April 16, 1957 M. B. NEUWORTH 2,789,145

METHOD OF REMOVING THIOPHENOLS FROM PHENOLS

Filed Aug. 10, 1954 2 Sheets-Sheet 1

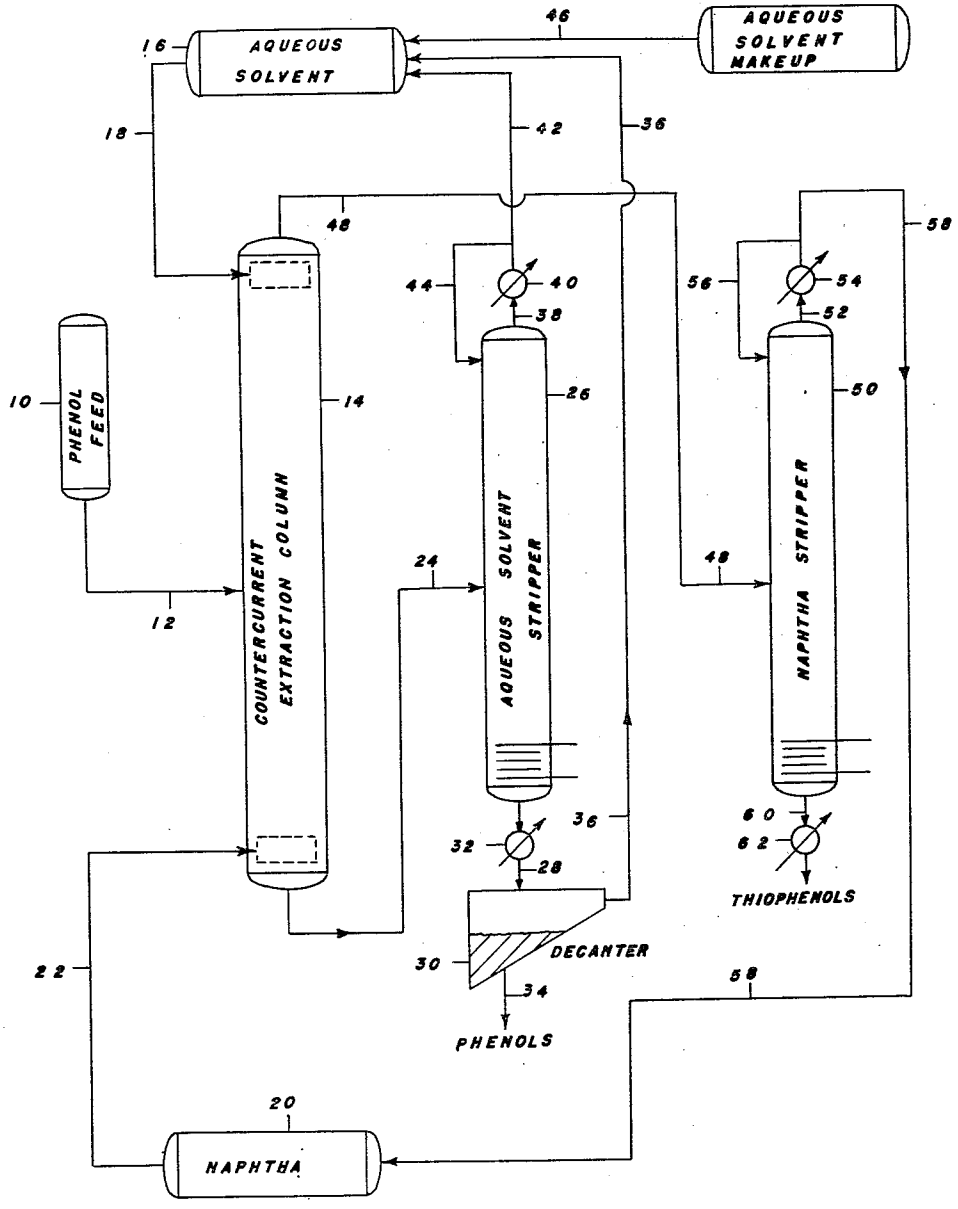

FIGURE 1.

