

Oct. 9, 1956

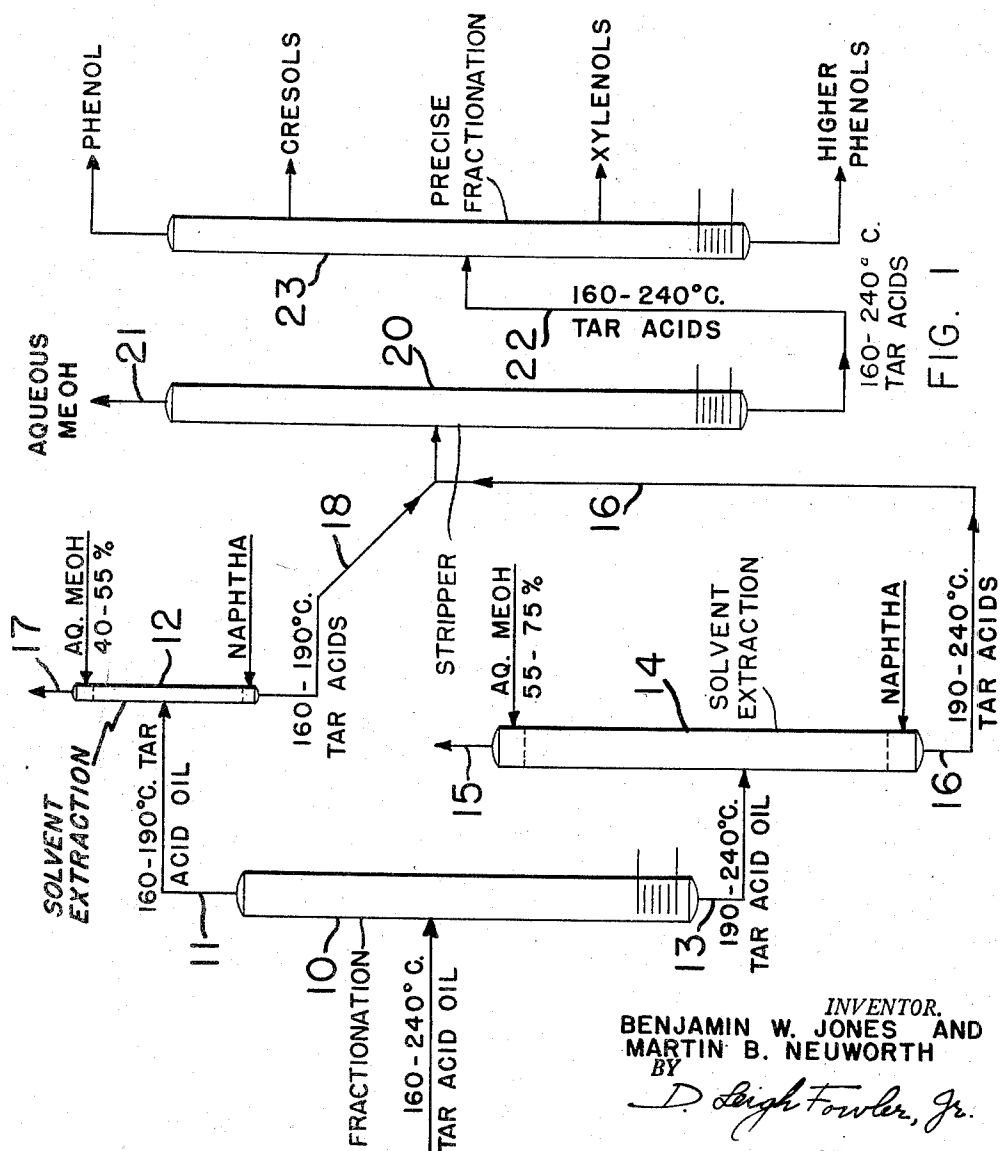
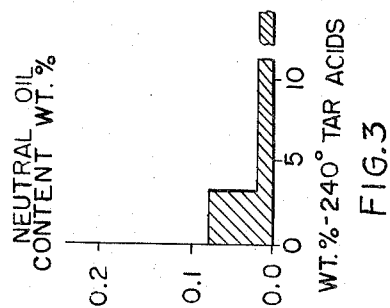
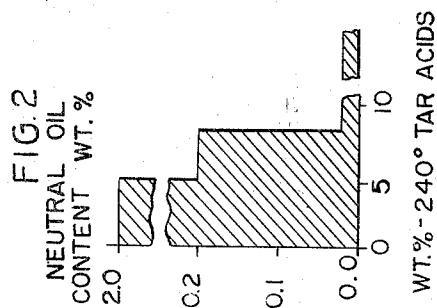
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2,766,296

