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PROCESS OF SEPARATING THE CONSTITUENTS OF TALL OIL AND SIMILAR MIXTURES

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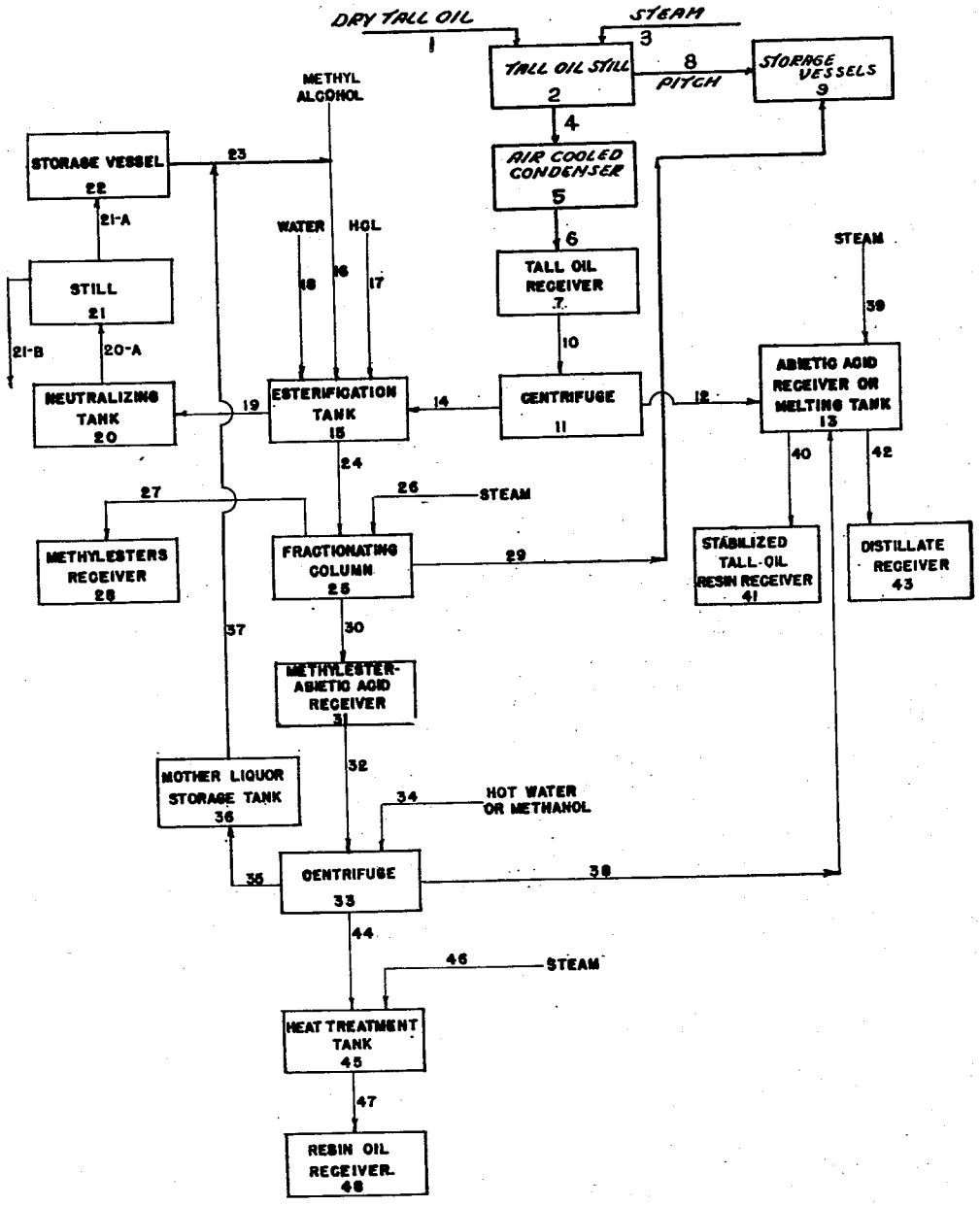


