April 24, 1934. E. H. ELLMS 1,955,742

DIRECT RECOVERY OF TAR ACIDS

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Fig. 1.

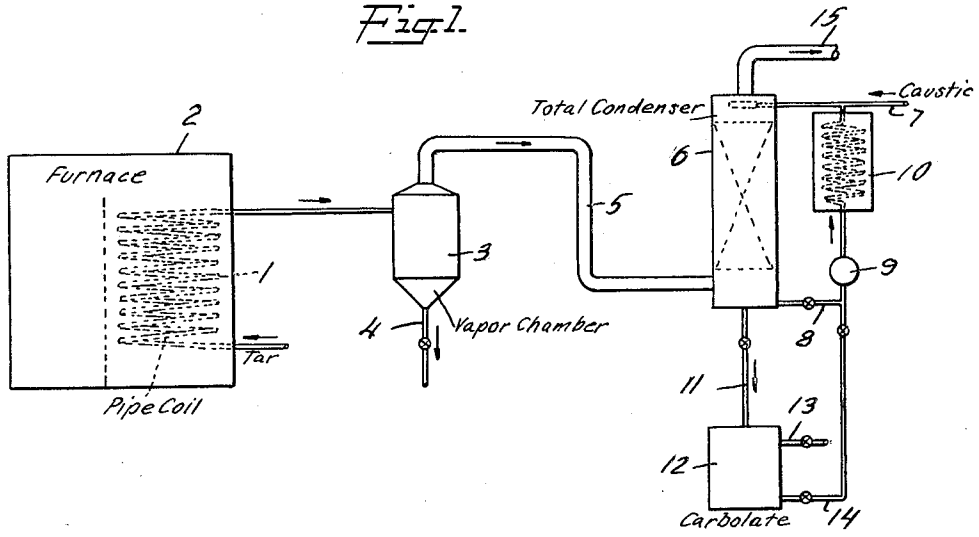
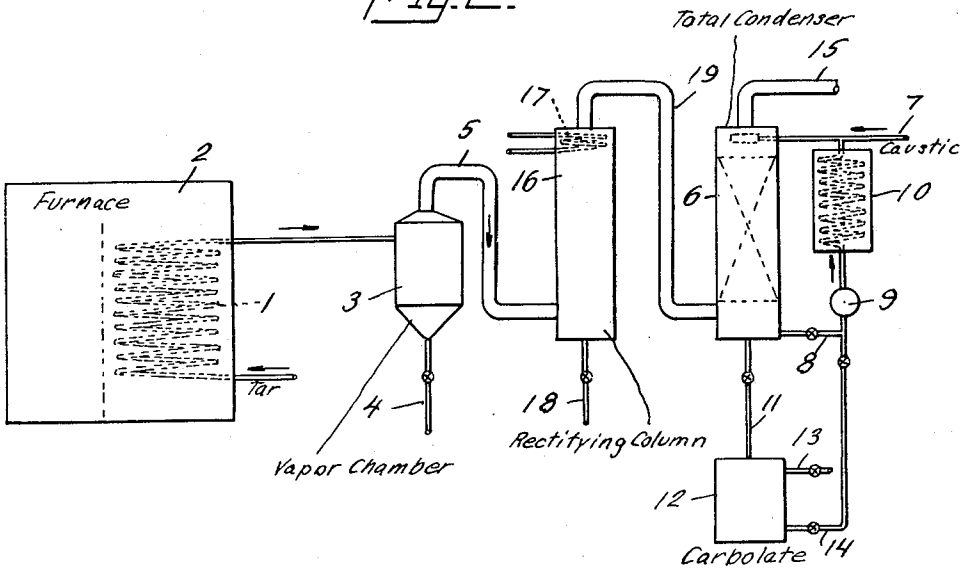


Fig. 2.



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Fig. 3.

