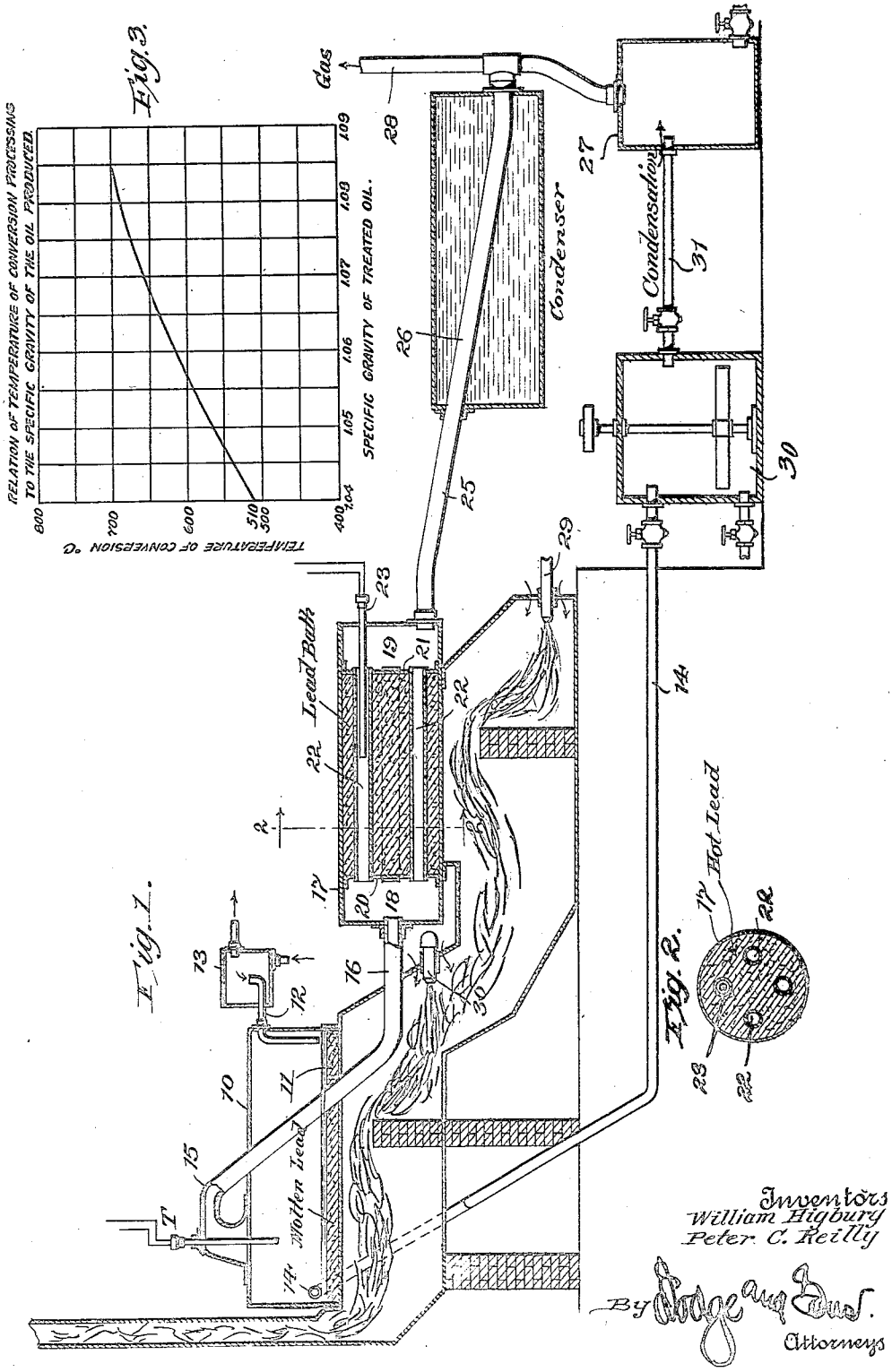
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METHOD FOR TREATING TAR AND LIKE OILS

