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METHOD OF PRODUCING A WOOD PRESERVATIVE OR THE LIKE

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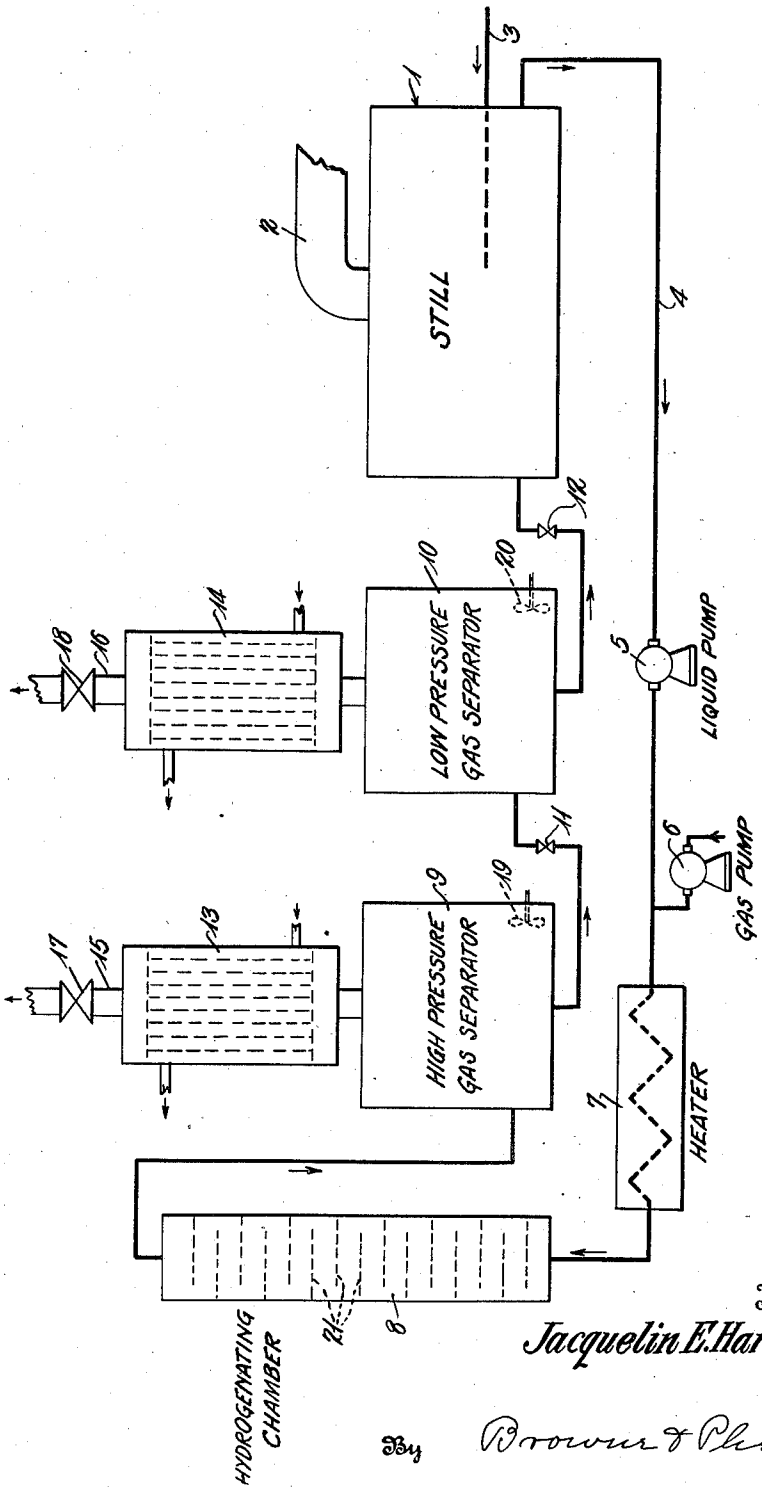

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METHOD OF PRODUCING A WOOD PRESERVATIVE OR THE LIKE

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This invention relates to a process of producing a wood preservative or the like and has as an object the carrying on of hydrogenation in such a manner as to exercise a control of the characteristics of the finished product.

It is a further object of the invention to provide a process for hydrogenation of pitch in such a manner as to finally convert the entire quantity into a synthetic creosote having less than 10% distilling to 200° C., and not less than 50% distilling to 355° C., when distilled according to American Wood Preservers' Association standard distillation of creosote, Schedule 11E.