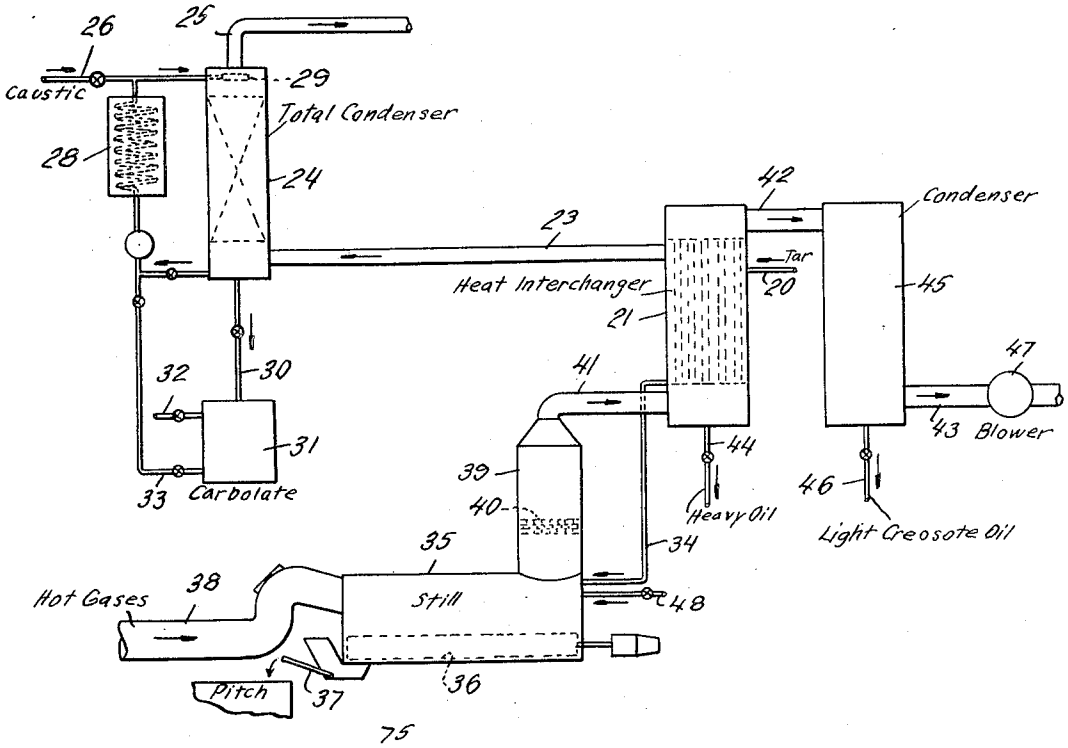
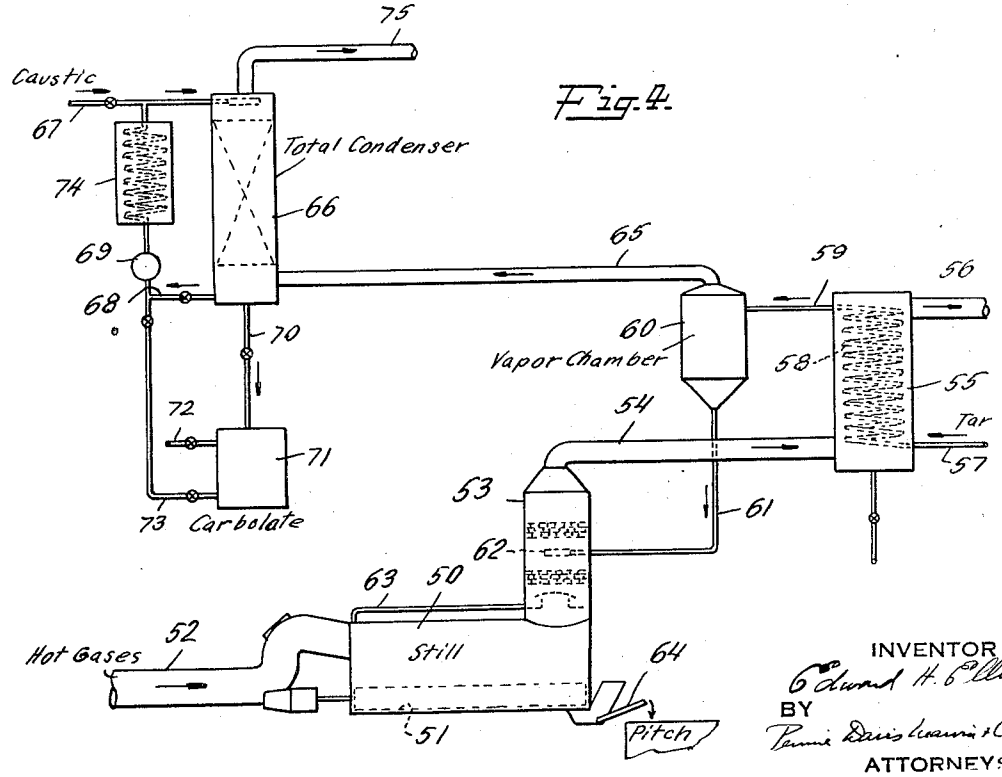


Fig. 4.



