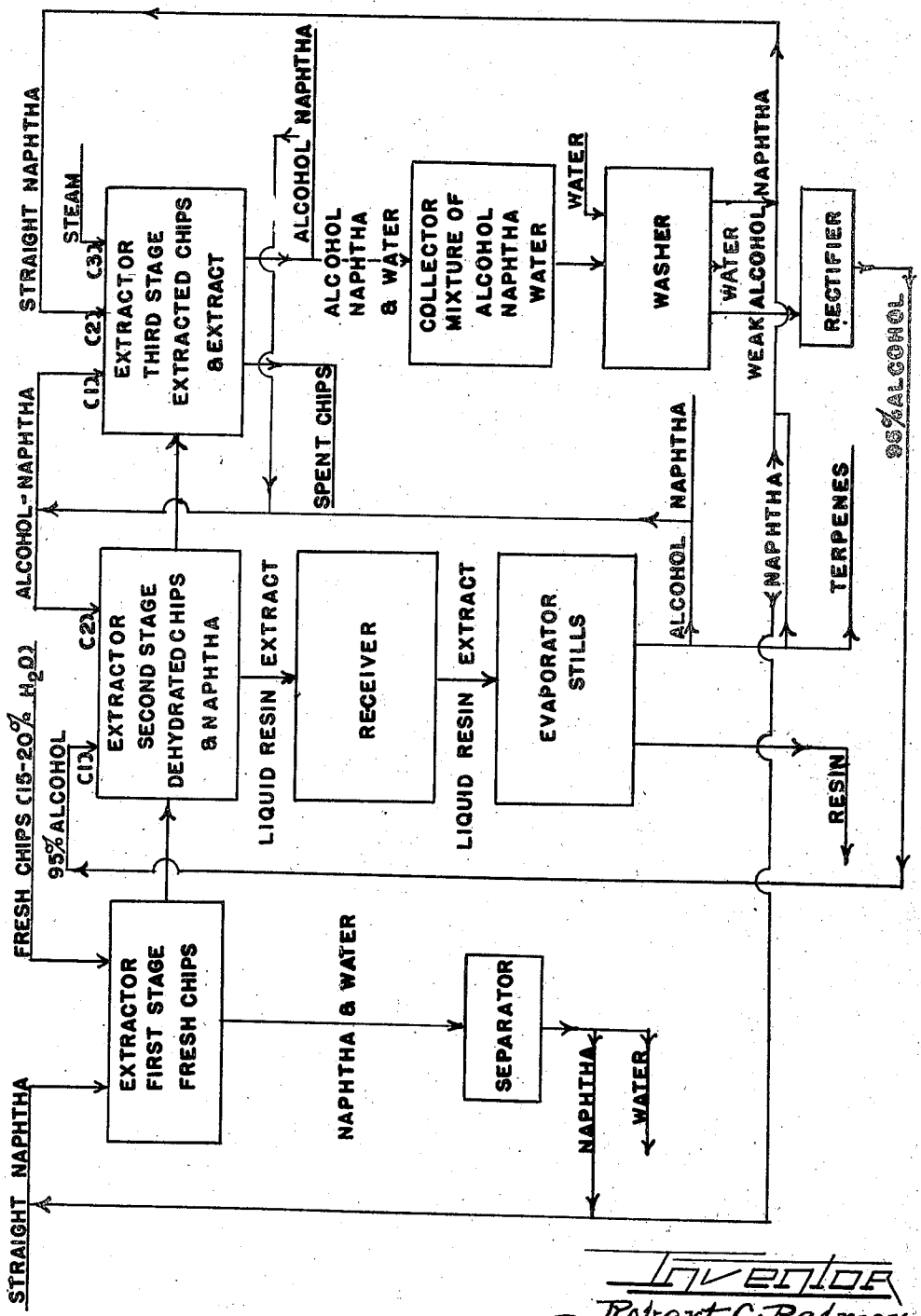
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PROCESS OF EXTRACTING RESINOUS WOOD

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PROCESS OF EXTRACTING RESINOUS WOOD

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This invention relates to a process of extracting resinous wood. More particularly the invention relates to a process of extracting resinous wood with a mixture of a petroleum solvent and an alcohol to obtain a resinous product in much higher yield than petroleum solvent alone. From such a product can be recovered a resin that is substantially petroleum-insoluble and the yield of this resin is several times that when petroleum solvent alone is used for extraction. Also a rosin may be recovered in higher yield from the wood than when using petroleum solvent that may be further purified in accordance with well-known processes to yield a pale wood rosin.