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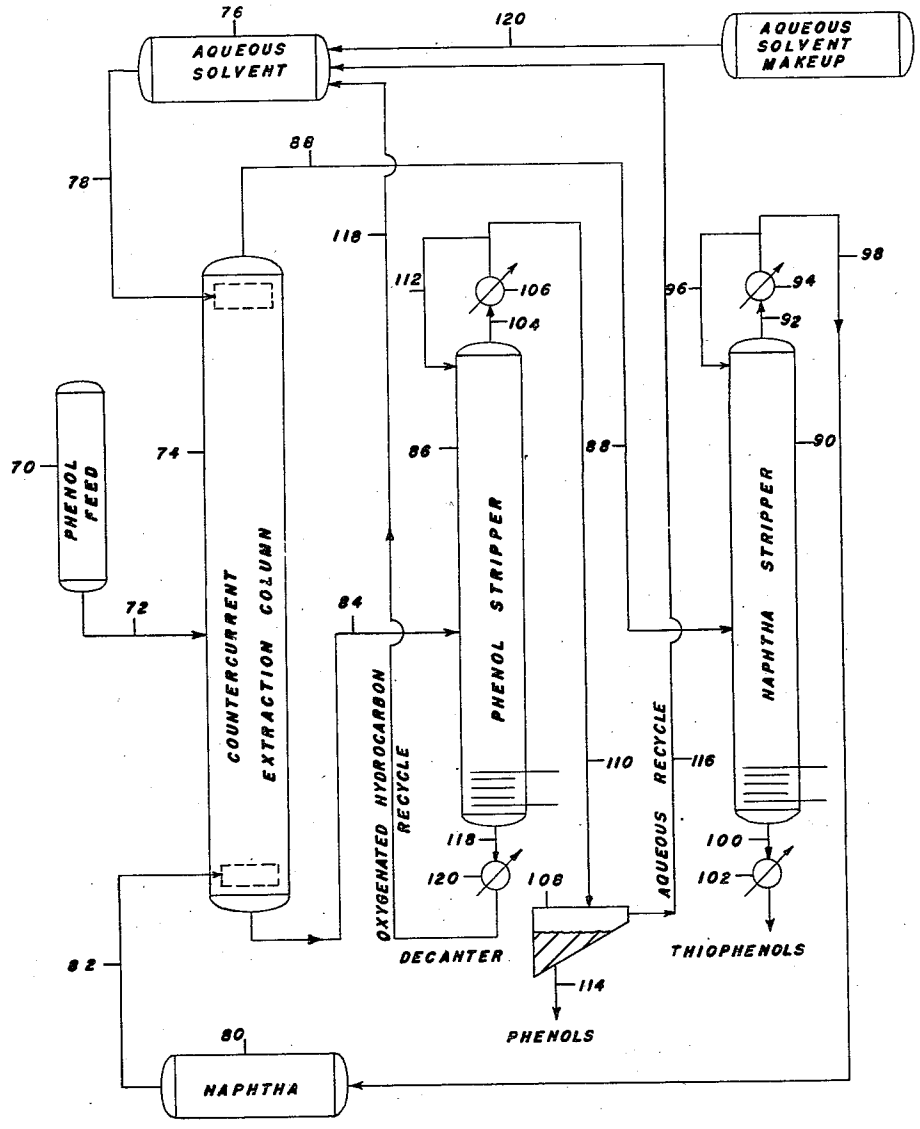

FIGURE 2.

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2,789,145

METHOD OF REMOVING THIOPHENOLS FROM PHENOLS

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Application August 10, 1954, Serial No. 448,947

9 Claims. (Cl. 260—627)

This invention relates to the art of refining phenols, and more particularly, to the removal of thiophenols from phenols.