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UNITED STATES PATENT OFFICE

1,955,742

DIRECT RECOVERY OF TAR ACIDS

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Application February 3, 1930, Serial No. 425,629

8 Claims. (Cl. 260—154)

This invention relates to an improved process for the direct recovery of tar acids during the distillation of tar.

The method commonly employed for obtaining tar acids is to distill tar and produce a fraction containing the tar acids, commonly called coal tar light oil, or carbolic oil, and to extract the tar acids or phenols from such oil with a caustic soda solution.

According to the present invention, the distillation of the tar and the condensation of the distillate is combined with the extraction of the tar acids so that the tar acids are extracted during and as a part of the condensation.

In the practice of the invention, I subject tar to distillation to an extent sufficient to produce a tar acid oil distillate therefrom and I then subject this distillate, in vapor form, to condensation by direct contact with an alkaline solution, such as caustic soda solution, so that there will be condensation of the carbolic oil fraction simultaneously with the extraction of tar acids from that fraction. This solution is advantageously recirculated thru cooling means and thru the condenser so as to effect complete or nearly complete saturation of the caustic soda with tar acids and to absorb in the cooling means the heat of condensation of the distillate. Instead of distilling the tar so as to obtain only a carbolic oil fraction, I may distill the tar to produce a greater total distillate and a higher melting point pitch, and the distillate vapors may then be subjected to partial condensation and rectification to remove therefrom the higher boiling oils which it is not desired to extract, and to leave the vapors of the tar acid oil which are then passed to a total condenser where the condensation is effected with caustic soda solution, thereby extracting the tar acids simultaneously with the condensation of the oil fraction in which the tar acids are contained.

The distillation of the tar, and the production of distillate oil vapors, can be carried out in various types of tar stills, including externally heated tar stills, or tar stills heated internally. The distillation can be carried out batch-wise or continuously, but is preferably a continuous operation in which the distillate oils are continuously produced and the tar acids continuously extracted during the continuous condensation of the tar acid oil fraction. The distillation can be carried out as a single operation, distilling the tar to produce a high melting point pitch and a large proportion of the oils as distillates, or the distillation can be carried out in stages, distilling first a lighter fraction, and then a heavier fraction. With pipe coil stills, for example, the distillation can be carried out by heating the tar first to a temperature which will distill off a carbolic oil fraction therefrom, and the residue can then be subjected to further heating to distill off one or more additional fractions therefrom.

Ordinarily, various fractions will be desired when tar is distilled, and a more or less high melting point pitch residue will be produced. During such distillation, the higher boiling point oils will leave the still in vapor form at a high temperature, and they can advantageously be employed for preheating tar to a temperature such that a low boiling distillate can be removed from it, thus effecting an economy in heat for the total distillation, and giving a low boiling point distillate which can advantageously be extracted and condensed according to the present invention.

The condensation of the oil fraction containing the tar acids, and the simultaneous extraction of tar acids therefrom, according to the present invention, is carried out as an extraction and total condensation operation. In this operation an alkaline cooling liquid, which contains caustic soda or other alkaline reagent in an amount sufficient to combine with the tar acids, is employed to condense the oil vapors which are condensable down to the temperature of the condensing liquid, and the heat of condensation is absorbed by suitable cooling means. By recirculating cooled caustic solution the vapors will be cooled to a temperature approximating that of the solution and condensation of all oils condensable at that temperature will be effected simultaneously with the extraction of the tar acids by the caustic liquor.

