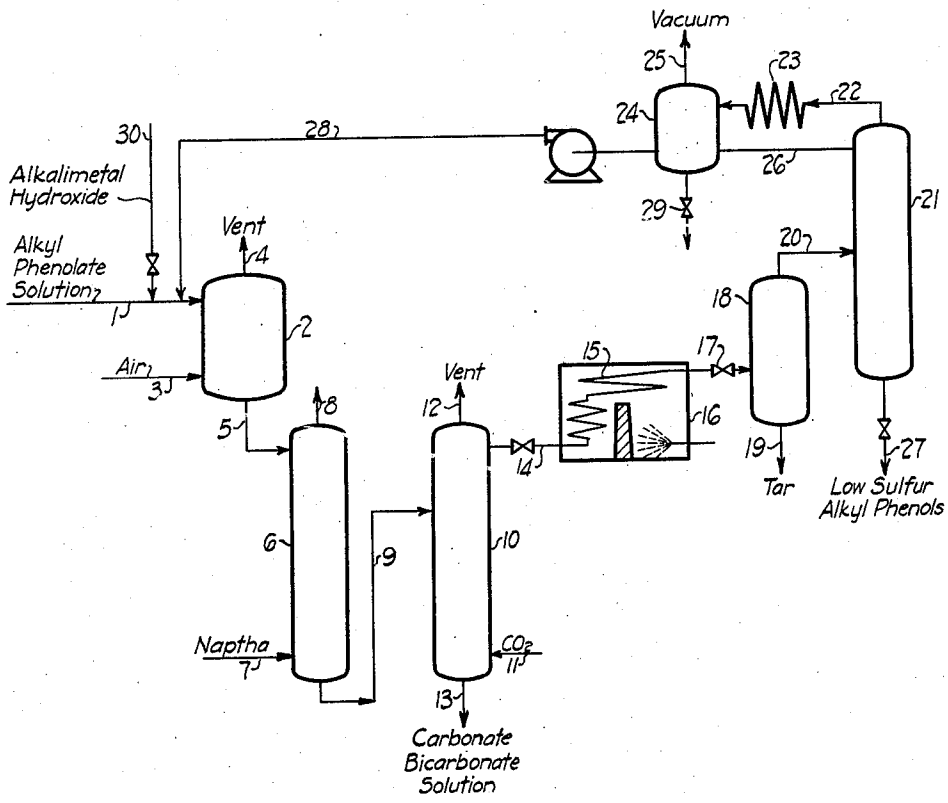
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PROCESS FOR DESULPHURIZING ALKYL PHENOLS

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PROCESS FOR DESULPHURIZING ALKYL PHENOLS

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This invention relates to an improved method for desulphurizing alkyl phenols and more particularly is concerned with an improvement in the desulphurization of alkyl phenols by air blowing.

The term alkyl phenols as herein used refers to mixtures of alkyl phenols normally obtained by extraction of cracked minerals oils or coal tar distillates with strong aqueous solutions of alkali metal hydroxides, said mixtures containing varying amounts of phenols and impurities, particularly organic sulphur and nitrogen compounds. Most of the sulphur compounds associated with alkyl phenols are of the type of thiophenols. Because alkyl phenols like the phenols themselves, are acid reacting and form water-soluble alkali metal salts, they are difficult to separate from alkyl phenol mixtures. Alkyl phenols recovered from cracked petroleum oils are more likely to contain substantial amounts of thiophenols than coal tar phenols, the latter normally containing very small amounts only, if any.

In a co-pending application, Serial No. 175,876, filed November 22, 1937, by Hund, Thomas and Luten, it has been disclosed that alkyl phenol mixtures containing thiophenols can be desulphurized effectively by air blowing aqueous solution of their alkali metal salts at about normal room temperature. The air blowing converts the thiophenols to disulphides which are normally neutral and can be removed from the aqueous solution by washing same with naphtha or other suitable solvent which is insoluble in the aqueous solution and is capable of dissolving the disulphides. According to the Hund et al. disclosure, the blown and washed phenolate solution is then sprung to liberate the alkyl phenols, and liberated alkyl phenols are distilled, preferably under high vacuum to avoid their decomposition.

