May 12, 1936. S. P. MILLER 2,040,098

TREATMENT OF TAR

Original Filed Jan. 23, 1931 2 Sheets-Sheet 1

Fig. 1.

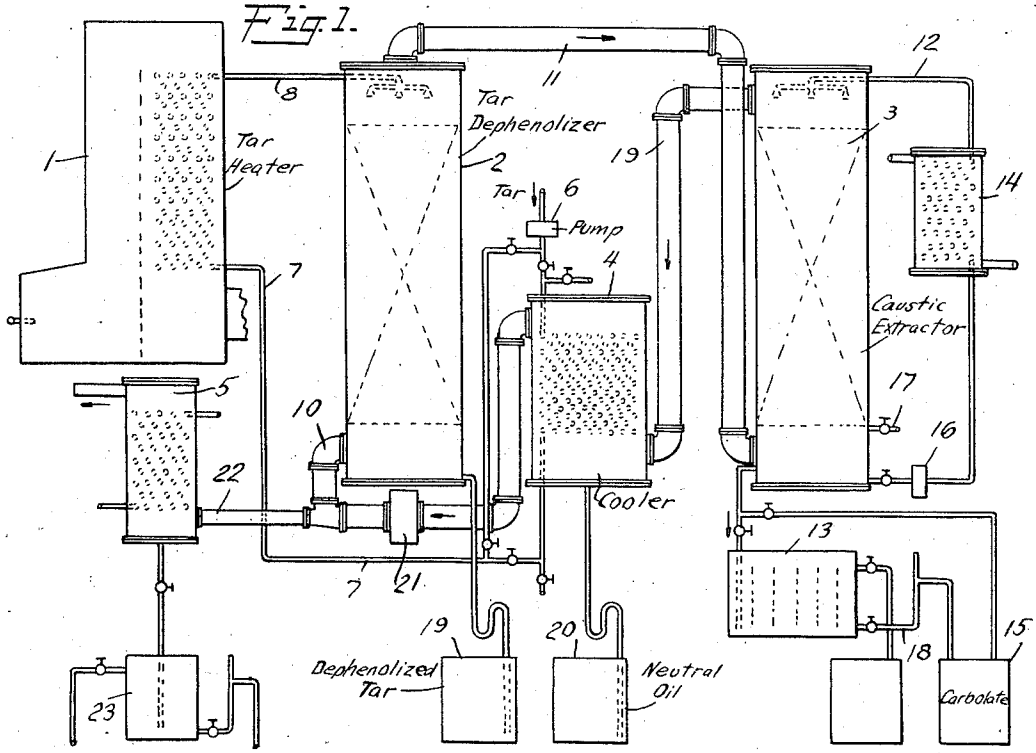
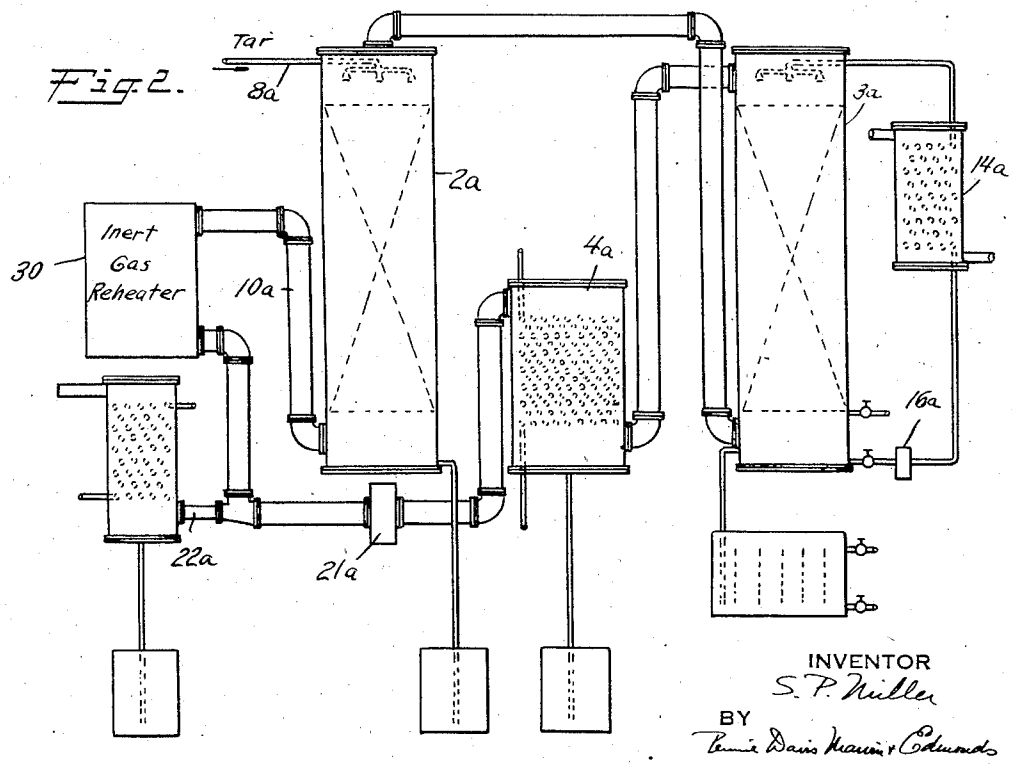



Fig. 2.