FIG. 1

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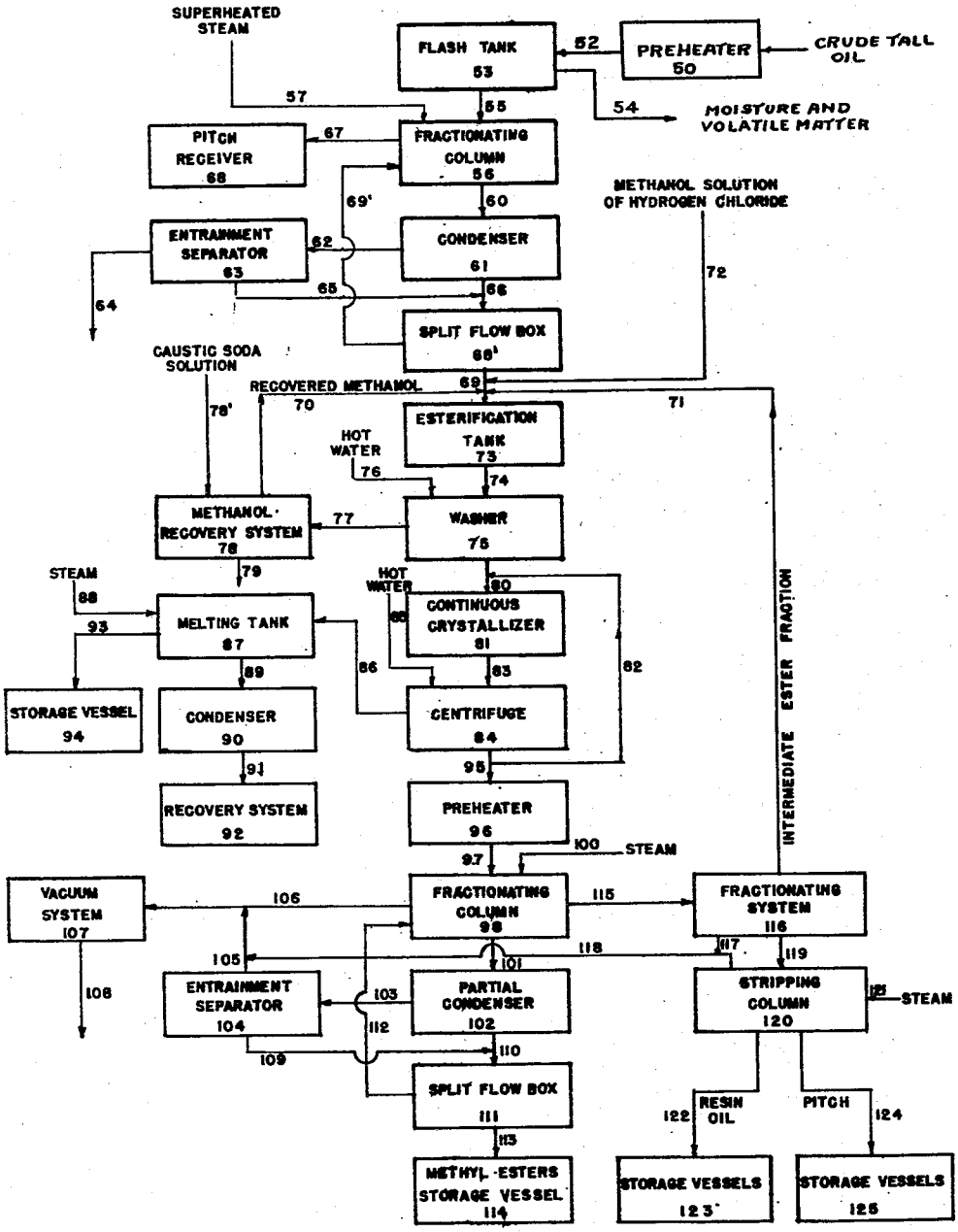


FIG. 2.

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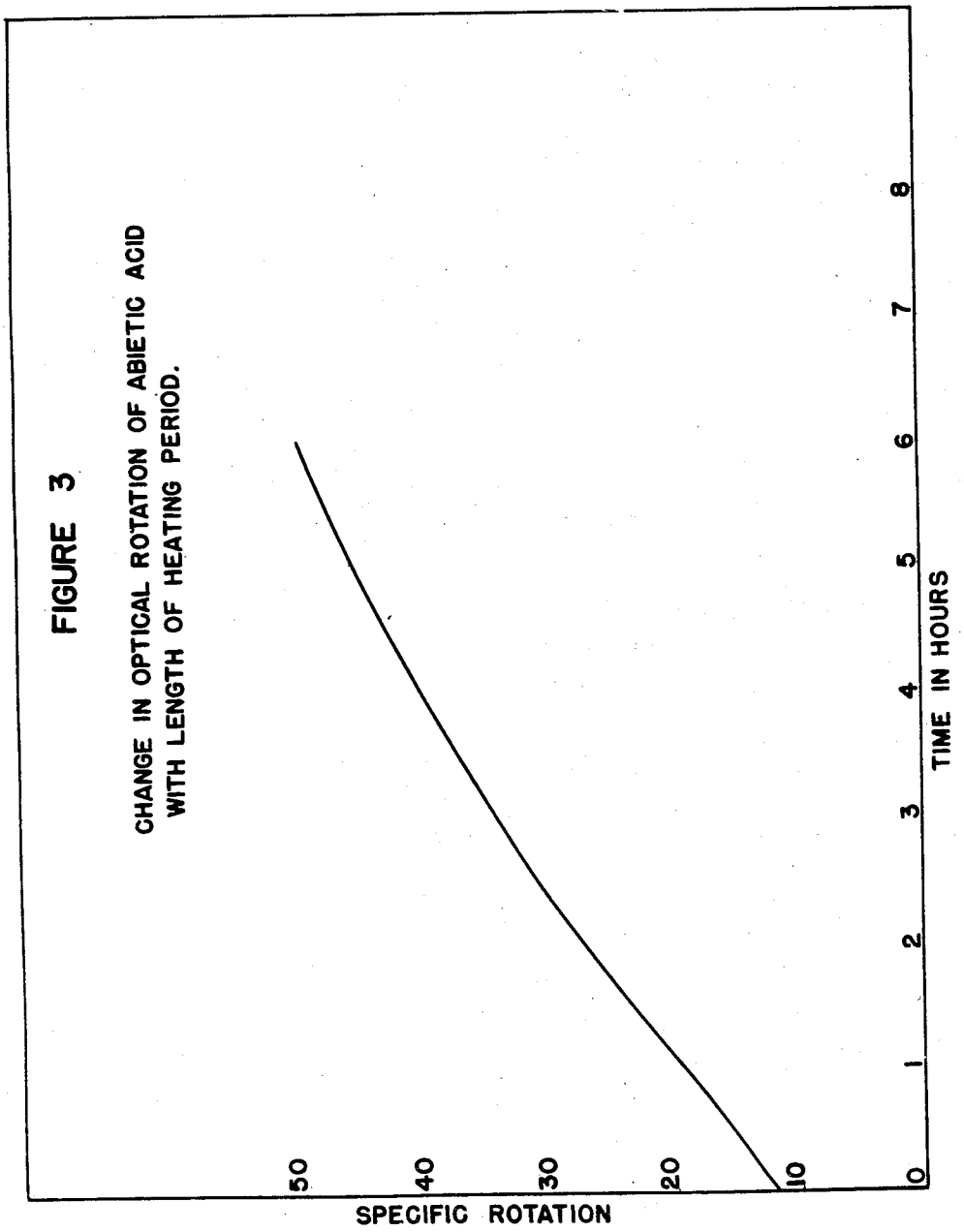
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PROCESS OF SEPARATING THE CONSTITUENTS OF TALL OIL AND SIMILAR MIXTURES

