, a partial fractionation of phenols has been accomplished, the extract fraction comprising the solvent containing predominantly ortho alkyl phenols of relatively high molecular weights, while meta and para alkyl phenols and phenols of relatively low molecular weights in general tend to remain in the aqueous alkaline solution. Thus, Kester in U. S. Patent No. 2,043,102 discloses a continuous process for removing phenols from coal tar distillates by treating same with an aqueous solution of an alkali metal hydroxide and regenerating the spent hydroxide-containing phenols by extracting same with a suitable solvent for phenols. The regenerated hydroxide which retains a portion of the phenols is then returned for the treatment of further amounts of the distillate. This continuous process is applicable only to distillates which are substantially free from acids stronger than phenols, i. e. thiophenols, carboxylic acids, sulfonic acids, etc., because the latter cannot be removed in practical amounts by extraction from aqueous solutions of their alkali metal salts and therefore accumulate rapidly, thereby neutralizing the hydroxide solution and rendering it unregenerable by solvent extraction.

In contrast to the Kester process which thus is predicated on the absence of thiophenols our process deals with the fractionation of mixtures of phenols with thiophenols.

Processes for the desulfurization of acid oils have mostly dealt with various oxidation methods for the conversion of organic hydrosulfides to disulfides. While it has been possible to convert thiophenols to disulfides and remove the latter from the phenols by distillation in the acid state or by solvent extraction in the alkaline state, undesirable side reactions during the oxidation often destroy or chemically change at least a portion of the desired phenols; and if it is desired to recover the thiophenols in the above process, yields of the latter are greatly reduced because portions thereof are converted to oxidation products which cannot be reconverted to thiophenols.

Now we have discovered that acid oils containing thiophenols can be refined effectively to yield phenols substantially free from thiophenols, and thiophenols of high degrees of purity, by extracting the acid oil with a limited amount of an aqueous solution of an alkali metal hydroxide in the presence of a solvent for phenols which is substantially insoluble in aqueous solutions of alkali salts of acid oils. When effecting the extraction of acid oils in accordance with our invention two layers are formed, a solvent layer

containing essentially phenols and an aqueous layer containing thiophenolates in amounts normally predominantly over phenolates.

We are aware that in U. S. Patent 1,445,668 it has been proposed to grind raw cresylic acids with 5% to 10% solid caustic soda to form a paste, adding to this paste an aromatic hydrocarbon solvent and treating the resulting mixture with water. Upon standing two layers are formed, an aqueous layer containing essentially sodium carbolate and an oily layer containing free cresylic acids and the sodium salts of sulfur and other impurities. However, in contrast to the above, in our process organic hydrosulfides accumulate in the aqueous phase and all phenols are concentrated in the oil phase, so that a more or less complete separation of phenols from thiophenols is achieved.

Thiophenols are in the average slightly more strongly acidic than phenols, and we have found that this difference is sufficient to enable a separation between the two types of compounds, if the proper conditions are maintained, notwithstanding the fact that there is a considerable overlap of acidities, some thiophenols having dissociation constants within the average range of phenols, and conversely some phenols having dissociation constants within the range of thiophenols. Apparently other factors, such as the size of the organic portion of the molecules, presence of additional polar radicals, etc., have a corrective influence and make possible an almost complete separation of phenols from thiophenols by our method despite these overlaps.

The extraction is preferably carried out at about room temperature although higher or lower temperatures may be used. However, no particular advantages are gained by substantially deviating from room temperatures, and, on the contrary, considerable difficulties may be experienced at substantially lower temperatures because of at least partial solidification, and at higher temperatures because of mechanical operating difficulties and the danger of oxidation of a portion of the thiophenols to neutral disulfides which cannot be separated from the phenols by our process and require additional manipulation for their removal.