Filed Jan. 12, 1926 2 Sheets-Sheet 1



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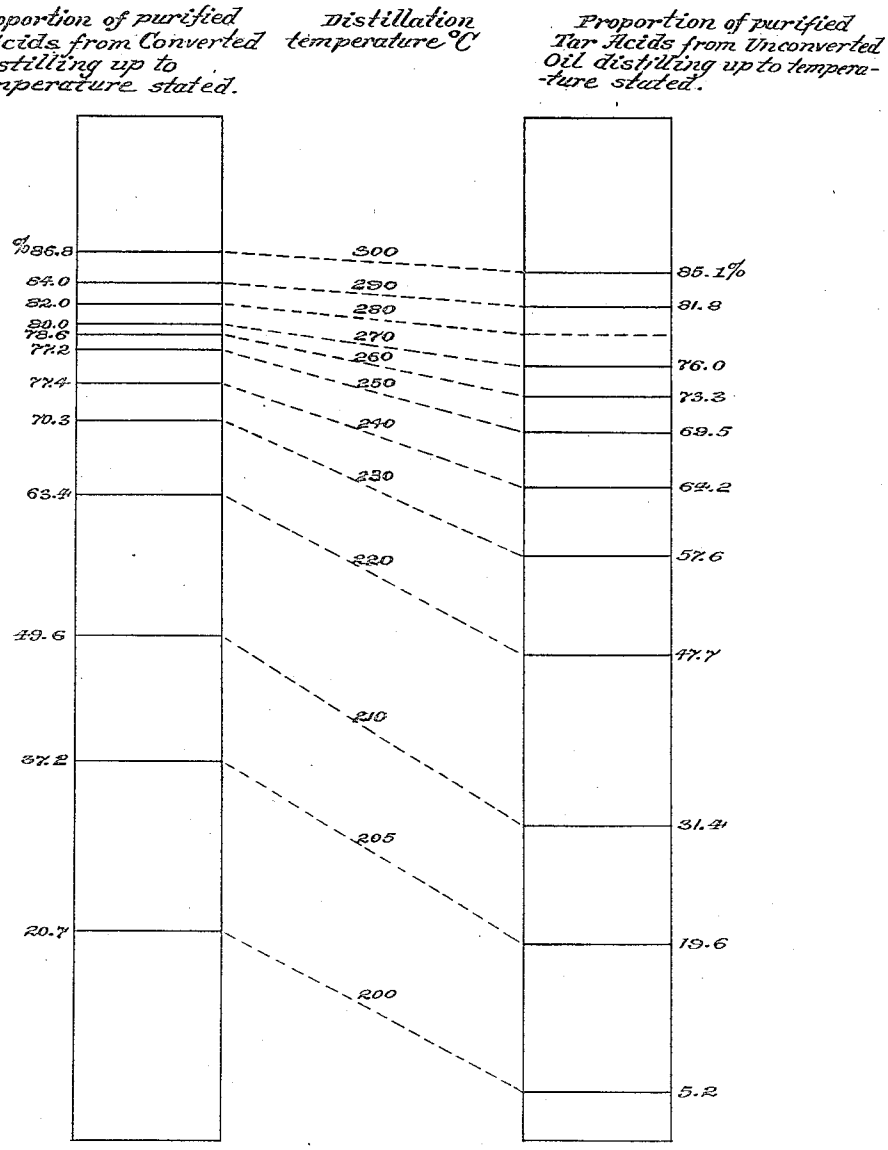
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Fig. 4.



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UNITED STATES PATENT OFFICE

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METHOD FOR TREATING TAR AND LIKE OILS

Application filed January 12, 1926. Serial No. 80,792.

The present invention relates to physically and chemically altering hydrocarbons, as will be more fully described herein.

An object of the invention is the provision of a process whereby any paraffin or straight chain hydrocarbon content (or what is termed "sulphonation residue") of coal tar or coal tar distillates or hydrocarbon mixtures (if there be such sulphonation residue present therein) may be substantially or completely removed, a large portion thereof being transformed into cyclic and aromatic hydrocarbons (material capable of being sulphonated) and gases. We note however that the total amounts of gas and of free carbon produced, corresponds to only a minor fraction of the total oil treated. The utility of such a process is evidenced by the fact that specifications for certain of the industrial applications of coal tar and coal tar distillates specifically inhibit the use of a tar or oil that contains appreciable amounts of paraffinoid or straight chain hydrocarbons or sulphonation residue. Thus, in certain specifications for the use of tars and tar oils, the amount of sulphonation residue in the fraction distilling between 300–360° C. is limited to not more than one and one-half per cent. It therefore follows that tar materials that have more than this amount of sulphonation residue are unfit for use under these specifications.