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FIGURE 3

CHANGE IN OPTICAL ROTATION OF ABIETIC ACID WITH LENGTH OF HEATING PERIOD.



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PROCESS OF SEPARATING THE CONSTITUENTS OF TALL OIL AND SIMILAR MIXTURES

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31 Claims. (Cl. 260—97.5)

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This invention relates to an economical and commercially feasible process for separating and recovering the fatty and resin acids present in tall oil or other mixtures containing both of these materials.

An object of the invention is to provide a process for recovering fatty acids in the form of alkyl esters from mixtures of the above type.

Another object is to provide a process for recovering abietic acid from tall oil and similar mixtures containing same in combination with fatty acids.

An additional object is to provide a process for heat treating abietic acid whereby this material is converted into a stabilized product simulating commercial rosin.

Other objects of the invention will be apparent to those skilled in the art as the description unfolds.

Tall oil is the resinous and fatty by-product obtained in the production of paper pulp from resin bearing woods by the soda, sulfite and sulfate processes. It is a dark colored viscous liquid consisting essentially of a mixture of roughly equal proportions of unsaturated fatty acids and resin acids together with a relatively small proportion of unsaponifiable matter, including sterols. Tall oil being a crude semi-natural product varies in composition considerably. Thus the fatty acid content may vary from 36% to 54%, the resin acid content from 38% to 58% and the unsaponifiable material from 6.5% to as high as 18%.

Owing to a number of objectionable properties, tall oil itself has not been extensively used on a commercial scale. For example, it is not suitable as such for the manufacture of soaps on account of its dark color and disagreeable odor nor can it be used as a rosin substitute because it is too high in fatty acid content. On the other hand, the components of tall oil, particularly the resin and fatty acids are of considerable value if they can be separated from tall oil as such or in the form of useful compounds. It is therefore, apparent that a process which will achieve this end is highly desirable and of great commercial value in view of the vast potential supply of relatively cheap tall oil.

Heretofore, numerous proposals for separating and recovering the fatty and resin acids of tall

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oil have been proposed. These proposals have involved fractional crystallization, fractional distillation, selective esterification, selective splitting of fatty and resin acid soaps, selective splitting of tall oil glycerides and extraction by means of selective solvents. These and other known methods have achieved varying degrees of success, but they have not been entirely satisfactory since they produce at best only a very rough separation of the components of tall oil with the result that the fatty acids or their esters are contaminated with resin acids and the latter are invariably contaminated with substantial quantities of fatty acids or fatty acid esters and unsaponifiable materials.

Now we have developed a process by which it is possible to obtain a much more efficient and economic separation of resin acids and fatty acids from tall oil and similar mixtures. This process yields fatty acid esters, abietic acid, heat stabilized abietic acid and a viscous resin oil, all of which are obtained in a commercially saleable form.

In carrying out the process of the present invention, dry crude tall oil is subjected to vacuum distillation or vacuum steam distillation until about 85% of tall oil is collected as a distillate. This distillate is then cooled and centrifuged to remove crystalline abietic acid, leaving a mother liquor consisting of tall oil of decreased abietic acid content.

The mother liquor is charged into a suitable reactor where it is reacted with methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl or isoamyl alcohol, in the presence of an acid catalyst, to form a mixture of fatty acid esters and abietic acid.

The resulting reaction mixture is washed with water to remove excess acid catalyst and alcohol and then fractionally distilled under reduced pressure, with or without steam, to recover an initial fraction consisting of substantially pure esters, a second fraction comprising abietic acid and a relatively small proportion of fatty acid esters, and a third fraction consisting of a high boiling resinous pitch.