If the higher boiling oils are condensed simultaneously with the lower boiling oils, the tar acids extracted will include the higher boiling tar acids as well as the lower boiling tar acids. For many purposes, the lower boiling tar acids are more valuable and, in order to obtain such acids, the process of condensation is advantageously carried out with effective rectification to condense the higher boiling point oils containing the higher boiling tar acids at a temperature which will leave the lower boiling oils containing the more valuable lower boiling tar acids in vapor form, and such oil vapors are then passed to a total condenser where the condensation is completed by direct contact with a caustic cooling solution.

The caustic solution can be used over and over

again until the caustic is used up. Additional caustic can be supplied as needed, in continuous operation, and the carbolate solution produced can be drawn off either intermittently or continuously. The tar acids can be set free from the carbolate solution in any suitable manner, as by treatment with carbon dioxide, etc.

The temperature of the vapors which are brought into contact with the caustic solution may be much greater than that of the caustic solution employed. If concentration of the caustic takes place sufficient water may be added to the solution to counterbalance the concentration of the caustic carbolate solution. If the caustic solution becomes diluted thru condensation of water from the tar, sufficiently concentrated caustic may be used in the make-up to produce carbolate of desired concentration. The caustic solution can be used cold; when recirculated, it must be cooled during recirculation. It is evident that the caustic carbolate solution will be heated by the vapors with which it is brought into contact. Sufficient heat absorption capacity must therefore be provided to cool the caustic solution enough to secure total condensation of vapors.

In referring to total condensation, I do not include the condensation of such light oils (benzol, toluol, etc.) as may be carried off by the inert gases produced during the distillation, since it is well known that the light oil constituents of coal tar are not completely condensable at the boiling point of water if diluted with inert gases; but except for such low boiling constituents in the presence of small amounts of inert gases, the condensation step of the present process, during which extraction of tar acids takes place, is intended to condense all constituents readily condensable at the temperatures of the caustic solution employed.

The tar which is subjected to distillation in carrying out the present process, may be ordinary coal tar, "low temperature" tar, gas house tar, or any tar containing tar acids. It may be total tar, or it may be a heavier tar fraction, but it may advantageously be the lighter tar fraction or tarry oils commonly recovered in the condensers of a coke oven by-product recovery plant. Such lighter tar fraction contains a much greater proportion of low boiling tar acids and, when it is subjected to distillation, and the carbolic oil fraction is condensed and simultaneously extracted according to the present invention, a large yield of tar acids can be obtained in proportion to the amount of tarry oil distilled. The invention is applicable to vapors from a distillation carried out at atmospheric pressure or under vacuum, or under pressures greater than atmospheric.

The invention will be further described in connection with the accompanying drawings, which illustrated, in a somewhat conventional and diagrammatic manner, an arrangement of apparatus embodying the invention and adapted for the practice of the process of the invention.

In the accompanying drawings;

Fig. 1 shows a pipe coil still with a total condenser and tar acid extractor for the vapors;

Fig. 2 shows a similar still with a rectifying column for removing heavier oils before the total condensing and extracting operation;

Fig. 3 shows a still in which the hot gases and vapors resulting from the distillation of tar to produce high melting point pitch are employed for preheating tar to distill a carbolic oil fraction therefrom with a total condenser and extractor for such fraction; and

Fig. 4 shows a similar but modified construction in which the pitch produced by such preheating and distilling operation is then supplied to the first mentioned still for further distillation.

In Figs. 1 and 2 the still is a pipe coil still, shown conventionally, having the pipe coil 1 in furnace 2 through which tar is pumped and heated under pressure and discharged into the vapor box or vapor separating chamber 3 where the oil vapors separate from the pitch residue. The pitch residue is drawn off through the line 4 and may, if desired, be subjected to further distillation to produce additional distillate oil and a higher melting point pitch residue.

In Fig. 1 the vapors separating in the vapor chamber 3 pass through the line 5 to a total condenser 6, which may be of any suitable construction, such as a packed tower, etc. Fresh caustic is supplied through the line 7, and carbolate solution is recirculated from the decanter 12 through the lines 14 and 8' by means of the pump 9 and may be cooled by the cooler 10 during recirculation. The caustic and recirculating carbolate solution enter the top of the tower and pass downwardly countercurrent to the upwardly flowing vapors and serve to cool and condense the same. The admixed carbolate and condensed oil escape through the line 11 to the decanter 12 where separation of neutral oil and carbolate takes place, the neutral oil being drawn off, e. g. at 13, and the carbolate at 14. Fixed gases produced in the distillation, together with any small amounts of uncondensed low boiling point vapors carried by these gases escape thru pipe 15 and may be disposed of as desired.