PURIFICATION OF TAR ACIDS

Filed Nov. 27, 1953

2 Sheets-Sheet 1



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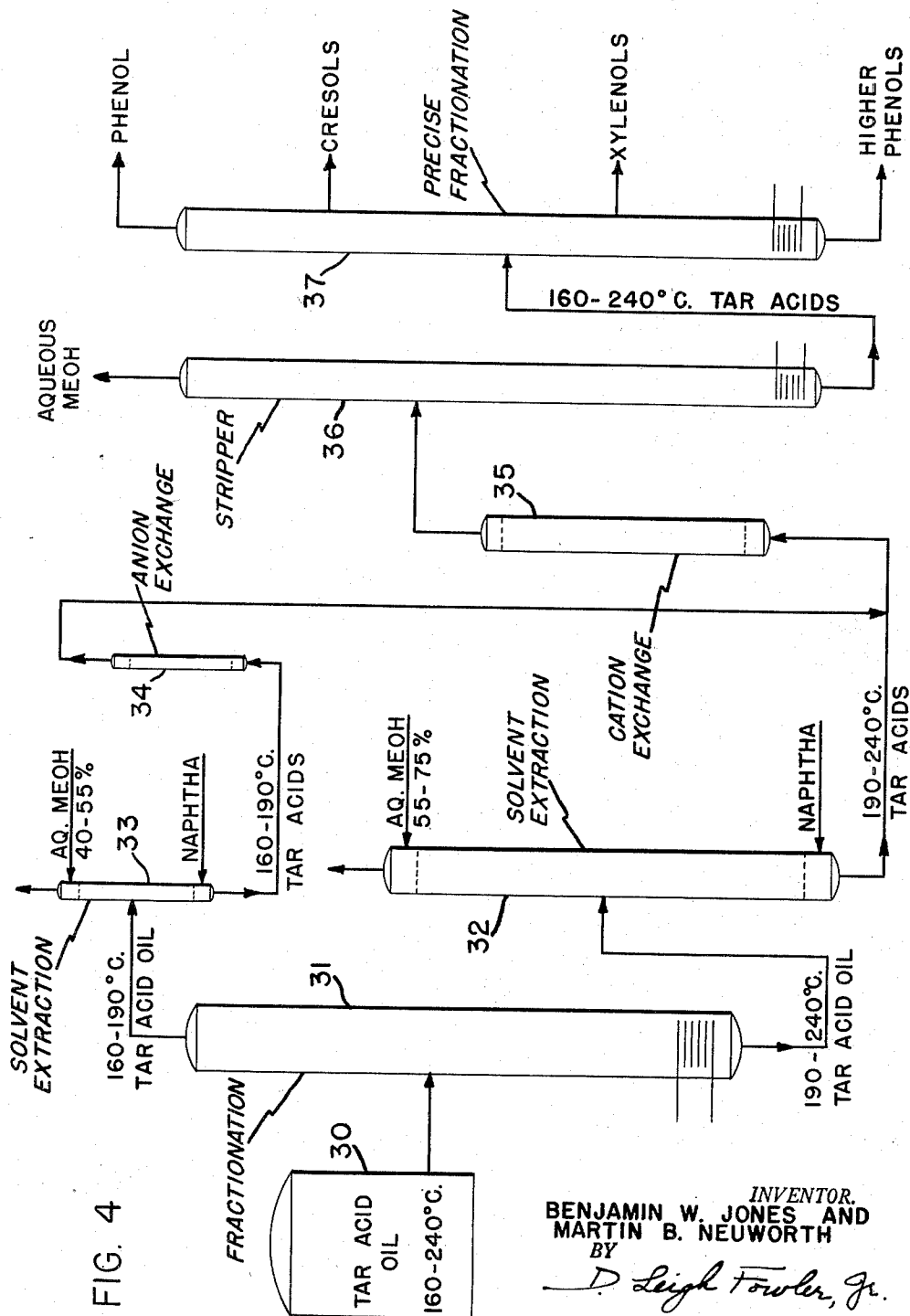
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PURIFICATION OF TAR ACIDS

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3 Claims. (Cl. 260—627)

The present invention relates to the production of pure tar acids and more particularly to an improved process for recovering pure tar acids by double solvent extractive methods.