The second fraction is cooled to separate out a second portion of abietic acid which is centrifuged to separate esters, free fatty acids, etc., and then washed with hot water or alcohol. The

mother liquor and washings thus obtained are combined and accumulated for recycling to the esterification step. After the accumulated mother liquor has been reworked, a final mother liquor is recovered which, upon heat treatment, yields a substantial amount of a viscous resin oil.

The abietic acid obtained in the manner described above is melted and simultaneously steamed or subjected to vacuum distillation to remove relatively small amounts of fatty acids, esters, resin oils, etc. This treatment has the effect of materially lowering the fusion point of the abietic acid, decreasing its acid and rosin acid number, lowering the iodine number and increasing its content of unsaponifiable matter. It also converts the crystalline abietic acid into a product simulating rosin which has up to 30% by weight of dehydro abietic acid and a color grade of WW to X or better.

Instead of recovering the abietic acid in a plurality of steps, the distilled tall oil may be esterified directly and the abietic acid separated from the esterified mixture in a single step by cooling and centrifuging. Moreover, the separation of the abietic acid from the ester mixture may be carried out prior to or after the step of fractionally distilling the ester mixture, see for example, Figures 2 and 1 respectively.

For a more complete understanding of the present invention, reference is made to the accompanying drawings.

Figure 1 illustrates one embodiment of the process of the present invention and

Figure 2 represents an alternative and preferred embodiment of the invention.

Figure 3 is a graphical representation of the effect of heat treatment on the optical properties of abietic acid. The optical rotation values were determined at a temperature of about 22° C. by means of a Lippich half-shadow polarimeter using a 20 cm. sample tube containing the heat treated abietic acid and a sodium arc lamp as a source of yellow light. The optical rotation values were converted into specific rotation values in the usual manner and the latter were then used in plotting the graph.

Referring to the drawings by reference characters, crude tall oil which has been dried in any suitable manner is charged into a tall oil still 2 by means of pipe 1 where it is subjected to steam distillation under an absolute pressure of about 10 mm. to 50 mm. of mercury and at a temperature of from 145° C. to 285° C., the steam used for this purpose being supplied by means of pipe 3. The steam distillation is carried out until about 85% of the tall oil is distilled, and the resulting distillate is discharged by pipe 4 into air-cooled condenser 5 where it is condensed. The condensate consisting of refined tall oil is conducted by pipe 6 into tall oil receiver 7.

The still residue, designated pitch in the flow sheet, is discharged by pipe 8 into storage vessels 9. This product is a black, tacky to brittle solid which is insoluble in water, soluble in xylene, toluene and benzene and slightly soluble in alcohol.

The purpose of distilling the tall oil is to improve its odor and color and to remove sulfonic acids and other impurities which tend to hydrolyze the methyl esters which are produced and distilled at a subsequent stage of the present process. Distillation is the preferred method of accomplishing these results, but it should be clearly understood that other methods of refining the tall oil are within the scope of the invention.

The distilled tall oil is cooled to room temperature and a substantial amount of crystalline abietic acid separates out. The crystal slurry thus obtained is conveyed by pipe 10 into centrifuge 11 in which the crystalline abietic acid is separated from its mother liquor. The abietic acid recovered is washed in the centrifuge with hot water or methanol and is then transported by means of a suitable conveyor 12 to an abietic acid receiver or melting tank 13.

The mother liquor consisting of distilled tall oil of decreased abietic acid content and the washings are discharged from centrifuge 11 and then conducted after drying in any suitable manner to esterification tank 15 by means of pipe 14.

In the esterification tank the fatty acids of the distilled tall oil are selectively esterified by reaction with methanol in the presence of an acid catalyst such as HCl, the reaction taking place at a temperature of from 40° C. to 60° C. and preferably from 40° C. to 45° C. The methanol and HCl used in this reaction are fed into the esterification tank by means of pipes 16 and 17 respectively. The amount of methanol employed may vary widely so long as the theoretical requirements are met, but we prefer to use it in an amount equivalent to about 50% by weight of the distilled tall oil treated. HCl in an amount corresponding to about 2% to 5% by weight of the distilled tall oil is preferably used in the reaction, but larger or smaller amounts may be employed if desired.

After the esterification reaction is completed, the excess methanol and HCl are separated from the reaction mixture by extraction with water which is introduced into esterification tank 15 by means of pipe 18. The extract containing HCl and methanol flows by pipe 19 into neutralizing tank 20 where it is neutralized with caustic soda or another suitable alkali. The neutralized extract is then conveyed by pipe 20A into still 21 where the methanol is distilled and discharged by pipe 21A into storage vessel 22 from which it may be returned for reuse in the next batch by means of pipes 23 and 16. The brine solution separated as a result of the methanol distillation step is discharged from still 21 by means of pipe 21B.

The washed esterified tall oil mixture is conveyed by pipe 24 into fractionating column 25 wherein it is subjected to vacuum steam distillation, the steam used for this purpose being introduced by pipe 26. The distillation is carried out at an absolute pressure of from 10 to 50 millimeters of mercury and at a temperature of from 220° C. to 250° C., and an initial fraction consisting essentially of methyl tall oil fatty acid esters is separated, which fraction leaves the fractionating column 25 and passes through a suitable condenser (not shown) and pipe 27 into a receiver 28.

