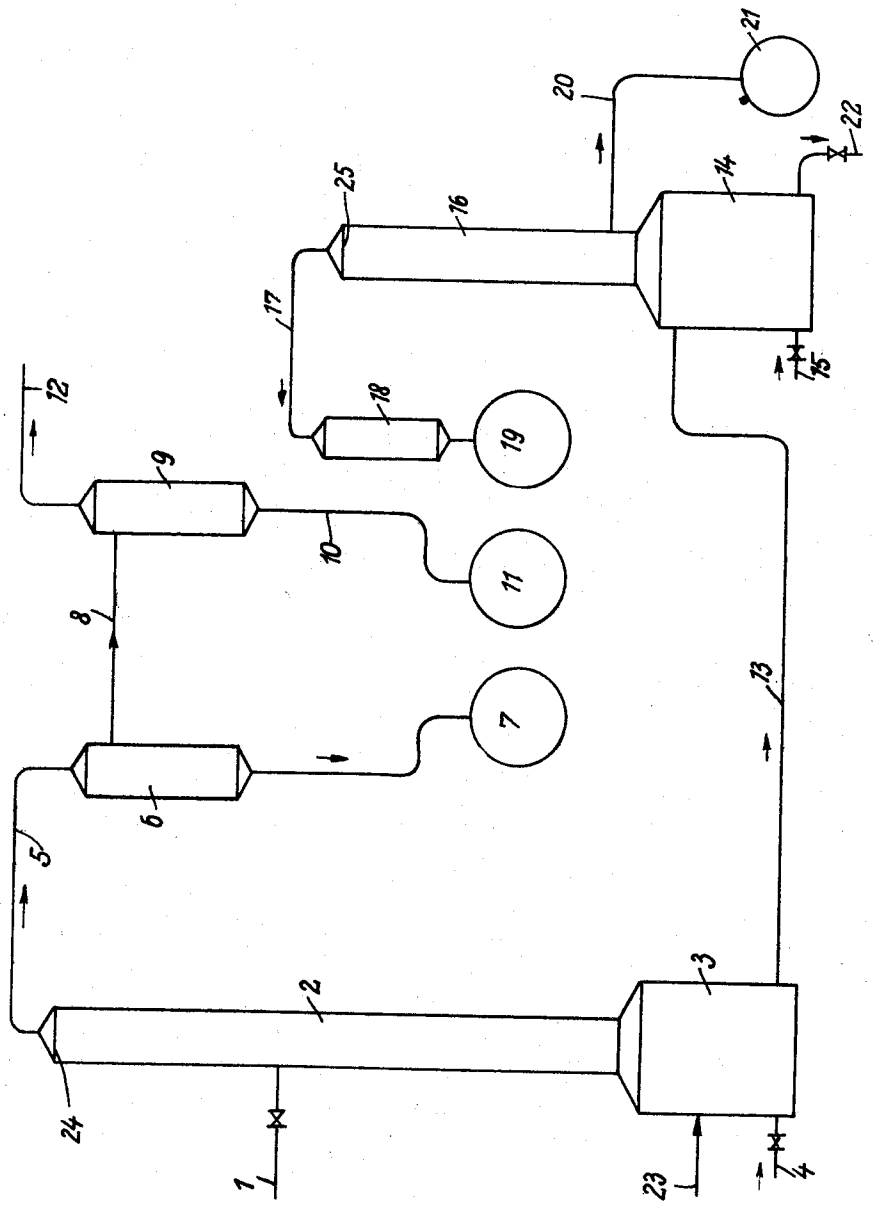
Aug. 30, 1955 W. J. A. SPANGENBERG ET AL 2,716,630

DISTILLATION OF TALL OIL

Filed Jan. 26, 1951



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United States Patent Office 2,716,630 Patented Aug. 30, 1955

2,716,630

DISTILLATION OF TALL OIL

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Application January 26, 1951, Serial No. 207,883

9 Claims. (Cl. 202—52)

This invention relates to improvements in the distillation of tall oil.