It has, however, been found that alkyl phenols derived from certain sources respond poorly to the above desulphurization process by air blowing. Whereas the sulphur content of alkyl phenols derived, for instance, from Mid-Continent, West Texas, etc., cracked distillates containing .5% and more sulphur can usually be reduced to .05% and less in a single treatment, the sulphur content of alkyl phenol mixtures from other sources e. g. California cracked distillates, usually cannot be reduced below about .2 to .4% in a single treatment, no matter how long the blowing time is extended. Only by redissolving the blown and distilled alkyl phenols in aqueous alkali metal hydroxide to form a second solution of alkyl phenolates, air blowing, washing and springing the latter solution and redistilling the liberated alkyl phenols, can the sulphur content be reduced further. This procedure though effective as shown in the above mentioned Hund et al. application is obviously cumbersome as well as costly.

It is a purpose of this invention to provide a method of desulphurizing alkyl phenols by air blowing whereby the sulphur can be reduced approximately to a point heretofore obtainable only by repeating the air blowing process as described above, in a manner more simple and less expensive than has been possible heretofore.

The newly observed fact that repetition of the entire blowing process leads to a reduction in sulphur content below that of a single treatment is somewhat unexpected, for it seems anomalous, indeed, that sulphur compounds which refuse to form neutral disulphides in the first air blowing treatment should be convertible to such compounds in the second treatment. Unfavorable equilibrium conditions in the aqueous phase are not expected to exist and as far as predictable should not prevent the conversion of substantially all thiophenols to neutral disulphides in a first air blowing treatment, because the disulphides so far as has been known are substantially insoluble in the aqueous layer, forming a separate phase.

Upon investigating the reasons for this apparent anomaly I discovered certain facts which form the basis of the present improvement. I have found that when air blowing sulphur-containing alkyl phenols under conditions to convert thiophenols to disulphides which are supposedly insoluble in the aqueous phase, a certain amount of high boiling sulphur compounds are formed which remain soluble in the aqueous phase. The nature of these soluble compounds is not definitely known but there is reason to believe that they are acid reacting disulphides. Washing the blown alkali metal phenolate solution with a solvent for disulphides fails to remove them from the aqueous layer, and upon springing the alkyl phenols they are also liberated.

I have further found that when fractionally distilling under substantially non-cracking conditions the alkyl phenols containing the high boiling acidic sulphur compounds which for the purpose of this disclosure I shall call acidic disulphides, to produce at least three fractions i. e., a top, middle and bottom fraction, the end fractions possess a much higher sulphur content than the middle fraction. Moreover, it was noted that if the time of distillation is prolonged, or the

temperature of distillation is raised or both, the sulphur contents of the top and middle fractions may increase at the expense of the sulphur content of the bottom fraction. Apparently the acidic disulphides which themselves are high boiling and should remain in the bottom fraction tend to decompose upon distillation, thereby forming relatively low boiling sulphur compounds which by oxidation may be converted to neutral disulphides.

Based on this discovery to the effect that a carefully distilled middle fraction may possess a very much lower sulphur content than the two end fractions, I have improved the method of desulphurization by air blowing as follows:

A clear steamed aqueous solution of alkali metal alkyl phenols is oxidized, e. g., air blown as usual at a temperature between about 0° to 90° C. and preferably below about 50° C. whereby a portion of the organic sulphur compound is converted to neutral disulphides. These disulphides are removed without substantially raising the temperature of the blown alkyl phenolate solution, as by washing same exhaustively with a suitable solvent for organic disulphides, such as naphtha, filtering through a bed of solids, etc. The alkyl phenolate solution freed from neutral disulphides is then sprung with a suitable acid, such as CO_2, H_2SO_4, HCl, etc., to liberate the alkyl phenols. Liberated alkyl phenols are separated from the remaining aqueous solution and are fractionally distilled under non-cracking conditions, preferably under high vacuum to prevent formation of an excessive amount of undistillable tar. The vaporized portion is fractionated into a light top fraction amounting to 25% or less of the still charge which top fraction is separately withdrawn, and a heavier fraction herein called the middle fraction. The top fraction which has a much higher sulphur content than the middle fraction and the exact amount of which depends upon the conditions of the distillation and the desired degree of desulphurization, is now dissolved in an aqueous solution of an alkali metal hydroxide to form an alkali metal alkyl phenolate solution. The resulting solution is then air blown under conditions to convert thiophenols to disulphides. Instead of blowing this solution separately it may be advantageous to combine it with fresh unblown alkali metal alkyl phenolate solution, i. e., a phenolate solution obtained by extracting cracked distillates or the like containing alkyl phenols, with aqueous solutions of alkali metal hydroxide, which extract has received a steaming treatment to remove neutral oils and other impurities, but which has received no previous air blowing treatment. Or instead of dissolving the high sulphur top fraction of alkyl phenols in fresh alkali metal hydroxide, I may dissolve it in unblown alkyl phenolate solution containing a substantial excess of alkali metal hydroxide over the amount equivalent to its content of alkyl phenols, which excess enables the dissolution of at least a portion of said top distillate fraction in the unblown alkyl phenolate extract. If necessary alkali metal hydroxide may be added in an amount sufficient to raise the alkali metal content of the solution containing the added top fraction to at least the equivalent of its combined alkyl phenol content.