Commercial tar acids include phenols, cresols, xylenols and certain higher boiling phenols such as ethyl phenols and trimethylphenols. Most of these tar acids boil in the range of 180 to 240° C. and are marketed as pure compounds or as closely boiling distillate fractions. Tar acids occur in coal tars, coal hydrogenation liquid products, shale oils, petroleum oils and the like. They are generally recovered as a tar acid oil by distillation of the source material and appear in mixture with neutral oils, tar bases and other contaminants, such as sulfur compounds and certain carboxylic acids. Tars produced by the low temperature carbonization of Pittsburgh seam coal contain in their tar acids distillate fractions about 40 to 60 percent tar acids, about 40 to 60 percent neutral oils and less than about 5 percent tar bases. The exact composition depends upon the particular coal as well as upon the method of carbonization. However it is apparent that the principal separation problem in connection with tar acids is the removal of the neutral oils. Commercial specifications for tar acids frequently prescribe the neutral oil content to be less than 0.1 weight percent.

The term "tar acid oil" defines any distillate fraction containing tar acids in mixture with neutral oils. The lowest boiling tar acid, phenol, boils at 180° C., although azeotropes of phenol boil as low as 160° C. The xylenols generally boil below 240° C. Other tar acids, however, have boiling ranges as high as about 300° C. Thus tar acid oil is a distillate fraction boiling anywhere in the range of about 160° C. through about 300° C. To recover the commercially valuable phenol, cresols and xylenols, however, only the fractions boiling from about 160° C. to about 240° C. are required. The present process is applicable to any tar acid oil boiling in the range of about 160 to 300° C., provided the lower boiling tar acids are present.

A solvent extraction process for separating tar acids from neutral oils has been developed and is described in U. S. patent application S. N. 184,474, entitled "Refining of Tar Acid Oil" by Martin B. Neuworth and Everett Gorin, filed September 12, 1950, now U. S. Patent 2,666,796 issued January 19, 1954 as a continuation-in-part of U. S. patent application S. N. 110,932, filed August 18, 1949, now abandoned. To separate tar acids from tar acid oil according to the process of application S. N. 184,474 supra, the tar acid oil is contacted in a center-feed extraction column with two solvents: (1) a paraffinic hydrocarbon solvent (naphtha) having a boiling range of 60 to 130° C. and a density of less than 0.8; and (2) aqueous methanol containing 55 to 75 weight percent methanol. The tar acids are selectively recovered in the aqueous methanol whereas the neutral oils are selectively recovered in the paraffinic solvent. The total tar acids recovered from this process satisfy the specifications of

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commerce, i. e. the neutral oil contamination of the product tar acids is less than 0.1 weight percent.

However, upon precise fractionation of the tar acids recovered in the process of U. S. patent application S. N. 184,474, it has been found that the residual neutral oil contaminant is not uniformly distributed throughout the distillate fractions. Instead, the neutral oils are preferentially concentrated in the lowest boiling distillate fractions containing the phenol (boiling point 181° C.) and ortho-cresol (boiling point 191° C.). In fact the neutral oil contamination of these lowest boiling fractions is as high as 0.2 weight percent and higher. To dispose of these lower boiling tar acids as a premium product, it is desirable that the neutral oil contamination be reduced.

We have found that these lowest boiling tar acids can be separated from the neutral oils which accompany them in distillate fractions by treating the fractions in a two-solvent extraction process similar to that shown and described in U. S. patent application S. N. 184,474 supra. However the aqueous methanol solvent for these lower boiling tar acids should contain from 40 to 55 weight percent methanol where it is desired to separate these low boiling tar acid oils into high purity tar acids, i. e. having less than 0.1 weight percent neutral oil contamination, for example.