During the manufacture of cellulose by the sulphate process a mass separates from the sulphate liquors which, after decomposing with acid, gives raw tall oil, which is a dark coloured liquid with an unpleasant smell and consists of resin acids, such as abietic acid and pimaric acid, unsaturated fatty acids, such as oleic and linoleic acids, smaller amounts of hydroxy acids and saturated fatty acids and of sterols, higher fatty alcohols and other unsaponifiable matters. Raw tall oil contains about 30–60% resin acids, 30–60% fatty acids and about 8–14% of unsaponifiable matters.

Tall oil is used to an increasing degree for soap manufacture and lacquer preparation, and must for these purposes be purified by distillation, whereby a part of the colouring matter and the undesired odorous substances is removed. Attempts have been made for a long time to separate tall oil into its components and to obtain pure fatty acids and pure resin acids. However, it has not proved possible up to the present to separate further the complicated mixture, of which the boiling points lie very close together and which form hitherto inseparable azeotropic mixtures. One had to be satisfied therefore with resin acid concentrates which contained up to about 60–70% of resin acids and 30–40% of fatty acids, and with fatty acid concentrates which contained 60–75% fatty acids and 25–40% of resin acids. A further decomposition into pure resin acids and pure fatty acids was not attained even with use of the modern steam distillation process in high vacuum.

The surprising observation has now been made that substantially pure resin and fatty acids are obtained if tall oil is submitted to steam distillation in high vacuum by rectification in a separating apparatus of sufficient separating power. In a first stage of the process, the fatty acids are driven off together with the more easily volatile compounds, the distillation residue thereupon being separated in a second stage by fractionation into the higher boiling and undistillable components (pitch) and the components containing substantially the resin acids. The resin acids are subjected to rectification in order to separate off the last residues of fatty acids on the one hand, and on the other the residues of the non-volatile and the higher boiling components.

The fatty acids obtained in the first stages are separated from the more easily volatile compounds by rectification.

According to a special form of carrying out the invention, a fraction which consists principally of the unsaponifiable matters and fatty acids with 16 and fewer carbon atoms is separated by fractionation from the vapours of the volatile compounds of the first stage. The separated fatty acids and/or the resin acids can be subjected to a subsequent, preferably repeated rectification.

According to a particular method of carrying out the invention the separation is carried through in the first stage above the boiling point of the fatty acids and

below the boiling point of the resin acids, preferably at about 230–240° C. the separation for the isolation of the fatty acids and removal of the more volatile components below the boiling temperature of the fatty acids, preferably below about 150–180° C. and the separation in the second stage to obtain the resin acids, above the boiling temperature of the resin acids, preferably at about 290–310° C. all these separations are carried out in high vacuum below about 20 mm. of mercury, preferably however below 3 mm. of mercury. The resin acids can preferably be so separated in the second stage that the higher boiling and undistillable components (pitch) are isolated and the remainder of the lighter, volatile compounds are distilled off from the resin acids.

The distillation is preferably so carried out, with the support or aid of high pressure wet steam supplied to the distillation zone, under a high vacuum of less than about 20 mm. of mercury, preferably however below about 3 mm. of mercury, that the material is treated in layers of less than 20 cm., preferably however in layers of less than about 3 cm. The speed of flow of the material through the distillation plant is so regulated that the time of sojourn in the distillation vessels or in the fractionation columns amounts to less than 15 minutes. The small amounts of fatty acids separating on the rectification of the resin acids can be fed to the fatty acid rectification zone, which comprises the first stage of treatment, or the attendant condensation.

The invention will be more clearly understood by reference to the diagrammatic drawings which are purely illustrative.