It has heretofore been proposed to employ an alcohol in the extraction of resinous woods, and also to extract resinous woods with a coal tar hydrocarbon to obtain a resin that is insoluble in light petroleum hydrocarbons, but to the best of my knowledge no one has heretofore proposed to extract resinous woods with a mixture of an alcohol and a petroleum solvent.

I have found that there are several advantages in the use of a mixed solvent comprising an alcohol and a petroleum solvent. Such a mixed solvent is economical because a major proportion of the mixture is the less expensive petroleum solvent. Moreover, a mixed solvent of alcohol and petroleum solvent does not present the health hazards that are present when using benzene, which is a commercial solvent commonly employed in the extraction of pinewood.

In addition, the extracting power of the mixed solvent used in accordance with my invention exceeds that of coal tar solvents so long as the concentration of alcohol in the mixed solvent is about 30% by volume or greater. For instance, pine stumpwood chips were completely extracted with a petroleum solvent to yield 20.5% resin (free of terpenes) by weight, based upon wood of 15% moisture content by weight. A sample of this same wood was completely extracted with benzene to yield 24% of resin on the same basis. Another sample of the same wood was completely extracted with a mixture of 95% denatured alcohol and a petroleum solvent, the mixture containing 33% by volume of 95% alcohol, to yield 26% of resin on the same basis. In another series of complete extractions of wood chips taken from the same lot to compare the extraction efficiency of different alcohols in each case, using 33% by volume of the alcohol and 67% by volume of the petroleum solvent, in the case of 95% ethyl alcohol, the yield was 24.5% of resin; with methyl alcohol the yield was 25.1%; with isopropyl alcohol the yield was 23.8% and with secondary butyl alcohol the yield was 24%.

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Ethyl alcohol, in the form of ordinary commercial denatured alcohol, is preferred because of its availability and the ease with which it may be handled, but the process is not limited to ethyl alcohol. Methyl alcohol, isopropyl alcohol, secondary butyl alcohol and others can be used so long as the alcohol exhibits the desired solvent power when diluted with the petroleum solvent.

Ordinary 95% ethyl alcohol is miscible in all proportions with a petroleum solvent at temperatures above about 35° C. The mixture of alcohol and petroleum solvent that I prefer to use is one containing between 30 and 35% of alcohol and between 65 and 70% of petroleum solvent, by volume. These proportions, however, are not critical, since my process operates satisfactorily so long as the mixed alcohol-petroleum solvent contains at least 30% by volume of 95% ethyl alcohol, or the equivalent of another alcohol. The advantages of my process are not fully realized, however, if more than about 75% of alcohol by volume of the mixed alcohol-petroleum solvent is used.

Mixtures of alcohol and petroleum can be readily kept from separating into two layers if the strength of the alcohol with respect to the water content is kept sufficiently high. While it would be possible, although not so economical, to allow separation to occur between the alcohol and petroleum solvent, and then recover the alcohol by rectification, and reintroduce the alcohol into the hot naphtha at the point of extraction, the use of a premixture of the alcohol and petroleum solvent is greatly to be preferred for ease of recovery and re-use, as will be apparent from the following description.

An important discovery, made in my study of the use of a mixed solvent such as above described, greatly simplifies the operation as regards the maintenance of a solvent system which will not separate into two layers at ordinary atmospheric temperatures, a phenomenon that would otherwise occur in actual practice. This discovery was that partially dehydrated pinewood chips act as a dehydrating agent for alcohol dissolved in a petroleum solvent where the alcohol is about 95% strength, so that the mixed solvent recovered from the extract contains alcohol of a concentration of over 95% with respect to the water content present. The dehydration of the mixed alcohol-petroleum solvent is first noticed when the water content of the wood chips being extracted goes below 10%, and is markedly notice-

able when the water content of the chips is below 8%. When wood chips having a water content as low as 5% are extracted, the concentration of alcohol with respect to the alcohol-water solution recovered from the extract was found to be as high as 98%.

