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PROCESS OF RECOVERING TAR ACIDS FROM CRUDE TAR

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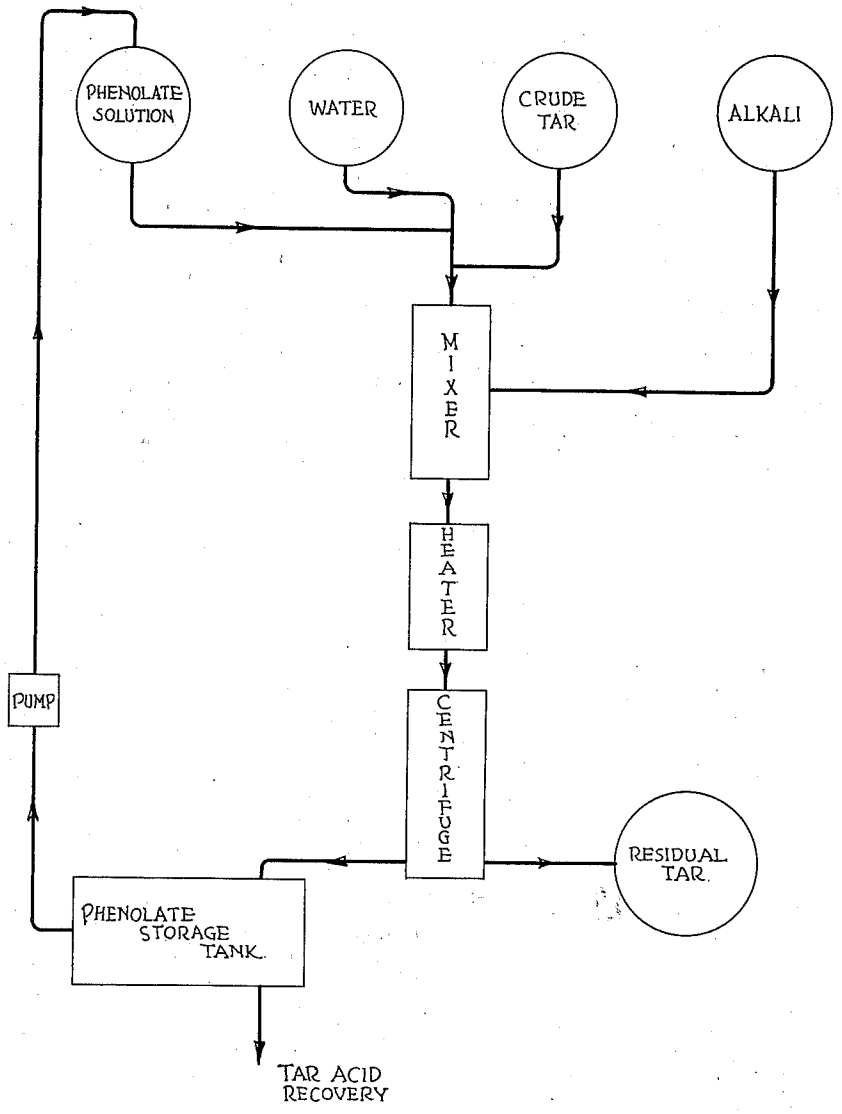

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PROCESS OF RECOVERING TAR ACIDS FROM CRUDE TAR

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5 Claims. (Cl. 260—154)

The present invention relates to the recovery of tar acids from coke oven tar, and it consists in an improvement in the processes described in the application of Charles M. Ambler, Jr. and Charles E. Underwood, Serial No. 754,718, filed November 26, 1934 and in the application of the present applicant, Serial No. 16,240, filed April 13, 1935.

In accordance with the usual practice of manufacturing coke, a quantity of tarry material results as a by-product. This tarry material, or crude tar as it will hereafter be called, ordinarily contains from 2½ to 6% of tar acids and a substantial quantity of water, which may amount to as much as 10% of the volume of the crude tar. The tar acids, which consist mainly of phenol and its homologues, such as the cresols and xylenols, are valuable commercially, but are quite difficult to separate from the crude tar in accordance with known procedures.

The method of effecting such separation in accordance with prior art procedure has usually been to dehydrate the crude tar by evaporation or centrifugation and thereafter to distil this crude tar in such a manner as to separate the acid naphthalene fraction, boiling below 270° C. and commonly known as tar oil, from the heavier tarry material, which is known as tar residue. Practically all of the tar acids contained in the crude tar boil within the tar oil range and are therefore distilled over with the tar oil fraction. The amount of tar oil distilled depends on the use to which the tar residue is put. These tar acids usually constitute between 10 and 25% of such fraction.