Irrespective of any change in the sulphonation residue, the invention further relates to increasing the specific gravities and decreasing the volatility of hydrocarbon materials, tars and tar fractions, whether or not such materials contain a high or low (or in fact any) sulphonation residue.

The process and apparatus of the present invention effects the rectification of such tars or hydrocarbon oils which are largely of cyclic or aromatic nature, (if unfit for use under the above mentioned specifications) making them entirely applicable for preservative or other use under approved specifications. The invention will be first described with reference thereto. The invention is also applicable to the conversion of unsulphonatable matter in water gas tar, such tar being obtained in the destructive distillation of petroleum oil in the manufacture of gas, the unsulphonatable matter in such tar or tar distillate being reduced to a negligible quantity by the application of this invention. This constitutes a most important application of the present process. Tars produced by low temperature carbonization of coal (which tars contain a relatively large percentage of straight chain hydrocarbons) yield equally satisfactory products on conversion by this process.

The purpose of this phase of the present invention is to process, rectify, transform, or convert such tars, or tar distillates, or similar oils as contain paraffinoid hydrocarbons or constituents that are not soluble or reactable with hot concentrated sulphuric acid (i. e. herein termed "unsulphonatable") into tars or oils that contain only traces or immaterial amounts of these materials; and at the same time to change the material treated in some other of its physical and chemical properties (especially as noted below); or the treatment of any tar or tar distillate or similar oil by this process to cause such desired changes in its physical and chemical properties. This process as outlined herein will be hereinafter designated as the "conversion process" and the process reaction as the "conversion reaction".

In this process a tar, pitch, tar distillate, creosote oil, dead oil, or other hydrocarbon oil consisting largely of cyclic hydrocarbons (or any desired fraction thereof) may be introduced directly as a liquid (but preferably as a vapor from a still or vaporizing device) into the treating or converting unit. The conversion unit consists of one or several tubes heated directly, or, preferably indi-

rectly, to a sufficiently high temperature to induce the reaction by which the paraffins or straight chain hydrocarbons or sulphonation residues are decomposed and converted into cyclic hydrocarbons and gases. At the same time other physical and chemical changes are effected in the material treated, such as changes in specific gravity, volatility, viscosity, color and odor.

Sheet 1 of the annexed drawings illustrates one form of apparatus which may conveniently be employed in carrying out the process.

Figure 1 of the annexed drawings shows a form of apparatus within the scope of our present invention, suitable for carrying out the process. This figure shows a longitudinal vertical section of the essential parts of the apparatus.

Figure 2 is a cross section on the line 2—2 of Figure 1.

Fig. 3 is a graph showing the relation between the temperature of treatment and specific gravity of the oil.

Fig. 4 is a graphic table showing the proportion of tar acids in the converted and unconverted oil.

In said drawings 10 is a still for distilling a tar oil or the equivalent, isothermally, and carrying a layer of molten lead or equivalent 11, in its bottom.

An inlet pipe 12 for oil or tar is provided and is in communication with a constant and uniform feed box 13. 14 represents the outlet for distillation residue, i. e. part not vaporized, and 15 is a vapor outlet.

In the vapor outlet, we provide a thermocouple T to indicate the temperature of the exit vapors. From this vapor outlet, the tube 16 conveys the vapors to the converting element 17. This device preferably takes the form of a cylindrical shell, having headers 18 and 19, formed by tube sheets 20 and 21 between which are connected a plurality of tubes 22, four of such being shown in the drawings. One of these tubes contains the thermocouple 23 for indicating the existing temperature in the tubes.

From the space adjacent the outlet header 19, a tube 25 leads to a condenser, shown conventionally at 26, the condensate flowing into receiver 27, and the gas formed passing out through pipe 28 to a point of use, say to one or the other of the burners 29 and 30 employed for heating the shell 17 and the still 10.