As indicated above the size of the top fraction of distilled alkyl phenols which should be separated for further air blowing depends upon the conditions of the distillation. If the distillation is carried out fairly rapidly and at low temperatures, i. e., under good vacuum and with steam, normally less than about 15% and often less than 10% of the still charge need be returned for reblowing with air. If the distillation is carried out by the batch method there is a considerable tendency, slowly to decompose high boiling sulphur compounds which remain in the bottom fraction, even after a suitable top fraction has been removed. Volatile sulphur compounds which are formed during this period contaminate the middle fraction. This is obviously undesirable, and in order to prevent this contamination I may subject the alkyl phenols containing acidic disulphides to a heat treatment at an elevated temperature, such as boiling for several hours prior to removing the top fraction under total reflux, in order to decompose substantially all of the acidic disulphides which are capable of decomposition under the conditions of distillation. Or instead I may distill the still charge to separate a substantially undistillable residue from the vaporizable portion, the latter containing volatile sulphur compounds formed by decomposition of acidic disulphides during the distillation. This overhead product may then be fractionally redistilled to separate a small top fraction which contains the largest portion of the volatile sulphur compounds. In this manner the products of decomposition of the acidic disulphides are removed together with the top fraction which is returned for further air blowing, as described.

If, on the other hand, the separation of the top fraction is carried out by continuous flash distillation, it is desirable to separate the top and middle fractions jointly in a first flash from the remaining undistilled residue and thereafter to separate the top and middle fractions from each other later, e. g., by partial condensation of the vapors. In this manner contamination of the middle fraction with sulphur compounds which become volatile after the top fraction has been removed is effectively prevented.

The advantages of my improved method over the older methods are obvious, in that it enables the production of alkyl phenols having sulphur contents as low as those heretofore obtainable only by subjecting the entire alkyl phenol mixture to a double desulphurizing treatment at substantially the cost of a single treatment. A further advantage is that the desulphurized recovered alkyl phenols are substantially anhydrous, water contained in the freshly liberated alkyl phenols being taken overhead during distillation as part of the top fraction. At least a portion of this water may usually be separated from the top fraction either by fractional condensation or after condensation by settling. However, such a separation is quite unnecessary since no harm is done by recirculating the condensate water together with a high sulphur alkyl phenol fraction to the air blowing zone.

The accompanying drawing showing a flow diagram serves to illustrate my process.

Aqueous alkyl phenolate solution containing thiopenolates is introduced through line 1 into blow case 2.

Air admitted to the blow case through line 3 is blown through the phenolate solution and is vented through vent line 4. The residence time for the solution in the blow case is normally of the order of about 10 to 60 hours in order to effect substantially complete oxidation of thiophenols to disulphides, although in the presence of certain catalysts such as Cu, Ni, or compounds thereof and/or by the application of superat-

mospheric air pressures the blowing time may be reduced to 2 hours or even less. The temperatures for blowing should be below 90° C. and preferably below 50° C. to prevent substantial losses of alkyl phenols due to partial oxidation thereof and formation of excessive amounts of tarry matter. During the air blowing thiophenols are converted to disulphides, normally the largest part of which are neutral and are insoluble in the alkyl phenolate solution.

The blown alkyl phenolate solution containing separated disulphides is transferred through line 5 to scrubber 6 where it is scrubbed with naphtha or other suitable solvent for the disulphides admitted through line 7, which solvent is immiscible with the alkyl phenolate solution. Spent solvent containing the separated disulphides is withdrawn from the scrubber through line 8. The washed alkyl phenolate solution, free from neutral disulphides but containing acidic impurities such as acidic disulphides, proceeds through line 9 to the carbonator 10. Into the bottom of the carbonator CO_2 is introduced through line 11 in an amount sufficient to convert the aqueous solution to a carbonate-bicarbonate solution substantially free from alkyl phenolates. Waste gas is released through vent line 12.