Creosote is the distillate recovered from coal tar, or the like. In past years, upwards of 50% creosote was recovered from coal tar, but as the present trend of the industry is toward lower residues, that is, the proportion above 355° C., smaller and smaller recoveries of creosote from coal tar are now being made. For instance, to produce a creosote having approximately 20% above 355° C., the producer must content himself with a 25 to 35% recovery of creosote from his tar. Such a condition necessarily sets up an increased amount of residuum in the distillation apparatus which must subsequently be marketed. This residuum is pitch.

Seasonal demands at times cause one or all these pitches (hard, soft and intermediate) to be distress products. Bearing such a distress condition in mind, it has long been a desideratum in the art to recover by simple distillation from coal tar, or the like, as much creosote as possible. Various investigators have proposed various procedures, one of the most notable being the Barrett direct recovery still which has recovered approximately 70% creosote from coal tar—but with a recovery of approximately 70%, the residue in the resultant creosote above 355° C., is 53%. Even when the recovery of creosote from coal tar in the Barrett direct recovery still has being dropped to 55%, the residue above 355° C., is only slightly under 50%.

The Barrett direct recovery still recovers as much creosote from coal tar as any other method heretofore known and more cheaply.

When recovering approximately 70% creosote from coal tar, the residue above 355° C. in the creosote is approximately 53%. Many creosote consumers will not permit a creosote having such a high residue; therefore, as the trend of the industry is toward creosotes having only 30% residue above 355° C., producers must decrease the percentage recovery of creosote from coal tar in the order of 25 to 35%.

I have found that I can recover 80 to 100% of creosote from coal tar or the like, neglecting normal manufacturing losses. When practicing my invention for the recovery of volume for volume of creosote from coal tar, I can control the residue in the creosote above 355° C., from zero to any desired point.

I claim as pioneer in the art my process for producing substantially volume for volume of creosote from coal tar, wherein not more than 10% will distill at 200° C., and wherein the residue above 355° C. can be controllably held from zero to any desired percentage.

"Coal tar" in the trade means the tar resulting from distillation of coal in a high temperature coke oven. This is the material now preferred for treatment by my process. Other usable starting materials are gas house tar, low temperature distillation tar, and rosin oil pitch.

Inasmuch as the first step in production of wood preservative from any of the above materials is the recovery by distillation of any fractions present of permissible wood preservative, the invention here resolves itself into the production of wood preservative from pitch.

By permissible creosote is meant a material which will meet the tests set up by the trade. At present among these tests is the requirement that not more than 5% shall distill at 200° C. It cannot be foretold, however, when methods of wood preservation may be modified so that lower boiling points may be permissible. This invention, therefore, contemplates any modification of the extent of hydrogenation at the successive steps described below to agree with any such modification.

I have at times secured more than 100% volumetric efficiency of creosote from coal tar or the like, and this recovery is more the rule than the exception. And, when practicing such recoveries, I have held the amount distilling up to 200° C. below 5%, and the amount of residue above 355° C. from zero to any desired percentage.

I may take a coal tar or the like and by simple distillation recover from it a distillate falling within the specifications of a permissible creosote. This simple distillation leaves a residuum of pitch in the still which because of its physical and other characteristics is not acceptable as a wood preservative. I have found that by taking the residual matter and subjecting it for a time to hydrogenating conditions, I can simple distil from said residual mass an oil falling within the

limitations of a specified and desired creosote. This oil is the desired creosote.

After the newly formed oil has been removed, the resultant residual mass may again be hydrogenated to produce a similar distillate and such procedure may be carried on until said residual mass has completely disappeared. The mechanics of the operation make possible the total conversion of the residual mass into an acceptable wood preservative.

The requirements for recovery of 100% or over of permissible wood preservative are: first, that the hydrogenation shall be carried out under such conditions as not to induce a fraction that is not commercially feasible of hydrogenation to creosote; and second, that at no time is the hydrogenation carried to an extent to produce a fraction having a boiling point lower than is permissible in the desired product as in such a case said fraction must be removed and discarded so far as the desired use is concerned.

By the word "pitch" as used herein and in the claims is meant any or all the material of coal tar not permissible in a wood preservative creosote. For instance, it is possible to distill off 75% to 80% of the coal tar and to label the distillate "creosote" but under present conditions the said creosote would not be permissible as a wood preservative. However if 80% cut is again distilled to yield a permissible wood preservative creosote, the residue of said last distillation is regarded as pitch in the sense used herein and in the claims and may be utilized as the starting material of the process of the present invention.