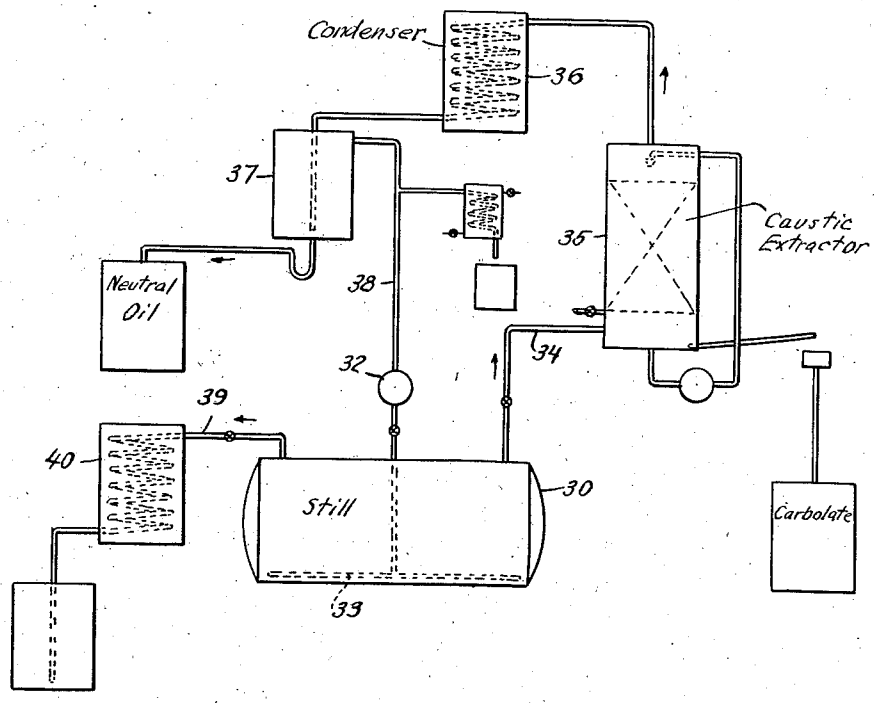

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Fig. 3.




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# UNITED STATES PATENT OFFICE

2,040,098

## TREATMENT OF TAR

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Application January 23, 1931, Serial No. 510,638
Renewed January 22, 1936

16 Claims. (Cl. 260—154)

This invention relates to the treatment of tar or oil for the recovery of tar acids and neutral oils and involves a process of heating and treating tar or oil in which a neutral oil distillate and tar acids are recovered simultaneously yet separately. The invention includes both the method of operation and apparatus therefor.

The process of the invention is applicable to the treatment of tars such as coke oven tar, gas retort tar, vertical retort tar, low temperature tars, and other tar-acid and neutral-oil containing hydrocarbon materials such as coal tar distillate. It may be applied to the separate treatment of tar fractions such as the heavy tar from the collector main of a coke oven plant or the light tar or tarry oil from the condensers of such a plant. It may be applied to the treatment of mixtures containing coal tars.

Coke oven tar, for example, ordinarily contains about three per cent of tar acids, although this may vary over a considerable range. In order to recover the tar acids from the tar it is customary to distill the tar and then extract the tar acids from the distillate by treatment with a caustic solution such as sodium hydroxide. The aqueous caustic solution is circulated through the distillate oil to effect the tar acid extraction, the mixture of oil and aqueous solution is then allowed to settle, and the aqueous carbolate solution and resulting neutral oil are separated by decantation.

According to the present invention the tar acids are recovered from tar without first obtaining an acid-oil distillate. The tar acids are volatilized from the tar, together with neutral oils, but by a selective process such that the ratio of the amount of tar acids removed to neutral oils recovered from the tar is greater than by the ordinary method of tar distillation. The volatilization of the tar acids and neutral oils takes place in a current of inert gases. These resulting gases and vapors are treated with an alkaline reagent for the removal of tar acids, and this treatment takes place preferably under conditions which prevent or inhibit cooling of the vapors and condensation of neutral oils. The gases and vapors resulting from this vapor phase extraction of the tar acids are cooled to separate neutral oils. Inert gases and uncondensed vapors are then recycled for further volatilization of tar acids and neutral oils from tar.

Any suitable inert gases may be used in the process, although ordinarily steam will be employed. If raw tar is being treated, the moisture present in the raw tar during the treatment will be converted into steam, so that although initially some inert gas other than steam may be passed through the tar, eventually this other gas will be replaced by the steam resulting from vaporization of the moisture in the tar being treated and such fixed gases as may be evolved during the treatment of tar. By carrying out the operation in a current of steam the tar acids and neutral oils in the tar vaporize at a temperature below their normal boiling points. By treating the mixture of steam and oil vapors resulting from the vaporization with an alkaline reagent such as caustic soda, tar acids are removed as carbolates and the resulting gases and vapors are substantially free from tar acids. A portion of the neutral oils is then removed from the cycle by partial condensation. The balance of the neutral oils is recycled together with the inert gases and any tar acids which may remain in vapor form, except for the inert gases and vapors which are bled from the system. The presence of neutral oil vapors in the recycled gases represses or inhibits to some extent the vaporization of neutral oils from the tar through which the recycled gases are passed. By such selective vaporization the ratio of the tar acids to the neutral oils vaporized from the tar is greater than by simple distillation.

