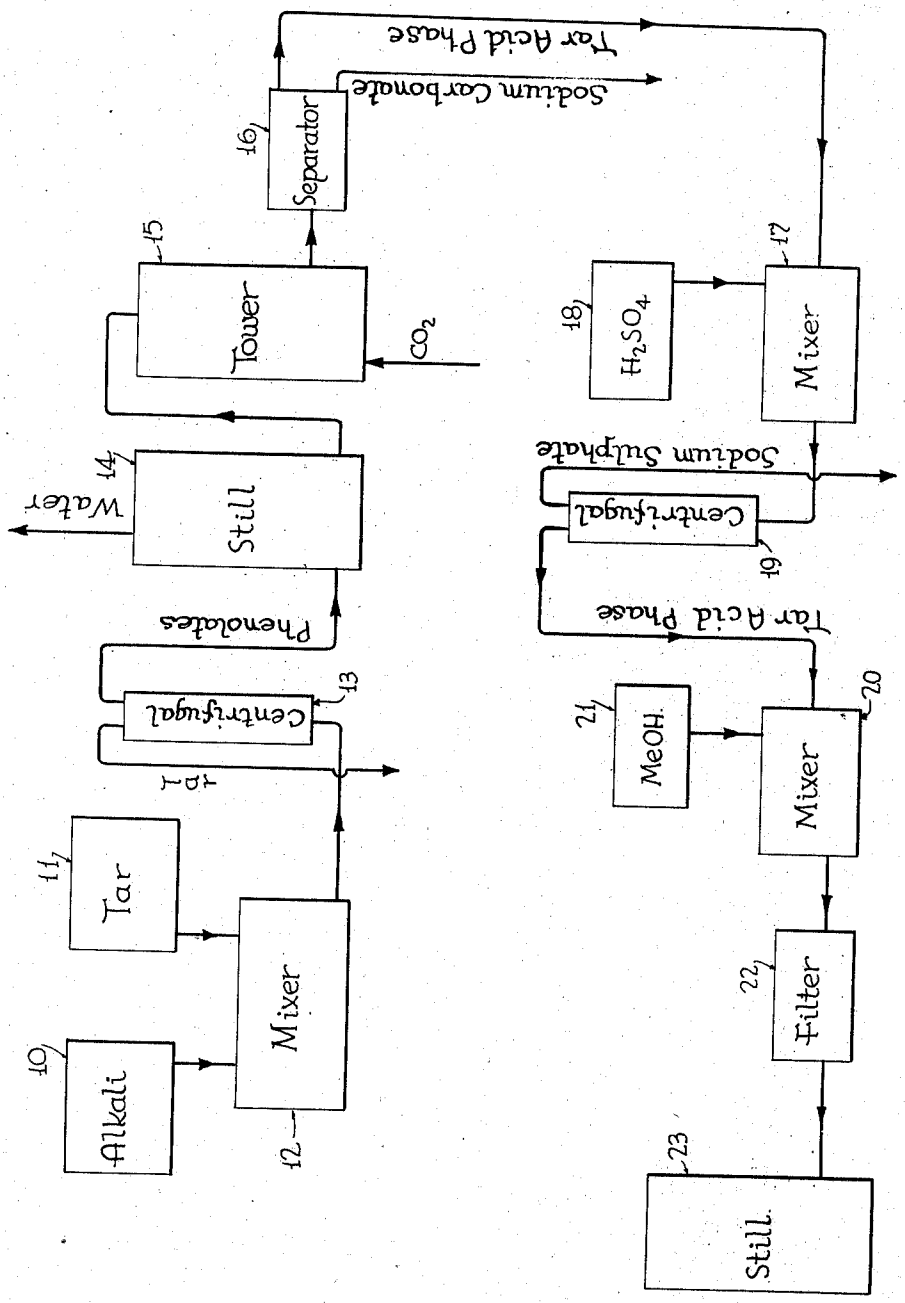
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RECOVERY OF TAR ACIDS

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RECOVERY OF TAR ACIDS

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The present invention pertains to the recovery of tar acids from phenolate-containing liquors derived from crude tar. It may be regarded as an improvement of the process of U. S. Patent 2,081,692 to Charles M. Ambler, Jr., and Charles E. Underwood.