In general, the methyl esters thus obtained have the following properties, it being understood that the properties will vary somewhat depending upon the degree to which the fatty acids are esterified and/or the efficiency of fractionation:

Acid No.		6.6
Rosin acid No.		3.0
Unsaponifiables	per cent	6.1
Free fatty acids	do	1.6
Abietic acid	do	1.6

These esters are saleable as such and are excellent raw materials for use in the production of higher alcohols, dicarboxylic acids, long chain al-

dehydes and ketones. They may also be partially hydrogenated to produce products which are eminently suitable for use as textile oils.

The separation of the methyl esters by distillation is preferably controlled by obtaining the acid number of the distillate samples. If a product having an average acid number of about 6.6 is desired, the distillation of the methyl esters is discontinued as soon as the distillate samples yield an acid number of from 10 to 12. However, if a product having a lower average acid number is desired, the recovery of methyl esters is discontinued when the acid number of the samples falls below 10. By this method of control, it is possible to obtain methyl esters having an average acid number of from about 2 to about 6.6 or a higher acid number, but as a product having a low acid number is desirable, it is preferred to carry out the distillation in such a manner that the product has an average acid number which does not substantially exceed 6.6.

After the desired methyl ester fraction has been recovered, the distillation is then continued at the same absolute pressure but at a temperature of from 250° C. to 300° C. and an intermediate fraction consisting essentially of abietic acid and a relatively small amount of methyl esters is separated, leaving a residue of pitch which is removed from the column and transported by means of a suitable conveyor 29 to storage vessel 9 where it is combined with the pitch recovered in tall oil still 2.

The intermediate fraction, after being condensed by means of a suitable condenser (not shown), is conveyed by pipe 30 into a methyl ester-abietic acid receiver 31 where it is cooled to a temperature sufficient to obtain substantially complete crystallization of the abietic acid. The resulting crystalline slurry is conducted by pipe 32 into centrifuge 33 where the abietic acid separated from its mother liquor is purified by washing with hot water or methanol. The hot water or methanol employed for this purpose is introduced by pipe 34 and is discharged from the centrifuge by means of pipe 35.

The washings and the abietic acid mother liquor separated in centrifuge 33 are combined and conveyed by pipe 35 into storage tank 36. The resulting mixture may be recycled to esterification tank 15 by means of pipes 37, 23, and 16, where it may be added to distilled tall oil of decreased abietic acid content and reworked in the manner indicated in the flow sheet.

As an alternative to this procedure, the mixture may be allowed to accumulate in storage tank 36 and then reprocessed separately in the same manner to recover additional quantities of abietic acid and methyl esters. When this is done, a final mother liquor is separated in centrifuge 33 and conveyed by pipe 44 into a heat treatment tank 45. In this tank the mother liquor is heated to about 280° C.–290° C. and treated with steam, the steam being introduced by means of pipe 46. The molten product thus obtained is discharged by pipe 47 into a suitable resin oil receiver 48 where it is allowed to cool in the presence of carbon dioxide, nitrogen or another suitable inert atmosphere.

The abietic acid separated in centrifuge 33 is removed and transported by any suitable means 38 to the abietic acid receiver or melting tank 13 where it is combined with the abietic acid separated in centrifuge 11.

The abietic acid recovered in the above described manner has substantially the following properties:

Acid No.	174.8–182.6
Rosin acid No.	172.7–180.4
Saponification No.	180.9–184.7
Unsaponifiables ——per cent—	1.3– 1.7
Abietic acids ——do——	91.5–96.0
Free fatty acids ——do——	1.0– 1.2
Methyl esters ——do——	3.6– 1.1
Color	White to cream colored crystals

This product has a tendency to become rancid and odorous due to the presence of fatty acids and its color darkens on ageing. It also differs from commercial rosin in that it has a negative specific rotation and has a marked tendency to crystallize after melting but before any extended heat treatment.

The abietic acid thus obtained may be stabilized as such or in the form of a non-crystalline product simulating commercial rosin.

In order to obtain stabilized abietic acid, the crystalline product is first melted in tank 13, preferably in an inert atmosphere, and then flaked on chilled rolls or extruded, molded, or otherwise shaped into blocks or other suitable forms. These products upon cooling are transformed into solid crystalline masses which, by virtue of their reduced surface, are much more stable to oxidation than the original loose mass of abietic acid crystals.

To produce a stable product simulating rosin, the crystalline abietic acid is preferably heated to a temperature of from 280° C. to 290° C., and then held at this temperature for 6 hours while a current of steam, introduced by pipe 39, is passed through the molten material. The molten mass is discharged by pipe 40 into a stabilized tall oil resin receiver 41 where it is permitted to cool to room temperature in an atmosphere of carbon dioxide, nitrogen or another suitable inert gaseous medium. The resulting product is a brittle glassy solid which resembles commercial rosin in appearance and chemical properties such as acid, saponification and iodine numbers, softening point, etc.

The distillate including fatty acids, esters, abietic acid and other low boiling impurities passes through a condenser (not shown) wherein the distillate is condensed and then discharged by pipe 42 into distillate receiver 43.