The separation of the tar acids from the tar oil fraction has ordinarily been accomplished by mixing this fraction with an aqueous caustic soda solution in a concentration and proportion adapted to convert the tar acids into their sodium salts. These compounds, which will hereafter be referred to generally as phenolates, are readily dissolved in the residual caustic soda solution and are separated from the tar oil after the neutralization treatment has been completed by allowing the mixture to settle into an aqueous layer containing the phenolates and an oil layer containing residual tar oil and then decanting. The aqueous solution so obtained is thereafter treated with carbon dioxide gas or acidulated by means of sulphuric acid and the resulting tar acids are separated from the sodium carbonate or sodium sulphate produced by this last mentioned treatment by gravity settling.

In accordance with the above mentioned application filed by Ambler and Underwood, this prior art procedure is simplified by the extraction of the tar acids from the original tarry material without subjection of this material to any preliminary distillation. This is accomplished by mixing the crude tar directly with a basic solution such as an aqueous solution of caustic soda or caustic potash and thereafter separating the resulting phenolates from such solution promptly by means of centrifugal force.

While the procedure of the Ambler and Underwood application represents a substantial improvement over prior art processes, a certain amount of difficulty and expense is encountered in its practice because of the necessity of acidulating relatively dilute phenolate solutions to recover tar acids therefrom. This difficulty is overcome in connection with the procedure forming the subject matter of application Serial No. 16,240 described above, by returning a substantial proportion of the phenolate solution obtained during the early stages of the practice of such a process to the mixing apparatus employed in the step of mixing the crude tar with the alkali solution. By recycling the phenolate solution in this manner the concentration of the phenolate solution leaving the centrifuge may be substantially increased and the expense of distillation incident to the recovery of tar acids from the solution resulting from treatment of this material may accordingly be substantially reduced.

In the practice of a process of the character described in the above mentioned application, difficulty has sometimes been encountered in the centrifugal separating step because of the formation of an emulsion which is difficult to resolve into its constituents and the object of the present invention has been to avoid this emulsion difficulty.

The present invention relates to modifications in the process described in the applicant's prior case, in which the order and manner of adding the aqueous phase materials to the crude tar is somewhat altered, in order to obviate these difficulties. In accordance with the present invention, water and phenolate solution are added to the crude tar and are mildly mixed therewith prior to the addition of alkali solution to the tar. While the physical basis for the improvement in separating conditions attained by such a sequence of operations is not fully understood, it has been found that a much more effective separation of water and phenolate solution from the crude tar can be accomplished by such a sequence of operations than by the operations

described in the above identified applications. A further feature of the invention consists in the discovery that the separate addition of water and phenolate solution to the crude tar prior to the mixing step results in a better separation of phenolates and water from the tar upon the subsequent addition of alkali and centrifugation than can be obtained in cases in which phenolate solution is recycled to the mixer as the one aqueous phase and no water is separately added. A still further feature of the invention consists in the employment of a sequence of mixing and heating operations better adapted to effect separation of aqueous phase from tar than are the operations described in said applications.

The nature of the present invention can be best understood by reference to the attached flow sheet. In practicing the invention, crude tar and water are initially passed to a multi-stage mixing apparatus adapted to mildly mix these influents, and alkali solution which may be of approximately 8% concentration is introduced into this mixer at a later stage of the operation in order that the crude tar may be somewhat mixed with water prior to the addition of such alkali. The mixing operation is preferably performed at a temperature between 50 and 65° C. The material leaving the mixer is then passed through a heater which is adapted to heat it to a temperature between 70 and 90° C. and is passed from this heater to a continuous centrifugal separator where it is resolved into phenolate solution and residual tar. The phenolate solution is passed to a phenolate storage tank from which it may be withdrawn from time to time for acidulation and distillation to recover tar acids therefrom.

During the early stages of the operation of a system of this character, the major proportion of phenolate solution passed to the storage tank is recycled and returned directly to the inlet end of the mixer. This recycling operation is continued until the aqueous effluent from the centrifuge reaches a concentration, for example, 15%, at which it may be economically treated for the recovery of tar acids as discussed above. When the phenolate solution has reached this desired concentration, the proportion of such solution returned to the inlet end of the mixer is diminished in order to effect such a balance between influent phenolate solution, alkali and water, as to produce as an aqueous effluent from this centrifuge a phenolate solution having this same desired degree of concentration.

