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METHOD OF PRODUCING A RESIN

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This invention relates to an improved method of producing from pine wood a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons.

In my U. S. Patent 2,193,026 I described a process of producing a new resin from pine wood which was characterized by solubility in alcohol, substantial insolubility in petroleum hydrocarbons and substantial freedom from rosin. My process for producing the novel resin as described in the above patent involved extracting pine wood with a coal tar hydrocarbon so as to remove from the wood my novel resin characterized by substantial insolubility in petroleum hydrocarbons, in addition to rosin. After evaporation of the coal tar hydrocarbon from the extract, I treated the solid residue consisting of a mixture of rosin and my novel petroleum hydrocarbon-insoluble resin with a solvent for the rosin component which would not dissolve the petroleum hydrocarbon-insoluble component of the coal tar hydrocarbon extract and separated the rosin solution from the undissolved insoluble novel resin.

The above process has the disadvantage that the petroleum hydrocarbon-insoluble resin must be handled as a solid in the plant equipment used for the process. This is a cumbersome and difficult procedure particularly in large plant scale operations, since it involves the subsequent operations of washing the solid residue with solvent to purify the novel resin component and the difficult handling of the solid material in the equipment.

It is an object of this invention to provide an improved method of producing from pine wood a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons.

It is a further object of this invention to provide an improved method of producing from pine wood a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons which overcomes the disadvantages of the earlier process of producing such a resin.

It is a further object of this invention to provide a method of producing from pine wood a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons by a process which is inherently more adaptable to commercial plant production than prior methods.

Other objects of the invention will appear from the description of my improved process hereinafter.

In accordance with the method embodying this invention, pine wood, preferably that from the southern long leaf pine, in the form of stump wood, root or "top" wood is extracted with a coal tar hydrocarbon such as, for example, benzol, toluol, xylol, etc. The pine wood may be steamed before extraction with the coal tar hydrocarbon or the extraction may be carried out without previous steaming of the wood. The coal tar hydrocarbon removes from the pine wood the rosin and the resin which is soluble in alcohol but insoluble in light petroleum hydrocarbon. Where the pine wood has not been previously steamed, turpentine and pine oil will also be extracted by the coal tar hydrocarbon. The coal tar hydrocarbon solution is then evaporated to remove the coal tar hydrocarbon and the turpentine and pine oil, if the latter are present in the extract. Where turpentine and pine oil are present in the extract, they will be evaporated off after the coal tar hydrocarbon has been removed.

The solid extract obtained is a lark-colored residue comprising a mixture of FF wood rosin and the petroleum hydrocarbon-insoluble resin. This solid residue is then extracted with a solvent mixture comprising a light petroleum hydrocarbon and another liquid solvent which is capable of substantial immiscibility with the petroleum hydrocarbon at normal temperatures and which is a solvent for the resin portion of the said solid extract which is insoluble in light petroleum hydrocarbons. The proportion of the light petroleum hydrocarbon present in the said solvent mixture is sufficient to dissolve the FF wood rosin of the solid residue and is generally of such an amount as to provide a light petroleum hydrocarbon solution which will contain the FF wood rosin in an amount within the range of about 18% to about 28% by weight. The proportion of the other liquid solvent present in the solvent mixture which is a solvent for the petroleum hydrocarbon-insoluble resin portion of the said solid residue is such as to be sufficient to dissolve substantially all of the resin portion of the solid residue which is insoluble in light petroleum hydrocarbons and insufficient to permit the solution of any appreciable amount of the rosin in the second solvent.

When the solid residue from the coal tar hydrocarbon extraction of the pine wood has been sufficiently extracted by the solvent mixture to dissolve substantially all of the resinous matter, the solvent solution obtained is permitted to settle at a temperature at which two separate layers will form. The two solutions are then separated and the petroleum hydrocarbon solution evapo-

rated to recover petroleum hydrocarbon for reuse, if desired, leaving FF rosin of marketable grade. The solvent is also evaporated from the solution of the petroleum hydrocarbon-insoluble resin to recover the resin which is soluble in alcohol but insoluble in light petroleum hydrocarbons.