As an alternative to the above method of handling the heat treated abietic acid, the molten product may be poured between two smooth faced water-cooled rolls, preferably steel rolls, to rapidly chill the melt. The solidified product which is removed from the rolls by means of a suitable scraper, has a clear glassy-like appearance and consists of flakes which may vary from 0.001 to 0.5 of an inch in thickness depending upon the conditions of operation. These flakes are in a very convenient form for handling since they do not stick together during storage and consequently they may be readily removed from the storage container in a dry free flowing condition. Moreover, due to their physical characteristics, they are in a form in which they may be readily dissolved in solvents without the necessity for additional treatment such as grinding.

The rolls used in the above operation are preferably of small diameter, for example, from three to twelve inches, and are rotated toward each other at a speed of from 300 to 1800 R. P. M. The thickness of the flakes may be controlled to a considerable extent by variation of the distance between the rolls and the speed of rotation. The

rolls may be cooled in a variety of ways, but generally such cooling is carried out by circulating water on the interior of the rolls.

Starting with 100 pounds of dry tall oil and following the above process for recovering abietic acid, the following products are obtained in substantially the quantities indicated:

	Pounds
Pitch	15
Abietic acid	21.3
Methyl tall oil fatty acid esters	44.2
Rosin oil	16
Loss	4.5

The following examples will serve to illustrate in greater detail the procedure used to heat treat the abietic acid recovered by the above described process:

Example 1

Crystalline abietic acid having the following properties:

Acid No.	182.6
Rosin acid No.	180.4
Saponification No.	184.7
Unsaponifiables	1.7
Specific rotation	12.2

is melted and brought up to a temperature of from 280° C.–290° C. in the presence of an atmosphere of carbon dioxide. When up to temperature, steam is bubbled into the molten mass at the rate of 5 grams per minute for a period of 80 minutes or until 400 grams of steam has been added. The steaming is discontinued and the product is then maintained at a temperature of 280° C. to 290° C. under an atmosphere of carbon dioxide for about 3 hours. At the end of this time, the product is cooled in an inert atmosphere to 150° C.–170° C. and poured into a paper boat. On setting a product is obtained which has substantially the following properties:

Acid No		158
Rosin acid No		157
Saponification		162.5
Unsaponifiables	per cent	9
Dehydroabietic acid	do	23
Specific rotation	degrees	41
Softening point	do	80

This product is adapted for use in the production of pale varnishes, ester gum, modified synthetic resins, white paper size, soap, medicinal adhesive tape and many other commercial products.

Example II

21.3 lbs. of crystalline abietic acid having the following properties:

Acid No		174.8
Rosin acid No		172.7
Saponification No		180.9
Unsaponifiables	per cent	1.3
Abietic acid	do	91.5
Free fatty acids	do	1.0
Methyl esters	do	3.6

is heated to a temperature of from 287 C.–289° C. and then treated with steam for 4 hours until about 8.4 lbs. of steam has been added or until about 20% by weight of the abietic acid has been distilled. The undistilled product is then cooled in an atmosphere of carbon dioxide to a temperature of from 150° C.–170° C. and poured into a suitable receptacle. On setting 16.3 lbs. of a high melting resin simulating commercial rosin is obtained, which has substantially the following properties:

Acid No		173.9
Rosin acid No		171.6
Saponification No		175.7
Unsaponifiables	per cent	3.1
Softening point	°C	86
Color		X

In view of the fact that most manufacturers prefer ester gum and synthetic resins having as high a softening point as possible, the above heat treated abietic acid is particularly suitable for use in the production of these products since it has a high softening point and this property is carried through to the finished resin or gum. This heat treated product is also suitable for use in the production of paper size, pale varnishes, high grade rosin soaps, molding compositions, paints and lacquers.

Any one of the various properties of heat treated abietic such as specific rotation, acid number, saponification number, percent unsaponifiables, softening point and disproportionation may be varied over wide limits but not without effect on the others. Therefore, the conditions of heat treatment will depend upon the desired specifications of the product.

Thus by the process of the instant invention heat treated abietic acid having the following range of properties has been obtained:

Acid No	140–175
Saponification No	142–182
Softening point	74.5–87°
Color	WW to X or better
Dehydroabietic acid	Up to 30%
Unsaponifiables	0.8 to 16%
Specific rotation	12.2 to 48.7

As indicated above the abietic acid heat-treatment is preferably carried out at a temperature of from 280° C. to 290° C. but temperatures ranging from 250° C. to 350° C. may be employed if desired. The time of heating varies inversely with the temperature. The higher the temperature the lower is the heating time and vice versa. Thus at 350° C. the heat treatment may be carried out in about ½ hour whereas at 250° C. about 8 hours' heat treatment is required to obtain the same results.

The heat treatment may be carried out in a single step or a plurality of steps, that is, the abietic acid may be heated, preferably in an inert atmosphere, to a temperature from 250° C. to 350° C. and then steamed or subjected to reduced pressure to remove volatile impurities or these two operations may be carried simultaneously. The latter procedure is preferred one because it is more economical, easier to control and it provides a means whereby products having predetermined properties may be obtained.

The heat treatment of abietic acid brings about a change in its chemical and physical characteristics. It converts the abietic acid into a glassy brittle solid simulating commercial rosin; it reduces its iodine number to marked degree; it increases its optical rotation from a negative or a low positive value to a high positive value; it reduces its tendency to crystallize from a solution or melt thereof; it decreases its acid and rosin acid numbers; and it increases its content of unsaponifiable matter, although the last mentioned effect may be more than counteracted by properly correlating the steaming operation with the heating step.

