The present invention relates to the separation of 2,6-xylene from cresols, and more particularly, to a double solvent extraction process for removing 2,6-xylene from a distillate fraction of cresols.

2,6-xylene is a naturally occurring phenol amounting to as much as 20% of the cresol distillate derived from low temperature carbonization of bituminous coal. It also occurs in petroleum creosites, in coke oven tars, oil shale distillates, coal hydrogenation oils and the like. Its boiling temperature is above that of ortho-cresol and below that of meta and para-cresol. Accordingly it is concentrated in what is normally termed the cresol distillate fraction of the distillation. The cresol density should be less than 0.80 and preferably less than 0.75 to insure sufficient gravity difference between the two phases in the extraction column 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 in this invention.

The polar solvent, aqueous methanol, should contain 30-50% by weight of methanol. So long as the cresol feedstock is essentially uncontaminated with neutral oils no emulsification problems arise. In concentrations exceeding about 50 weight percent methanol, the purity of the 2,6-xylene recovered in the hexane phase decreases sharply. With aqueous methanol solutions having concentrations less than about 30%, the recovery of 2,6-xylene diminishes.

The process of this invention may be practiced with either the naphtha or the aqueous methanol solution as the continuous phase in the phase contacting portion of the extraction column.

For a better understanding of my invention, its objects and advantages, reference should be had to the following description and accompanying drawing which is a diagrammatic illustration of the preferred embodiment of the apparatus adapted to the practice of this invention.

Referring to the drawing, a cresol distillate containing cresols and 2,6-xylene is pumped from a storage tank continuously through a pipeline into a continuous, countercurrent, double solvent feed extraction column. 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 2,6-xylene. A conventional packed tower may be used, for example, as well as a fiber, plate column, a bubble plate column or a column containing alternate zones of quiescence and turbulence.

The cresol feed should be essentially free of neutral oils, tar bases, sulfur compounds and other contaminants. Small quantities of neutral oils and sulfur compounds may be present (up to about 5%). These are recovered in the naphtha solvent where they contaminate the 2,6-xylene. The preferred feedstock is the cresol distillate fraction of phenols consisting essentially of cresols and 2,6-xylene. A distillate fraction of phenols having an atmospheric boiling range of about 190 to 205° C. combines these properties, i.e. it contains all the 2,6-xylene and essentially all the cresol in the crude tar acid source. Frequently small quantities (e.g. a few percent) of other phenols may occur in this fraction, for example, phenol and some of the other xylene isomers. The presence of phenols other than cresols and 2,6-xylene, however, does not alter the effectiveness of the present process.

Aqueous methanol solvent is fed continuously from the aqueous methanol storage tank into the top of the extraction column. Naphtha solvent is sent continuously from the naphtha storage tank through a pipeline into the base of the extraction column.

Since the density of the aqueous methanol solvent exceeds the density of the naphtha solvent, the aqueous methanol descends through the column dissolving the cresols in the feed, while the lighter naphtha solvent passes countercurrently upward through the column dissolving the 2,6-xylene. Trace quantities of neutral oils and sulfur compounds from the feedstock will be recovered in the naphtha phase along with the 2,6-xylene.

In the preferred embodiment, the feedstock is introduced into the center of a vertical, countercurrent extraction column. In some instances, the feedstock might be mixed with one of the two solvents to permit the use of end-feed columns.

For every volume of phenols fed to the extraction column, from 1.0 to 15.0 volumes of aqueous methanol
and from 1.0 to 15.0 volumes of naphtha should be employed. Aqueous methanol extract, containing phenols freed of 2,6-xyleneol, is recovered from the bottom of column 24 through conduit 24 and sent into a stripping column 26 for separation of the extract and the solvent. Methanol is recovered overhead through conduit 30 and returned to the methanol storage tank 16 for recycle. A condenser and refluxing system may be installed in the conduit 30. Water, together with the phenols freed of 2,6-xyleneol, is recovered from the base of the stripping column 26 through conduit 28. If desired a cooling condenser may be inserted in the conduit 28. The water is separated from the extracted phenols by phase separation in a decanter 40 and returned through conduit 42 to the aqueous methanol storage tank 16 for recycle. Additional methanol can be added to the solvent circulation system through conduit 44 to compensate for solvent losses in the system.

The naphtha solution containing 2,6-xyleneol is recovered from the top of the extraction column 14 through a conduit 52 and sent to a naphtha stripping column 34. The naphtha solvent is recovered overhead through conduit 36 and returned to the naphtha storage tank 20 for recycle. If desired, a condenser and refluxing system may be inserted in conduit 36. 2,6-xyleneol is recovered from the bottom of the stripping column 34 through the conduit 38. A cooling condenser may be inserted in the conduit 38.

The fractionation process is preferably operated at atmospheric pressures and temperatures.

To illustrate the present process, tar from low temperature carbonization of bituminous coal was fractionated by distillation to produce a distillate boiling from 180 to 230° C. This fraction, containing all the phenol, cresol and xyleneol in the tar, together with neutral oils, was processed in accordance with U. S. Patent 2,666,796 (abovementioned) to recover the phenols free of neutral oils. Upon precise fractionation, the distillate fraction boiling from 190 to 203° C. had the following analysis:

<table>
<thead>
<tr>
<th>Phenol</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Cresol</td>
<td>28</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>25</td>
</tr>
<tr>
<td>p-Cresol</td>
<td>18</td>
</tr>
<tr>
<td>2,6-xyleneol</td>
<td>18</td>
</tr>
</tbody>
</table>

Thus the 2,6-xyleneol contained in the tar acid oil remains with the phenol extract produced in the double-solvent extraction process described in U. S. Patent 2,666,796.