The heat for the selective vaporization will ordinarily be supplied by heating the tar before it enters the still or "dephenolizer", in which the tar acids and neutral oils are vaporized from the tar. The recycled gases will be reheated in part before entering the dephenolizing zone by coming in contact with the relatively hotter treated tar. Additional heat may be added to the gases from some outside source, but ordinarily no more than a portion of the heat for the selective vaporization will be supplied in this manner. Additional heat may be supplied to the system by heating either the dephenolizer or the caustic extractor or both.

The quantity of the gases passed through the dephenolizer per unit volume of tar will vary depending upon the per cent of tar acids present in the tar, the per cent of these tar acids which it is desired to recover from the tar, etc., and the temperature at which the gases and vapors leave the dephenolizer may vary accordingly. If ordinary coke oven tar containing approximately three per cent tar acids is being treated good recovery is obtained using 175 to 200 cubic feet of gas per gallon of tar treated and an outlet gas temperature in the neighborhood of 175° C. Using a larger volume of gas, the same percentage of recovery of

tar acids is obtained with a lower outlet temperature. For example, by increasing the rate of gas recirculation to 300–350 cubic feet per gallon of tar treated the temperature of the outlet gases and vapors may be dropped to around 150° C. to obtain a tar acid yield comparable with that obtained using 175 to 200 cubic feet of gas and an outlet temperature of 175° C.

From the dephenolizer the gases and vapors pass to a caustic extractor. Condensation of neutral oil vapors in the extractor may be prevented by providing heavy insulation on the extractor and by using concentrated caustic solution at a temperature sufficiently high to avoid such condensation.

Although it is preferable to operate without any substantial condensation in the caustic extractor, some condensation may result due to loss of heat through radiation, or when caustic colder than the gases and vapors is employed, or where dilute caustic is used and there is evaporation of water from the caustic solution.

The carbolate formed in the extractor may contain, for example, 50 to 70 per cent of tar acids, and will also include excess caustic, sodium carbonate, water, dissolved neutral oils, etc. The tar acids may be recovered from the carbolate by the usual methods, as by acidification with carbon dioxide, etc.

Although complete removal of the tar acids from the gases passing through the extractor is possible, it will usually not be found economical to install the apparatus necessary for removal of the last traces by insuring contact of the alkaline reagent with every particle of the gas. For example, the oil content of the gases returned to the dephenolizer may be as much as three per cent of tar acid vapors although under good commercial operating conditions it may not contain more than a few tenths of a per cent of tar acids.

From the caustic extractor the inert gases together with all or a large proportion of the neutral oil vapors and any vapors of tar acids not recovered in the extractor, pass to a condenser where a portion of the neutral oils is condensed. The extent to which the gases and vapors are cooled may be varied to recover, for example, ten per cent up to twenty per cent of neutral oils based on the volume of the tar treated. These neutral oils may contain up to three per cent of tar acids although ordinarily they will contain only a few tenths of one per cent of tar acids. They are called "neutrals oils" because they are deficient in or substantially free from tar acids.

The gases and uncondensed oil vapors will preferably leave the condenser at a temperature above the steam dewpoint which will be in the neighborhood of 90–98° C. The operating temperature will ordinarily be between 105° C. and 120° C.

The blower for recycling the gases will normally be located between the condenser and the dephenolizer. In order to maintain a constant pressure in the cycle, gases and vapors will be bled from the cycle to compensate for the steam and gases generated in the dephenolizer plus or minus water boiled off from the caustic or absorbed by the caustic and minus the gases such as carbon dioxide which are absorbed by the caustic. A bleed condenser is advantageously provided to recover oil from the vapors in the bleed. The bleed line may be located at any point in the gas circulatory system but is preferably located between the blower and the dephenolizer or between the condenser and the blower.

However, it is within the scope of the invention to cool the gases below the steam dewpoint, in which case, additional neutral oils will be condensed and the steam will be partially condensed. The cooling and condensation of neutral oil vapors and steam may be controlled so that a small amount of steam is condensed which is just the amount necessary to compensate for the steam generated from moisture in the tar and thus keep the system in balance.

Fresh steam may be introduced into the dephenolizer in addition to that generated from the moisture in the tar, or other gas may be introduced into the system as by introducing nitrogen, preferably heated, into the dephenolizer to aid in the vaporization of the tar acids, etc., from the tar. In this case the bleed will be sufficient to compensate for such additions or else the cooling will be so regulated as to condense the added amount of steam employed.

Between the blower and the dephenolizer may be inserted a contact means, called a "pitch cooler", to provide intimate contact between the hot tar residue from the dephenolizer and the circulated gases, for recovery of some of the heat from the tar residue discharged from the system. Or the same result may be accomplished by making the dephenolizer sufficiently large to include a zone for recovering heat from the pitch.