In order to bring the water content of the pine-wood chips from its normal value of between 15 and 20% moisture by weight down to below 10% by weight, the chips are immersed in a petroleum solvent and the solvent brought to a boil under distillation conditions. Alternatively, the chips may be first steamed to remove turpentine and some of the high boiling terpenes and then boiled with a petroleum solvent under distillation conditions. Water distills off as vapor with the petroleum solvent vapor, thereby reducing the water content of the chips. Accordingly, it is possible by carrying the distillation far enough to reduce the water content of the chips to below 10% by weight. By this method, it has been possible to devise a very practical extraction process using an alcohol-petroleum solvent mixture.

It is, therefore, an important object of this invention to provide a process for the extraction of resinous wood for the economical recovery of a resinous product in good yield.

It is a further important object of this invention to provide a process of extracting resinous wood that includes the preliminary partial dehydration of the wood followed by the extraction of the partially dehydrated wood by means of a hot mixed solvent containing an alcohol and a petroleum solvent.

It is a further important object of this invention to provide an economical and practical process for the extraction of resinous wood in which the solvent used is a mixture of an alcohol and a petroleum hydrocarbon in such proportions as to be miscible under the temperature conditions to which the mixture may be subjected in the system, whereby separation of the alcohol and petroleum hydrocarbon into layers is avoided.

It is a further important object of this invention to provide a process for the recovery of a resinous product from resinous wood, in accordance with which the resinous wood in the form of chips is first partially dehydrated and then extracted with a mixture of ordinary denatured ethyl alcohol and petroleum naphtha, the partially dehydrated chips serving to maintain the alcohol as at least 95% alcohol with respect to its water content and thereby facilitating the maintenance of the alcohol-naphtha mixture in a single liquid phase under the temperature conditions obtaining in the system.

Other and further important objects of this invention will become apparent from the following description and appended claims.

The drawing comprises a flow sheet illustrating the process of my invention.

In accordance with my process, fresh chips of a resinous wood, such as pine stumps, are placed in a suitable extractor. The chips may, if desired, be first steamed to remove some turpentine and pine oil, and then subjected to the first stage of the process illustrated on the accompanying flow sheet, or the preliminary steaming may be omitted. A sufficient amount of a petroleum solvent, such as a light petroleum hydrocarbon, is added to immerse the wood chips. The petroleum solvent that is preferred is a naphtha that is not so low boiling as to give excessive vapor losses and yet one the dry point of which is sufficiently low to permit complete separation from pinenes, such as turpentine, by fractional distillation. A petroleum naphtha having a dry point between 100 and 120° C. is a specific example of a suitable petroleum solvent. Other normally liquid aliphatic hydrocarbons are intended to be included within the term "petroleum solvent."

The mass of wood chips immersed in the petroleum solvent is brought to the boiling point of the solvent under distillation conditions, either at atmospheric or superatmospheric pressure, and continued until the desired degree of dehydration of the wood chips has been reached, as determined by measuring the water obtained from the condensed vapors coming from the extractor. By this means, the water content of the wood chips can be reduced from the normal value of from 15 to 20% by weight down to below 10% by weight. When this point has been reached, that portion of the liquid petroleum solvent extract that will readily drain from the wood chips is discharged from the extractor. A substantial portion, as much as from 20 to 35%, of the solvent necessary to immerse the chips is left behind adsorbed in the wood.

Ordinary denatured ethyl alcohol (95% ethyl alcohol) as shown in the second stage of the extraction in the accompanying flow sheet, is next introduced into the extraction vessel in an amount sufficient to bring the residual petroleum solvent up to the desired alcohol concentration of the mixed solvent, which concentration will ordinarily be at least 30% of 95% alcohol by volume of the mixed solvent. The alcohol is allowed to reflux for a short period to effect a uniform admixture with the residual petroleum solvent. The extractor is then filled with a mixed alcohol-petroleum solvent from another source and the extraction step carried out either at atmospheric pressure or under superatmospheric pressure, as desired. The percentage of 95% alcohol in the extracting solvent may be considerably higher than 30% by volume, but, in general, no increase in resin yield has been observed even when the percentage of alcohol is carried as high as 50% by volume of the mixed solvent. The extraction may suitably be carried out at a gauge pressure of 25 pounds per sq. in., which required a temperature of only about 90 to 100° C. The extraction of the chips is carried to substantially complete removal of the resinous content of the wood by dissolution into the extracting solvent.