Having described my improved method in broad terms, I will now proceed to describe the specific steps and features of the improved method with greater particularity. Coal tar hydrocarbons, such as, for example, benzol, toluol, xylol, etc., are particularly well suited for the first step of my process, namely, the extraction of pine wood, since they have the property of extracting from pine wood, such as Southern Long Leaf pine, resinous material not extracted from such wood by the use of gasoline, or other light petroleum hydrocarbons. They will, therefore, extract from the pine wood a larger quantity of resinous material than may be obtained by use of petroleum hydrocarbons. Thus, the resinous extract will amount to about 0.9 barrel per ton of wood with use of gasoline, whereas with the use of benzol, toluol, xylol, etc., I am able to extract from a ton of the same grade of pine wood about 1.13 barrels of resin. This resin obtained with coal tar hydrocarbons generally contains from about 8% to about 30% or more of resinous material which is insoluble in petroleum hydrocarbons. The extraction of the pine wool with coal tar hydrocarbons, with or without preliminary steaming of the wood chips to remove the turpentine and pine oil content, may be accomplished in any suitable manner, such as, for example, by flooding the pine wood chips with the solvent with or without the use of heat. After the extraction of the chips is sufficiently complete, the coal tar hydrocarbon solution is drawn off from the chips and the solvent evaporated and reused in the process, if desired. Evaporation of the coal tar hydrocarbon leaves turpentine, pine oil, rosin and the petroleum hydrocarbon-insoluble resin, all in admixture. In the case of extraction of steamed wood, the turpentine and pine oil content will be greatly reduced. The turpentine and pine oil are then removed by distillation, leaving a dark colored residue comprising a mixture of FF wood rosin and the petroleum hydrocarbon-insoluble resin.

As the next step in my improved process the dark colored solid residue obtained after exaporation of the coal tar hydrocarbon and any turpentine and pine oil which may be present is subjected to treatment with a solvent mixture comprising a light petroleum hydrocarbon component which will be a solvent for the FF wood rosin contained in the solid residue, and another liquid solvent which will be a solvent for the petroleum hydrocarbon-insoluble resin portion of the solid resinous extract. This solvent mixture will be capable of dissolving substantially all of the solid extract from the coal tar hydrocarbon extraction. The light petroleum hydrocarbon solvent component may be any solvent such as petroleum ether, gasoline, heptane, hexane, etc., or an operable equivalent therefor. The other liquid solvent may be any solvent which is capable of dissolving the petroleum hydrocarbon-insoluble resin portion of the coal tar hydrocarbon extract and which is capable of immiscibility at some definite temperature with the petroleum hydrocarbon solution. At such a solvent, I have found to be useful solvents such as, for example, furfural, aniline, phenol, usually liquified by water, furfuryl alcohol, nitromethane, ethylene chlorhydrin, ethyl alcohol, methyl alcohol, methyl thiocyanate, methyl lactate, 2-nitro-1 propanol, liquid sulfur dioxide, etc. I prefer to use such solvents which will be capable of immiscibility with the petroleum hydrocarbon solvent at a temperature within the range of about 5° F. to about 125° F. and which are capable of miscibility with the petroleum hydrocarbon solvent at elevated temperatures.

The particular composition of the solid resinous extract from the coal tar hydrocarbon solution will determine to a certain extent the proportions of light petroleum hydrocarbon desirable in the solvent mixture. I prefer to use an amount of light petroleum hydrocarbon solvent in the solvent mixture which will dissolve all of the FF rosin contained in the coal tar hydrocarbon extract to give a petroleum hydrocarbon solution containing within the range of about 18% to about 28% by weight of dissolved FF rosin. If a smaller amount of petroleum hydrocarbon is used, I find that some of the petroleum hydrocarbon-insoluble resin constituent dissolves in the light petroleum hydrocarbon-rosin solution, thus lowering the yield of the petroleum hydrocarbon-insoluble resin and also contaminating the FF rosin. On the other hand, if a larger amount of petroleum hydrocarbon solvent is used in the solvent mixture a greater amount of the petroleum hydrocarbon solvent must be removed by evaporation in the recovery of the rosin. For purposes of economy and efficiency in the process, this is undesirable.

The amount of the liquid solvent for the petroleum hydrocarbon-insoluble resin portion of the coal tar hydrocarbon extract used in the solvent mixture is rather critical for satisfactory operation of my process. I have found that if the proportion of this solvent present in the solvent mixture is such as to be sufficient to dissolve substantially all of the resin portion of the solid coal tar hydrocarbon extract which is insoluble in light petroleum hydrocarbons, successful operation of the improved process is possible. I have found, further, that the amount of this solvent must be also insufficient to dissolve any appreciable amount of the FF wood rosin. Thus, the proportion of this second solvent must be varied with the petroleum hydrocarbon-insoluble resin content of the coal tar hydrocarbon extract. For example, if any large excess of the second solvent over such an amount is included in the solvent mixture, it will be difficult to effect a satisfactory separation of the rosin from the petroleum hydrocarbon-insoluble resin component. The amount of the second solvent used in the solvent mixture is further dependent on the temperature at which the two layers of the solution will be permitted to separate.