In accordance with the process of U. S. Patent 2,081,692, crude tar is mixed with an alkali solution to effect reaction between the alkali and the phenolic constituents of the crude tar and solution of the phenolate reaction products in the aqueous phase. The aqueous phase is thereafter separated from the crude tar by centrifugation, sprung with an acid to free the phenolic compounds and subjected to distillation for recovery of these phenolic compounds. Such a process affords an important advantage in the avoidance of the distillation step by which a tar oil fraction has been first separated from crude tar in the practice of the prior art before treatment of this tar oil fraction separately for recovery of phenolic compounds. There are certain difficulties encountered in connection with the process of Patent 2,081,692, however, and an object of the present invention has been to correct these difficulties.

In the process of Patent 2,081,692, the aqueous phenolate phase discharged from the centrifugal may be sprung with sulfuric acid, or it may be sprung by treatment with carbon dioxide. When sulfuric acid is used as the springing agent, the alkali freed by the springing step combines with the sulfuric acid to form the alkali metal salt of the springing acid (sodium sulfate), and this alkali metal salt has practically no value.

When carbon dioxide is used as the springing agent, the tar acids derived from the springing step and subsequent distillation are relatively impure, and the tar acid fraction obtained by springing and distillation has hydrophilic properties, indicating that the tar acids have not been adequately purified. They contain an undesirably high proportion of ash, and this is an indication that the separation of the alkali from the phenolates in the springing step is incomplete.

Regardless of whether the springing step is accomplished by carbon dioxide or by sulfuric acid in the practice of the process of Patent 2,081,692, a coke-like residue is formed in the still incident to distillation, rendering continuous distillation impossible, and introducing difficulties in connection with the removal of this residue even in cases in which the distillation is accomplished by batch operation.

An object of the present invention has been to accomplish the springing and purification of the phenolate liquor obtained in the practice of Patent 2,081,692 in such a way as to avoid all of the above-mentioned difficulties.

Further objects and advantages of the invention, and the manner in which they have been attained, will be evident from a reading of the following specification in connection with the attached flow sheet, in which the single figure is a diagrammatic representation of one embodiment of the practice of the invention.

Referring to the drawing by reference characters, an alkaline solution (preferably sodium hydroxide, and hereinafter assumed to be such, although equivalent reagents may be used) from tank 10 is first mixed with tar from tank 11 in mixer 12. The mixture of aqueous phenolate solution with crude tar, obtained as a result of the mixing operation in mixer 12, is next passed to a centrifugal separator 13, and the equeous phenolate solution is continuously separated from the crude tar by the centrifugal separation accomplished in that centrifugal. These steps of mixing and centrifugation are identical with the corresponding steps of the above-mentioned patent to Ambler and Underwood.

The aqueous phenolate liquor discharged from centrifugal 13 is next passed to a still 14, in which it is concentrated by evaporation of a substantial proportion of the water content. The concentrated solution resulting from this evaporating step is next reacted with carbon dioxide to effect springing of a substantial part of the sodium phenolates, and formation of sodium carbonate. This results in precipitation of the phenols freed by the springing reaction from solution in the aqueous phase, and solution of the sodium carbonate formed by the springing reaction in the aqueous phase. The springing reaction may be accomplished by passing the aqueous phenolate phase downwardly through the tower 15 while passing carbon dioxide upwardly into that tower, as will be well understood by those skilled in the art. The mixture of sodium carbonate solution with the oil phase, resulting from liberation of the tar acids, is next passed to a separator 16, which may be either a gravity or centrifugal separator, to effect subsidence of the sodium carbonate solution from the sprung tar acids. Sodium hydroxide may be regenerated by causticization with lime of the aqueous sodium carbonate solution discharged from the separator 16, and the resulting sodium hydroxide solution may be used in the treatment of a further quan-

tity of tar in the mixer 12, or for any other desired use.