At the end of the extraction period, the liquid contents of the extractor are discharged, preferably by downward displacement, into a receiver, from which the liquid resin extract is conducted to evaporator stills, or any other conventional equipment, for the recovery of the resin extracted as well as to separate the mixed solvent for recycling.

In the evaporation of the mixed solvent from the liquid resin extract, alcohol is readily concentrated by fractionation even without the benefit of a fractionating column. This is particularly true of alcohol-petroleum solvent mixtures where the concentration of alcohol with respect to water present is above 95%. All of the alcohol from a 33% alcohol, 67% petroleum solvent mixture can be distilled off before all of the naphtha is distilled off. This makes it possible to recover terpenes, which may have been extracted, since after the alcohol has been distilled off there is left in the concentrated extract naphtha and terpenes free of alcohol. As pointed out above, a naphtha is preferably used that can be readily fractionated from terpenes.

After discharging the liquid resin extract from the extractor, as much more of the mixed solvent in a heated condition is introduced as will effectively rinse the extracted wood free of extract. This may be done either at atmospheric or at superatmospheric pressure, as desired, but is preferably carried out under pressure by downward displacement. It may also be conducted in a cycle system with several extractors in series in different stages of extraction or rinsing. No attempt has been made in the accompanying flow sheet to illustrate a cycle system, but for the sake of simplicity the flow sheet does show the extractor in three different stages: a first stage in which the extractor is charged with fresh chips and subjected to the action of boiling straight naphtha to partially dehydrate the chips; a second stage in which the partially dehydrated chips and naphtha remaining from the first stage are fortified with 95% alcohol and with an alcohol-naphtha mixture for effecting the extraction step; and a third stage in which the extracted chips containing extract from the second stage are rinsed with mixed solvent, then with straight naphtha, then heated to remove the remaining alcohol and finally steamed. It is thus obvious from the flow sheet that the partial dehydration of the chips, extraction of the chips and the rinsing of the extracted chips could be carried out in a cycle system.

After the rinsing of the extracted chips with mixed solvent is complete, the chips are given a final rinse with straight petroleum solvent, containing no alcohol. This amounts in effect to a displacement of the mixed solvent with the petroleum solvent, so that when the concentration of alcohol in the effluent shows a decrease as compared with the alcohol concentration in the preferred alcohol-petroleum solvent mixture, the displacement is stopped. This avoids reducing the alcohol content of the effluent solvent, since this effluent solvent being displaced is to be used for extraction, as indicated on the flow sheet, or for rinsing.

The next step in the process is to free the extracted wood from alcohol. This is done by supplying indirect heat, such as steam under pressure in a jacket or coil located around or in the extractor, and distilling out the alcohol by boiling off the petroleum solvent. This may be done under pressure or at atmospheric pressure, as desired. The use of pressure hastens the rate of distilling off the alcohol. Any residual water not removed from the wood in the first extraction-dehydration stage, as well as water adsorbed from the alcohol, is distilled off along with the alcohol. In usual practice, if the distillation of the petroleum solvent and alcohol and/or water is conducted at, say, about 25 lbs. gauge pressure, all of the alcohol and/or water is removed from the wood chips by the time approximately two-thirds of the solvent required to immerse the wood chips has been distilled off.

The wood chips are then freed of any remaining petroleum solvent by any of the methods commonly practiced in the pinewood extraction industry, such as by direct steaming.

The alcohol-petroleum solvent distilled from the wood in this step of the process is below a 30% alcohol content (95%) by volume of the mixed alcohol-petroleum solvent, and the alcohol itself is below 95% concentration with respect to the water present. The alcohol is then recovered free of petroleum solvent by further washing of the distillate with water, after which the weak alcohol recovered is rectified back to 95% concentration. Enough 95% alcohol is thus provided to introduce into the extraction step in the second stage, as illustrated in the flow sheet. The rectified 95% alcohol can also be used in the system to make up for vapor losses.

By this novel system, therefore, only a minor proportion of the total alcohol necessary for the extraction need be separated from the petroleum solvent and recovered by rectification.