In Fig. 2 a rectifying column is interposed between the vapor separating chamber 3 and the total condenser 6, the vapors from the vapor box 3 passing to the bottom of the rectifying column 16 through the line 5. The rectifying column is cooled in any suitable manner, as by a cooling coil 17 in the top of the tower which causes condensation and refluxing of part of the vapors. The heavier oil condensate is withdrawn from the bottom of the column through the line 18 while the uncondensed vapors pass from the top of the tower through the line 19 to the total condenser and extractor 6.

In the apparatus of Fig. 1, all of the vapors passing from the vapor box 3 are subjected to extraction and total condensation with the caustic solution. This arrangement of apparatus enables the total distillate to be extracted to recover the tar acids therefrom simultaneously with the production of a total condensate of neutral oils.

In the apparatus of Fig. 2 the vapors produced by the distillation in the pipe coil still are first subjected to rectification to remove higher boiling constituents therefrom while leaving the lower boiling constituents which are rich in the lower boiling and more valuable tar acid constituents in vapor form. The vapors then pass to the total condenser where extraction of tar acids combined with simultaneous total condensation will take place, giving a neutral oil and a carbolate solution containing the lower boiling tar acids.

In operating the apparatus of Fig. 1 the conditions may be so controlled as to permit, say, 15% by weight of the oil distilled from the tar, to pass in vapor form to the condenser 6. This oil may contain, for example, 13% tar acids. One thousand gallons of tar may thus produce

150 gallons of carbolic oil containing 19.5 gallons tar acids. To condense this fraction approximately 635,000 B. t. u. must be removed; to fix the tar acids 64.4 pounds of caustic soda must be used. A solution of 10% NaOH may be used, 70 gallons being employed for each 1000 gallons of tar distilled. In continuous operation fresh caustic solution is added at 7 and carbolate removed at 14 at such a rate as corresponds to a consumption of 70 gallons caustic soda per 1000 gallons of tar distilled. Cooling water is circulated thru the cooler 10 at a sufficient rate to remove the above quantity of heat.

Figs. 3 and 4 show stills in which the distillation of the tar to produce high melting point pitch is accomplished by the use of highly heated gases such as hot coke oven gases, and in which the hot gases leaving the still, admixed with the oil vapors, are employed in a heat interchanger for preheating tar to a temperature such that tar acid oils will be removed therefrom. These tar acid oils are then subjected to simultaneous condensation and extraction of tar acids in the total condenser.

In Fig. 3 the tar entering through the line 20 is heated to a temperature sufficient to distill low boiling tar acid oils therefrom in a still or heat interchanger 21 where the tar is brought into indirect heat interchanging relation with hot gases and vapors from the still 35. The vapors produced by this preheating and partial distillation pass through the line 23 to the total condenser and extractor 24 where they are brought into direct contact with a caustic solution and condensation and simultaneous extraction of tar acids is effected. Fresh caustic solution is supplied through the line 26, and the carbolate solution which may contain excess caustic is recirculated through the cooler 28 by means of pump 27 and discharges into the top of the tower through suitable spray or distributing devices 29. A vent or outlet 25 permits escape of the usual small amount of uncondensable gases to the atmosphere.

The operation of the total condenser and extractor 24 is similar to that above described in connection with Figs. 1 and 2. The carbolate and neutral oil are drawn off through the line 30 to a decanter 31 where separation takes place and from which the neutral oil may be drawn off at 32 and the carbolate solution at 33 either for recirculation or to storage.