The two principal commercial sources of phenols are coke oven tar and petroleum distillates resulting from oil cracking processes. The conventional method of recovering phenols from either source is to extract them with aqueous caustic solution to produce water soluble phenolate salts. The latter are separated from the source material by decantation and reconverted to phenols upon reaction with mineral acids. Other sources of phenols include tar from low temperature coal carbonization and oil shale distillates. The term phenols encompasses those hydroxy aromatic compounds, principally the mononuclear compounds, but also including the polynuclear compounds, for example, phenol itself, cresols, xylenols, higher methyl substituted phenols, ethyl phenols and higher alkylated phenols, bicyclic, polycyclic and dihydric phenols. The fraction of phenols boiling below 230° C. includes most of the commercially valuable phenols, i. e., phenol itself, cresols, xylenols and ethyl phenols.

Extraction of phenols by means of aqueous caustic solution is accompanied by the extraction of thiophenols since the latter are even stronger acids than the phenols themselves. The quantity of thiophenols in the original source material varies widely, being sometimes as little as one percent by weight of the phenols and ranging as high as 25 percent and above. Their presence in the extracted phenols is undesirable for most industrial applications.

Many schemes have been proposed for the removal of the thiophenols from the caustic extracted phenols. The successful ones are based upon the ease of oxidation of the thiophenols to disulfides. It is difficult to keep thiophenols free of disulfides since normal handling will expose them to air and result in at least partial oxidation. Accordingly the proposed schemes, in view of this behavior, have resorted to deliberate oxidation by air blowing to completely convert the thiophenols to disulfides. The latter are readily separable from the phenols because of their insolubility in an aqueous medium.

The general method of oxidizing thiophenols to disulfides has three disadvantages; Firstly, destruction of a significant quantity of the valuable phenols results from the oxidation; secondly, redistillation of the phenols causes a reversion of any remaining disulfides to thiophenols; there thirdly, the thiophenol content of the resulting phenols is still not reduced sufficiently for some commercial applications.

Analysis of a typical commercial product of petroleum cresylics (i. e. phenols boiling below 230° C.) that were recovered by caustic extraction and oxidized to remove thiophenols shows 97.7% by weight of phenols; 1% by weight of neutral oil; 1% by weight of sulfur compounds (total); and 0.3% by weight of tar bases. The sulfur is, of course, present in organic sulfur compounds, principally unoxidized or reconverted thiophenols, and disulfides resulting from oxidation of the thiophenols.

For many industrial resin applications, 1% by weight of sulfur compounds is too high.

In accordance with the present invention, I have provided a method for removing thiophenols from phenols which are substantially free of neutral oil. The method comprises contacting the contaminated phenols in a continuous, countercurrent extraction zone with a low boiling paraffinic naphtha fraction as one solvent and an aqueous solution of an oxygenated hydrocarbon as the other solvent. The oxygenated hydrocarbons used in the present invention are glycols, polyglycols and their methyl and ethyl ethers.

When one contacts a mixture of phenols and thiophenols with a polar and a nonpolar solvent, one would expect the more strongly acidic thiophenol to remain in the polar solvent (aqueous solutions of oxygenated hydrocarbons). However, I have found that the reverse is true. The less acidic phenols remain in the polar solvent (aqueous oxygenated hydrocarbons) and the more acidic thiophenols are recovered in the nonpolar solvent (low boiling paraffinic naphtha). The separation resulting from the present extraction treatment is extremely effective; phenols of high purity can be recovered in virtually quantitative yields.

In the process of my invention, the feedstock consists of phenols from which substantially all the neutral oil has been separated. The efficiency of separating sulfur compounds from phenols decreases as the neutral oil content of the mixture increases. In general, the neutral oil contamination of the feed material should be less than about 10 percent, preferably less than about 5 percent. This feed stock generally but not necessarily has a boiling range from 160–300° C., or some portion thereof, particularly the fraction boiling up to 230° C. The organic sulfur contaminants comprising principally thiophenols (i. e. thiophenol itself, thiocresols, thioxylenols, etc.) may be present in amounts from about 0.5 to 25% by weight of the feed stock. The present process is effective in removing thiophenols from phenols and also effective in eliminating the more readily separated sulfur compounds, such as disulfides. Thus the present process can be applied to fresh phenols as well as those which have been subjected to airblowing for partial oxidation of the thiophenols.