The resin recovered from the liquid resin extract contains an abnormally high proportion of naphtha-insoluble resin and, of course, wood rosin. The naphtha-insoluble resin fraction may be separated by adding naphtha gradually, with agitation, to the hot liquid resin, and continuing dilution with cold naphtha to the desired concentration. After settling and cooling, the bulk of the clear solution containing wood rosin can be decanted to tanks for water washing. The petroleum-insoluble resin is melted out of the settling cone and removed to recovery stills, from which it is recovered free from naphtha. The resulting petroleum-insoluble resin is not 100% soluble in alcohol.

The clear naphtha solution containing wood rosin can be further processed in the usual manner for the production of pale wood rosin.

It will, of course, be understood that various details of the process may be varied through a wide range without departing from the principles of this invention and it is, therefore, not the purpose to limit the patent granted hereon otherwise than necessitated by the scope of the appended claims.

I claim as my invention:

1. The process of extracting resinous wood which comprises at an elevated temperature extracting the wood in subdivided form and containing less than 10% moisture by weight with a mixed solvent containing a petroleum solvent and from 28.5% to 71.25% of said mixture of a hydrous monohydric alcohol containing less than five carbon atoms, the ratio of alcohol to water in said solvent being at least 19 to 1, to form a liquid resin extract and separating a resin from said extract.

2. The process of extracting resinous wood which comprises extracting resinous wood in the form of chips containing less than 10% moisture by weight with a mixed solvent comprising a petroleum hydrocarbon and a hydrous monohydric alcohol containing less than five carbon atoms, said solvent containing from 28.5% to 71.25% of said alcohol and the ratio of alcohol to water in said solvent being at least 19 to 1, separating the resulting liquid resinous extract from the wood and recovering the resin content from said extract.

3. In the process of recovering from resinous wood a resin that is relatively insoluble in a light petroleum hydrocarbon, the step of extracting the resinous wood in chip form and containing less than 10% of moisture by weight with a hot solution of a light petroleum hydrocarbon and a hydrous monohydric alcohol containing less than five carbon atoms, said solvent containing from 28.5% to 71.25% of said alcohol and the ratio of alcohol to water in said solvent being at least 19 to 1.

4. In the process of recovering from resinous wood a resin that is relatively insoluble in a light petroleum hydrocarbon, the steps of extracting the resinous wood with a hot solution of hydrous ethyl alcohol and a light petroleum hydrocarbon,

said solution containing from 28.5% to 33.25% ethyl alcohol and from 70% to 65% of said light hydrocarbon by volume of said solution, the ratio of ethyl alcohol to water in said solution being at least 19 to 1.

5. In the process of recovering from resinous wood a resin that is relatively insoluble in a light hydrocarbon, the steps of subjecting the resinous wood to the action of a hot liquid aliphatic hydrocarbon under distillation conditions to reduce the moisture content of the wood to less than 10% by weight, and extracting the partially dehydrated wood with a hot mixed solvent comprising a liquid aliphatic hydrocarbon and from 28.5% to 71.25% of a hydrous monohydric alcohol containing less than five carbon atoms, the ratio of alcohol to water in said solvent being at least 19 to 1.

6. In the process of recovering from resinous wood a resin that is relatively insoluble in a light petroleum hydrocarbon, the steps of subjecting the resinous wood to the action of a hot liquid aliphatic hydrocarbon under distillation conditions to reduce the moisture content of the wood to less than 10% by weight, and extracting the partially dehydrated wood with a hot mixed solvent comprising from 28.5% to 71.25% of hydrous ethyl alcohol and a light petroleum hydrocarbon, the ratio of alcohol to water in said solvent being at least 19 to 1.

7. In the process of recovering from resinous wood a resin that is relatively insoluble in a light hydrocarbon, the steps of subjecting the resinous wood to the action of a hot liquid aliphatic hydrocarbon under distillation conditions to reduce the moisture content of the wood to less than 10%, and extracting the partially dehydrated wood with a mixed solvent comprising from 28.5% to 71.25% of a hydrous monohydric alcohol containing less than five carbon atoms and a light petroleum hydrocarbon, the ratio of said alcohol to water in said solution being at least 19 to 1.