The raw tall oil, which has a blackish-brown colour and a penetrating, unpleasant smell and contains about 45% of resin acids, 45% of fatty acids, 2% of hydroxy-acids and 8% of unsaponifiable matter, is led into a fractionating column 2 through a pipe 1 and into a distillation vessel 3 through a pipe 23 in a first process stage. The introduction is advantageously effected in the middle of the fractionating column 2 in as fine as possible a uniform distribution over the whole cross section of the column. Simultaneously high pressure, wet steam is led through a pipe 4 in the opposite direction or countercurrent to the down flowing tall oil.

The rectification carried out under high vacuum is preferably so conducted that the fatty acids and the lighter, volatile components pass out of the top of column 2 while the resin acids and the non-volatile components are collected in the lower part of the column.

The fatty acid vapours evolved are led through the pipe 5, they are condensed in a cooler 6 which is held below about 150–180° C. and then flow into a fatty acid container 7 in which substantially fatty acids with 18 carbon atoms collect. The uncondensed vapours pass out of the condenser 6 through a pipe 8 into an after-cooler 9 where further amounts of lighter, more volatile fatty acids, and in fact such as contain substantially about 16 carbon atoms, are separated and flow through a pipe 10 into a vessel 11. The lighter, volatile components such as steam, lower molecular weight fatty acids and low molecular hydrocarbons are led off by a pipe 12 and can be further condensed or worked up. Condensers (not shown) are connected to the pipe 12 and these condensers have such an output that the steam is practically completely condensed, preferably with the use of cooling agents, so that a high vacuum is attained, if possible under 5 mm. of mercury, e. g. 3 mm. Hg or less, thereby effecting a vacuum of below approximately 20 mm. in the system comprising the distillation, rectification and condensation zones.

The distillation residue from the distillation vessel 3, which contains the main amount of resin acids as well

as the non-volatile unsaponifiable components, is now fed in a second stage through a pipe **13** to a distillation vessel **14** which is also operated with the aid of high pressure steam, preferably in the wet state, supplied by means of a pipe **15**. Both this vessel **14** and the column **16** are under high vacuum and the temperature at the upper end of the column **16** is so maintained that the residue of the fatty acids still present distils off and passes by means of a pipe **17** through a condenser **18** into a fatty acid container **19**, whilst the pure resin acids run off through a pipe **20** and flow into a resin acid container **21**. The non-volatile residue is drawn off through pipe **22**.

The temperatures of evaporation and the amount of reflux condensate in the columns **2** and **16** are held so that substantially only pure fatty acid and the lighter volatiles pass over in column **2** whilst the resin acids remain behind with the residue in vessel **3**. At a high vacuum of less than 20 mm. Hg this temperature amounts to about 200° C. To this end a dephlegmator is arranged in the head **24** of the column which is held at a temperature of about 200° C. In the fractionating column **16** the evaporation temperatures and the amount of reflux condensate must be so adjusted that only the more easily volatile fatty acids pass over and the resin acids are separated from the non-volatile residue. The temperature must thus amount to 190–200° C. in the dephlegmation zone at the head **25** of the fractionating column **16** and in the distillation vessel **14** to about 290–310° C. at a high vacuum of less than about 20 mm. Hg. These temperatures alter according to the origin and composition of the tall oil, and are dependent upon the pressure conditions applicable during the treatment of the tall oil.

Instead of the fractionating columns horizontal reaction vessels according to the Wecker system can also be employed and further fractionating columns or reaction chambers can also be provided as well as condensers or dephlegmators if a further fine rectification is desired.

It has been found preferable to use compressed very wet steam which contains water droplets in the form of a mist as carrier for the distillation because thereby the speed of distillation is considerably increased. Also the time of sojourn of the distillation material in the single vessels, on the separating plates of the fractionating columns or in the divisions of the distillation vessels should be kept as short as possible, for example to less than 15 minutes. The thickness of the layers must be kept low so that polymerization processes and decomposition do not occur. The fraction of unsaponifiables in the distillate is thus kept low, and the rise in the amount of pitch which occurs with the customary processes is prevented. The distillation can be effected continuously or discontinuously. According to the present invention it is possible for the first time so to split up tall oil into its components that these occur in technically pure form as resin acids (e. g. abietic acid, pimaric acid), fatty acids (e. g. oleic, linoleic acids) besides the distillation residues (sterols in easily recoverable form).