The several limitations which must be observed to effect satisfactory separation of phenols from thiophenols are as follows:

The amount of alkali metal hydroxide used in the extraction must be less than that which is equivalent to the acid oil. Suitable amounts may range from the low limit equivalent to

$$\frac{(m-1)X}{m}\%$$

to an upper limit equivalent to

$$\frac{(m-1)X+100}{m}\%$$

where X is the percentage of thiophenols in the acid oil and m is a numeral not lower than 2 and preferably 4 or higher. If m is 2, then the lower limit is an amount equivalent to ½ of the thiophenol content and the upper limit is equivalent to the thiophenols plus ½ of the phenol content of the acid oil. Likewise, if $m=4$, the lower limit is equivalent to ¾ of the thiophenol content and the upper limit equivalent to the thiophenol content plus ¼ of the phenols. If m is infinite, then both limits are the same, i. e. the amount of alkali metal hydroxide is equivalent to the thiophenol content. This last condition represents the optimum and, if maintained, normally results in the production of two fractions, a thiophenol and a phenol fraction of fair degrees of purity and in substantially theoretical yields. The smaller m is, the farther removed is the amount of alkali metal hydroxide from the optimum. Deviating from the optimum under otherwise identical conditions results in an increasing yield of one fraction at the expense of the other, the growing fraction becoming progressively more impure, whereas the shrinking fraction at first becomes more pure. However, when m becomes less than 4, further improvements in the purity of the shrinking fraction are small, and when m becomes 2 or less purity of this fraction remains substantially unchanged, while losses continue to grow.

As a general proposition if the amount of alkali metal hydroxide is less than the equivalent of the thiophenols the phenol fraction normally retains substantial amounts of thiophenols; and vice versa, if the amount of the alkali metal hydroxide is greater than the equivalent of the thiophenols, the thiophenol fraction will tend to retain substantial amounts of phenols.

Frequently it is difficult to obtain substantially pure phenol and thiophenol fractions simultaneously by a single extraction of acid oils containing thiophenols, because the alkali metal hydroxide requirements may differ for the production of the respective pure fractions. In such a case resort may be had to two or more successive extractions, in which different amounts of caustic alkali are used. For instance, in a first extraction a relatively large amount of alkali metal hydroxide may be used which yields a highly purified phenol fraction and a mixed thiophenol-phenol fraction. The latter may then be processed in a second extraction in the presence of a smaller amount of alkali metal hydroxide to yield a relatively pure thiophenol fraction and a residual mixed fraction. This residue may be re-extracted together with original acid oil in the presence of relatively large amounts of alkali metal hydroxide.

The concentration of the caustic alkali may be varied between wide limits. As is known, however, dilution of aqueous solutions of alkali metal phenolates with water promotes hydrolysis, and if hydrolysis is excessive the sharpness of the fractionation may be reduced, thiophenols having a tendency under such conditions to be washed out by the organic solvent together with the phenols. Therefore, we prefer in general to employ alkali metal hydroxide solutions which are not substantially less than about .5 normal and preferably not less than 1 normal. The upper concentration limits are normally determined by considerations of solubilities, the alkali metal phenolates for instance tending to become insoluble in alkali metal hydroxide solutions having concentrations greater than about 7 normal. The formation of a third layer of insoluble phenolates may interfere with the proper refining or fractionation.

The amount of organic solvent used may also be varied within wide limits. For practical purposes we usually employ from about 50 to 1000 volume per cent of solvent based on the acid oil to be refined or separated, and more often from about 100 to 300 volume per cent. Amounts of solvent less than 50% by volume may leave considerable portions of the phenols in the thiophenol fraction, and excessive amounts of solvent tend to remove thiophenols together with the phenol fraction from the aqueous layer under otherwise proper conditions for good separation.

Suitable solvents are all those which dissolve acid oils at room temperatures, are substantially chemically inert under the conditions of the extraction and substantially insoluble in aqueous solutions of alkali salts of acid oils. Moreover, it is desirable that the solvent be separable from phenols by simple means other than extraction with strong caustic alkali, for instance by distillation. Preferred solvents are alcohols, ethers and ketones of 4 or more carbon atoms such as butanol, pentanol, cyclohexanol, etc.; normally liquid ethers as diethyl ether, diisopropyl ether, propyl butyl ether, chlorinated ethers; and ketones as methyl ethyl ketone, diethyl ketones, ethyl propyl ketone, methyl isobutyl ketone, etc. However, normally liquid hydrocarbons may be used such as naphtha, natural gasoline, pentane, hexane, benzene, toluene, xylene; chlorinated hydrocarbons as carbon tetrachloride, ethylene dichloride, trichlorethylene, chlor propane; and organic bases as pyridine, quinoline, picoline, piperidine, normally liquid mono alkyl amines, petroleum bases, etc. Mixtures of such solvents may also be used to advantage. Of the foregoing solvents, cyclohexanol is particularly effective.