Accordingly, to recover high purity tar acids from the total tar acid oil, the feed material is subjected to a first fractionation to separate it into (1) a low boiling distillate fraction having an end boiling point of about 180 to 210° C., containing all the phenol and some of the cresols from the tar acid oil feedstock and (2) a higher boiling distillate fraction having an initial boiling point of about 180 to 210° C., and containing some ortho-cresol but no phenol from the tar acid oil feedstock. The higher boiling fraction thereupon is treated in accordance with the solvent extraction process of U. S. patent application S. N. 184,474 supra. The lower boiling fraction however is treated in a solvent extraction process similar to that set forth in U. S. patent application S. N. 184,474 supra, but differing in that the polar solvent is a 40 to 55 weight percent solution of aqueous methanol. Pure tar acids having low residual neutral oil contamination are recovered from each solvent extractive process.

For a full explanation of the present invention, its objects and advantages, reference should be had to the following description and to the accompanying drawings in which:

Figure 1 is a schematic flow sheet showing the preferred embodiment of the present invention;

Figure 2 is a graphical illustration of the purity of tar acids produced without pre-fractionation;

Figure 3 is a graphical illustration of the purity of tar acids produced according to the present invention; and

Figure 4 is a schematic flow sheet showing a modification of the process of our invention for recovering water-white tar acids, free of neutral oils, free of tar bases and free of foul-smelling carboxylic acids.

Referring to Figure 1, the feed material is tar acid oil having a boiling range of about 160 to about 240° C. for this example. The tar acid oil is introduced into a primary fractionation zone 10 where it is separated into two distillate fractions. The cut point between the two fractions in general ranges from about 180 to about 200° C. and is determined by the composition of the tar acid oil feedstock and the desired products. The lower boiling distillate from the fractionation zone 10 should contain all the phenol and some of the cresols in the tar acid oil feedstock. The light fraction containing the phenols comprises less than 20 percent of the 160 to 240° C. tar acid oil from tar produced by low temperature carbonization of bituminous coal. The bottoms from the fractionation zone 10 should contain some cresols but no

phenol. For the purposes of illustration, the fractionation zone of Figure 1 is shown as operating at a cut point of 190° C.

The lower boiling distillate fraction from the fractionation zone 10 passes through a conduit 11 to a solvent extraction zone 12. The extraction process carried out in the zone 12 is similar to that described in U. S. patent application S. N. 184,474 supra, but differs in that the methanol concentration of the aqueous polar solvent is about 40 to 55 weight percent. A paraffinic naphtha fraction boiling in the range of 60 to 130° C. and having a density of less than 0.8 is introduced into the bottom of the extraction zone 12. Aqueous methanol having a methanol concentration of about 40 to 55 weight percent is introduced into the top of the extraction zone 12. For every volume of tar acid oil fed through the conduit 11, from 0.5 to 5.0 volumes of aqueous methanol and from 0.5 to 5.0 volumes of paraffinic naphtha should be used. The ratio of naphtha to aqueous methanol, moreover, should be from about 0.25 to about 4.0.

The paraffinic naphtha passes upwardly through the extraction zone 12 and selectively absorbs the neutral oil constituents of the tar acid oil. The aqueous methanol passes downwardly through the extraction zone 12 and selectively absorbs the tar acid constituents of the tar acid oil. Neutral oils in naphtha solvent are recovered through a conduit 17; aqueous methanol and tar acids are recovered through a conduit 18. Effluent tar acids from the extraction zone 12 possess low residual neutral oil contamination. In general these tar acids comprise all the phenol in the tar acid oil feedstock together with some of the cresols. If desired, the aqueous methanol solution of pure tar acids in conduit 18 can be stripped of methanol and the remaining tar acids may be separately recovered. In Figure 1, however, for the purposes of illustration, the purified tar acids in aqueous methanol solution, are recombined with higher boiling tar acids for further refining.

The higher boiling tar acid oil fraction from the fractionation zone 10 passes through the conduit 13 to a solvent extraction zone 14 where it is treated in accordance with the process set forth in U. S. patent application S. N. 184,474 supra. Aqueous methanol having a concentration of 55 to 75 weight percent and a paraffinic naphtha are employed as solvents. The naphtha passes upwardly through the extraction zone and selectively absorbs the neutral oil constituents of the feedstock. The aqueous methanol passes downwardly through the extraction zone and selectively absorbs the tar acid constituents. Neutral oils in naphtha solvent are recovered through the conduit 15. Effluent tar acids from the extraction zone 14 possess a low residual neutral oil contamination, and comprise generally all of the tar acids from the feedstock except for the phenol and a portion of the cresols. These tar acids may be separately recovered from their aqueous methanol solvent or may be recombined as shown in Figure 1 and fractionated as a blend of all tar acids.

