May 25, 1937. C. M. AMBLER, JR., ET AL 2,081,692

METHOD OF EXTRACTING TAR ACIDS FROM CRUDE TAR

Filed Nov. 26, 1934

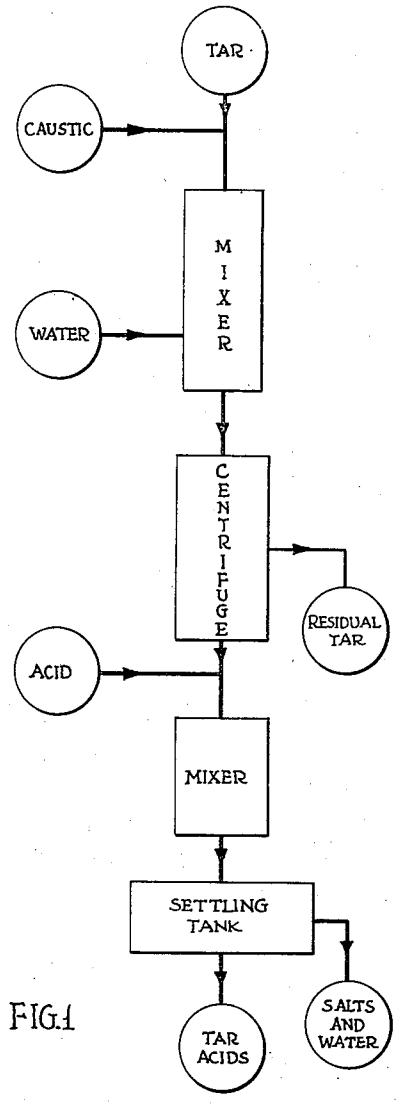


FIG.1

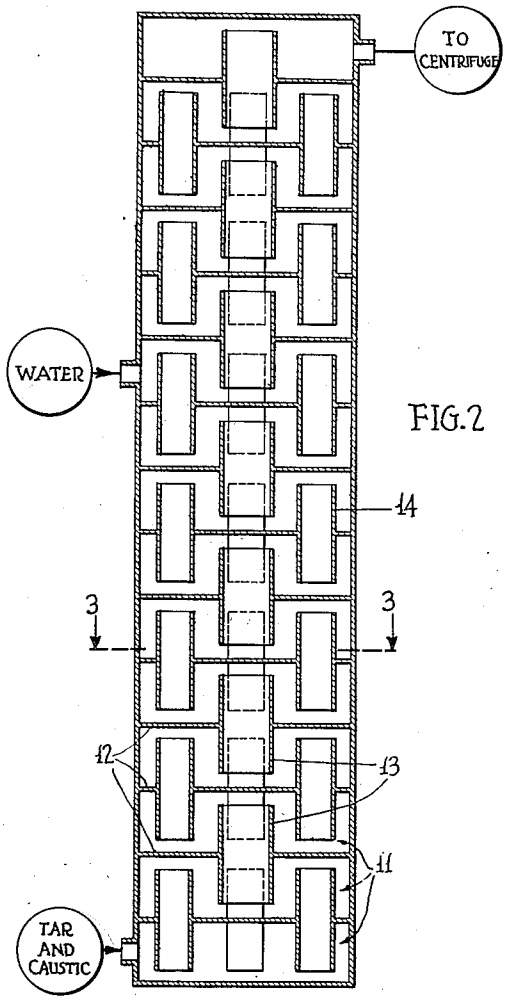


FIG.2

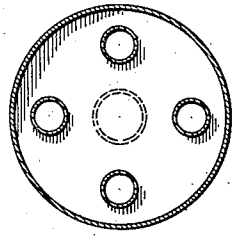


FIG.3

INVENTORS
CHARLES E. UNDERWOOD
CHARLES M. AMBLER JR.
BY Maurice A. Crews
ATTORNEY.