The contaminated feed stock is fed into a continuous, countercurrent, double solvent, extraction zone. Aqueous oxygenated hydrocarbon solution is fed into one end of the zone, and a low boiling, essentially paraffinic naphtha fraction is fed into the other end of the zone. The aqueous solvent passes through the extraction zone dissolving substantially all the phenols. The naphtha passes countercurrently through the zone dissolving the thiophenols and any residual neutral oil. The phenols then may be recovered readily from the aqueous solvent by distillation, provided the boiling ranges of the phenols and solvent are different. Similarly, the thiophenols may be recovered from the naphtha solution for disposal as waste or for commercial use depending upon the quantity.

The oxygenated hydrocarbon materials which I have found to be effective in the present invention are glycols, polyglycols, and their methyl and ethyl ethers. These compounds may be represented by the following formula:

$$R(OCH_2\overset{H}{C}R')_nOH$$

where R is H, CH_3 or C_2H_5; R' is H or CH_3; and n is an integer from 1 to 10 inclusive. It is necessary that these oxygenated hydrocarbon materials be used in an aqueous solution containing from about 50 to 80% by weight of the oxygenated hydrocarbons. In concentrations below about 50 percent by weight of oxygenated hydrocarbons, recovery of phenols is too low to be practical. Above about 80 percent concentration of oxygenated hydrocar-

bons, the aqueous solvent dissolves the thiophenols so that the extracted phenols remain contaminated to an undesirable extent.

Suitable materials for the aqueous solvent include ethylene glycol, propylene glycol, monomethyl and monoethyl ethers of ethylene glycol, diethylene glycol, dipropylene glycol, monomethyl and monoethyl ethers of diethylene glycol, triethylene glycol and various other commercially available polyethylene glycols, polypropylene glycols, and monomethyl and monoethyl ethers of polypropylene and polyethylene glycols.

The process of this invention is further critically conditioned by the characteristics of the naphtha solvent. It must be essentially paraffinic in character. Such solvents may be obtained from the distillation of paraffinic petroleum stock. Its boiling range should be 60–130° C. but preferably 60–100° C. in order to facilitate the subsequent stripping of the naphtha solvent from the naphtha extract. And finally, the naphtha density should be less than 0.80 and preferably less than 0.75 to insure a gravity difference between the two phases in the extraction column sufficient to effect a ready separation of the phases. The hexane cut of paraffinic naphtha combines all these critical properties and accordingly is preferred as the nonpolar solvent.

For a clear understanding of my invention, its objects and advantages, reference should be had to the following description and accompanying drawings in which:

Figure 1 is a diagrammatic illustration of apparatus adapted for the practice of the preferred embodiment of this invention; and

Figure 2 is a diagrammatic illustration of an alternate embodiment of this invention.

Referring to Figure 1, a feedstock comprising phenols contaminated with sulfur compounds as previously defined, is pumped continuously from a storage tank **10** through a pipeline **12** into a continuous countercurrent, double solvent extraction zone consisting, in the preferred embodiment, of a multistage, vertical, center feed extraction column **14**. The extraction column may be of any convenient design capable of providing a sufficient number of theoretical extraction stages to effect the desired separation of phenols. A conventional packed tower may be used, as well as a pierced plate column, a bubble plate column, or a column containing alternate zones of quiescence and turbulence.

A polar aqueous solvent, as previously defined, is fed continuously from an aqueous solvent storage tank **16** through pipeline **18** into the top of the extraction column **14**. Naphtha is fed continuously from the naphtha storage tank **20** through a pipeline **22** into the base of the extraction column **14**. Since the density of the aqueous solvent exceeds the density of the naphtha, the aqueous solvent descends through the column, dissolving phenols while the lighter naphtha passed countercurrently upward through the column, dissolving the thiophenols contained in the feed. Column throughput and contact time are dependent upon column design.

For every volume of feedstock, from 0.5 to 5.0 volumes of aqueous solvent and from 0.5 to 5.0 volumes of naphtha should be employed, where both high phenol recovery and high phenol purity are desired. These flow ratios are therefore preferred. While either of the two solvents may be employed as the continuous phase in the extraction column, it is preferred that the naphtha be selected as the continuous phase.