An illustrative embodiment of apparatus which may be used to carry out the process is shown in the accompanying drawing in which the figure is a diagrammatic showing of a flow sheet.

In the drawing a still is shown at 1, which may be of any desired character having an outlet for vapors at 2, and a charging inlet for fresh material at 3. Residues from the distillation are drawn at 4 under influence of pump 5, and hydrogen or hydrogen carrying gas may be supplied by pump 6 from any source. The residues and gas then pass through heater 7, through the hydrogenation chamber 8, to and through a high pressure gas separation chamber 9, then to and through a low pressure gas separator 10, from which latter the hydrogenated liquid passes back to the still. Pressure regulating and reducing valves are shown at 11 and 12.

The gases from separators 9 and 10 are passed into reflux condensers 13 and 14 respectively and escape at 15 and 16 from which points the escaping gases may be led to apparatus, not shown, to recover hydrogen for reuse.

The fresh material introduced to the still at 3 may be "pitch" as defined herein. However in many cases it may be desirable to introduce coal tar at 3 both initially and thereafter to keep up the supply as the volume of material is reduced by hydrogenation and distillation, allowing the creosote distilled from the coal tar direct to mingle with the synthesized creosote produced by the process of the invention.

It will be understood that the gas recovery apparatus connected at 15 and 16 must be arranged to preserve the desired pressures in 9 and 10, which fact I have illustrated by indicating reducing pressure regulation valves at 17 and 18 although in practice no such valves would be necessary at those points. If desired for more complete separation of entrained gas from the hydrogenated liquid, agitators 19 and 20 may be placed in the separators 9 and 10 respectively. The baffle plates 21 in hydrogenating chamber 8 may be depended upon for agitation of the gas and liquid therein but it will be obvious that any form of hydrogenation chamber and any form of agitator may be utilized.

In the following I set forth fully several examples of steps for substantially a hundred per cent volumetric recovery of desired creosote from coal tar or the like:

Example 1.—I take a given coal tar and subject it to simple distillation until all permissible wood preservative creosote has been recovered which under present trade requirements means until a creosote is recovered which will distill approximately 5% up to 200° C., and that will have a residue of not substantially more than 20% at 355° C. The resultant pitch, as is well known, will have a specific gravity in the order of 1.23 and approximately nothing off at 355° C. as well as having substantially no toxic value as a wood preservative. This pitch is charged to an autoclave designed to withstand high pressure and temperature, and subjected to a temperature of from 300 to 500° C., and a hydrogen pressure of from 20 to 300 atmospheres while, as is usual with such processes, keeping the contents of the autoclave agitated. This step of the process is continued until test samples withdrawn show that fractions have been induced falling within the range of permissible wood preservative creosote, that is, under present trade conditions distilling not more than 5% at 200° C., and having a residue of not substantially more than 20% at 355° C.

Depending on the nature of the pitch and within the ranges of temperature and hydrogen pressure named, this result will be found to be accomplished in from one to ten hours. It is at present preferred to operate at from 350° to 400° C. and with hydrogen pressures of about 200 atmospheres under which conditions the result named will be found to be accomplished in a time of the order of four hours.

After hydrogenating as and to the extent described, the contents of the autoclave are discharged into a suitable distilling apparatus and distilled up to a temperature of substantially 355° C. until approximately nothing further is coming off. This distillation will be found to yield approximately 12% as a distillate which is the wood preservative creosote desired, which under the conditions set forth will give off not substantially more than 5% at 200° C. and will have a residue not substantially more than 20% at 355° C.

The residue from the distilling operation may then be charged back to the autoclave and the cycle repeated, enabling a total conversion of the pitch into creosote. As is well known, the usual coal tar pitches have a hydrogen content of substantially 4% to 6.5%. Analysis of the result of the above described process will show a hydrogen content of substantially 7%. This means that the process as described adds to the pitch from .5 to 3% hydrogen.

It is impossible to produce volume for volume of creosote from pitch in a single cycle of hydrogenation since if the pitch be hydrogenated in a single step to the point that it will all pass over at 355° C., the resultant distillate will contain an undue amount (more than 5%) that will distill at 200° C. and this low boiling fraction must be eliminated and discarded for the purpose intended. Therefore volume for volume in

permissible wood preservative creosote will not result.

The starting material, pitch, is not acceptable as a wood preservative impregnant for two reasons: 1st, Its physical properties are not such as to make it acceptable; and 2d, it has no, or very slight, toxic value. It is a discovery of the present invention that hydrogenation of pitch having no toxic value will induce toxic properties such that the resultant product will be equal or superior to creosote distilled from coal tar from which distillation the pitch is the residue.