Mixtures, whose exact compositions are set forth in Table I, were treated in accordance with the present invention for separation and recovery of 2,6-xyleneol. Results are presented in Table I.

The naphtha solvent, a commercial grade of hexane derived from petroleum, was the continuous phase in the extraction column. A one-inch diameter, eight-feet long, center feed, countercurrent extraction column was employed and contained in its contacting zone 29 settling stages alternately disposed with 28 agitation stages.

Aqueous Methanol Concentration, Wt. Percent

<table>
<thead>
<tr>
<th>Solvent/Feed Ratio, vol./vol.:</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Methanol</td>
<td>45</td>
<td>45</td>
<td>35</td>
</tr>
<tr>
<td>Naphtha</td>
<td>5</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Feed Composition, Wt. Percent:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Cresol</td>
<td>42.2</td>
<td>43.0</td>
<td>42.2</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>28.0</td>
<td>24.0</td>
<td>28.6</td>
</tr>
<tr>
<td>p-Cresol</td>
<td>18.9</td>
<td>16.0</td>
<td>18.9</td>
</tr>
<tr>
<td>2,6-xyleneol</td>
<td>15.3</td>
<td>17.0</td>
<td>15.3</td>
</tr>
</tbody>
</table>

The feedstock in the three runs of Table I contained from 15.3 to 17.0 wt. percent 2,6-xyleneol. This concentration of 2,6-xyleneol was reduced to 6.1 to 6.8 wt. percent of the product cresol fraction. The 2,6-xyleneol was recovered in purities ranging from 95.2 to 91.2% by weight. It is of interest to note that the azeotropic distillation technique described in British Patent 708,925 (above-mentioned) increased the concentration of 2,6-xyleneol from an initial level of 5% to a final value of only 22 to 30%.

From 60.1 to 65.5 wt. percent of the 2,6-xyleneol in the feed tar acids was removed and recovered. The naphtha-to-feed ratio ranged from 5 to 10 parts by volume; the aqueous methanol to feed ratio ranged from 2 to 10 parts by volume.

The purity of cresol in the feedstock ranged from 83 to 84.7% by weight. The purity of the recovered cresols ranged from 93.2 to 93.9% by weight. By proper adjustment of the solvent-to-feed flow rates, the purity and recovery of the cresol can be regulated. Improving the stage efficiency of the extraction column results in improved purity and recovery.

Recovery of higher purity fractions of 2,6-xyleneol can be accomplished by treating the naphtha extract through fractional crystallization.

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. The method for separating 2,6-xyleneol from a mixture consisting essentially of cresol and 2,6-xyleneol which comprises introducing said mixture into a vertical, countercurrent extraction zone, introducing paraffinic naphtha solvent boiling in the range of 60 to 130° C. and having a density less than 0.8 in the bottom of said extraction zone, introducing an aqueous methanol solution containing 30 to 50 wt. percent of methanol into the top of said extraction zone, recovering from the bottom of said extraction zone an aqueous methanol extract containing cresols and recovering from the top of said extraction zone a naphtha extract containing 2,6-xyleneol.

2. The method for separating 2,6-xyleneol from a cresol distillate fraction consisting essentially of phenols including 2,6-xyleneol which comprises introducing said distillate fraction between the ends of a vertical, countercurrent extraction zone, introducing 1 to 15 volumes of paraffinic naphtha solvent boiling in the range of 60 to 130° C. and having a density of less than 0.8 in the bottom of said extraction zone, introducing 1 to 15 volumes of aqueous methanol solution containing 30 to 50 wt. percent methanol into the top of said extraction zone, recovering from the bottom of said extraction zone an aqueous methanol extract containing cresols and recovering from the top of said extraction zone a naphtha extract containing 2,6-xyleneol.

3. The method for separating 2,6-xyleneol from a distillate fraction consisting essentially of phenols including 2,6-xyleneol boiling in the range of 190 to 203° C. which comprises introducing said distillate fraction between the ends of a vertical, countercurrent extraction zone, introducing 1 to 15 volumes of paraffinic naphtha solvent boiling in the range of 60 to 130° C. and having a density of less than 0.8 in the bottom of said extraction zone, introducing 1 to 15 volumes of aqueous methanol solution containing 30 to 50 wt. percent methanol into the top of said extraction zone, recovering from the bottom of said extraction zone an aqueous methanol extract containing phenols and recovering from the top of said extraction zone a naphtha extract containing 2,6-xyleneol.
4. The method of claim 3 in which the paraffinic naphtha solvent is the continuous phase in the extraction zone.

5. The method of claim 3 in which the paraffinic naphtha solvent is the hexane distillate fraction of petroleum naphtha.

6. The method of claim 3 in which the paraffinic naphtha solvent has a boiling range of 60-100°C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,556,213 Pierotti et al. June 12, 1951
2,666,796 Gorin et al. Jan. 19, 1954

FOREIGN PATENTS

708,925 Great Britain May 12, 1954