The resulting aqueous solution is removed through bottom draw off 13 while the free alkyl phenols go through line 14 to heating coil 15 in furnace 16, where they are heated to a non-cracking distilling temperature. The heated alkyl phenols pass through release valve 17 into flash tower 18 maintained under substantial vacuum. The largest portion of the alkyl phenols, e. g., normally about 90%, is flashed off, the residue consisting of a heavy black tar which is removed through tar line 19.

The alkyl phenol vapors pass through vapor line 20 to fractionator 21 from which a small top fraction comprising alkyl phenols and thiophenols not exceeding about 25% of the total alkyl phenols is withdrawn through vapor line 22 to be condensed in condenser 23, condensate accumulating in receiving tank 24. Line 25 connects the distilling system to a source of vacuum. Condensed and separated water may be withdrawn through line 29, if desired.

The remainder of the alkyl phenols in fractionator 21 constituting the largest portion, is condensed by reflux from tank 24 admitted through reflux line 26, and leaves the fractionator through bottom line 27. This portion normally has a very low sulphur content.

Condensed alkyl phenols in tank 24 which have a much higher sulphur content than the bottom fraction from column 21 are returned through line 28 to blow case 2 to be reblown, if desired, in combination with fresh alkyl phenolate solution from line 1. Aqueous alkali metal hydroxide in amounts sufficient to convert all of the returned alkyl phenol fractions to the respective alkali metal salt may be introduced into blow case 2 through line 30.

It is understood that the described flow diagram is merely illustrative and that the use of pumps, tank, valves, etc., as well as the substitution of equipment susbtantially equivalent to that shown is within the skill of the average designer for such equipment.

While in the foregoing I have limited the oxidation to oxidation by air blowing, it shall be understood that other oxidation methods capable of converting thiophenols to disulphides without materially attacking alkyl phenols may be used instead. Particularly useful are peroxides, such as hydrogen peroxide or organic peroxides. Hypochlorites are less desirable because of the danger of chlorination of at least a portion of the alkyl phenols.

In the following examples my invention is further illustrated.

Example I

A steamed aqueous solution of sodium alkyl phenolate was blown with air at normal atmospheric temperature for 6 hours. The blown solution was washed with naphtha and sprung with CO_2 to liberate the alkyl phenols. When the latter were redistilled in a 2500 gallon batch still to produce a single overhead fraction amounting to 90% of the charge, a sulphur content of .29% was found in the distilled alkyl phenols. However, when a still charge of about 2000 gallons of the raw alkyl phenols was fractionally distilled under vacuum of 25 mm. mercury at the rate of about 2 gallons per minute, the entire distillation lasting more than 15 hours, the first 50 gallons had a sulphur content of .52%, the second 50 gallons .41% and the third 50 gallons .36%. Thereafter the sulphur content of the overhead dropped rapidly to .1% and less.

The high sulphur fractions were combined and redissolved in aqueous caustic soda to produce an aqueous sodium alkyl phenolate solution of about 10% concentration. This solution was air blown for several hours, washed with naphtha and sprung with CO_2. The liberated alkyl phenols before distillation had a sulphur content of .07%. Redistillation further reduced the sulphur content to below .06%.

The middle fraction which constituted about 75% of the total charge, (10% being undistillable bottoms), had received but a single treatment and had an average sulphur content of .12%.

Example II

15,140 ml. of a steamed aqueous solution of sodium alkyl phenolates was air blown with 40 cu. ft. of air at room temperature at a rate of .1 cu. ft. per minute. The blown phenolate solution was washed with successive volumes of 750 ml., 750 ml. and 500 ml. of a hydrocarbon distillate having a boiling range of 150° to 195° C. The washed solution was then carbonated with 40 cu. ft. CO_2 at a rate of .3 cu. ft. per minute, leaving an aqueous phase containing sodium carbonate-bicarbonate in the ratio of 3:1, and releasing 2,940 ml. crude alkyl phenols. The latter were subjected to a vacuum distillation with the following results:

Products	Yield ml.	Percent S in product
Water	298	
Hydrocarbon distillate	49	
Alkyl phenols:		
Low boiling fraction	141	0.97
Middle fraction (225° C. at 95% distilled)	768	.21
Residue	1,684	.48
Total	2,940	

The low boiling alkyl phenol fraction from the foregoing distillation was redissolved in 15,140 ml. of a fresh batch of steamed aqueous solution of the same alkyl phenolates used in the previous treatment, making a total of 15,281 ml. The resulting solution was air blown, washed with

naphtha and carbonated as in the first case described above, and the liberated raw alkyl phenols amounting to 3115 ml. were vacuum distilled. This time results were as follows:

Products	Yield ml.	Percent S in product
Water	300	
Hydrocarbon distillate	61	
Alkyl phenols:		
Low boiling fraction	142	0.64
Middle fraction (225° C. at 95 percent distilled)	922	.21
Residue	1,690	.43
Total	3,115	

As will be noted the sulphur contents of the middle fractions having boiling points of 225° C. at 95% distilled were the same in both treatments, whereas the yield in the second treatment was greater by 154 ml. This amount is approximately equal to the amount which was returned from the first treatment for retreatment.