The two streams 16 and 18 contain substantially all the tar acids from the tar acid oil feedstock in aqueous methanol solution. Aqueous methanol is stripped from the tar acids in a stripping zone 20 and recovered for reuse as solvent through the conduit 21. Tar acids, freed of solvent, are recovered from the stripper 20 through a conduit 22 and sent to a precise fractionation zone 23 where closely boiling distillate fractions of the tar acids are recovered as final products.

To show the improvement resulting from the present invention, the neutral oil contamination of the distillate fractions of purified tar acids is plotted in Figures 2 and 3 against the percentage of the tar acids distilled. For Figure 2, raw tar acid oil was treated in accordance with U. S. patent application S. N. 184,474 and the purified tar acids contained about five percent water but had less than 0.1 weight percent neutral oil contamination. As indicated in Figure 2, the neutral oil contaminants

appear to be concentrated in the lowest boiling tar acids, i. e. in the lowest boiling ten percent of the purified tar acids. Throughout the phenol and ortho-cresol boiling range the neutral oil contamination was of the order of 0.2 weight percent; the initial fraction of the tar acids had as much as 2.0 weight percent contamination.

When the same raw tar acid oil was treated according to the present invention, a lower neutral oil contamination of the lower boiling tar acids resulted as indicated in Figure 3. Even the lowest boiling tar acids had a residual neutral oil contamination of less than 0.1 weight percent. Thus, by employing the present invention it is possible to produce pure tar acids which satisfy many commercial specifications over the entire boiling range, i. e., the neutral oil contamination is less than 0.1 weight percent.

Separation of the lowest boiling tar acids from tar acid oil by the double solvent extraction process results in high yields of tar acids throughout the range of aqueous methanol concentrations from 40 to 75 weight percent. However only in the range of 40 to 55 percent aqueous methanol can high purity tar acids be recovered from the lower boiling tar acid oil. Similarly, the higher boiling tar acids can be recovered in high yield and high purity only with aqueous methanol having a concentration of 55 to 75 percent. Treatment of the higher boiling tar acid oils with an aqueous methanol solvent having a concentration of 40 to 55 percent would produce pure tar acids in low yields, since many tar acids would appear in the naphtha phase.

Another advantage resulting from pre-fractionation of the tar acid oil is a saving in intermediate refining processes for the tar acids. To understand this intermediate saving, reference should be had to Figure 4 which is a schematic flow sheet of an overall tar acids refining system according to the present invention.

As shown in Figure 4, tar acid oil having a boiling range of 160 to 240° C. from a source 30 is pre-fractionated in a distillation zone 31 into two distillates, one boiling from 160 to about 190° C. and the other boiling from about 190 to 240° C. The exact temperature of the fractionation is determined by the composition of the tar acid oil. The overhead fraction should contain substantially all the phenol whereas the bottoms fraction should contain substantially no phenol. The heavier fraction (190–240° C.) is treated in a solvent extraction zone 32 in accordance with the process of S. N. 184,474 as previously described.

The 160 to 190° C. overhead fraction is treated in a solvent extraction zone 33 with paraffinic naphtha and 40 to 55 weight percent aqueous methanol. The aqueous methanol extract, containing the 160 to 190° C. tar acids, is substantially free of neutral oils, but does contain some carboxylic acids which create foul odors and also some tar bases which must be removed. An anion exchange process for removing the foul smelling carboxylic acids has been described in copending U. S. patent application S. N. 276,991 by Martin B. Neuworth, now U. S. Patent 2,734,925 issued Feb. 14, 1956, entitled "Purification of Low Boiling Tar Acids" and filed on March 17, 1952 as a continuation-in-part of U. S. patent application S. N. 215,214, filed March 13, 1951, now abandoned. According to the process of S. N. 276,991, foul smelling carboxylic contaminants may be removed from tar acids by passing an aqueous methanolic solution of tar acids through a vessel containing certain anion exchange materials. A vessel 34 containing anion exchange material is provided for treating the light fraction of tar acids in aqueous methanol solvent. We have found that the foul-odor-producing materials also are concentrated in the light fraction of the tar acids. Hence it is not required that the heavy fraction (190–240° C.) be treated in the anion exchange vessel corresponding to vessel 34.