The tar acid phase, discharged as a supernatant oil from the separator 16, is next passed to a mixer 17 where it is mixed with sulfuric acid from tank 18 to effect completion of the springing reaction and formation of sodium sulfate by reaction of the sulfuric acid with the phenolates. This reaction results in the formation of a mixture consisting of an aqueous phase comprising principally sodium sulfate solution, and an oil phase containing liberated tar acids. This mixture is passed to a centrifugal separator 19 which effects continuous separation of these two phases and separate discharge thereof.

The tar acid phase discharged from the centrifugal 19 contains practically no alkali, but still contains constituents which would result in the formation of a coke-like residue in the still if this tar fraction were to be distilled without further intermediate treatment after discharge from the centrifugal 19. An important feature of the invention consists in the manner in which this coking incident to distillation is avoided.

The tar acid phase discharged from the centrifugal 19 is passed to a mixer 20, where it is mixed with a naphthenic solvent from tank 21. The mixing of the tar acid phase with the naphthenic solvent effects precipitation from solution of the constituents which would otherwise cause coking in the still, and these constituents can thereafter be removed from the tar acids by filtration in the filter 22. An excellent solvent for use in precipitating the undesired constituents (which will be referred to hereinafter in the specification and claims as coking constituents) is methyl alcohol, and excellent results have been obtained in the practice of the invention in cases in which the tar acid phase discharged from the centrifugal 19 is mixed with twice its volume of methyl alcohol.

The tar acids discharged as a filtrate from the filter 22 may be passed to a still 23, which may be of either the batch or continuous type, and subjected to distillation in that still to remove methyl alcohol from the tar acids and effect separation of tar acids from residual oil.

The invention has been described above in the simplest and preferred embodiment thereof. Various details may be modified without departing from the spirit of the invention. For example, the step of distilling off water in the still 14 may be entirely eliminated. The purpose of this step is two-fold. In the first place, the concentration of the phenolate fraction at this stage is desirable because of the fact that it improves the efficiency of the salting out effect on the tar acid compounds upon subsequent treatment with carbon dioxide In the second place, it is desirable that the sodium carbonate solution obtained from the separator 16 be relatively concentrated in order to facilitate regeneration of sodium hydroxide therefrom, and this object can be accomplished most efficiently by removal of water from the phenolate fraction prior to the treatment thereof by carbon dioxide Since neither of the above features of advantage is absolutely essential to the successful performance of the process, however, the material discharged as an aqueous phase from the centrifugal 13 may be treated with carbon dioxide in the tower 15 without the performance of the intermediate distillation step in still 14.

The step of effecting further springing of phenolates, and formation of an aqueous solution containing the sodium salt of the springing acid has been described above as being accomplished by treatment of the tar acid phase in mixer 17 with sulfuric acid. It will be evident, however, that any other acid capable of springing the phenolates may be substituted for the sulfuric acid. Phosphoric, hydrochloric or acetic acid, for example, may be substituted for the sulfuric acid.

While the preferred practice of the process of the invention involves performance of all of the steps described above and illustrated in the attached flow sheet, a substantial part of the advantages of the invention may be accomplished in spite of the omission of the springing and separating steps performed in tower 15 and separator 16, or of the springing and separating steps performed in the elements 17, 18 and 19 of the flow sheet. Thus, the advantages in avoiding passage of coking constituents to the still may be obtained in connection with the use of naphthenic solvent as described in connection with reference numerals 20, 21 and 22 of the flow sheet, in cases in which carbon dioxide is used as the springing reagent and the acid springing step is eliminated, or in cases in which an acid alone is used as the springing reagent and the carbon dioxide springing is eliminated. It is desirable, however, that both the carbon dioxide springing step and the acid springing step be performed prior to the step of precipitating coking constituents, since the performance of the springing step with carbon dioxide affords an important advantage in that it results in the formation of sodium carbonate, which is much more valuable than the sodium sulfate into which the sodium content of the phenolates would be converted if sulfuric acid alone were used for springing. The acid treatment after the carbon dioxide treatment also affords an important advantage in that a much more complete springing reaction and more effective removal of sodium compounds from the mixture can be accomplished by the inclusion of the acid springing step after the carbon dioxide springing, than can be accomplished if the acid springing step is eliminated.