It will be understood that the respective distillation vessels, fractionating or rectification columns, and the various condensers comprise zones of treatment in the stages of the process, as defined in the appended claims.

We claim:

1. A two-stage process for obtaining substantially pure fatty acids and resin acids from tall oil containing the same as well as comparatively non-volatile and unsaponifiable components which comprises in the first stage subjecting the tall oil to distillation in comparatively thin layers under substantially high vacuum with the aid of wet steam, the distillation temperature being maintained above the boiling point of the fatty acids therein and below that of the resin acids content, said temperature being within the approximate range of 230° C. to 240° C., conducting the vapors evolved by the said distillation to a rectification zone for fractionally separating vapor constituents, maintaining a dephlegmation zone, at a temperature of approximately 200° C., at the outlet end of the rectification zone, whereby components condensed in the said rectification zone return to the distillation zone containing tall oil residue, conducting the vapors evolved from the rectification zone to a first zone of condensation maintained at a temperature approximately within the range of 150° C. to 180° C., thereby condensing fatty acids of approximately 18 C atoms, conducting the vapors evolved from said first condensation zone to a second condensation zone maintained at a temperature below that of the first condensation zone for separating additional fatty acids having a lower number of C atoms, subjecting the remaining volatile components from the said second condensation zone to further condensation, said final condensation being adapted to produce a vacuum below approximately 5 mm. Hg, the vacuum during all of the aforesaid treatment, including that in the distillation, rectification and condensation zones, being maintained below approximately 20 mm. Hg; and in the second stage, conducting the tall oil residue, comprising resin acids and the comparatively non-volatile unsaponifiable components of the tall oil, from the first stage distillation treatment to a second distillation zone, subjecting the said residue in the latter zone to distillation with the aid of wet steam in comparatively thin layers under substantially high vacuum, the temperature in the distillation zone being maintained approximately within the temperature range of 290° C. to 310° C., conducting the vapors evolved by the said distillation to a rectification zone for fractionally separating vapor constituents, maintaining a dephlegmation zone at a temperature approximately within the range of 190° C. to 200° C., at the outlet end of the latter rectification zone, whereby the relatively volatile components, including any fatty acid constituents, are separated from the resin acids condensed in said rectification zone, conducting the said volatile components to a condensation zone for recovering fatty acids, and conducting the resin acids from a point approximately adjacent the inlet end of the rectification zone to collect the same, the vacuum conditions during the aforesaid second stage of treatment being maintained below approximately 20 mm. Hg.

2. The method as in claim 1, wherein tall oil is supplied directly to the distillation zone at a point above the supply of the steam to the said distillation zone, and wherein tall oil is supplied at approximately the middle of the rectification zone in a relatively finely divided and uniformly distributed state.

3. The method as in claim 1, wherein the steam is compressed wet steam containing moisture droplets therein.

4. The method as in claim 2, wherein the steam is compressed wet steam containing therein moisture droplets in the form of a mist.

5. The method as in claim 1, wherein the distillation and rectification in the respective zones is applied to layers of material approximately within the thickness range of 3 mm. to 20 cm.

6. The method as in claim 2, wherein the distillation and rectification in the respective zones is applied to layers of material approximately within the thickness of 3 mm. to 20 cm.

7. The method as in claim 2, wherein the distillation and rectification in the respective zones are applied to layers of material in thickness below approximately 3 cm., and the vacuum in said zones is approximately 3 mm. Hg.

8. The method as in claim 2, wherein the fatty acids obtained from the second stage of distillation and rectification are returned to the zone of fatty acid rectification in the first stage treatment.

9. The process as in claim 2, wherein the time for treatment in the respective zones is less than approximately 15 minutes.

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