By this method of selective vaporization in which constituents of the tar are vaporized in an atmosphere containing neutral oil vapors, from 40 to 85 per cent or more of the tar acids in the tar may be recovered directly in the carbolate without first producing a tar-acid and neutral-oil-containing distillate such as is customary at the present time. The removal of tar acids from the tar can be carried to the point where the tar is practically completely stripped or nearly stripped of tar acids or to the point where only the lower boiling acids, for example chiefly the phenols and the cresols, are removed and recovered. A partial removal of the more readily vaporizable tar acids can be effected without removing the higher boiling and more difficultly removable acids. Although complete removal of tar acids from the tar will not ordinarily be effected by this process, the treated tar will contain a lower percentage of tar acids than the product obtained by the removal of the same per cent of volatile matter from the tar by straight distillation. The tar product obtained by this selective vaporization of tar acids is referred to herein as "dephenolized tar" and although it may, and generally will, contain some of the higher boiling tar acids it will be substantially free of the low boiling tar acids.

The amount of neutral oil recovered from the tar as distillate may be regulated by controlling the temperature at which the gases and vapors enter and leave the condenser so as to produce an oil of a desired boiling range or so as to produce a dephenolized tar of desired characteristics. For example, a dephenolized tar with a melting point of 105° F. to 110° F. (cube-in-water method) may be produced which is suitable as a binder for making roads. By condensing and thus separately removing a smaller percentage of neutral oils, a lighter dephenolized tar suitable for saturating felts for roofing, or for road surfacing material or as a base to be mixed with other material for making road surfacing material, or as a flux for mixing with heavier, more viscous or higher melting point material for making road binders for tar roads, may be obtained. Dephenolized tars suitable as bases for tar paint

may be produced. The dephenolized tar may be used for fuel.

For example, if vertical retort tar is treated and the tar acids and neutral oils separately recovered total up to about 25% of the tar, a dephenolized tar with a melting point of 105°–110° F. may be produced. If the oil and tar acids recovered total 20% of the tar treated the dephenolized tar will be lighter and may have a viscosity of about 170 seconds Engler for 100 cc. at 100° C. for example. Using ordinary coke oven tar, if 15–18% of the tar acids and neutral oil are separately collected the dephenolized tar will have a viscosity of about 170 seconds Engler for 100 cc. at 100° C.; and if 20–25% a melting point in the neighborhood of 105°–110° F.

The tar which is subjected to the dephenolizing treatment may be preheated by the use of a steam preheater or by the use of waste heat from the flue gases in the flues at coke or gas plants or by the use of waste flue gases from tar stills, steam boiler plants, etc., or by the use of heat interchangers in which hot tar or pitch is employed as the heating medium or by separate heating stills, etc.

Where the recovery of tar acids from the tar is carried out at coal distillation plants at which coal tar is produced, such as coke oven plants or gas plants, the tar separated from the gases at an elevated temperature may be kept hot and employed in a heated condition. In some cases the temperature will be sufficient for carrying out the tar acid removal process without added heat or at least without any great amount of additional heat. Where the collector mains of a coke oven plant are operated at high temperature with the use of hot tar for flushing the main, the hot tar drawn off from the main may be at a sufficiently high temperature so that it does not require further heating and so that it can be led directly from the main to the apparatus for the selective vaporization.

In the case of an ordinary tar still containing a large batch of tar, the still can be heated until the tar is at the proper temperature and inert gases can then be recirculated thru the tar, the resulting gases and vapors passed thru the caustic solution and the gases recirculated until the tar acid oils have been driven off to the desired extent after which the recirculation can be stopped and the still may be heated to a higher temperature to effect further distillation of the dephenolized tar. Where the tar is distilled in a pipe coil still in which the tar is heated in a pipe coil and the heated tar discharged into a vapor box or vapor separating chamber, the initial heating of the tar can be so regulated that the tar will be at the proper temperature in the vapor-separating chamber and the current of inert gases can be passed thru the tar in such chamber to remove tar acids, after which the dephenolized tar can be heated to a higher temperature by circulation thru another pipe coil which discharges into another vapor-separating chamber, etc.

Oil vapors will in many cases serve satisfactorily as the gaseous medium employed for the removal of the tar acids from the tar. This will particularly be the case with tars containing lower boiling oils, for example tars containing benzol, toluol and the xylols and especially when dehydrated tars are treated. By heating the tar to the point at which these lower boiling oils are vaporized, the vapors may be recirculated thru the tar and the caustic solution. These oil vapors serve as the inert gases employed in the process.

The caustic solution employed for scrubbing tar acid vapors from the gases may be ordinary caustic solution of suitable strength. Caustic potash or sodium sulfide solutions may also be employed in some cases. Where the gases and vapors pass thru the caustic scrubber at a much higher temperature than the caustic soda solution, the gases will be cooled by contact with the solution and the solution itself will be heated and may be concentrated by evaporation of part of the water. In this way relatively dilute caustic solutions may be employed. The strength of the carbolate solution formed in the caustic absorber may be regulated either by regulating the strength of the caustic soda solution employed, or the temperature of the scrubber, or the temperature of the gases and vapors passing thru the scrubber. If any steam is allowed to condense on its way thru the scrubber, the carbolate will be diluted, while by maintaining the gases and the scrubber at a regulated temperature any particular strength of carbolate solution that is desired may be produced. It will be understood that the tar acids contained in vapor form and carried by the gases will combine with the sodium or other metal of the caustic solution at least to some extent to form sodium or other metal phenolates which will remain in solution until the absorbing capacity of the solution is exhausted or reduced to the desired extent.