Patented May 25, 1937 2,081,692

UNITED STATES PATENT OFFICE

2,081,692

METHOD OF EXTRACTING TAR ACIDS FROM CRUDE TAR

Charles M. Ambler, Jr., Philadelphia, and Charles E. Underwood, Bethlehem, Pa.; said Ambler assignor to The Sharples Specialty Company, Philadelphia, Pa., a corporation of Delaware, and said Underwood assignor to Bethlehem Steel Company, Bethlehem, Pa., a corporation of Pennsylvania

Application November 26, 1934, Serial No. 754,718

17 Claims. (Cl. 260—154)

The present invention relates to an improved process for separating tar acids from tar and particularly to a process by which tar acids are separated in a simple expeditious manner from the tar which is produced incidental to the manufacture of coke. Certain apparatus that it has been found advantageous to use in the performance of the new process is also claimed as a part of this invention.

In accordance with the usual process 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, has a specific gravity of around 1.06 to 1.18 and ordinarily contains from 2½ to 6% of tar acids and up to about 10% of water. 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 isolate according to known procedures.

The practice heretofore has usually been to dehydrate the crude tar either by evaporating off the water or centrifuging. After dehydrating, the crude tar is distilled in a tar still and separated into two fractions, the fraction boiling below 250° C. being known as tar oil and the remainder simply as tar, or as tar residue, the tar acids, being substantially wholly contained in the tar oil, and being present therein in a concentration of between 15 and 25%.

This tar oil fraction is subjected to further treatment to separate these acids. Such treatment ordinarily consists in intermixing the tar oil with an aqueous caustic soda solution of a concentration sufficient to convert the tar acids into phenolates, cresolates and the like. These compounds, which will hereafter be referred to generally as phenolates, dissolve readily in the caustic solution and are subsequently separated from the tar oil by allowing the mixture to settle into an aqueous layer and an oil layer and then decanting. The aqueous solution so obtained is thereafter treated with an acid, usually sulphuric, to convert the dissolved compounds back to tar acids. The tar acids, being insoluble, are thereafter separated from the resulting solution of sodium sulphate by gravity settling.

The difficulty with such a process is that it requires a dehydration and distillation of the heavy tarry material which is difficult and troublesome and which many coke plants are not equipped to accomplish. Hence the tar must often be sold without extracting the tar acids therefrom, to refineries especially equipped for this work and these refineries must be equipped to carry out the relatively long and involved process outlined above.

The present process has been conceived to overcome difficulties involved in the practice of the process now in use and to produce relatively pure tar acids simply and expeditiously, directly from the original tarry material as it is produced by the coke plant. According to the invention it has been found that if this original tarry material is mixed directly with a basic solution such as an aqueous solution of caustic soda or caustic potash, capable of converting the tar acids into the corresponding phenolates, and thereafter separated from such solution with sufficient promptness to avoid emulsion difficulties, such separation can be effected by the technique of the invention and the separated solution will contain substantially all of the tar acids in the form of soluble phenolates. These compounds may thereafter be reconverted into tar acids by the addition of acid and separated.

A feature of this invention of considerable importance relates to the manner of mixing the basic solution with the crude tar. The invention can be practiced in a general way by simply mixing a dilute basic solution with this material and thereafter promptly separating. However, the process may be performed in a far more expeditious manner by taking advantage of an apparently anomalous phenomenon that these inventors have discovered.

According to this newly discovered phenomenon, if a relatively concentrated basic solution be first added to the tar and intermixed therewith and then subsequently a quantity of water be added to the mixture, the resultant mixture may be expeditiously separated, for example, by centrifuging, by the addition of a much smaller quantity of liquid than would be necessary to condition the mass for the ultimate separating step if all of the liquid were added as a part of the original basic solution.

While an academic consideration of the problem might make it seem rather obvious to extract the tar acids directly from the tarry residue rather than from the separated tar oil, such is not the case. Tar oil is a material of relatively low viscosity as compared with the original tarry material from the coke plant and hence the fact that the tar oil can be treated with a basic solution and thereafter separated from the solution, in no way indicates that the original tarry material can be so treated in commercial quantities. This original tar, in contra-distinction to the tar oil, is a heavy, viscous material and when

mixed with a basic solution with sufficient intimacy to insure reaction, tends to become emulsified therewith and thereafter is separable only with the greatest of difficulty.

According to the present invention, however, these difficulties are obviated and the process made economically usable on a commercial scale.

In order to convey a thorough understanding of the details of the new process and the features which contribute to the avoidance of the difficulties mentioned, reference may be had to the accompanying drawing and to the following detailed description of the process, although it is to be understood that the present invention is not limited to the details of this process nor to the particular apparatus described, but that the apparatus and steps of the process may be modified or certain of the steps of the process or parts of the apparatus omitted without departing from the scope of the invention as defined in the appended claims.