The above changes in physical and chemical characteristics are apparently due to an intra and inter molecular rearrangement of the hydrogen atoms which takes place without affecting the carbon skeleton. This is further manifested by the fact that the products are more resistant to oxygen absorption indicating a marked change in the type unsaturation and also by the fact that the saponification number is not substantially changed, thus demonstrating that the carboxyl groups are not appreciably affected by the heat treatment, which, therefore, must act upon the hydrocarbon skeleton only.

In order to demonstrate the effect of the heat treatment employed in the process of the instant invention, the following experiments were carried out.

Samples of crystalline abietic acid recovered by the above process were heat treated as follows:

The weighed sample was melted in a flask under an atmosphere of carbon dioxide and heated to a temperature of about 285° C. at which point steam was bubbled into the liquid. Any material distilling out of the flask with steam was condensed hot and termed distillate.

At the end of a specified period of time the steaming was stopped and carbon dioxide blown over the surface of the molten product. Several runs were made in which the heating period extended beyond the steaming.

After completion of the heat treatment, the sample was allowed to cool (under CO_2) to 155° C.–170° C. at which time it was weighed, poured into a paper boat and allowed to set.

The distillate was dried and weighed and the steam consumption was measured by loss in weight of the flask used as a steam generator.

The above experiments are summarized in the following table, it being understood that the total heating time includes the steaming time.

Weight Sample g.	Total Heating Time, min.	Steaming Time, min.	Weight Steam, g.	Weight Product, g.	Acid number	Percent Unsap.	Percent dehydro Abietic Acid	Softening Point, °C.	Optical Rotation
454	30	30	110	400	175.8	2.6	----------	85	
538	35	30	76	477	176.4	2.4	12.7	82	
501	60	60	123	435	175.2	4.0	14.1	83	
454	60	60	147	374	173.9	3.6	----------	85	
500	120	80	205	346	169.0	4.9	10.5	82	
925	120	80	481	687	178.2	5.2	----------	82	
500	180	180	444	295	178.0	3.0	----------	86	
453	180	180	----------	----------	173.7	3.5	----------	83	See accompanying graph.
500	240	80	211	355	158.7	6.7	22.1	80	
1,000	240	240	683	715	175.0	2.3	----------	87	
1,475	240	240	660	1,125	172.5	4.4	----------	85	
2,090	240	240	727	1,650	168.6	5.2	----------	83	
1,700	240	240	665	1,299	173.9	3.1	----------	86	
1,700	240	240	658	1,310	172.4	2.7	----------	85	
500	345	80	179	367	152.4	11.8	26.5	75.5	
454	450	80	182	351	151.0	12.4	----------	75	
500	450	80	198	361	149.1	14.5	28.0	74.5	

From the above table and the accompanying graph which shows the effect of heat treatment on the optical rotation of abietic acid, the following conclusions can be drawn:

During the heat treatment the molten abietic acid disproportionates into dehydro abietic acid and a mixture of dihydro and tetra hydroabietic acid and the rate of disproportionation is fairly constant.

Some decomposition of the abietic acid also occurs as is evidenced by an increase in the unsaponifiable material produced and also by the reduction in acid number.

As the time of heating increases, the unsaponifiable content increases and the acid number of the abietic acid is reduced.

The tendency of heat treated abietic acid to crystallize when cooling is diminished by prolonged heating. This is apparently true regardless of the amount of unsaponifiables present, although dehydro abietic acid tends to make the product more crystalline.

Although a considerable amount of abietic acid is removed, steaming tends to remove the lower boiling free acids and unsaponifiables. Analyses of various distillates showed the presence of only small amounts of dehydro abietic acid, indicating that the bulk of this material is left in the product.

The rate of steaming is very important in determining the acid value and the softening point of the heat treated abietic acid. Thus the rate can be such that the unsaponifiables will be removed about as fast as they are formed, and the product will have a high acid value and a high softening point. If a lower steam rate is used, a gradual drop in acid values and softening points occurs throughout the steaming period. If the heating period extends beyond the steaming time, the acid values and softening points decrease rapidly due to the formation of unsaponifiables which are not removed.

The total amount of steam used in the above experiments is roughly proportional to the amount of distillate obtained, but actually this factor may vary considerably depending upon the temperature and time of heat treatment and also the properties desired in the final product.

As indicated by the accompanying graph (see Fig. 3) the specific rotation values of the heat treated abietic acid increase in proportion to the heating period.

The foregoing disclosure has been restricted to a batch process, but it will be apparent from the following description that the process may be carried out continuously.

In describing this embodiment of the invention, reference will be made to Figure 2 which illustrates the flow sheet of our continuous process.

Crude tall oil is continuously pumped from a suitable source into a two stage preheater **50** which is heated with steam at 50 pounds per square inch in the first stage and with chlorinated diphenyls at 24 lbs. per square inch in the second stage. The preheater discharges into flash tank **53** by way of pipe **52** wherein moisture and volatile matter are removed from the tall oil and

exhausted into the atmosphere through outlet pipe 54. The flash tank during this operation is maintained under a vacuum and at a temperature of from 120° C. to 280° C. The hot dry tall oil is pumped through pipe 55 into a suitable fractionating column 56, preferably a bubble cap fractionating column, by means of a positive displacement pump (not shown).