The treatment of the solid residue obtained from the coal tar hydrocarbon extraction with the solvent mixture described above may be carried out at normal temperatures or at elevated temperatures. The treatment is preferably carried out at such a temperature that the light petroleum hydrocarbon solvent and the other liquid solvent present in the mixture will form a homogeneous solution. This temperature will be dependent on the particular solvents employed in the solvent mixture. A preferable temperature of treatment will be within the range of about 150° F. to about 165° F. The treatment will be continued for a time which will be sufficient to dissolve substantially all of the soluble components of the extract. Generally, complete

solution occurs, but small amounts of extraneous matter may be present and may be removed in any convenient manner.

The temperature of the solvent solution is then brought to a point at which the two solutions will be immiscible with each other. This temperature again will depend on the particular solvents being employed and also on the amount of dissolved components in the solution. Generally speaking, the temperature of separation will fall within the range of about 5° F. to about 125° F. In the case of furfural, for example, when used with gasoline, the temperature of separation which gives the best results is a temperature within the range of about 85° F. to about 95° F. The two solutions may then be separated in any convenient manner such as by siphoning or by decantation or by separation in any suitable form of separator. The evaporation of the light petroleum hydrocarbon from the rosin solution will then leave the FF rosin of marketable grade as a residue. Evaporation of the other liquid solvent from the solution containing the petroleum hydrocarbon-insoluble resin will leave as a residue the latter resin. The FF rosin obtained and the petroleum hydrocarbon-insoluble resin may, if desired, be purified in any suitable manner.

As a specific example of the process in accordance with this invention, pine wood chips were extracted with benzol at a pressure of about 70 pounds per square inch gauge at a maximum temperature of about 260° F. without first steaming the chips. After the extraction was complete the benzol was removed by evaporation and the turpentine and pine oil subsequently removed by evaporation. The dark colored solid resinous extract contained about 80% FF wood rosin and about 20% petroleum hydrocarbon-insoluble resin. This extract in the molten condition at a temperature of about 300° F. was fed to a centrifugal pump simultaneously with a solvent mixture containing 90% gasoline and 10% furfural by weight in the proper proportion to produce a gasoline layer containing about 25% of dissolved rosin after cooling. The hot solution was forced through a set of water jacketed cooling coils of sufficient capacity to cool the solvent mixture to a temperature of 85° F. to 95° F. and passed into a separator. After permitting the solution to separate, the subnatant or furfural layer was drawn off and separated from the gasoline layer. The gasoline solution containing about 25% by weight of FF wood rosin was then evaporated to free the rosin. The furfural solution containing approximately 55% by weight of the petroleum hydrocarbon-insoluble resin was evaporated to free the latter resin.

While the exact chemical composition of the petroleum hydrocarbon-insoluble resin produced in accordance with the process of this invention is not known to me, I have found that it will be substantially completely soluble in 95% ethyl alcohol, will have an acid number within the range of about 90 to 110, a melting point within the range of about 95° C. to about 125° C. (Hercules drop method), a methoxyl content of about 3% to about 6% and a petroleum naphtha insoluble content of about 90% to about 99%.

The highly desirable advantages of my improved process of producing an alcohol-soluble resin from pine wood which is substantially insoluble in light petroleum hydrocarbons will be readily apparent to those skilled in the art.

It will be understood that the improved method described in accordance with my invention does not require for its practical adaptation the use of any particular form of apparatus, and it will be understood that the details given herein for carrying out the improved method are for the purpose of illustration only and are not to be construed as limitation upon the scope of the invention.