Pipe 14 for the distillation residue may extend to a mixing chamber 30, which chamber is also connected with the receiver 27 by a pipe 31. The various pipes and outlets will, of course, be properly valved as indicated in the drawings.

As a specific example of the process of the present invention the following is given, without in any manner limiting the scope of the invention thereto. A coal tar oil of specific gravity 1.034 at 38° C. derived from the distillation of a vertical retort tar showed a sulphonation residue in the fraction distilling between the limits 300–360° C. of six and eight tenths per cent and was therefore a prohibited material for use as a preservative under specifications. This oil (before treatment) had a distillation range as follows:

	Per cent
Up to 210 C.	0.5
Up to 235 C.	4.4
Up to 270 C.	31.0
Up to 300 C.	47.8
Up to 315 C.	55.7
Up to 360 C.	76.4

This oil was vaporized or distilled isothermally in still 10, at a temperature of 350° C. and the vapors were passed directly from the still to the conversion unit 17. The conversion unit consisted of several parallel tubes 22, one inch internal diameter, submerged in a bath of molten lead. The tubes and bath of molten lead were heated to a temperature of 700° C. (registered by thermocouple 23), for this run and this temperature was maintained during the process. As the vapors from the still passed through the tubes of the conversion unit and were subjected to the temperature there maintained, the conversion reaction proceeded rapidly. The progress and extent of this reaction was evidenced by the efflux of considerable quantities of fixed gases from the condenser together with the condensed oil. The condensed oil when incorporated with the distillation residue over 350° C., that was drawn from the still through pipe 14, had the following properties:

Specific Gravity 1.069 at 38° C.

Sulphonation Residue (300–360° C. fraction) 1.0%.

Distillation:

	Per cent
Up to 210 C.	2.1
Up to 235 C.	9.5
Up to 270 C.	29.8
Up to 300 C.	42.6
Up to 315 C.	48.6
Up to 360 C.	68.0

In this example, instead of using a tar oil, we could introduce a tar into still 10, but in such a case we would not necessarily mix the residue of the tar from still 10 with the condensate from tank 27, since such still residue would contain material which under certain specifications would be unsuitable for use as a constituent of a preservative oil.

By the process as detailed in the present case, we have in this example reduced the paraffin, straight chain hydrocarbon content or sulphonation residue of this oil from six and eight tenths percent to one percent

in the test fraction (300–360° C.). Based on the whole oil the sulphonation residue is reduced from seven and two tenths per cent to half of one percent. We have at the same time in this operation raised the specific gravity of the oil from 1.034 at 38° C. to 1.069 at 38° C., and have altered the oil in such manner that a somewhat greater proportion of the oil distills up to a temperature of 235° C., and a somewhat lesser proportion of the oil distills off up to a temperature of 360° C.; these distillates being determined by the approved distillation tests for the examination of creosote oil. We have in this example converted a prohibited oil under commercial specifications into one that is entirely acceptable.

In the above example only the vapors distilling off up to 350° C., were passed through the converting process for the reason that practically all of the material that it was desired to convert distilled off below this temperature. In other cases it may be desirable to pass only the material distilling up to other temperatures (say 300° C. or 375° C.) through the conversion apparatus or it may be desirable to pass through only the vapors distilling through a certain temperature range. In other cases it may be desirable to distill the oil or tar to a coke and pass all or part of the vapors of distillation through the conversion unit. Such variations in operation depend upon the character of material to be treated and are so included in the present invention.

Thus the temperature at which the original oil or tar or fraction is distilled (or in other words the portion of the original which is vaporized) can be varied to suit the particular material under treatment, it being usually advisable to vaporize all or substantially all of the constituents which are not subject to sulphonation.

Directly heated tubes for the conversion of the vapors may be and have been used by us in the practice of the present process. The advantage of using a lead bath in which the tubes for carrying out the reaction are submerged is twofold; first in that the lead bath to which the heat is supplied acts as a mobile distributor and equalizer of heat and prevents the otherwise unavoidable local superheating of the tubes when direct heat by gas or oil burners is supplied; secondly the lead bath holds within itself a large supply of stored up heat that is continuously supplied to the converting tubes and the vapors to carry on the reactions of conversion and to effectually neutralize any sudden and transient temperature fluctuations.