The limits of temperature and pressure given are important. A lower temperature or pressure or both are operable but the time required is greatly extended and the process therefore ceases to be commercially feasible at present. Higher temperatures or pressures than those mentioned tend to induce the residual fraction not capable of feasible hydrogenation under commercial conditions. The conditions at present preferred are a temperature of 375° to 400° C. and a pressure of from 180 to 200 atmospheres hydrogen pressure.

After total conversion of the residual matter into an acceptable oil by hydrogenation, it falls within the scope of this invention to blend said synthetic and first recovered natural creosotes to produce an acceptable oil useful as a wood preservative on account of its toxic value.

It is a known and accepted fact that the fungicidal power of a creosote decreases as the boiling point increases. It is also a known and accepted fact that the neutral hydrocarbons are fully as effective as the phenolic compounds of similar distillation range. That this is accepted as fact is borne out by an article by F. H. Rhodes and F. T. Gardner of Cornell University which was published in February 1930 issue of Industrial and Engineering Chemistry under the caption "Comparative efficiencies of the components of creosote oil as preservatives for timber."

Example 2.—Using as a starting material soft, intermediate or hard pitches, they are subjected to hydrogenation at necessary pressures, temperatures and for the desired time as above described until a new oil has been formed that will not distil more than 5% up to 210° C., and such that when distillation is carried to a point of 355° C. the residue will not be greater than permitted by the trade standard. The thus partially hydrogenated material is then simple distilled at a maximum temperature of 500° C. preferably to an upper limit of substantially 400° C. to remove a distillate comprising the desired product for use as a wood preservative.

The residual matter resulting from said simple distillation is then again charged back to the hydrogenation vessel, compensation being made if desired by new material for the distillate removed and hydrogenating conditions again repeated as above stated. Economic and commercial operations dictate the advisability of the addition of fresh compensating material, however this is not necessary to the success of the process inasmuch as total conversion of the residual matter into a desired oil can be effected without compensation of new material for the distillate removed by simple distillation.

Instead of operating intermittently as described in the foregoing, it falls within the scope of the invention to operate the process continuously. For example, material in the hydrogenation vessel may be continuously withdrawn at a controlled rate preferably with pressure reducing means in its path, and delivered to a conventional still where the newly formed fractions are removed by distillation. A portion of the liquid charge in the simple still stripped of the newly induced fractions is then continuously withdrawn and returned to the hydrogenating vessel for further hydrogenation. Means must be provided to continuously or at intervals restore the volume of the material to the reaction chamber.

The conventional use of heat exchangers and the like may be incorporated if and when desired.

Example 3.—This process is also especially applicable to the treating of high residue oils from a conventional direct recovery still. Those versed in the art will immediately know what is meant by the direct recovery still and no explanation here is thought necessary.

The direct recovery still may be set so as to recover all possible volatile matter with the sending of the resultant vapors into a fractionating column whereby permissible oil is thrown into one channel and non-permissible oil is thrown into another channel, the non-permissible oil being then subjected to hydrogenating conditions as above described to produce an acceptable and desired oil in regards its float test, coke test, and insolubility in benzol. I have repeatedly found that hydrogenation as practiced and described by me has the effect of lowering insolubility in benzol.

It is well to note that when practicing my special form of hydrogenation for the production of acceptable and desired creosote from coal tar or the like, I do not desire cracking conditions. Whatever the usual definition of cracking may be, I refer to cracking as a condition wherein polymerization has the effect of salting out carbon. This salting out of carbon I do not desire because it would make more or less impossible the total volumetric conversion of coal tar or the like into an acceptable and specified creosote.

It may be that hydrogenation as practiced in my form of invention is really only partial hydrogenation. However I do not desire to assign any definite name to the effect that I have secured but only desire to point markedly to the fact that my hydrogenation is carried only to the point where a new oil is synthesized that will distil not more than 5% up to 210° C. However inasmuch as future creosote specifications may be changed, that is, a larger percentage of low boiling fractions may be made permissible, it necessarily falls within the scope of this invention to hydrogenate the aforementioned residual matter until an oil is produced which will distil in its lower boiling range in accordance with creosote specifications.

It is also important to again note that the neutral fractions of coal tar are equally as toxic as the phenolic compounds of similar distillation range. Therefore my invention does not presuppose a condition wherein a starting material must have phenolic compounds or the like. Attention is directed to the fact that the lowering of the boiling point of neutral fractions has the effect of increasing their toxicity. In other words, using as starting material neutral fractions not acceptable as wood preservatives I can transform them into acceptable and toxic fractions of a desired wood preservative.