I claim as my invention:

1. In the process of desulphurizing alkyl phenols containing thiophenols by oxidizing an aqueous solution of an alkali metal salt thereof to produce neutral disulphides which are insoluble and other sulphur compounds which are soluble in said solution, separating said neutral insoluble disulphides from the solution, acidifying the latter to liberate alkyl phenols containing said sulphur compounds, and distilling the liberated alkyl phenols whereby said sulphur compounds are converted to thiophenols, the improvement comprising fractionally distilling said liberated alkyl phenols to separate a low boiling fraction containing thiophenols, and a higher boiling fraction substantially free from tar and thiophenols, redissolving the first fraction in aqueous alkali metal hydroxide to produce an aqueous solution of the alkali metal salt of said fraction, oxidizing the solution under conditions to convert thiophenols to disulphides insoluble in the solution, separating the insoluble disulphides from the solution and acidifying the latter to liberate alkyl phenols.

2. The process of claim 1 in which the oxidation is by air blowing.

3. The process of claim 1 in which the low boiling fraction is less than 25% of the total alkyl phenols.

4. In the process of desulphurizing alkyl phenols containing thiophenols by oxidizing an aqueous solution of an alkali metal salt thereof to produce neutral disulphides which are insoluble, and other sulphur compounds which are soluble in said solution, separating said neutral insoluble disulphides from the solution, acidifying the latter to liberate alkyl phenols containing said sulphur compounds, and distilling the liberated alkyl phenols whereby said sulphur compounds are converted to thiophenols, the improvement comprising fractionally distilling said liberated alkyl phenols to separate a low boiling alkyl phenol fraction containing thiophenols and a higher boiling fraction substantially free from tar and thiophenols, combining said low boiling fraction with an aqueous solution of alkali metal phenolate and thiophenolate containing an amount of alkali metal at least equivalent to the resulting content of the combined alkyl phenols and thiophenols, oxidizing the combined solution under conditions to convert thiophenols to disulphides insoluble in the solution, separating the insoluble disulphides from the combined solution and acidifying the latter to liberate alkyl phenols.

5. In the process of the desulphurizing alkyl phenols containing thiophenols by oxidizing an aqueous solution of an alkali metal salt thereof to produce neutral disulphides which are insoluble, and other sulphur compounds which are soluble in said solution, separating said neutral insoluble disulphides from the solution, acidifying the latter to liberate alkyl phenols containing said sulphur compounds, and distilling the liberated alkyl phenols whereby said sulphur compounds are converted to thiophenols, the improvement comprising distilling the liberated alkyl phenols to produce a substantially undistillable bottom fraction and an overhead fraction, thereby converting substantially undistillable acidic disulphides to volatile sulphur compounds, fractionating the overhead fraction into low and high sulphur fractions, separately withdrawing the low sulphur fractions, dissolving the high sulphur fractions in aqueous alkali metal hydroxide to produce an aqueous solution of an alkali metal phenolate, oxidizing the solution under conditions to convert thiophenols to disulphides insoluble in the solution, separating the insoluble disulphides from the solution and acidifying the latter to liberate the alkyl phenols.

6. In the continuous process of desulphurizing alkyl phenols containing thiophenols by selective oxidation, the steps comprising oxidizing in an oxidizing zone an aqueous solution of alkali metal phenolates and thiophenolates containing an amount of alkali metal at least equivalent to its content of alkyl phenols and thiophenols, under conditions to convert thiophenols to disulphides at least a portion of which are insoluble in the solution, separating the insoluble disulphides from the solution, acidifying the remaining solution to liberate alkyl phenols, fractionally distilling liberated alkyl phenols to produce three fractions, a top fraction containing thiophenols, a middle fraction substantially free from tar and thiophenols, and a substantially undistillable bottom fraction, and continuously returning said top fraction to said oxidizing zone.

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