In some cases it will be desirable to operate at relatively high temperatures in the dephenolizer. In such a case the steam or other inert gases will pass at high temperature to the caustic absorber. To avoid evaporation of the caustic or carbolate solution beyond any particular desired point, the caustic or carbolate solution may be cooled by means of cooling coils, or water may be continually or intermittently added to the caustic-carbolate solution to maintain the desired concentration. Under such conditions part of the oil vapors in the gas stream may be condensed and may remain with the carbolate. They may be continuously separated off and returned to the dephenolized tar or may be kept separate as a secondary product of the process.

The caustic soda absorber may be constructed in stages so that a completely saturated carbolate can be made in the first stage or in the lower compartment of a series of compartments while there is still an excess of caustic in the second or upper stage. In this way the caustic solution can be exhausted of caustic soda and at the same time the tar acid vapors extracted with substantial completeness from the gases.

A selective extraction of tar acids from gases and vapors containing a mixture of tar acid vapors can be effected by installing and employing several caustic scrubbers and carrying out the scrubbing operation in stages. If, for example, a carbolate rich in phenol and a second carbolate rich in higher boiling tar acids including cresols is desired, a three stage absorber or scrubber can be employed with the supply of caustic to the lower or first section or scrubber equivalent only to the phenol entering the system with the inert gas being circulated. The carbolate will be allowed to be completely saturated and to build up to the maximum percent of the phenols before any is withdrawn. Phenol, being more strongly acidic than the higher phenols (e. g. cresols and xylenols) will replace these higher phenols from their combination with caustic soda

so that when the caustic soda is consumed and a carbolate solution is produced, the passing of additional gases carrying phenols and higher phenols will result in the driving off of higher phenols and the absorption of phenol until the carbolate solution in the lower section will be greatly enriched in sodium phenolate while the higher phenolates will be absorbed in the higher section. With a multistage operation of this kind it is possible to produce carbolates predominating in phenol, the cresols, the xylenols, etc. If still more selective extraction is desired, the carbolate absorber may be constructed in a larger number of stages, for example, five or six, and a plurality of different tar acid fractions obtained.

The recovery of tar acids from tars, according to the present invention, may be carried out batch-wise or continuously, i. e. from successive batches of tar or from tar which is continuously supplied, and with continuous discharge of the dephenolized tar and likewise with batch-wise or continuous operation of the caustic absorber using successive batches of caustic soda solution for forming phenolates or supplying additional fresh caustic continuously and withdrawing the carbolate solution continuously. With batch-wise operations the caustic absorbers may be installed in parallel or at least in duplicate with piping arranged for allowing saturated carbolates to be produced first in one and then in the other absorber. At tar distillation plants, particularly at continuous tar distillation plants, with continuous supply of tar to the dephenolizing scrubber, the system of dephenolizing can be made a part of the distillation unit so that it will function continuously and require no labor in addition to that normally required for the continuous distillation.

The invention will be further described in connection with the accompanying drawings, but it is intended and is to be understood that the invention is not limited thereto.

In the drawings Fig. 1 shows in a more or less diagrammatic manner apparatus for recovering tar acids and neutral oils from tar according to this invention. Fig. 2 is a modification of Fig. 1. Fig. 3 shows a modified form of apparatus.

The apparatus of Fig. 1 comprises a tar heater 1, a tar dephenolizer 2, a caustic extractor 3, a cooler or partial condenser 4, and a bleed condenser 5. The condenser 4 is shown as a heat interchanger in which the tar is heated before it enters the heater 1. Instead of using the tar as the cooling medium in the condenser 4, water or any other suitable cooling medium may be employed. Tar may be employed for cooling the gases in part, and this cooling may be supplemented by cooling with water or other means.

The tar enters the condenser 4 at 6 and passes through the pipe 7 up through the heater 1. It passes from the heater 1 to the dephenolizer 2 through the line 8. The dephenolized tar from which at least a portion of the tar acids and part of the neutral oil have been distilled is drawn off through the pipe 9. This may be disposed of in any suitable manner. The inert gases which enter the dephenolizer through the pipe 10 vaporize tar acids and neutral oils from the tar. The gases and vapors pass from the dephenolizer to the caustic extractor through the pipe 11. In the caustic extractor they are sprayed with caustic from the pipe 12. In order to provide a considerable quantity of liquid for contact with the gases and vapors in the caustic extractor, it is desirable to recirculate a portion of the carbolate solution and respray it into the caustic extractor together with some fresh caustic. A pump 16 is provided to recirculate the carbolate for this purpose. Fresh caustic is admitted to the system through the line 17. The caustic combines with tar acid vapors and carbolate is formed, which is drawn off into the receiver 15 or otherwise disposed of. The carbolate which is formed is ordinarily treated with acids for the recovery of tar acids. The treatment may be carried out in the usual manner with carbon dioxide, et cetera.