The effectiveness of the anion exchange treatment

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for the lower boiling tar acids furthermore is improved by the fact that the higher boiling tar acids do not contact the anion exchange materials. The high boiling tar acids and particularly those boiling above 240° C., have a tendency to clog the pores of the anion exchange material, diminishing its activity and reducing its effective life. Without the pre-fractionation afforded by the present invention, it would be required to treat the entire 160-240° C. fraction of tar acids in an anion exchange zone. According to the present invention, only the lighter fraction, which comprises perhaps ten percent of the weight of the tar acid oil, must be treated with the anion exchange process. Accordingly only sufficient anion exchange capacity for about ten weight percent of the total tar acid oil is required. The capital investment in such a tar acid oil refinery is reduced. Moreover the relatively expensive anion exchange material is not subjected to contact with the higher boiling tar acids which have a tendency to sludge the anion exchange material.

Tar bases can be removed from the tar acids by a cation exchange process described in U. S. patent application S. N. 382,866 by Everett Gorin, Martin B. Newworth and Benjamin W. Jones, entitled "Separation of Tar Acids and Tar Bases," filed on September 28, 1953 as a continuation-in-part of U. S. patent application S. N. 215,376 by the same inventors and having the same title, filed on March 13, 1951, and now abandoned.

Since the tar base contaminants are distributed throughout the entire boiling range of the tar acid oil, it is necessary that both fractions be treated by a cation exchange process in order to remove the tar base contamination. The light fraction is combined with the heavy fraction and the mixture is treated in a cation exchange vessel 35. Effluent from the vessel 35 contains substantially no tar bases, substantially no odor-producing carboxylic acids, and essentially no neutral oil contaminants. Aqueous methanol solvent is removed from the purified tar acids in a stripper 36. The resulting tar acids are separated into closely boiling marketable fractions in a precise fractional distillation zone 37.

By pre-fractionating the tar acid oil and separately treating the two fractions by solvent extraction, it is possible to produce tar acids which satisfy the commercial specifications throughout the entire distillate range. Moreover it is possible to eliminate the foul-smelling carboxylic contaminants from the tar acids products by treating only the lighter fraction with anion exchange materials; increased life of the exchange material results since contact between the heavier tar acids and the anion exchange materials is avoided.

Now, according to the provisions of the patent statutes, we have explained the principle, preferred construction, and mode of operation of our invention and have illus-

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trated and described what we now consider to represent its best embodiment. However, we 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.

We claim:

1. A method for refining low boiling tar acid oil to recover pure tar acids which comprises separating the low boiling tar acid oil into two distillate fractions, a first containing substantially all the phenol and some cresol and a second containing some cresol but substantially no phenol, treating said first fraction in a first countercurrent, center-feed, double solvent extraction system using paraffinic naphtha having a density less than 0.8 and 40 to 55 percent aqueous methanol as solvents, treating said second fraction in a second countercurrent, center-feed, double solvent extraction system using paraffinic naphtha having a density less than 0.8 and 55 to 75 percent aqueous methanol as solvents, recovering the aqueous methanol extracts from both solvent extraction systems and recovering from said aqueous methanol extracts tar acids containing substantially no neutral oils.

2. The method of claim 1 in which the tar acid oil is derived from tar produced by the low temperature carbonization of bituminous coal.

3. A method for recovering tar acids from tar acid oil boiling in the range 160 to 240° C. which comprises separating the tar acid oil into two distillate fractions, the first having an end boiling point in the range 180 to 200° C. and the second distillate fraction having an initial boiling point in the range 180 to 200° C., treating the low boiling fraction in a first countercurrent, center-feed, double solvent extraction system using 40 to 55 percent aqueous methanol and paraffinic naphtha having a density less than 0.8 as solvents, treating the higher boiling fraction in a second countercurrent, center-feed, double solvent extraction system using 55 to 75 percent aqueous methanol and paraffinic naphtha having a density less than 0.8 as solvents, recovering and combining aqueous methanol extracts from each solvent extraction system, and recovering from the combined extracts tar acids substantially free of neutral oils.

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