It may be desirable to add a portion of the naphtha solvent to the feedstock, especially when a high viscosity phenol fraction is being treated, i. e., one having a high end boiling point. When such technique is employed, the naphtha so added should be considered as solvent for the purpose of determining solvent ratios.

While the method of the present invention is relatively independent of the temperature at which the column is operated, it is preferred to operate the extraction column within the range of 60–120° F. The increased viscosity of the phenol feedstocks below this range introduces column operation difficulties, while the increasing solubility of the thiophenols in the aqueous solvent at higher temperatures decreases the purity of the recovered phenols. If necessary, the extraction column may be heated or cooled in any convenient manner.

The aqueous solvent, containing purified phenols, is withdrawn continuously from the bottom of the extraction column **14** through a pipeline **24** and fed into a stripping column **26** for the separation of the aqueous solvent from the recovered purified phenols. Where the aqueous solvent contains oxygenated hydrocarbons having a boiling range below that of the recovered phenols, the oxygenated hydrocarbons will pass overhead through a conduit **38**, a condenser **40** and a conduit **42** to the aqueous solvent tank **16** for recirculation in the process. A portion of the condensed distillate may be returned to the column **26** as reflux through conduit **44**. The water entering the stripping column **26** also will pass overhead with the oxygenated hydrocarbon solvent. Purified phenols are recovered at the bottom of the stripping column **26** through a conduit **28** and a condenser **32**. Any water remaining with the purified phenols is separated in a decanter **30** and returned for recirculation as solvent through conduit **36**. Purified phenols essentially free of thiophenols are recovered from the decanter **30** through conduit **34**. Fresh oxygenated hydrocarbon solvent may be added as makeup through conduit **46**.

Naphtha with dissolved thiophenols and any residual neutral oil leaves the top of the extraction column **14** through pipeline **48** and passes to a stripping column **50** where the naphtha is separated from the thiophenols. Naphtha passes overhead from the stripper **50** through a pipeline **52** and reflux condenser **54**. A portion of the condensed naphtha may be recirculated through pipeline **56** as reflux for the stripper **50**. The remainder of the naphtha is returned to the naphtha storage tank **20** through pipeline **58** for recirculation. Thiophenols leave the column **50** as a bottom product through pipeline **60**. A cooler **62** may be inserted in the exit pipeline **60** to cool the sulfur containing product.

Where the oxygenated hydrocarbon solvent of this invention has a boiling range higher than that of the phenols being treated, the process should be conducted in accordance with Figure 2. Referring to Figure 2, a feedstock containing phenols and sulfur compounds is introduced from a storage tank **70** through a conduit **72** into a countercurrent extraction column **74**. An aqueous solution of an oxygenated hydrocarbon material is introduced into the top of the column **74** from a solvent tank **76** through a conduit **78**. A low boiling paraffinic naphtha solvent from storage tank **80** is introduced through conduit **82** into the bottom of the extraction column **74**. The aqueous solvent passes downwardly through the column dissolving the phenols contained in the feed material. The paraffinic naphtha solvent passes upwardly through the column dissolving thiophenols and any residual neutral oils which may exist in the feed. The naphtha extract is recovered from the top of the column **74** through conduit **88** and sent to a naphtha stripping column **90**. In the naphtha stripper **90** the low boiling solvent is vaporized and recovered through conduit **92**, condensed in a reflux condenser **94** and returned through conduit **98** to the naphtha storage vessel **80**. A portion of the condensed naphtha may be returned to the stripper **90** through the conduit **96** as reflux. Thiophenols are recovered from the stripping column **90** through a conduit **100**. If desired a cooling condenser **102** may be provided in the withdrawal conduit.