The tar which has been preheated and partly distilled, and from which a greater or less proportion of the tar acid oils have been removed by distillation, passes from the heat interchanger or still 21 through the line 34 to the still 35 where the tar is subjected to further distillation. The still 35 has therein a rapidly rotatable roll 36 adapted to atomize or spray the tar or pitch into the gases passing therethrough. Hot gases, such as hot coke oven gases directly from the coke ovens, are supplied through the insulated line or header 38 and serve to heat the tar or pitch in the still to a high temperature. With thorough spraying of the pitch into the gases, the temperature of the gases is rapidly lowered and that of the pitch is rapidly raised. The high melting point pitch produced escapes through the outlet 37. The hot gases and vapors escape from the still through the settling chamber 39 having suitable baffles therein for assisting in removing entrained constituents from the gases and vapors which then pass through the line 41 to the bottom of the heat interchanger or still 21 where they serve to heat and distill the fresh tar at the same time that cooling and condensation of the higher boiling oil constituents in the gases takes place, the condensate of heavy oil escaping at 44 and the uncondensed vapors and the gases escaping at 42 to a further condenser 45 where further cooling and condensation takes place and light creosote oil is condensed and drawn off through the line 46. The remaining gases and light oil vapors then escape through the line 43 to the blower 47 and may be admixed with other gases or passed to a light oil scrubber, etc.

Instead of showing a plurality of heat interchangers for preheating and distilling the tar by indirect contact with the hot gases and vapors from the still, I have, for simplification, shown only a single heat interchanger in Fig. 3, and I have omitted a rectifying tower between the preheater or still and the total condenser and tar acid extractor.

In Fig. 4 a still 50 is similar in construction and operation to the still 35 of Fig. 3. It has in it a rapidly rotatable spray roll 51 and is supplied with hot gases through the insulated gas header 52 and the hot gases and vapors from the still escape through the settling chamber 53 to the vapor outlet pipe 54 thence to the preheater and partial condenser 55 and the gas outlet pipe 56. The tar to be distilled is supplied through the line 57 and is preheated by indirect contact with the hot gases and vapors to a temperature sufficient to distill a carbolic oil fraction therefrom. This preheated tar then escapes through the line 59 to the vapor separating chamber 60 where separation of vapors from unvaporized pitch constituents takes place, the vapors passing through the line 65 to the total condenser 66 and the low melting point pitch passing through the line 61 to the distributor 62 located in the settling chamber 53. The pitch comes in contact with the hot gases and vapors leaving the still 50 and the residue then flows through the line 63 to the end of the still 50. Pitch is discharged from the still 50 through line 64.

The vapors from the vapor box 60 pass through the line 65 to the total condenser 66 where they are brought into intimate contact with a caustic soda solution and extraction of tar acids and condensation are effected. Fresh caustic is supplied through the line 67 and the caustic solution containing carbolate is recirculated through the line 68 by the pump 69 and may be cooled in the cooler 74 before being returned to the top of the total condenser. Admixed carbolate and neutral oils are drawn off through the line 70 to the decanter 71 from which neutral oil can be withdrawn at 72 and carbolate solution at 73 for recirculation or to storage.

In the operation of the apparatus of Fig. 4 the tar is preheated by indirect contact with the hot gases and vapors to a temperature such that a tar acid oil fraction is distilled therefrom. This fraction separates in the vapor box 60 and is subjected to total condensation and simultaneous extraction of tar acids in the condenser 66. The low melting point pitch then passes into the still 50 where it is distilled to produce a high melting point pitch, e. g. a pitch of 400° F. melting point by utilization of hot gases such as hot coke oven gases. The gases and vapors leaving the still are utilized for preheating the fresh tar to a sufficient temperature to effect preliminary distillation of light oils from it.

In distilling tar to produce pitch of around 400° F., melting point in stills such as the stills

35 and 50 of the Figs. 3 and 4 around 75% or more of the tar can be recovered as distillate oil and the gases and vapors leaving the still may be at a temperture around 300° C. The large amount of heat contained in the gases and vapors at such a high temperature is advantageously utilized for preheating the tar to a temperature sufficient to distill a carbolic oil or tar acid oil fraction therefrom. This fraction will be substantially free from admixed inert gases and it can, therefore, be readily subjected to total condensation and simultaneous extraction of tar acids therefrom. At the same time the hot gases and vapors are cooled and the heavier oil constituents are condensed therefrom, thus recovering a considerable part of the heat contained in the hot gases and vapors and utilizing it at a lower temperature for the preheating and distillation of the tar. The tar which has thus been preheated and partly distilled can then be supplied in a preheated and partly distilled state to the still in which it is to be subjected to further distillation for the production of a high melting point pitch and a heavier distillate therefrom.

