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THE SELECTIVE EXTRACTION OF PHENOLS FROM TARS  
( METASOLVAN PROCESS ) IN GERMANY

Phenols are generally obtained by extraction with sodium hydroxide. The process is divided into several stages, such as evaporation, liberating the phenols from the phenolates by means of CO<sub>2</sub>, and regeneration of the NaOH. Thus, a number of suggestions for selective extraction with solvents have been made.

These methods are all applied to low temperature distillation tars of lignite and bituminous coal. The best known of these methods is the alcohol washing process for lignite distillation tars, German Patents 272 689 (Dougall Brothers and Howles) and 302 398 (Graefe and Krey, Riebeck-Montan Werke). Another method is that of Erdmann, German Patent 360 745, in which the solvent is 50 percent acetone. The use of the Edeleanu process, using SO<sub>2</sub> for separating creosotes and neutral oil, has also been suggested.

The purification of lignite oils was carried out to obtain raw material which could easily be processed into paraffin, since quality and yield of paraffin are increased if the products are free of creosote.

In the distillation of bituminous coal, products with much higher phenol content were found, and attempts were made to transfer the experiences gained in the distillation of lignite to this field.

However, it was found that bituminous coal tar deviates from the characteristics of lignite tar. Weindel (Patent 433 268 of Mathias Stinnes Mine, Essen) dissolved coal tar completely in 90 percent ethyl alcohol, but only with alcohol of a concentration of 60 percent or less could good results be obtained, yielding phenols of 99 percent purity. This process was later expanded by a pitch separation process using gasoline. Another modification, by the same author, described in Patent 436,444, employs an addition of NH<sub>4</sub>OH to the alcohol, phenols having a greater solubility in this medium. It is not known whether this method was ever used on an industrial scale.

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A number of other suggestions have been made for the separation of acid and neutral oils. Croy, in German Patent 529 321, uses strong HCl or 50 percent  $H_2SO_4$  as an extracting agent. The extract is then washed with gasoline, the 60 percent phenols contained in the extract being concentrated to 90 percent thereby.

The more recent development of the synthetics industry increased the demand for phenols free from neutral oils. A number of suggestions for their production have been made, all based on the principle of using selective solvents. Among these is the suggestion of the Imperial Chemical Industry made in 1936 to remove the phenols by means of  $NH_4OH$  in a salt solution, e.g.,  $Ca(NO_3)_2$ . Another suggestion along this line is that of Goeckil, made in 1940, for using gaseous ammonia or amines. Patents 449 400 and 556 640 suggest the use of formic acid to extract phenols. However, these two above methods also extract a considerable quantity of neutral oils, and are therefore not superior to the alcohol method. Furthermore, they are corrosive, and thus not very suitable for industrial purposes.

Another possibility for removing the phenols from oils in the "Phenosolven" method, used mainly for obtaining carbolic acid and cresols, as described in detail in Chemiker - Zeitung, 1942.

The Metasolvan process is a further development of the alcohol washing process in which pure phenols are obtained. Methyl alcohol is used, since its selectivity is greater and its cost lower than that of ethyl alcohol. The process was developed by Alfred Dierichs, in cooperation with the firm of Lurgi, Frankfurt-am-Main. Experiments on tar fractions in the boiling range from 160 to 200 degrees centigrade, at room temperature, and using equal volumes, showed that the amount of the refined material increases with decreasing methyl alcohol concentration, but that the phenol content remains fairly constant up to a methyl alcohol concentration of approximately 70 percent. At the same concentration value, the extract has its maximum content of phenols, 81.5 percent, and this value cannot be increased by dilution below 70 percent. If this method is carried out as a counter-current process, practically all the phenol can be removed.

The neutral oil content of the phenol oil, however, is still too high for practical utilization of this product. It turned out, however, that these neutral oils could be easily removed from the methyl alcohol solution by extraction with hydrocarbons, especially straight-chain gasoline. The content of neutral oils of the phenol oils can be brought down to as low as 0.5 percent and less, thus making the phenols produced by this method equal in quality to those obtained by the sodium hydroxide process.