I consider as pioneer in the art my process for the total volumetric conversion of coal tar or the like into a permissible and acceptable and desired creosote.

In the procedure of the process hydrogen is

conveniently secured by dissociation of methane. The hydrogen is placed under pressure, preheated and delivered to the reaction chamber. A portion of the gas from the reaction chamber may be withdrawn, purified, restored as to volume by addition of fresh hydrogen and again introduced as at first. The material is desirably agitated while bubbling the gas therethrough. However any procedure may be adopted whereby intimate contact between gas and material is secured. It is a well known fact that the hydrogenation of coal tar or the like necessarily at times produces undesirable amounts of methane and hydrogen sulphide. For the sake of economy it may be desirable to remove undesirable amounts of methane and hydrogen sulphide from the hydrogen or hydrogen-containing gases. This procedure is necessary and advisable for economic reasons that are immediately apparent to those skilled in the art.

Hydrogenation in liquid phase is preferred but it also falls within the scope of the invention to hydrogenate in vapor phase if and when advisable and such operating conditions may be incorporated in any of the above examples.

The above description is silent as to the presence or absence of catalysts. It is well known that the material of the wall of the reaction chamber may have a catalytic action. For commercial reasons it is preferred to carry out the invention without an added or apparent catalyst, assuming any such effect of the material of the apparatus itself as not an "apparent" catalyst.

To reduce the required pressure or temperature or to shorten the process, catalysts may be used. Many catalysts are possible of use, such as Luxmasse (the residual material after alumina has been removed from bauxite), all oxides, halides, and sulphates of common metallic elements under proper conditions known to the art.

It necessarily follows that a preferred catalyst is one partially or entirely immune to the poisoning effect of sulphur. I therefore in practice if and when a catalyst is desired use such a catalyst. Examples of catalysts somewhat immune to sulphur poisoning are molybdenum oxide and chromium oxide.

Well known methods, either batch or continuous, of revivifying catalysts may be practiced.

Purifying the gases has been referred to. It is found that a considerable quantity of nitrogen compounds are found in the system as a result of the operation. The purification of the gases may include the removal of these compounds as by scrubbing with sulphuric acid with recovery of ammonium sulphate as a valuable by-product.

Minor changes in the steps of the process may be made within the scope of the appended claims without departing from the spirit of the invention.

I claim:

1. The method of producing a preservative wood impregnant which comprises: subjecting a pitch obtained from a material in the group consisting of coal tars and rosin pitch to hydrogenation with the temperature, pressure, and time so controlled that when the hydrogenated product is distilled up to a temperature to recover the desired product as a distillate said distillate will have no greater percentage of ends boiling below 210° C. than is permitted in specifications accepted in the trade for a wood preservative creosote directly recovered by distillation of coal tar and when the percentage of materials in said distillate boiling between 210° C. and 355° C. required by said specifications is produced; and distilling said hydrogenation product until the distillate has no greater percentage of ends boiling above 355° C. than is permitted by said specifications.

2. The method of claim 1 wherein the said hydrogenation and distillation steps are repeated in cycles upon the residue of each preceding distillation step.

3. The method of producing a preservative wood impregnant which comprises: subjecting a pitch obtained from a material in the group consisting of coal tars and rosin pitch to a hydrogenation with the temperature, pressure, and time controlled so that less than 10% of the hydrogenated fractions recoverable as the wood preservative distills up to 210° C. and not less than 50% of the distillate boils below 355° C. when the product is distilled; distilling the hydrogenation product until the distillate has a no greater percentage of ends boiling below 210° C. and above 355° C. than is permitted in specifications accepted in the trade for a wood preservative creosote directly recovered by distillation of coal tar.

4. The method of claim 1 performed as a continuous operation by substantially continuous circulation of hydrogenated material from the hydrogenation chamber to the still and of residue from the still to said chamber at a rate to properly control the extent of the hydrogenation.

5. The method of producing a preservative wood impregnant which comprises: subjecting a pitch obtained from a material in the group consisting of coal tars and rosin pitch to hydrogenation with the temperature, pressure, and time so controlled that if the hydrogenated product is distilled up to a temperature to recover the desired product as a distillate said distillate will have no greater percentage of ends boiling below 210° C. than is permitted in specifications accepted in the trade for a wood preservative creosote directly recovered by distillation of coal tar and so controlled that the percentage of materials in said distillate boiling between 210° C. and 355° C. required by said specification is produced.

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