In the drawing, Fig. 1 is a flow sheet indicating diagrammatically the operation of the process of this invention.

Fig. 2 is a showing in vertical section of the tortuous path mixer which it is preferred to use in the practice of the process.

Fig. 3 is a cross-sectional view of the mixer shown in Fig. 2, being taken on the line 3—3 of Fig. 2.

In the preferred practice of the invention the crude tar from the coke plant is first treated by the addition thereto of a solution of an alkali metal hydroxide, preferably caustic soda, containing approximately one pound of caustic for each two and one-half pounds of tar acids in the tar. The caustic solution is usually varied in strength between 10% by weight of caustic and 25% by weight of caustic according to the proportion of tar acids in the tar. If the tar contains around 2½% tar acids, the solution used is usually of around 10% concentration, whereas if the percent of tar acids in the tar is around 6% the caustic solution will be of around 25% concentration.

The caustic solution and the tar are passed into a mixer, preferably of the tortuous path type, such as shown in Figs. 2 and 3, where they are intimately mixed. During the course of the mixing operation, and preferably toward the end thereof, a quantity of water is added and this tends to make the phases of the mixture separate readily. Ordinarily an amount of water about equal in volume to that of the original caustic solution is added and this amount is usually sufficient to reduce the specific gravity of the aqueous phase far enough below the specific gravity of the tar phase to render subsidence separation possible. If not, more water may be added. In some instances, however, a smaller quantity of water may be added so that the aqueous solution remains the heavier phase and is separated as such. Since the mixing step is of considerable importance in that the manner of its performance greatly affects the subsequent separation of the aqueous solution and unreacted tar, the mixer which it is preferred to use has been illustrated and will be described in detail.

As shown in Fig. 2, the mixer consists of a stack of short cylindrical chambers 11, adjacent chambers being separated by partition walls 12. Tubular members 13 and 14 extending through these walls, permit the passage of the liquid from chamber to chamber throughout the stack. Alternate partition walls have similarly arranged tubular members projecting through them, while the tubular members passing through the remaining walls are offset in relation thereto. Thus in one set of partition walls, each wall has a relatively large diameter tube 13 passing axially through the center thereof while in the remaining set of walls which alternate with these walls in their position in the stack, each wall is pierced by four smaller tubes 14 also extending in an axial direction but offset from the larger tubes 13. Each of the tubes 13 and 14 extends not only into the chambers which it connects but nearly to the opposite walls of these chambers. The distance between each end of the tube and the corresponding wall is preferably such that the distance from the end of the tube to the wall is approximately equal to one fourth of the diameter of the tube itself. Furthermore, the cross-sectional area of the large tube 13 is substantially equal to the combined cross-sectional areas of the four smaller tubes 14.

It has been found most desirable to use about fifteen chambers in a mixer of this type and to add the water at approximately the tenth chamber from the entrance end. Usually the tar and caustic solution enter at the bottom of the stack and flow upward, being discharged at the top and conducted to a centrifuge. Various modifications may be made in the mixer construction and the water may be added at other times than when the mixture passes through the tenth chamber. Also a dilute caustic solution may be added instead of water.

If desired, instead of adding water during the mixing, the water may be added as a part of the original caustic solution. When the process is accomplished in this manner, however, the caustic solution originally used is much less concentrated, ordinarily varying from 2 to 5% by weight of caustic soda in concentration, and a somewhat larger quantity of caustic in proportion to the tar acids should be present. Although it is possible to perform the process in such a manner, when so performed it is much less economical and advantageous than when performed in the preferred manner by adding the water separately. More caustic must be used; the separation is more difficult; the quantity of solution to be separated is greater; and more tar acid is lost because of failure to recover it from this larger quantity of caustic solution, in the case of the addition of all of the water as a part of the original solution than in the case of dilution after mixing more concentrated caustic with the crude tar in accordance with our preferred procedure. Furthermore, in the performance of an operation in which all of the aqueous liquid is added at the beginning of the mixing operation, great difficulty is encountered in separating the residual tar from the phenolate solution in connection with treatments of crude tars of high acid content.