I claim:

1. The improvement in the distillation of tar and the production of neutral oils and tar acids therefrom, which comprises subjecting tar to distillation to produce vapors of neutral oils containing admixed tar acid vapors, and subjecting the admixed vapors to total condensation by direct contact with caustic solution to effect simultaneous extraction of tar acids and condensation to give directly a total condensate of neutral oils and a carbolate solution.

2. The improvement in the distillation of tar and the production of neutral oils and tar acids therefrom, which comprises subjecting tar to distillation to produce vapors of neutral oils containing admixed tar acid vapors, subjecting the admixed vapors to total condensation by direct contact with caustic solution to effect simultaneous extraction of tar acids and condensation to give directly a total condensate of neutral oil and a carbolate solution, using a caustic solution containing caustic in excess of that required to extract the tar acids and cooling and recirculating the carbolate solution containing the excess caustic thus obtained.

3. The improvement in the distillation of tar and the production of neutral oils and tar acids therefrom, which comprises subjecting tar to distillation to produce vapors of neutral oils containing admixed tar acid vapors, subjecting the admixed vapors to total condensation by direct contact with caustic solution to effect simultaneous extraction of tar acids and condensation to give directly a total condensate of neutral oil and a carbolate solution, using a caustic solution containing caustic in excess of that required to extract the tar acids, cooling and recirculating the solution containing the carbolate and excess caustic and simultaneously and continuously adding caustic to the solution being recirculated and drawing off a portion of the solution at that part of the cycle where the carbolate content is greatest.

4. The improvement in the distillation of tar and the production of neutral oils and tar acids therefrom, which comprises subjecting tar to distillation to distill therefrom carbolic oil and higher boiling oil constituents, subjecting the resulting vapors to partial condensation and rectification to remove higher boiling constituents therefrom while leaving tar acid oil vapors uncondensed, and subjecting such vapors to total condensation and simultaneous extraction of tar acids therefrom by bringing them into direct contact with caustic solution to give directly a total neutral oil condensate and a carbolate solution.

5. The improvement in the distillation of tar containing neutral oils and tar acids which comprises preheating said tar, flashing the preheated tar to vaporize therefrom a mixture of vapors comprising tar acid and neutral oil vapors, separating said mixture of vapors from the tar, passing the mixed vapors into direct contact with caustic solution at a temperature below the temperature of the vapors simultaneously to extract tar acids therefrom and to condense neutral oils.

6. The improvement in the distillation of tar and the production of neutral oils and tar acids therefrom, which comprises subjecting tar to distillation to distill therefrom carbolic oil and higher boiling oil constituents, subjecting the resulting vapors to partial condensation and rectification to remove higher boiling constituents therefrom while leaving tar acid oil vapors uncondensed, subjecting such vapors to total condensation and simultaneous extraction of tar acids therefrom by bringing them into direct contact with caustic solution to give directly a total neutral oil condensate and a carbolate solution, using a caustic solution containing caustic in excess of that required to extract the tar acids, cooling and recirculating the solution containing the carbolate and excess caustic and simultaneously and continuously adding caustic to the solution being recirculated, and drawing off a portion of the solution at that part of the cycle where the carbolate content is greatest.

7. The improvement in the distillation of tar to produce high melting point pitch and high boiling distillate oils, which comprises preheating tar by indirect heat interchange with the high boiling oil vapors from such distillaton to effect dstillation of a tar acid oil fraction from the tar and the production of a partially distilled tar, subjecting the tar acid oil vapors so produced to simultaneous total condensation and extraction of tar acids therefrom by bringing the vapors directly into contact with cooled caustic solution to give directly a neutral oil condensate and a carbolate solution, and recooling and recirculating the carbolate solution.

8. The improvement in the distillation of tar to produce high melting point pitch and high boiling distillate oils, which comprises preheating tar by indirect heat interchange with the high boiling oil vapors from such distillation to effect distillation of a tar acid oil fraction from the tar and the production of a partially distilled tar, subjecting the tar acid oil vapors so produced to simultaneous total condensation and extraction of tar acids therefrom by bringing the vapors directly into contact with cool caustic solution to give directly a neutral oil condensate and a carbolate solution, re-cooling and recirculating the carbolate solution and subjecting the partly distilled tar while still in a heated state to further distillation to produce the high melting point pitch and the high boiling distillate oils.

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