The amount or degree of conversion obtained in the practice of the present process depends upon and may be controlled by varying the factors of rate of flow of the vapors through the conversion tubes and by raising or lowering the temperatures of the conversion system and is so included in the present invention.

We call attention to the fact that the isothermal distillation or vaporization in the still 10, when under approximately atmospheric pressure, is not a cracking operation, as no substantial amount of cracking occurs in this still. The conversion occurring in the tubes 22 is, in this instance, largely confined to open chain compounds, whereby these are converted into sulphonatable constituents, and only small percentages thereof are converted into gases.

The conversion reactions as herein described are preferably conducted and the products produced thereby are formed under approximately atmospheric pressure. Experiments have been performed by us in which similar reactions progress and similar results are obtained by working under pressure below or above atmospheric, and the use of such pressures is within the scope of the invention. We prefer, however, to employ about atmospheric pressure throughout the system.

In the annexed drawings, the tubes 22 are shown as not being filled. It is permissible however, (and in some cases advisable, especially when relatively large tubes are being used), to fill these with a suitable filling material, in order to more effectively bring all the vapors into direct contact with the hot tube walls. Suitable filling for such purposes is well known and needs no detailed description. Such filling material may be catalytic in character, in order to cause the reactions to take place at a somewhat lower temperature, or to cause the reactions to be more complete. Examples of such catalytic material, are properly prepared iron, copper, alumina or nickel. It will of course be understood that small tubes without fillings, are more easily kept clean.

In the above description, we have stressed the importance of the feature of the removal or conversion of "sulphonation residue". Water gas tars are prevalent in the present industrial market and future practice in coal carbonization will, we believe, tend toward a continually increased production of low temperature tars. The distillates from these tars are in many cases (aside from "sulphonation residue" considerations) not acceptable to the users of preservative oils because of their low specific gravities and because of their high volatility. Our conversion process will increase specific gravity and reduce volatility and so will make these unfit hydrocarbons suitable for use under present specifications.

Example 2.—We have taken a pure coal tar distillate containing no sulphonation residue and have treated it, by the method above described, at temperatures as shown

below with the resulting increase in gravities as indicated.

The original oil had a gravity 1.026 at 38° C.

Temperature of treatment	Gravity	Yield
°C		Per cent
603	1.026	
698	1.032	93
750	1.050	82

Increase in the gravity of the oil means a corresponding decrease in its volatility.

The graph constituting Figure 3 of the drawings, shows the same relation between the temperature of treatment (between 510 and 800° C.) and specific gravity on another and entirely different oil of which the original gravity was 1.040. In a series of thermal treatments in which this oil was processed at temperatures ranging from 510 to 700° C., a series of oils of gravities ranging from 1.040 to 1.084 were obtained as plotted in Figure 3. In another case a water gas tar distillate of gravity .97 at 38° C. was converted at 710° C. The converted oil had a gravity of 1.003 at 38° C. Distillation tests on the two oils showed a corresponding decrease in volatility.

Example 3.—Results obtained from low temperature tars show even more advantageous results on conversion. A low temperature tar distillate, being 90% of the total distillate from this tar, had a density of .994 at 38° C. After conversion, as above described, at about 690° C., in our conversion apparatus the product produced from this oil had a gravity of 1.041 at 38° C. Distillation tests showed a great decrease in the volatility of the oil. The properties of the converted and unconverted oils are shown in the following table:

	Untreated	Treated
Gravity at 38° C.	.994	1.041
Sulphonation residue	8.4%	1.4%
Tar Acids in 0-315° C. Fraction	42.8	38.7
Distillation:		
Up to 170° C.	2.3	2.0
200	13.0	9.5
210	18.7	13.4
235	33.4	26.6
270	50.1	38.8
315	65.0	53.5
355	81.7	65.2

The decrease in tar acid content of this oil led us to examine the tar acids in each of the above oils to determine whether the character of the tar acids had been changed in the conversion process. The tar acids were extracted from each of the above oils and purified, and the graphic table constituting Figure 4 of the annexed drawings show the large increase in the amount of low boiling tar acids in the converted oil over that present in the original oil. This change in tar acid content and in the constitution of the tar acids themselves is due to the conversion processing. There is a much larger demand in the market for acids of the low boiling type than for those of the higher boiling points which fact adds to the value of the process. The low boiling point tar acids have a higher specific gravity or density than the high boiling point tar acids.