As has been stated, the material emerging from the mixer is promptly centrifuged. It is important that the centrifugation be performed without undue delay in order to avoid the formation of a tight emulsion between residual tar and the aqueous phases. The centrifuge used is of the separator type designed to effect continuous separation of two liquid phases. Because the residual tar usually has a specific gravity of around 1.06 to 1.18 and the solution of phenolates and caustic usually has a lower specific gravity if sufficient water has been added, the tar is continuously discharged from the outer portion of

the centrifuge bowl while the solution is discharged from the inner portion of the bowl. The mixture should be fed to the centrifuge at a temperature between 75° C. and 100° C. and best results are obtained in the centrifuging operation when the temperature is between 80° C. and 90° C. The maintenance of the tar and caustic at an elevated temperature during the mixing operation also facilitates the mixing function and it is therefore preferred to introduce these ingredients into the mixer at a temperature between 80° C. and 90° C., the water which is added after the initial mixing of crude tar and alkali being likewise introduced at a temperature within this range.

The caustic solution from the centrifuge is next treated with an acid, preferably sulphuric, although carbonic, as formed by passing blast furnace gas into the solution, may be used. This treatment decomposes the phenolates and again forms tar acids. The tar acids, being insoluble, are then separated, usually by subsidence. Further purification of the tar acids may be accomplished by distillation, but that is not an essential part of the present invention.

As stated above, it is desirable, in the practice of the invention, to avoid contact of tar with the phenolate solution for more than a brief period. This can best be accomplished by a continuous process in which crude tar and alkali are passed to the mixer in flowing streams, pass continuously through the mixer and in which the resultants of the reaction which takes place in the mixer are continuously passed from the mixer to the centrifuge, where they are promptly and continuously separated.

In a specific example of the practice of the invention the following procedure was adopted:

Crude tar containing 10% water and 6% tar acids was taken from a coke oven tar settling pit and pumped continuously to a mixer of a type illustrated in Fig. 2. The tar taken from the pit was at a temperature of 77° C. and live steam was passed into the crude tar during its passage from the pit to the mixer to raise it from the temperature at which it left the pit, to a temperature of 90° C. Caustic soda was passed into confluence with the flowing stream of tar just prior to passage of tar to the mixer, the caustic soda being likewise maintained at a temperature of 90° C., the total quantity of caustic soda added representing a slight molecular excess over the quantity of tar acids contained in the crude tar passing to the mixer. The crude tar and caustic were passed together through the mixer, and the mixture of residual tar and aqueous phase resulting from the treatment of the crude tar with caustic soda was passing continuously to a centrifugal separator, sufficient water being added to the mixer in the tenth stage to reduce the specific gravity of the aqueous effluent from the separator to 1.04. The specific gravity of the tar discharged from the separator was 1.16. The residual tar was titrated and found to contain ½% tar acids. This loss compares very favorably with the tar acid content of the tar oil fraction remaining after removal of tar acids therefrom by prior art procedure.

The treatment of crude tar from coke plants has been particularly described herein but it is to be understood that other similar crude tars containing tar acids may be similarly treated with similar results and that modifications in the process herein described may be made to adapt the process to particular technical situations, all within the scope of the appended claims.

Having thus described our invention what we claim as new and desire to secure by Letters Patent, is:

1. A process for removing tar acids from crude tar that comprises continuously mixing crude tar with an alkali solution and thereafter continuously separating unreacted tar from the resulting solution by centrifuging.

2. A continuous process for removing tar acids from viscous coke oven crude tar having a specific gravity at least as great as 1.06 that comprises continuously mixing the crude tar with a basic solution and promptly thereafter continuously separating unreacted tar from the resulting solution by centrifuging.

3. A process of removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises mixing substantial quantities of the crude tar with a basic solution, diluting said solution during the mixing operation and promptly thereafter separating unreacted tar from the resulting solution.

4. A continuous process for removing tar acids from coke oven viscous crude tar having a specific gravity at least as great as 1.06 that comprises continuously mixing the crude tar with a basic solution adding water during the mixing operation and promptly thereafter continuously separating unreacted tar from the resulting solution by centrifuging.

5. A process of removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 which comprises mixing the crude tar in substantial quantities with a basic solution by passing the crude tar and the solution through a tortuous path and promptly thereafter separating unreacted tar from the resulting solution by centrifuging.