The high boiling aqueous solvent extract is recovered from the bottom of the extraction column **74** through a

conduit 84 and sent to a phenol stripping column 86. Phenols and water pass from the top of the stripper 86 through a conduit 104 to a reflux condenser 106. Condensed water and phenols are sent to a decanter 108 through a conduit 110. A portion of the condensed water and phenols may be returned to the top of the stripping column 86 through a conduit 112 as reflux. Purified phenols are recovered from the decanter 108 through a withdrawal conduit 114. The water in the decanter 108 is separated from the phenols and returned for recirculation to the aqueous solvent storage vessel 76 through a conduit 116.

The high boiling oxygenated hydrocarbon material used in the aqueous solvent is withdrawn from the bottom of the stripping column 86 through a conduit 118 and a cooling condenser 120. High boiling oxygenated hydrocarbon material is returned to the aqueous solvent storage vessel 76 for recirculation in the system. Additional high boiling oxygenated hydrocarbon material may be introduced to the system as makeup through a conduit 120.

As mentioned previously, the system shown in Figure 2 is employed when the oxygenated hydrocarbon material has a higher boiling range than the phenols being separated. The advantage of the use of a high boiling oxygenated hydrocarbon material is that the large quantities of solvent required need not be vaporized prior to reuse in the process. In the practice of the present invention according to Figure 2 only the product purified phenols and water from the aqueous solvent need be vaporized to effect recovery of the phenols.

By way of example, a series of runs will now be described which were conducted on a commercially available product consisting of petroleum cresylics, i. e., phenols, having a boiling range of 375 to 450° F. The petroleum cresylics employed as the feed material contained the following contaminants; thiophenol 0.6%, disulfides 4.0%, and neutral oil 1.0%. The elemental sulfur in the feed material was 1.4% by weight.

The runs were conducted in a 1-inch diameter, 8-feet long, center feed, countercurrent extraction column containing in its contact zone 29 settling stages alternately disposed with 28 agitation stages. The column was operated at a temperature of 25° C. The continuous solvent phase was commercial grade hexane which was employed as the nonpolar solvent.

Six different oxygenated hydrocarbons having the following formula:

$$R(OCH_2\overset{H}{C}R')_nOH$$

where R is H, CH_3 or C_2H_5; R' is H or CH_3; and n is an integer from 1 to 10 inclusive, were employed as the primary component of the aqueous polar solvent. They included (1) ethylene glycol monomethyl ether; (2) ethylene glycol monoethyl ether; (3) ethylene glycol; (4) triethylene glycol; (5) polypropylene glycol 150; and (6) polyethylene glycol 600. The concentration of the aqueous solvent was from 70 to 80% by weight of the oxygenated hydrocarbon material.

The conditions and results of these runs are reported in the following Table I.

Table I.—Removal of thiophenols and disulfides from phenols using as solvents hexane and aqueous solutions of oxygenated hydrocarbons

Aqueous Solvent Component	Ethylene Glycol Monomethyl Ether	Ethylene Glycol Monoethyl Ether	Ethylene Glycol	Triethylene Glycol	Dipropylene Glycol [1]	Polyethylene Glycol 600 [2]
Boiling Temperature, ° C.	124.5	195	197	287	232	>400
R	CH_3	C_2H_5	H	H	H	H
R'	H	H	H	H	CH_3	CH_3
n	1	1	1	2	2	8–10
Aqueous Solvent Conc. (Wt. percent)	70	80	75	70	70	70
Feed Rates (Volumes):						
Phenols	1	1	1	1	1	1
Aqueous Solvent	2	3	2	2	2	2
Hexane	3	4	3	3	3	3
Recovery of Phenols in Extract (Wt. percent)	98.0	95.3	93.8	99.5	95.8	95.4
Contaminants in Recovered Phenols (Wt. percent):						
Thiophenols	0.07	0.07	0.007	0.14	0.04	0.2
Disulfides	0.13	0.06	0.023	0.10	0.08	0.03

[1] The dipropylene glycol in this run was a commercially available solvent sold under the name Polypropylene 150, consisting of a narrow boiling fraction of propylene glycol having an average molecular weight of about 150. It is marketed by the Carbon and Carbide Chemicals Corporation.

[2] Polyethylene glycol 600 is a commercially available solvent consisting of a narrow boiling distillate of polyethylene glycol having an average molecular weight of about 600. It is marketed under the trade name "Carbowax" by the Carbon and Carbide Chemicals Corporation.