8. The process of recovering from resinous wood a resin that is relatively insoluble in a light petroleum hydrocarbon, which comprises partially dehydrating chips of such resinous wood to less than 10% moisture content by weight, extracting the partially dehydrated chips with a hot mixture containing from 28.5% to 71.25% of a hydrous monohydric alcohol containing less than five carbon atoms and a liquid aliphatic hydrocarbon, the ratio of alcohol to water in said mixture being at least 19 to 1, separating a resinous residue from the resulting extract, and recovering a petroleum hydrocarbon-insoluble resin from said resinous residue.

9. The process of recovering from resinous wood a resin that is relatively insoluble in a light hydrocarbon, which comprises partially dehydrating chips of such resinous wood to less than 10% moisture content by weight by the action of a hot liquid aliphatic hydrocarbon under distillation conditions, adding a hydrous monohydric alcohol containing less than five carbon atoms to the resulting mass of partially dehydrated chips and the hydrocarbon to form a liquid mixture containing from 28.5% to 71.25% of said alcohol, the ratio of alcohol to water in said mixture being at least 19 to 1, separating a resinous residue from the resulting extract and recovering a petroleum hydrocarbon-insoluble resin from said resinous residue.

10. The process of recovering from resinous wood a resin that is relatively insoluble in a light petroleum hydrocarbon, which comprises partially dehydrating chips of such resinous wood to less than 10% moisture content by weight, extracting the partially dehydrated chips with a hot mixture containing from 28.5% to 71.25% of a hydrous monohydric alcohol containing less than five carbon atoms and a light petroleum hydrocarbon, the ratio of alcohol to water in said mixture being at least 19 to 1, distilling the resulting extract to separate the alcohol, the petroleum hydrocarbon, terpenes, and a resinous residue, and recovering a petroleum hydrocarbon-insoluble resin from said resinous residue.

11. In the process of extracting wood in chip form containing less than 10% moisture by weight with a mixture containing a petroleum solvent and from 28.5% to 71.25% of a hydrous monohydric alcohol containing less than five carbon atoms to form a liquid resin extract, the ratio of alcohol to water in said mixture being at least 19 to 1, and recovering a resin from said extract, the step of recovering said alcohol petroleum solvent mixture which comprises subjecting said liquid resin extract to distillation to distill off therefrom substantially all of the alcohol in admixture with petroleum solvent in proper proportion for reuse.

12. In the process of extracting resinous wood in chip form and containing less than 10% moisture by weight at an elevated temperature with a mixture containing from 28.5% to 71.25% of a hydrous monohydric alcohol containing less than five carbon atoms and a petroleum solvent to form a liquid resin extract, the ratio of alcohol to water in said mixture being at least 19 to 1, and recovering a resin from said extract, the steps of recovering said alcohol and petroleum solvent for reuse after rinsing the extracted wood with quantities of said mixture of alcohol and petroleum solvent to remove remaining extract from said chips, following with straight petroleum solvent to displace said mixture from said extracted chips and finally subjecting said extracted chips to heat to free the chips from alcohol, which steps comprise separately recovering a mixture of alcohol and petroleum solvent from said rinsing operation as long as the proportion of alcohol in said recovered mixture is at least 28.5%, adding water to the mixture of alcohol and petroleum solvent thereafter recovered from said rinsing operation in sufficient amount to form a tertiary mixture separable into petroleum solvent and aqueous alcohol fractions, separating the petroleum solvent from the diluted mixture to leave a dilute aqueous alcohol solution and rectifying said dilute alcohol solution to 95% strength alcohol.

13. In the process of recovering a resin by subjecting resinous wood to the action of a hot hydrocarbon under distillation conditions to reduce the moisture content to less than 10% by weight, extracting the partially dehydrated wood with a mixture containing from 28.5% to 71.25% of a hydrous monohydric alcohol containing less than five carbon atoms and a petroleum solvent to form a liquid resin extract, the ratio of alcohol to water in said mixture being at least 19 to 1 and recovering a resin from said extract, the steps of recovering the alcohol and petroleum solvent for reuse, which comprise recovering petroleum solvent and water from the partially dehydrated wood, separating and recovering said petroleum solvent and water from the partially dehydrated wood, separating and recovering said petroleum solvent from said water, and subjecting said liquid resin extract to distillation to distill

off therefrom substantially all of the alcohol in admixture with not more than 70% of petroleum solvent.

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