A process of this general character is described in the above mentioned co-pending application of the present applicant. The present application relates to three basic features of improvement over that application. In accordance with the first of these features the phenolate solution recycled to the mixer is introduced to the mixer at a point of said mixer more remote from the heater than the point of introduction of the alkali. By operating the process in this manner the phenolate solution is mixed with the crude tar to a mild extent before this crude tar is contacted by alkali solution.

As pointed out in the above identified applications, it is desirable that a substantial proportion of water be included among the materials fed into the mixer. In order to attain this end, it is suggested in the applicant's prior case that water be added to the phenolate solution prior to the re-introduction of this solution into the mixer.

A second basic feature of the present invention consists in the discovery that emulsion difficulties are still further decreased by the separate introduction of this added water and the phenolate solution. The applicant is unable to account for any reason why the separate addition of water as such should avoid emulsion difficulties occurring when a small amount of water is added to further dilute the phenolate solution and this diluted solution added to the tar, but experiments have proven this to be the case.

To this end, the present invention involves the addition of water to a part of the mixer more remote from the heater than the point of introduction of the alkali solution simultaneously with the re-introduction of the phenolate solution at a point which is likewise more remote from the heater than the introduction of such alkali. Water so added may be in the form of diluent for the phenolate solution in accordance with the broadest aspects of the invention, but the preferred procedure in accordance with the invention involves separate introduction of such water and such phenolate solution. It has been found that the addition of a quantity of water amounting to at least 5% of the quantity of recycled phenolate solution at such a stage of the flow of materials through the system substantially aids in the attainment of the desired end. It will of course be understood that a quantity of water amounting to substantially more than this proportion based upon the recycled phenolate solution is added during the early stages of the operation of the system.

In accordance with the practice of the process of the invention after the initial stages of operation discussed above, therefore, recycled phenolate solution and water are simultaneously added to the inlet end of the mixer as illustrated, and alkali is continuously added at an intermediate point to the mixer, the proportion of water to phenolate solution being gradually decreased as the concentration of the phenolate solution is increased, until a proportion of water varying between 5 and 15% based upon the quantity of recycled phenolate solution is added when the desired concentration of phenolate solution has been finally attained.

The temperature conditions maintained in the practice of the process also contribute very largely to the success thereof. It has been found that the mixing of the water, phenolate solution and alkali solution with the crude tar at a temperature between 50 and 65° C. contributes to the success of the process by obviating emulsion difficulties which are sometimes encountered when an attempt is made to perform this mixing operation at a higher temperature. When this mixing operation has been completed, the mixture so formed may be heated to a temperature between 70 and 90° C. in order to reduce the viscosity of the tar and facilitate centrifugal separation, provided care is taken to avoid turbulence of the material passing through the heater and consequent further mixing and emulsification which might otherwise occur at these higher temperatures. This feature of the invention accordingly involves mixing of the tar and aqueous phases at a reduced temperature and thereafter heating the mixture so obtained under non-mixing conditions to a temperature best adapted to facilitate centrifugal separation.

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 sub-joined claims.

I claim:

1. The process of separating tar acids from crude tar which comprises adding a phenolate solution to said crude tar and mixing said solution with said tar, thereafter mixing an alkali solution with the mixture so formed and separating the resulting aqueous phase from the resulting tar phase by centrifugal force.

2. The process of separating tar acids from crude tar which comprises adding a phenolate solution to said crude tar and mixing said solution with said tar at a temperature between 50 and 65° C., heating the resulting mixture to a temperature between 70 and 90° C. and separating the resulting aqueous phase from the resulting tar phase by centrifugal force.

3. The process of separating tar acids from crude tar which comprises separately adding a phenolate solution and water to said crude tar and mixing said added materials with said tar, thereafter mixing an alkali solution with the mixture so formed and separating the resulting aqueous phase from the resulting tar phase by centrifugal force.

4. The process of separating tar acids from crude tar which comprises adding a phenolate solution to said crude tar and adding water to said crude tar in a proportion based upon the quantity of phenolate solution added amounting to at least 5% of said phenolate solution, mixing said water and said solution with said tar, thereafter mixing an alkali solution with the mixture so formed and separating the resulting aqueous phase from the resulting tar phase by centrifugal force.

5. The process of separating tar acids from crude tar which comprises treating said crude tar with an alkali solution to produce a phenolate solution phase and a tar phase, separating the phenolate solution phase from the tar phase by centrifugal force, recycling the phenolate solution phase into contact with further crude tar, adding water to said crude tar, mixing the recycled phenolate solution and the water with said crude tar, thereafter mixing an alkali solution with the mixture so formed between said phenolate solution, water and crude tar, and separating the resulting aqueous phase from the resulting tar phase by centrifugal force.

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