While the step of precipitating coking constituents in a form in which they can be removed from the tar acid phase discharged from the centrifugal 19 has been described as performed by the addition of methyl alcohol, it will be understood that other naphthenic solvents, such as chloroform, carbon disulfide or sulfur dioxide, may be employed in connection with the practice of this step of the invention.

While the treatment of the tar in the mixer 12 has been described as being performed by the addition of sodium hydroxide, it will be understood that equivalent alkaline reagents can be substituted in this step. Potassium hydroxide, or any alkali capable of reacting with the tar acids to form a soluble alkali phenolate phase which may thereafter be separated from the tar by centrifugation, may, for example, be substituted for the sodium hydroxide used in this step.

Still further modifications will be obvious to those skilled in the art and I do not therefore wish to be limited except by the scope of the subjoined claims.

I claim:

1. In the recovery of tar acids from tar, the process comprising mixing the tar with an aqueous alkali metal hydroxide solution, separating the resulting aqueous alkali metal phenolate phase from the tar by centrifugation, concentrat-

ing the resulting aqueous alkali metal phenolate phase by evaporating water therefrom, adding carbon dioxide to the concentrated phenolate phase, separating the resulting alkali metal carbonate solution from the resulting tar acid phase, mixing the tar acid phase, from which the alkali metal carbonate solution has been separated, with a springing acid, separating the resulting tar acid phase from the resulting salt solution phase to obtain a tar acid phase substantially freed of salt solution, mixing the tar acid phase, from which said salt solution phase has been separated, with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulfide and sulfur dioxide to effect precipitation of coking constituents, thereafter removing said precipitated coking constituents from the solution of tar acids in said solvent, and separating the solvent and other impurities from the tar acids by distillation.

2. In the recovery of tar acids from tar, the process comprising mixing the tar with an aqueous alkali metal hydroxide solution, separating the resulting aqueous alkali metal phenolate phase from the tar by centrifugation, concentrating the resulting aqueous alkali metal phenolate phase by evaporating water therefrom, adding carbon dioxide to the concentrated phenolate phase, separating the resulting alkali metal carbonate solution from the resulting tar acid phase, mixing the tar acid phase, from which the alkali metal carbonate solution has been separated, with sulfuric acid, separating the resulting tar acid phase from the resulting salt solution phase to obtain a tar acid phase substantially freed of salt solution, mixing the tar acid phase, from which said salt solution phase has been separated, with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulfide and sulfur dioxide to effect precipitation of coking constituents, thereafter removing said precipitated coking constituents from the solution of tar acids in said solvent and separating the solvent and other impurities from the tar acids by distillation.

3. In the recovery of tar acids from tar, the process comprising mixing the tar with an aqueous alkali metal hydroxide solution, separating the resulting aqueous alkali metal phenolate phase from the tar by centrifugation, mixing the resulting aqueous alkali metal phenolate phase with a springing acid, separating the resulting tar acid phase from the resulting salt solution phase and obtaining a tar acid phase substantially freed of salt solution, mixing the tar acid phase, from which said salt solution has been separated, with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulfide and sulfur dioxide to effect precipitation of coking constituents, thereafter removing said precipitated coking constituents from the solution of tar acids in said solvent and separating the solvent and other impurities from the tar acids by distillation.

4. In the recovery of tar acids from tar, the process comprising mixing the tar with an aqueous alkali metal hydroxide solution, separating the resulting aqueous alkali metal phenolate phase from the tar by centrifugation, adding carbon dioxide to said phenolate phase, separating the resulting alkali metal carbonate solution from the resulting tar acid phase and obtaining a tar acid phase substantially freed of salt solution, mixing the tar acid phase with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulfide and sulfur dioxide to effect precipitation of coking constituents, thereafter removing said precipitated coking constituents from the solution of tar acids in said solvent and separating the solvent and other impurities from the tar acids by distillation.