6. A process of removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises mixing substantial quantities of the crude tar with an alkaline solution adapted to react with the tar acids to the exclusion of the main body of the crude tar, thereafter adding an aqueous liquid to the mixture so produced and finally separating the reaction products of the alkaline solution with the tar acids from the unreacted tarry material by subsidence.

7. A process of removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises mixing substantial quantities of the crude tar with an alkaline solution adapted to react with the tar acids to the exclusion of the main body of the crude tar, thereafter adding an aqueous liquid to the mixture so produced and finally separating the reaction products of the alkaline solution with the tar acids from the unreacted tarry material by centrifugal subsidence.

8. A process of removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises continuously flowing an alkaline solution into confluence with a flowing body of the crude tar, continuously mixing the alkaline solution with the crude tar to effect reaction of the tar acids of said crude tar with the alkaline solution, continuously flowing a more dilute liquid into confluence with the mixture of unreacted tar and reaction products between the tar acids and alkaline solution, continuously mixing said more dilute liquid with

the mixture to which it is added, continuously passing the resultant mixture to a centrifugal separator and continuously separating unreacted tar from the remaining material by centrifugal force.

9. A process for removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises mixing the crude tar with a basic solution and promptly thereafter separating unreacted tar from the resulting solution by centrifugation of the mixture of crude tar and solution at a temperature between 75 and 100° C.

10. A process for removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises mixing the crude tar with a basic solution and promptly thereafter separating unreacted tar from the resulting solution by centrifugation of the mixture of crude tar and solution, the mixing and centrifuging operations being conducted at a temperature between 75 and 100° C.

11. A process of removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises continuously flowing an alkaline solution into confluence with a flowing body of crude tar, continuously mixing the alkaline solution with the crude tar to effect reaction of the tar acids of said crude tar with the alkaline solution, continuously flowing a more dilute liquid into confluence with the mixture of unreacted tar and reaction products between the tar acids and alkaline solution, continuously mixing said more dilute liquid with the mixture to which it is added, continuously passing the resultant mixture to a centrifugal separator and continuously separating unreacted tar from the remaining material by centrifugal force, the crude tar being maintained at a temperature between 75 and 100° C. during the sequence of mixing and centrifuging operations.

12. A process for removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises separately mixing the crude tar with water and a basic solution and thereafter separating unreacted tar from the solution resulting from the mixing operation by centrifuging.

13. A process for removing tar acids from a mass of viscous tar having a specific gravity at least as great as 1.06 and containing a substantial proportion of tar having a boiling point over 250° C. that comprises continuously mixing said mass of tar with a basic solution and thereafter continuously separating unreacted tar from the resulting solution by centrifuging.

14. A process for removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises mixing the crude tar with a basic solution by passage of said crude tar and basic solution through a tortuous mixing chamber and thereafter separating unreacted tar from the resulting solution by centrifuging.

15. A process for removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises mixing the crude tar with a basic solution and thereafter separating unreacted tar from the resulting solution by centrifuging.

16. A process for removing tar acids from a mass of viscous tar having a specific gravity at least as great as 1.06 and containing a substantial proportion of tar having a boiling point over 250° C. that comprises mixing said mass of tar with a basic solution and thereafter separating unreacted tar from the resulting solution by centrifuging.

17. A continuous process for removing tar acids from viscous crude tar having a specific gravity at least as great as 1.06 that comprises continuously mixing the crude tar with a caustic solution by passing the solution and the crude tar through a tortuous path in a sequence of movements in which the materials are passed in a restricted stream in the general direction of movement of materials from the inlet end of said path to the outlet end thereof, thereafter allowing said stream to expand and passing it in a direction opposed to the general direction of said stream from the path inlet to the path outlet, thereafter again restricting the stream and passing it in the general direction from the path inlet to the path outlet, said succession of passage in the general direction from path inlet to path outlet, expansion, passage in a direction opposed to the direction from path inlet to path outlet, restriction and repeated passage in the direction from path inlet to path outlet being repeated a plurality of times and thereafter separating by centrifugal force the aqueous and tar phases.

CHARLES E. UNDERWOOD.
CHARLES M. AMBLER, JR.