The extraction in its most elementary form may be carried out by simply agitating an acid oil with a proper amount of an aqueous solution of alkali metal hydroxide and a suitable solvent, and then allowing the reaction mixture to separate. Two layers are formed, a solvent layer containing most of the phenols and an aqueous layer comprising alkali thiophenolates. The layers are separated, and the phenol and thiophenol fractions are liberated from the respective layers by appropriate means. Thus, the phenol fraction may be recovered from the solution for instance by distilling the solvent if the latter has a sufficiently low boiling temperature; and the thiophenol fraction is most easily liberated by acidifying the aqueous solution with sulfuric, hydrochloric or other suitable acid stronger than thiophenols.

In general, however, the above method of extraction is not very satisfactory because of the closeness and partial overlap of acidities of many of the phenols and thiophenols and the solvent power of the thiophenolate solution for phenols. Therefore we prefer an extraction system in which a solution of the acid oil in a solvent of the type hereinbefore described flows in countercurrent to a properly limited amount of an aqueous solution of caustic alkali. Still more efficient is a system in which a suitable solvent and an aqueous solution of alkali metal hydroxide flow in countercurrent to each other through a series of stages or a vertical tower, and the acid oil is admitted to an intermediate stage or point. Any efficient countercurrent extraction process in which there is a zone for stripping the acid oil solution from thiophenols with the aqueous solution of caustic alkali, and in which there is preferably a washing zone for washing the resulting aqueous solution containing thiophenolates and phenolates with a solvent for the acid oil, is applicable to our problem.

The following examples illustrate our invention:

Example I

An amount of 500 gm. of an acid oil containing 3.35% hydrosulfide sulfur was dissolved in 715 gm. diisopropyl ether. The resulting solution was extracted with 400 gm. of a 1 normal NaOH solution in a three-stage countercurrent extractor. The amount of the caustic soda used was exactly equivalent to the thiophenols present. An ether extract solution was obtained which was distilled to remove the ether. The residue was then vacuum distilled yielding 350 gm. of a distillate containing .061% hydrosulfide sulfur.

The aqueous solution resulting from the extraction was acidified with sulfuric acid to liberate the thiophenols. The liberated thiophenols were vacuum distilled and 117 gm. of an oil was obtained containing about 80% thiophenols.

Example II

1430 gm. per hour isopropyl ether and 700 gm. per hour of a 10% NaOH solution were fed at opposite ends to a four-stage countercurrent extraction system and allowed to flow in countercurrent to each other while an amount of 1000 gm. per hour acid oil containing 8.8% hydrosulfide sulfur was admitted to the second extraction stage along the path of the ether. The amount of caustic soda was 8% less than the equivalent of the thiophenols.

The ether extract was distilled to remove the ether and the residual phenols were vacuum distilled. A distillate fraction was produced amounting to 765 gm. and consisting of phenols containing less than .1% hydrosulfide sulfur.

The aqueous solution was acidified and the thiophenols liberated thereby were vacuum distilled. 170 gm. of a thiophenol fraction was obtained which contained 21.3% hydrosulfide sulfur consisting of 79% thiophenols.

Example III

An acid oil, containing about 21% by weight thiophenols obtained in the usual manner from a cracked mineral oil distillate boiling from 100° to 200° C., was extracted in a vertical extraction column filled with steel wool. The acid oil was admitted to about the middle of the column. Into the bottom of the column was continuously fed diisopropyl ether in an amount of 140 parts by weight per 100 parts of the acid oil; and into the top of the column was introduced an aqueous 3N-NaOH solution amounting to 90% by weight of the acid oil. The amount of NaOH so introduced was equivalent to the thiophenols plus 13% of the phenols contained in the acid oil.

From the bottom of the column a thiophenolate solution was withdrawn. Thiophenols liberated therefrom by acidification, amounting to 22% of the acid oil feed, contained 23.1% hydrosulfide sulfur and consisted of about 85% thiophenols. The ether extract solution, after removal of the ether by distillation, yielded a mixture of phenols containing less than .2% hydrosulfide sulfur, i. e. less than .7% thiophenols.

While in the foregoing examples only sodium hydroxide has been used it is understood that other alkali metal hydroxides such as lithium hydroxide and potassium hydroxide are equally well suited.