In the runs recorded in Table I recovery of phenols ranged from 93.8–99.5%. The thiophenol contamination was reduced from its initial value of 0.6 weight percent to a value ranging from 0.007–0.14 weight percent. The disulfide content was reduced from its initial value of 4.0% to a value in the range of 0.023–0.13 weight percent. Accordingly, even if the phenols containing thiophenols are subjected to a preliminary air blowing treatment, the resulting disulfides can be substantially eliminated by the present process.

To facilitate separation of the recovered phenols from the solvents, it is preferred that the oxygenated hydrocarbon used in the polar solvent have a boiling range outside that of the phenols in the feedstock. Thus preferred solvents of the examples in Table I would include ethylene glycol monomethyl ether as boiling below the range of the cresylics, and triethylene glycol, polypropylene glycol 150 and polyethylene glycol 600 as boiling above the range of the cresylics. The use of the other two examples, ethylene glycol monoethyl ether and ethylene glycol is well-suited for effecting the desired elimination of the sulfur compounds from the phenols, but it results in an extract which is not readily separable from the purified phenols by distillation.

And now according to the provisions of the patent statutes, I have explained the principle, preferred construction, and mode of operation of my invention and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

1. A method of separating thiophenols from a mixture of phenols and thiophenols that is substantially free of neutral oils which comprises the steps of feeding said mixture of phenols to an extraction zone, feeding to one end of said extraction zone an aqueous solution containing from about 50 to about 80 percent by weight of an oxygenated hydrocarbon having the formula

$$R(OCH_2\overset{H}{C}R')_nOH$$

where R is a radical selected from the class consisting of H, CH_3 and C_2H_5; R' is a radical selected from the class

consisting of H and CH_3; and n is an integer having a value in the range of 1 to 10, feeding a paraffinic naphtha fraction boiling in the range of 60° to 130° C. and having a density of less than 0.8 to the other end of said extraction zone, passing said aqueous solution and said naphtha fraction through said extraction zone in countercurrent relation, and recovering the phenols principally in the aqueous solution and the thiophenols principally in the naphtha fraction.

2. A method of separating thiophenols from a mixture of phenols and thiophenols that is substantially free of neutral oils which comprises the steps of feeding said mixture of phenols to a vertical extraction zone at a point located between the ends thereof, feeding to the upper end of said vertical extraction zone an aqueous solution containing from about 50 to about 80 percent by weight of an oxygenated hydrocarbon having the formula

$$R(OCH_2\overset{H}{C}R')_nOH$$

where R is a radical selected from the class consisting of H, CH_3 and C_2H_5; R′ is a radical selected from the class consisting of H and CH_3; and n is an integer having a value in the range of 1 to 10, feeding a paraffinic naphtha fraction boiling in the range of 60° to 130° C. and having a density of less than 0.8 to the bottom of said extraction zone, passing said aqueous solution and said naphtha fraction through said extraction zone in countercurrent relation, and recovering the phenols principally in the aqueous solution and the thiophenols principally in the naphtha fraction.

3. A method of separating thiophenols from a phenol distillate fraction boiling within the range 170 to 230° C. comprising phenols and thiophenols and being substantially free of neutral oils, comprising the steps of feeding said distillate fraction to a vertical extraction zone at a point located between the ends thereof, feeding to the upper end of said vertical extraction zone an aqueous solution containing from about 50 to about 80 percent by weight of an oxygenated hydrocarbon boiling below 170° C. and having the formula

$$R(OCH_2\overset{H}{C}R')_nOH$$

where R is a radical selected from the class consisting of H, CH_3 and C_2H_5; R′ is a radical selected from the class consisting of H and CH_3; and n is an integer having a value in the range of 1 to 10, feeding to the bottom of said extraction zone a paraffinic naphtha fraction boiling in the range of 60° to 130° C. and having a density of less than 0.8, passing said aqueous solution and said naphtha fraction through said extraction zone in countercurrent relation, and recovering the phenols principally in the aqueous solution and the thiophenols principally in the naphtha fraction.