The graphic table constituting Figure 4 shows a comparison of the distillation ranges of purified tar acids obtained from the same distillate fractions of converted and untreated oils.

With regard to apparatus used, we call attention to the fact that the space 18, into which the vapors are delivered, is relatively large, in order to allow the vapors to expand into and fully mix in this space. This allows equalization of pressure over space 20 and causes equal volumes of the vapors, thoroughly mixed, to travel through the several tubes, and to again thoroughly mix in the space 19.

While in this specification we have particularly shown and described the conversion operation as being performed on the material while in a vapor phase, we call attention to the fact that in some cases the material may be introduced into the high heating zone as liquids or sprays or even as solids, and the claims of the present case are to be construed as covering such operation, and also are intended to cover the carrying out of the process at pressures below, equal to, or above, atmospheric pressure.

Likewise in the claims, the expression "a tube" does not indicate that one single tube is necessary since several of such tubes may be employed if desired. Further, the broad process may be carried out without the use of tubes in which to conduct the selective cracking operation.

What is claimed is:

1. A process of lowering the sulphonation residue of oily tar fractions containing some unsulphonatable constituents, which comprises vaporizing the desired volatile portion of the same and thereafter superheating such vaporized portion sufficiently to convert a large part of said unsulphonatable constituents into sulphonatable constituents and gases, condensing the vapors and mixing the condensate with the distillation residue of the first step.

2. A process of lowering the sulphonation residue of water gas tar distillates containing a substantial amount of sulphonation residue, which comprises vaporizing a vola-

tile portion of the same and thereafter superheating such vaporized portion sufficiently to convert a large part of said unsulphonatable constituents into sulphonatable constituents and gases, condensing the product thus produced and mixing the same with the distillation residue of the first step.

3. A process of lowering the sulphonation residue of tar distillates other than high temperature coal tar distillates, which comprises vaporizing a volatile portion of the same and thereafter superheating such vaporized portion sufficiently to convert a large part of said unsulphonated constituents into sulphonatable constituents and gases, condensing the product and mixing the same with the distillation residue of the first step.

4. A process of producing a creosote oil which comprises subjecting a hydrocarbon material of a predominantly tarry character, and containing not more than a few percent of constituents which will distil below 210° C., and containing an undesirably large sulphonation residue, to a temperature above 510° C. and below 750° C. sufficient to selectively convert substantially all the unsulphonatable constituents thereof into sulphonatable materials, producing thereby a material of higher specific gravity and less volatility than the starting material.

5. A process of producing a creosote oil which comprises subjecting a hydrocarbon material of a predominantly tarry character, and containing not more than a few percent of constituents which will distil below 170° C., and containing an undesirably large sulphonation residue, while in the vaporized state, to a temperature of about 603° C. to 750° C., sufficient to selectively convert substantially all the unsulphonatable constituents thereof into sulphonatable materials and gases, producing thereby a material of a higher specific gravity and of less volatility than the starting material.

6. A process of making creosote oil which comprises subjecting a hydrocarbon material consisting largely of cyclic and aromatic substances of which only a small percentage will distil below 170° C., but containing sulphonation residue in excess of 1.5%, to a temperature of about 510° C. to 750° C. sufficient to selectively convert substantially all the unsulphonatable constituents thereof into sulphonatable materials.

7. A process of treating tars and tar oils containing substantially over 1.5% of sulphonation residue in the 300–360° C. fraction, and containing a substantial amount of high-boiling low density tar acids to produce a creosote oil containing tar acids of higher density, which comprises vaporizing the major part of the high-boiling low density tar acids along with the tars and tar oils, passing such vapors through a heated zone maintained at between 510° C. and 750° C. to change the low density tar acids largely into higher density tar acids without substantial loss of total tar acids, and in which the unsulphonatable constituents are largely decomposed into sulphonatable compounds and gases, and condensing the vapors.

In testimony whereof we have signed our names to this specification.

PETER C. REILLY.
WILLIAM HIGBURG.