By careful regulation of the concentration of the caustic and by controlling the temperature of the caustic as in the heat interchanger 14, the tar acid vapors will combine with the caustic without any substantial condensation of neutral oils. Should substantial condensation occur, the carbolate is drawn off from the caustic extractor into a decanter 13 to provide for the separation of neutral oil before being drawn off into the receiver 15. Any neutral oil separated may be separately collected or blended with other neutral oil collected in the receiver 20.

The gases and vapors which leave the caustic extractor through the line 19 comprise inert gases and vapors of neutral oils and ordinarily a small percentage of tar acids. In passing through the cooler 4 neutral oils are condensed from the cycle and these are drawn off through a draw-off pipe communicating with the cooler and collected in a suitable receiver 20. The cooling in the heat interchanger 4 is advantageously so controlled that the inert gases leave the cooler at a little above their dewpoint for water, for example, at 105 to 120° C.

A blower 21, is provided between the cooler and the dephenolizer for recycling the inert gases. A bleed pipe 22 is provided to remove from the system any excess steam which results from vaporization of moisture contained in the tar. The bleed condenser 5 condenses the steam and oil vapors carried by the steam, and the condensate passes to the decanter 23. The neutral oils which separate in this decanter may be separately recovered or they may be blended with the neutral oils which are collected in the receiver 20.

As an example of how the system is operated, the incoming tar may be heated in the heater 1 to a temperature around 250° C. In a specific instance the tar entered the dephenolizer at a temperature of 247° C. The inert gases were recirculated at such a rate that the cooled gases entered the dephenolizer at the rate of 335 cubic feet for every gallon of tar treated. These gases were heated by the tar and left the dephenolizer at a temperature of 150° C. After passing through the caustic extractor they were cooled in the cooler 4 to a temperature of 105° C. and then recycled through the dephenolizer. Under these conditions 17.1% of the tar was recovered as neutral oil distillate in the cooler and 62.3% of the tar acids in the tar were recovered as carbolate.

The temperature and other conditions may be varied with satisfactory results. The temperature of the incoming tar, for example, may be raised to 260° C. or above, and the gases and vapors may leave the dephenolizer at a temperature around 170 to 175° C. Under such conditions the gas circulation velocity may be reduced to around 200 cubic feet per gallon. In another specific instance tar was heated to 259° C. and inert gas vapors were circulated through the tar at a rate equivalent to 190 cubic feet per gallon of tar treated. The mixed steam, neutral oil and tar acid vapors left the tar dephenolizer at a tem-

perature of 176° C. The caustic extractor recovered 64.1% of the tar acids present in the tar. The gas temperature was reduced to 110° C. in the condenser before being recirculated to the tar dephenolizer. Under these conditions 17.7% of the tar was recovered as neutral oil from the cooler.

In Fig. 2 a caustic extractor **3A**, with a heater **14A** for controlling the temperature of the caustic, and a pump **16A**, are shown as in Fig. 1. The gases and vapors pass from the caustic extractor through the condenser **4A**. In this condenser the tar may be used as a cooling medium to be simultaneously heated or as shown in the drawings any other suitable cooling medium may be employed. The blower **21A** and the bleed **22A** are shown as in Fig. 1.

According to the modification shown in Fig. 2, the gases are heated in the preheater **30** before they enter the dephenolizer **2A**. This may be a steam heater or a hot oil heater or direct fire heater or any other suitable form of heater. The heated gases enter the bottom of the dephenolizer **2A** through the line **10A**. The tar enters the dephenolizer through the line **8A** and this tar may be at substantially room temperature, or it may be preheated to some extent as when it is used as the cooling medium in the cooler **4A**, or it may be further heated in a supplementary heater. The higher the temperature to which the gases are heated in the preheater **30**, the lower may be the temperature of the tar entering the dephenolizer and yet the same tar acid recovery may be obtained. When the gas enters at high temperature the dephenolized tar will leave at high temperature and part of the sensible heat content of the hot dephenolized tar is advantageously recovered by heat interchange as by partially preheating the incoming tar.

In Fig. 3 a simple fire-heated still **30** is shown with provision for forcing inert gas containing neutral oil vapors through a body of tar in the still. The gas is introduced into the still through the pipe **31** under pressure by means of the blower **32** and bubbles up through the perforated pipe **33** and is thus brought into intimate contact with the tar. Tar acids and neutral oil are vaporized in the still and the resulting gases and vapors pass through the line **34** to the bottom of the caustic scrubber **35**. The gases and vapors escaping from the top of the caustic scrubber pass through the condenser **36** where they are cooled to a regulated temperature. The condensate which collects in the receptacle **37** is drawn off, while the uncondensed vapors and admixed gases return through the line **38** to the blower **32** and are again recirculated through the tar in the still.

In starting up the apparatus shown in Fig. 3 when the tar has been heated to a suitable temperature, steam or other gas is forced through the body of tar to remove tar acid and neutral oil vapors and the resulting vapors and gases pass through the caustic absorber, then through the condenser to condense part of the neutral oil vapors, and the uncondensed vapors and admixed gases are then returned for recirculation in the still. After the tar acids have been driven off to the desired extent the recirculation can be discontinued and the still may be heated to a higher temperature and the distillate carried over through the line **39** to the condenser **40**. In this case more or less of the light neutral oil can be separately recovered during the dephenolizing treatment and drawn off from the receiver **37** while the oils subsequently distilled from the tar in the still will be collected in the usual way by condensation in the condenser **40**.