The process is a continuous one, as is shown in the appended diagram.

The tar oil, in this case lignite tar oil of the 160-to 200-degree-centigrade fraction, enters at the top, is mixed with the residue from the gasoline distillation which still contains phenol, and moves to the three-stage continuous washer. Practically all the phenol is removed here, and the remainders of the solvent (70 percent methyl alcohol) are removed from the phenol in distillation K 1. The methanol extract is then washed in a continuous scrubbing tower with gasoline, the neutral oil and slight amounts of phenols being extracted. The washed extract goes to distillation K 2, where most of the solvent is distilled out. In distillation K 3 the phenol oil obtained is freed from water and separated into fractions. In distillation K 4, the gasoline containing extracted material is freed from the extracted neutral oil and re-enters the cycle. In the mixer of the methyl alcohol cycle (on the left side in the diagram), the exact concentration of the methyl alcohol is set.

In a comparison with the customary NaOH process, the following features of the Metasolvan process become evident: The phenol oil will probably be just as

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expensive, due to losses of solvent, as the phenol oil obtained by the NaOH process. However, the original investment is smaller (less iron needed), the end products are free of alkali content, the equipment requires less space, and the process is simple and clean. The main disadvantage is that the process can be used only for certain types of oil and for certain fractions of this particular oil, while the NaOH process is universally applicable.

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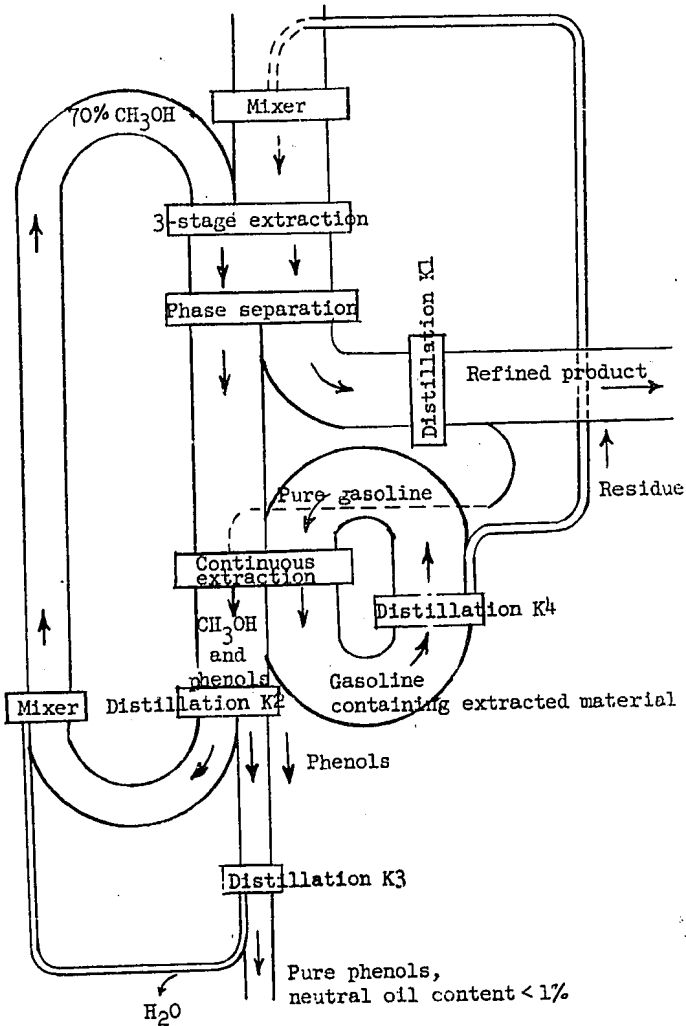
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Lignite Tar Oil, Fractions .160°- 205° C BP



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