4. A method of separating thiophenols from a phenol distillate boiling within the range of 170° to 230° C. comprising phenols and thiophenols and being substantially free of neutral oils, comprising the steps of feeding said distillate fraction to a vertical extraction zone at a point located between the ends thereof, feeding to the upper end of said vertical extraction zone an aqueous solution containing from about 50 to about 80 percent by weight of an oxygenated hydrocarbon boiling above 230° C. and having the formula

$$R(OCH_2\overset{H}{C}R')_nOH$$

where R is a radical selected from the class consisting of H, CH_3 and C_2H_5; R′ is a radical selected from the class consisting of H and CH_3; and n is an integer having a value in the range of 1 to 10, feeding to the bottom of said extraction zone a paraffinic naphtha fraction boiling in the range of 60 to 130° C. and having a density of less than 0.8, passing said aqueous solution and said naphtha fraction through said extraction zone in countercurrent relation, and recovering the phenols principally in the aqueous solution and the thiophenols principally in the naphtha fraction.

5. A method of separating thiophenols from a mixture of phenols and thiophenols that is substantially free of neutral oils which comprises the steps of feeding said mixture of phenols to an extraction zone, feeding to one end of said extraction zone an aqueous solution containing from about 50 to about 80 percent by weight of ethylene glycol monomethyl ether, feeding to the other end of said extraction zone a paraffinic naphtha fraction boiling in the range of 60° to 130° C. and having a density of less than 0.8, passing said aqueous solution and said naphtha fraction through said extraction zone in countercurrent relation, and recovering the phenols principally in the aqueous solution and the thiophenols principally in the naphtha fraction.

6. A method of separating thiophenols from a mixture of phenols and thiophenols that is substantially free of neutral oils which comprises the steps of feeding said mixture of phenols to an extraction zone, feeding to one end of said extraction zone an aqueous solution containing from about 50 to about 80 percent by weight of ethylene glycol monoethyl ether, feeding to the other end of said extraction zone a paraffinic naphtha fraction boiling in the range of 60° to 130° and having a density of less than 0.8, passing said aqueous solution and said naphtha fraction through said extraction zone in countercurrent relation, and recovering the phenols principally in the aqueous solution and the thiophenols principally in the naphtha fraction.

7. A method of separating thiophenols from a mixture of phenols and thiophenols that is substantially free of neutral oils which comprises the steps of feeding said mixture of phenols to an extraction zone, feeding to one end of said extraction zone an aqueous solution containing from about 50 to about 80 percent by weight of triethylene glycol, feeding to the other end of said extraction zone a paraffinic naphtha boiling in the range of 60° to 130° C. and having a density of less than 0.8, passing said aqueous solution and said naphtha fraction through said extraction zone in countercurrent relation, and recovering the phenols principally in the aqueous solution and the thiophenols principally in the naphtha fraction.

8. A method of separating thiophenols from a mixture of phenols and thiophenols that is substantially free of neutral oils which comprises the steps of feeding said mixture of phenols to an extraction zone, feeding to one end of said extraction zone an aqueous solution containing from about 50 to about 80 percent by weight of dipropylene glycol, feeding to the other end of said extraction zone a paraffinic naphtha boiling in the range of 80° to 130° C. and having a density of less than 0.8, passing said aqueous solution and said naphtha fraction through said extraction zone in countercurrent relation, and recovering the phenols principally in the aqueous solution and the thiophenols principally in the naphtha fraction.

9. A method of separating thiophenols from a mixture of phenols and thiophenols that is substantially free of neutral oils which comprises the steps of feeding said mixture of phenols to an extraction zone, feeding to one end of said extraction zone an aqueous solution containing from about 50 to about 80 percent by weight of polyethylene glycol, feeding to the other end of said extraction zone a paraffinic naphtha boiling in the range of 60° to 130° C. and having a density of less than 0.8, passing said aqueous solution and said naphtha fraction through said extraction zone in countercurrent relation, and recovering the phenols principally in the aqueous solution and the thiophenols principally in the naphtha fraction.

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