It has further been noted that if the extract phenol fractions which normally have initial boiling points above about 160° C., are subjected to a fractional distillation and the front and/or end fractions amounting to about 5 to 15 or more per cent each of the total charge are discarded, middle fractions may be obtained having considerably reduced sulfur contents. Care, however, should be taken to avoid decomposition of certain sulfur compounds, in particular aromatic disulfides, during distillation which, in the absence of de-

composition tend to concentrate in the heaviest fraction but will contaminate the overhead fractions if allowed to decompose. Rapid distillation under substantial vacuum is desirable to avoid their decomposition.

For example, a middle fraction obtained by vacuum distillation of the extract phenol fraction of Example III had a hydrosulfide sulfur content of .006%.

We claim as our invention:

1. In the process of separating a mixture of phenols containing substantial amounts of thiophenols to produce an alkyl phenol fraction of low hydrosulfide sulfur content and a thiophenol fraction consisting predominantly of thiophenols, the steps comprising extracting said mixture in the presence of cyclohexanol with an aqueous solution of an alkali metal hydroxide in an amount equivalent to not less than ½ of the thiophenols nor more than the thiophenols plus ½ of the phenols contained in said mixture, under conditions to form two layers, a solvent layer containing a solute consisting predominantly of phenols and an aqueous layer containing alkali metal thiophenolates.

2. In the process of separating a mixture of phenols containing substantial amounts of thiophenols to produce an alkyl phenol fraction of low hydrosulfide sulfur content and a thiophenol fraction consisting predominantly of thiophenols, the steps comprising extracting said mixture in the presence of cyclohexanol with an aqueous solution of an alkali metal hydroxide in an amount equivalent to not less than ¾ of the thiophenols nor more than the thiophenols plus ¼ of the phenols contained in said mixture, under conditions to form two layers, a solvent layer containing a solute consisting predominantly of phenols and an aqueous layer containing alkali metal thiophenolates, and separating the layers.

3. The process of claim 1 in which the amount of alkali metal hydroxide is approximately equivalent to the thiophenols contained in the acid oil.

4. The process of claim 1 in which the organic solvent is present in an amount between 50 and 1000 volume per cent of the acid oil.

5. The process of claim 1 in which the aqueous solution of alkali metal hydroxide is .5 to 7 normal.

6. In the process of separating a mixture of phenols containing substantial amounts of thiophenols to produce an alkyl phenol fraction of low hydrosulfide sulfur content and a thiophenol fraction consisting predominantly of thiophenols, the steps comprising dissolving said mixture in 50 to 1000 volume per cent of cyclohexanol, flowing the resulting solution through an extraction zone in countercurrent flow to an aqueous solution of an alkali metal hydroxide in an amount equivalent to not less than ½ of the thiophenols nor more than the thiophenols plus ½ of the phenols contained in said mixture, to produce a solution of phenols in said organic solvent and a separate aqueous solution containing thiophenolates, and separately withdrawing said solutions from the extraction zone.

7. In the process of separating a mixture of phenols containing substantial amounts of thiophenols to produce an alkyl phenol fraction of low hydrosulfide sulfur content and a thiophenol fraction consisting predominantly of thiophenols, the steps comprising extracting said mixture in the presence of cyclohexanol and under substantially non-oxidizing conditions with an aqueous solution of an alkali metal hydroxide in an amount equivalent to not less than ½ of the thiophenols nor more than the thiophenols plus ½ of the phenols contained in said mixture, under conditions to form two layers, a solvent layer containing a solute consisting predominantly of phenols and an aqueous layer containing alkali metal thiophenolates, and separating the layers.

8. In the process of separating a mixture of phenols containing substantial amounts of thiophenols to produce an alkyl phenol fraction of low hydrosulfide sulfur content and a thiophenol fraction consisting predominantly of thiophenols, the steps comprising extracting said mixture in the presence of cyclohexanol with an aqueous solution of an alkali metal hydroxide in an amount equivalent to not less than ½ of the thiophenols nor more than the thiophenols plus ½ of the phenols contained in said mixtuure, under conditions to form two layers, a solvent layer containing a solute consisting predominantly of phenols and an aqueous layer containing alkali metal thiophenolates, and acidifying the aqueous layer to liberate thiophenols, and recovering them from the resulting solution.

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