What I claim and desire to protect by Letters Patent is:

1. The method of producing a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons, which includes extracting pine wood with a coal tar hydrocarbon to produce an extract containing coal tar hydrocarbon, volatile materials and normally solid resinous materials, evaporating the coal tar hydrocarbon and volatile portions of the extract to produce a solid residue comprising a rosin portion soluble in light petroleum hydrocarbons and a resin portion insoluble in light petroleum hydrocarbons, treating said solid residue with a solvent mixture comprising a light petroleum hydrocarbon and another liquid solvent which is capable of substantial immiscibility with the petroleum hydrocarbon at normal temperatures and which is a solvent for the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons, the amount of light petroleum hydrocarbon present in said solvent mixture being sufficient to dissolve the components of the said solid residue which are soluble in the light petroleum hydrocarbon to give a light petroleum hydrocarbon solution containing within the range of about 18% to about 28% by weight of dissolved rosin, the amount of the other liquid solvent which is a solvent for the petroleum hydrocarbon-insoluble resin portion of the said solid residue present in said solvent mixture being sufficient to dissolve substantially all of the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons but insufficient to dissolve any appreciable amount of the rosin, then permitting the solution to settle at a temperature at which two separate layers will form, separating the two solutions and recovering rosin from the light petroleum hydrocarbon solution and a petroleum hydrocarbon-insoluble resin from the other solution.

2. The method of producing a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons, which includes steaming pine wood chips to remove volatile substances therefrom, extracting the steamed wood chips with a coal tar hydrocarbon, evaporating the coal tar hydrocarbon and other volatile constituents of the extract to produce a solid residue comprising a rosin portion soluble in light petroleum hydrocarbons and a resin portion insoluble in light petroleum hydrocarbons, treating said solid residue with a solvent mixture comprising a light petroleum hydrocarbon and another liquid solvent which is capable of substantial immiscibility with the petroleum hydrocarbon at normal temperatures and which is a solvent for the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons, the amount of light petroleum hydrocarbon present in said solvent mixture being sufficient to dissolve the components of the said solid residue which are soluble in the light petroleum hydrocarbon to give a light petroleum hydrocarbon solution containing within the range of about 18% to about 28% by weight of dissolved rosin, the amount of the other liquid solvent which is a solvent for the

petroleum hydrocarbon-insoluble resin portion of the said solid residue present in said solvent mixture being sufficient to dissolve substantially all of the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons but insufficient to dissolve any appreciable amount of the rosin, then permitting the solution to settle at a temperature at which two separate layers will form, separating the two solutions and recovering rosin from the light petroleum hydrocarbon solution and a petroleum hydrocarbon-insoluble resin from the other solution.

3. The method of producing a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons which includes extracting pine wood with a coal tar hydrocarbon to produce an extract containing coal tar hydrocarbon, volatile materials and normally solid resinous materials, evaporating the coal tar hydrocarbon and volatile portions of the extract to produce a solid residue comprising a rosin portion soluble in light petroleum hydrocarbons and a resin portion insoluble in light petroleum hydrocarbons, treating said solid residue with a solvent mixture comprising a light petroleum hydrocarbon and furfural, the amount of light petroleum hydrocarbon present in said solvent mixture being sufficient to dissolve the components of the said solid residue which are soluble in the light petroleum hydrocarbon to give a light petroleum hydrocarbon solution containing within the range of about 18% to about 28% by weight of dissolved rosin, the amount of the furfural present in said solvent mixture being sufficient to dissolve substantially all of the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons but insufficient to dissolve any appreciable amount of the rosin, then permitting the solution to settle at a temperature at which two separate layers will form, separating the two solutions and recovering rosin from the light petroleum hydrocarbon solution and a petroleum hydrocarbon-insoluble resin from the furfural solution.

4. The method of producing a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons which includes extracting pine wood with a coal tar hydrocarbon to produce an extract containing coal tar hydrocarbon, volatile materials and normally solid resinous materials, evaporating the coal tar hydrocarbon and volatile portions of the extract to produce a solid residue comprising a rosin portion soluble in light petroleum hydrocarbons and a resin portion insoluble in light petroleum hydrocarbons, treating said solid residue with a solvent mixture comprising a light petroleum hydrocarbon and furfural, the amount of light petroleum hydrocarbon present in said solvent mixture being sufficient to dissolve the components of the said solid residue which are soluble in the light petroleum hydrocarbon to give a light petroleum hydrocarbon solution containing within the range of about 18% to about 28% by weight of dissolved rosin, the amount of furfural present in said solvent mixture being sufficient to dissolve substantially all of the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons to give a concentration of about 50% to about 60% by weight of said resin portion in the furfural, then permitting the solution to settle at a temperature at which two separate layers will form, separating the two solutions and recovering rosin from the light petroleum hydrocarbon solution and a petroleum hydrocarbon-insoluble resin from the furfural solution.