5. In the recovery of tar acids from phenolate solutions obtained by extraction of tar with an aqueous alkali metal hydroxide solution, the process comprising, adding carbon dioxide to the phenolate solution, separating the resulting alkali metal carbonate solution from the resulting tar acid phase, mixing the tar acid phase, from which the alkali metal carbonate solution has been separated, with a springing acid, separating the resulting tar acid phase from the resulting salt solution phase to obtain a tar acid phase substantially freed of salt solution, mixing the tar acid phase, from which said salt solution phase has been separated, with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulfide and sulfur dioxide to effect precipitation of coking constituents, thereafter removing said precipitated coking constituents from the solution of tar acids in said solvent and separating the solvent and other impurities from the tar acids by distillation.

6. In the recovery of tar acids from phenolate solutions obtained by extraction of tar with an aqueous alkali metal hydroxide solution, the process comprising, adding carbon dioxide to the phenolate solution, separating the resulting alkali metal carbonate solution from the resulting tar acid phase and obtaining a tar acid phase substantially freed of salt solution, mixing the tar acid phase, from which said salt solution phase has been separated, with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulfide and sulfur dioxide to effect precipitation of coking constituents, thereafter removing said precipitated coking constituents from the solution of tar acids in said solvent and separating the solvent and other impurities from the tar acids by distillation.

7. In the recovery of tar acids from phenolate solutions obtained by extraction of tar with an aqueous alkali metal hydroxide solution, the process comprising, mixing the phenolate solution with a springing acid, thereafter separating the resulting tar acid phase from the resulting salt solution phase to obtain a tar acid phase substantially freed of salt solution, mixing the tar acid phase, from which said salt solution phase has been separated, with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulfide and sulfur dioxide to effect precipitation of coking constituents, thereafter removing said precipitated coking constituents from the solution of tar acids in said solvent and separating the solvent and other impurities from the tar acids by distillation.

8. In the recovery of tar acids from phenolate solutions obtained by extraction of tar with an aqueous alkali metal hydroxide solution, the process comprising, mixing the phenolate solution with a springing acid, thereafter separating the resulting tar acid phase from the resulting salt solution phase to obtain a tar acid phase substantially freed of salt solution, mixing the tar acid phase, from which said salt solution phase has been separated, with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulfide and sulfur dioxide to effect precipitation of coking constituents and

thereafter removing said precipitated coking constituents from the solution of tar acids in said solvent.

9. In the production of tar acids, the process comprising separating from tar a fraction consisting principally of tar acids, but containing constituents which cause a coke precipitate to form upon distillation, mixing said tar acid fraction with methyl alcohol to effect precipitation of said coking constituents, and thereafter separating the precipitated coking constituents from the resulting solution of tar acids in methyl alcohol.

10. In the production of tar acids, the process comprising separating from tar a fraction consisting principally of tar acids, but containing constituents which cause a coke precipitate to form upon distillation, mixing said tar acid fraction with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulfide and sulfur dioxide to effect precipitation of said coking constituents from the solution of tar acids in said solvent, and thereafter separating said precipitated coking constituents from said solution.

11. In the recovery of tar acids from tar, the process comprising mixing the tar with an aqueous sodium hydroxide solution, separating the resulting aqueous sodium phenolate phase from the tar by centrifugation, concentrating the resulting aqeuous sodium phenolate phase by evaporating water therefrom, adding carbon dioxide to the concentrated phenolate phase, separating the resulting sodium carbonate solution from the resulting tar acid phase, mixing the tar acid phase from which the sodlium carbonate solution has been separated with sulphuric acid, separating the resulting tar acid phase from the resulting salt solution phase by centrifugal force to obtain a tar acid phase substantially free of salt solution, mixing the tar acid phase, from which said salt solution phase has been separated, with a solvent chosen from the class consisting of methyl alcohol, chloroform, carbon disulphide, and sulphur dioxide to effect precipitation of the coking constituents, thereafter filtering the resulting mixture to remove precipitated coking constituents from the solution of tar acids in said solvent and separating the solvent and other impurities from the tar acids by distillation.

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