The various units of the apparatus in which gas and liquid are brought into direct contact are preferably of the type in which there is a low pressure drop. This is desirable so that a low pressure blower can be used for recirculating the gases. For example, the dephenolizer may be provided with sprays for spraying the tar into the recycled gases. The spray may be produced by the rapid rotation of a horizontal cylinder member so situated in the dephenolizer that it dips to but a slight extent into the tar to be treated and sprays the tar into the gases and vapors passed through the dephenolizer. Packed towers or plate columns may be used for the dephenolizer and caustic extractor. Injectors may be used for bringing the tar or caustic into contact with the gases.

The drawings show condensers of the heat interchanger type. Tar may be used for the cooling medium as shown or water may be so used. The caustic may be heated in such a heat interchanger and where only dilute caustic is available it may be heated in the heat interchanger as a step in its concentration prior to use in the extractors. The steam from the concentration of the dilute caustic may enter the circulating gas stream. Condensers of the direct contact type may be employed, where desirable. Water may be used as the condensing medium or the distillate produced may be cooled and recirculated through the condenser for further condensation of oils. The oils may be fractionally condensed and collected in two or more cuts. The dephenolized tar may be separately cooled and then brought into contact with the gases to condense neutral oils and blend them with the pitch simultaneously with the condensation. When the oils are separately condensed they may be blended with the pitch, if desirable.

The removal of neutral oils from the gases may be effected only in part by cooling and in part by absorption in a suitable absorbent such as a heavy coal tar oil or a petroleum distillate such as gas oil. The absorption may be accomplished with or without substantial cooling of the recycled gases. The neutral oil may then be recovered from the absorbent by distillation or other suitable treatment.

By varying the temperature and the rate at which the gases and vapors are recycled through the system, and other conditions, the boiling range of the neutral oil and the characteristics of the dephenolized tar produced can be controlled. The process affords a method by which tar acids can be recovered from tar and simultaneously a portion of the neutral oil constituents of the tar may be recovered. This oil is substantially free from tar acids. By cooling in the condenser to a temperature just above the dew point of the gases for water, maximum condensation of dry neutral oils is effected, and on recirculation maximum distillation of the neutral oils which can be obtained under these conditions is obtained. By cooling to a temperature just enough below the dew point for water to condense the steam equivalent to the moisture in the tar, maximum condensation of neutral oils is obtained without use of make up steam or other inert gas.

By vapor phase extraction of the tar acids and return of a portion of the neutral oils to the dephenolizer as herein disclosed, the volatilization of tar acids from the tar is selective and a relatively

larger yield of tar acids is obtained than accompanies the same amount of neutral oils when tar is distilled in the ordinary manner.

This application is in part a continuation of my application Serial No. 383,859, filed August 6, 1929.

I claim:

1. The method of treating tar-acid and neutral-oil-containing hydrocarbon material to recover therefrom both tar acids as carbolates and neutral oils as distillate, which comprises vaporizing tar acids and neutral oil constituents from the hydrocarbon material in an atmosphere of inert gases and neutral oil vapors, recovering tar acids from the resulting gases and vapors by direct contact with an alkaline reagent, cooling the resulting gases and vapors to condense part of the neutral oil vapors therefrom, and then using the resulting gases which contain neutral oil vapors for selective vaporization of tar acids from hydrocarbon material.

2. The method of treating tar to recover therefrom both tar acids as carbolates and neutral oils as distillate, which comprises vaporizing tar acids and neutral oils from tar in an atmosphere of inert gases containing neutral oil vapors, extracting tar acids from the resulting gases and vapors by direct contact with an alkaline reagent, cooling the gases and vapors to a temperature above the dew point thereof for water to condense part of the neutral oils therefrom, and employing the resulting mixture of inert gases and vapors of neutral oils for selective vaporization of tar acids from tar.

3. The method of treating tar to recover therefrom both tar acids as carbolate and neutral oils as distillate which comprises vaporizing tar acids and neutral oils from tar in a current of inert gases containing neutral oil vapors and steam, bringing the resulting gases and vapors into contact with an alkaline reagent to extract tar acids therefrom, condensing a portion of the vapors of neutral oil by cooling the gases, bringing the cooled gases containing neutral oil vapors into direct contact with the heated tar residue left from the removal of tar acids and neutral oils, whereby the gases are heated and the hot tar residue is cooled, and utilizing the resulting gases and vapors for further selective vaporization of tar acids and neutral oils from tar.

4. The method of treating tar to recover therefrom both tar acids as carbolate and neutral oil as distillate, which comprises bringing tar into direct contact with a current of hot inert gas containing vapors of neutral oils and steam, whereby tar acid and neutral oil constituents are vaporized from the tar, removing tar acids from the resulting gases and vapors by bringing them into direct contact with an alkaline reagent, cooling the gases and vapors to a temperature below the dew point thereof for water to condense part of the neutral oils and a portion of the water vapor therefrom, and employing the resulting mixture of inert gases containing vapors of neutral oils for selective vaporization of tar acids from tar.