5. The method of producing a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons which includes extracting pine wood with a coal tar hydrocarbon to produce an extract containing coal tar hydrocarbon, volatile materials and normally solid resinous materials, evaporating the coal tar hydrocarbon and volatile portions of the extract to produce a solid residue comprising a rosin portion soluble in light petroleum hydrocarbons and a resin portion insoluble in light petroleum hydrocarbons, treating said solid residue with a solvent mixture comprising a light petroleum hydrocarbon and furfural, the amount of light petroleum hydrocarbon present in said solvent mixture being sufficient to dissolve the components of the said solid residue which are soluble in the light petroleum hydrocarbon to give a light petroleum hydrocarbon solution containing within the range of about 18% to about 28% by weight of dissolved rosin, the amount of the furfural present in said solvent mixture being sufficient to dissolve substantially all of the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons to give a concentration of about 50% to about 60% by weight of said resin portion in the furfural, then permitting the solution to settle at a temperature within the range of about 5° F. to about 125° F. to form two layers, separating the two solutions and recovering rosin from the light petroleum hydrocarbon solution and a petroleum hydrocarbon-insoluble resin from the furfural solution.

6. The method of producing a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons which includes extracting pine wood with a coal tar hydrocarbon to produce an extract containing coal tar hydrocarbon, volatile materials and normally solid resinous materials, evaporating the coal tar hydrocarbon and volatile portions of the extract to produce a solid residue comprising a rosin portion soluble in light petroleum hydrocarbons and a resin portion insoluble in light petroleum hydrocarbons, treating said solid residue with a solvent mixture comprising a light petroleum hydrocarbon and furfural, the amount of light petroleum hydrocarbon present in said solvent mixture being sufficient to dissolve the components of the said solid residue which are soluble in the light petroleum hydrocarbon to give a light petroleum hydrocarbon solution containing within the range of about 18% to about 28% by weight of dissolved resin, the amount of the furfural present in said solvent mixture being sufficient to dissolve substantially all of the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons to give a concentration of about 50% to about 60% by weight of said resin portion in the furfural, then permitting the solution to settle at a temperature within the range of about 85° F. to about 95° F. to form two layers, separating the two solutions and recovering rosin from the light petroleum hydrocarbon solution and a petroleum hydrocarbon-insoluble resin from the furfural solution.

7. The method of producing a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons which includes extracting pine wood with a coal tar hydrocarbon to produce an extract containing coal tar hydrocarbon, volatile materials and normally solid resinous materials, evaporating the coal tar hydro-

carbon and volatile portions of the extract to produce a solid residue, said solid residue containing within the range of about 8% to about 30% of resin portion insoluble in light petroleum hydrocarbons, treating said solid residue with a solvent mixture comprising gasoline and furfural, the amount of gasoline present in said solvent mixture being sufficient to dissolve the components of the said solid residue which are soluble in the gasoline to give a gasoline solution containing within the range of about 18% to about 28% by weight of dissolved rosin, the amount of furfural present in said solvent mixture being sufficient to dissolve substantially all of the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons but insufficient to dissolve any appreciable amount of the rosin, then permitting the solution to settle at a temperature at which two separate layers will form, separating the two solutions and recovering rosin from the gasoline solution and a petroleum hydrocarbon-insoluble resin from the furfural solution.

8. The method of producing a resin which is soluble in alcohol but substantially insoluble in light petroleum hydrocarbons which includes extracting pine wood with benzol to produce an extract containing benzol, volatile materials and normally solid resinous materials, evaporating the benzol and volatile portions of the extract to produce a solid residue containing within the range of about 8% to about 30% of a resin portion insoluble in light petroleum hydrocarbons, treating said solid residue with a solvent mixture comprising gasoline and furfural, the amount of gasoline present in said solvent mixture being sufficient to dissolve the components of the said solid residue which are soluble in gasoline to give a gasoline solution containing within the range of about 18% to about 28% by weight of rosin, the amount of furfural present in said solvent mixture being sufficient to dissolve substantially all of the resin portion of the said solid residue which is insoluble in light petroleum hydrocarbons to give a concentration of about 50% to about 60% by weight of said resin portion in the furfural, then permitting the solution to settle at a temperature within the range of about 85° F. to about 95° F. to form two layers, separating the two solutions and recovering rosin from the gasoline solution and a petroleum hydrocarbon-insoluble resin from the furfural solution.

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