5. The method of treating tar to recover therefrom both tar acids as carbolates and neutral oils as distillate, which comprises heating coal tar, vaporizing tar acid and neutral oil constituents of the hot tar in a current of inert gases containing neutral oil vapors, extracting tar acids from the resulting gases and vapors by direct contact with the alkaline solution, cooling the resulting gases and vapors to a temperature above the dew point thereof for water to condense part of the neutral oils therefrom, and utilizing the resulting inert gases and vapors of neutral oils for selective vaporization of tar acids from tar.

6. The process of the preceding claim, according to which wet coal tar is treated and sufficient steam and accompanying neutral oil vapors are continuously bled from the cycle prior to being again brought into contact with the wet tar to compensate for the generation of steam from the moisture in the tar.

7. The method of treating coal tar to recover therefrom both tar acids as carbolates and neutral oils as distillate, which comprises bringing tar into direct contact with a current of hot inert gases and vapors of neutral oils, whereby tar acids and neutral oil constituents are vaporized from the tar, removing the tar acids from the resulting gases and vapors by bringing them into direct contact with an alkaline agent, cooling the resulting gases and vapors to separate part of the neutral oils therefrom, heating the resulting inert gases and neutral oil vapors contained therein, and utilizing them for selective vaporization of tar acids from tar.

8. The method of claim 7, in which the gases and neutral oil vapors are cooled to a temperature above the dew point of these gases and vapors for water in the step in which part of the neutral oils are condensed therefrom.

9. The method of claim 7, in which wet tar is treated and in which sufficient steam and accompanying neutral oil vapors are continuously bled from the system prior to preheating the gases and vapors to compensate for the generation of steam from the moisture in the tar.

10. The method of treating tar to recover therefrom both tar acids as carbolate and neutral oils as distillate, which comprises repeatedly circulating gases and vapors through a dephenolizing zone in which tar acids are vaporized from tar, an extracting zone and a condensing zone in the order named, introducing heated tar into the dephenolizing zone, extracting tar acids from the gases and vapors in the extracting zone while leaving neutral oil vapors in the gases, condensing a portion of the neutral oil vapors from the gases and vapors in the condensing zone and returning inert gases, vapors of neutral oils and not more than a small percentage of tar acid vapors to the dephenolizing zone to effect selective vaporization of tar acids from the tar therein.

11. The method of treating wet tar to recover therefrom both tar acids as carbolate and neutral oils as distillate, which comprises repeatedly circulating gases and vapors through a dephenolizing zone in which tar acids are vaporized from tar, an extraction zone and a condensing zone in the order named, heating and continuously flashing the tar into the dephenolizing zone, extracting tar acids from the gases and vapors in the extracting zone while leaving neutral oil vapors in the gases, condensing a portion of the neutral oils in the condensing zone, returning steam, vapors of neutral oils and not more than a small percentage of tar acid vapors to the dephenolizing zone to effect selective vaporization of tar acids therefrom and continuously withdrawing dephenolized tar from the dephenolizing zone.

12. The method of treating tar to recover therefrom both tar acids as carbolate and neutral oils as distillate, which comprises vaporizing tar acids and neutral oils from tar in a current of inert gases and neutral oil vapors, bringing the result-

ing gases and vapors into contact with an alkaline reagent both to extract tar acids therefrom and to condense a portion of the vapors of neutral oils by cooling and then utilizing the resulting inert gases and vapors of neutral oils for selective vaporization of tar acids from tar.

13. The method of recovering tar acids from tar, which comprises passing inert gases into intimate contact with hot tar to effect vaporization of tar acid oils, passing the resulting admixed gases and vapors into intimate contact with an alkaline solution to absorb tar acid vapors, cooling the resulting gases and vapors to condense part only of the neutral oils present therein and then recirculating the gases and remaining admixed vapors through the tar in a cyclic manner.

14. The method of treating tar to recover therefrom both tar acids as carbolates and neutral oils as distillate which comprises vaporizing tar acids and neutral oils from tar in a current of inert gas, bringing the resulting gas and vapors into contact with an alkaline reagent to extract tar acids therefrom and then cooling the thus treated gas and vapors to condense neutral oils.

15. The method of treating tar to recover therefrom both tar acids as carbolates and neutral oils as distillate which comprises vaporizing tar acids and neutral oils from tar in an atmosphere of inert gas containing neutral oil vapors, extracting tar acids from the resulting gas and vapor mixture by direct contact with an alkaline reagent, and then cooling the gas and vapors to condense neutral oils therefrom.

16. The method of extracting tar acids from tar which comprises passing inert gases and tar in intimate contact with each other at elevated temperatures to effect vaporization of tar acid oils, maintaining the tar and inert gases in contact with each other at a temperature such that after passing in contact with the tar the resulting admixed gases and vapors are at a temperature of about 150° C. or above, passing the admixed gases and oil vapors from the aforesaid treatment of the tar into intimate contact with hot alkaline solutions at temperatures above the condensation temperature of said oil vapors to absorb tar acid vapors and cooling the resulting admixed gases and vapors to condense neutral oils therefrom.

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