Fractionating column 56 is provided with a reboiler (not shown) which is located near the bottom of the column. The reboiler supplies the latent heat required to vaporize the high boiling constituents; the latter in turn give up their latent heat to vaporize the lower boiling constituents in the incoming feed and the reflux.

Superheated steam is charged through pipe 57 into column 56, the steam being introduced into the bottom of the reboiler in order to accelerate the thermosyphon effect between the reservoir in the bottom of the column and the reboiler.

The low boiling components, abietic acid and fatty acids, vaporized by the steam pass up through the rectification system of the column and here the high boiling constituents are separated from the vapors and returned to the reboiler section of the column. The tall oil vapors pass by means of pipe 60 into a partial condenser 61 which condenses the tall oil vapors and permits the steam vapors to pass on through pipe 62 into an entrainment separator 63 where the steam is separated and discharged from the system by means of pipe 64. The condensates separated in separator 63 and condenser 61 drain through pipes 65 and 66 respectively into split flow box 68', the latter being employed to maintain the composition of the refined tall oil substantially constant. This is accomplished by circulating a fixed portion of the tall oil back to the top of fractionating column 56 as reflux by means of pipe 69' and taking the remaining portion as product.

The high boiling pitch overflows continuously from the bottom of the column into pitch receiver 68 by means of pipe 67.

The refined tall oil is discharged from the split flow box into pipe 69 at a predetermined rate where it is combined with recycled methanol, an intermediate ester fraction and a solution of hydrogen chloride in methanol, these three materials being introduced into pipe 69 by pipes 70, 71, and 72 respectively. The resulting mixture is fed into a three stage continuous mixer (not shown) where it is thoroughly mixed and discharged into an esterification tank 73 of sufficient size to allow at least one hour's sojourn time to permit the reaction to go to completion. The temperature of the refined tall oil supplied to the mixer is controlled so that the esterification reaction can be carried out at approximately 60° C.

The esterification tank discharges the crude esters into washer 75 by means of pipe 74 wherein the excess alcohol and hydrochloric acid are extracted by means of hot water which is introduced into the washer through pipe 76.

The methanol-water-hydrochloric acid mixture is conducted by pipe 77 into a methanol recovery system 78 which includes a neutralizing tank and a fractionating column. In this system the solution is neutralized with a caustic soda solution or other suitable alkali introduced by pipe 78 and then the resulting solution is charged into a fractionating column where the alcohol is removed, condensed and recycled by pipe 70 to the esterification tank. The remaining salt solution is drawn off continuously from the bottom of the column and discharged from the system by means of pipe 79.

The hot crude esters are conveyed by pipe 80 into a continuous crystallizer 81 which may take the form of a water jacketed trough containing a long pitch ribbon conveyor. Simultaneously therewith, a fixed quantity of resin free mother liquor is pumped through pipe 82 from the discharge outlet of centrifuge 84 or other suitable source into the inlet of the crystallizer. The purpose of this is to provide sufficient carrier for the abietic acid crystals and to produce a thin crystal slurry which can be efficiently handled in centrifuge 84.

The continuous crystallizer discharges by means of pipe 83 into centrifuge 84 wherein the crystalline abietic acid is separated from the mother liquor containing methyl fatty acid esters. Hot water is introduced by pipe 85 into the discharge end of the centrifuge in order to purify the crystals and the contaminated water is discharged with the esters at the opposite end of the centrifuge.

The washed abietic acid crystals are discharged onto a conveyor 86 by which they are transported to a melting tank 87, this tank being provided with a dowtherm or another suitable heating coil. The abietic acid is melted and treated with live steam, introduced by pipe 88, to convert it into a product simulating rosin. For this purpose, a temperature of about 285° C. is preferably maintained in the melting tank, but it should be clearly understood that other temperatures within the range of from 250° C.–350° C. may also be used. The time of heating and the amount of steaming will depend on the desired properties of the final product.

The distillate containing small amounts of abietic acid, fatty acids and esters passes from the melting tank by means of pipe 89 into a condenser 90 where it is condensed and discharged into a recovery system 92 by pipe 91. The hot liquid resin residue is continuously drawn off through pipe 93 into storage vessels 94.

The semi-crude esters leaving centrifuge 84 by pipe 95 (after a fixed portion has been removed for recycling to continuous crystallizer 81) flow at a predetermined rate to a preheater 96 where they are heated to a temperature of about 310° C. The preheated esters are discharged by pipe 97 into a fractionating column 98 where they are distilled by means of steam which is introduced through pipe 100. The distillation is carried out at a temperature of from 220° C. to 250° C. and at an absolute pressure of about 10 to 50 millimeters of mercury. The distilled esters flow continuously by pipe 101 into partial condenser 102 wherein substantially all of the esters are condensed. The steam, non-condensible gases and a relatively minor amount of esters are conveyed by pipe 103 into entrainment separator 104 where the steam and non-condensible gases are separated and discharged by pipe 105 into pipe 106 leading to vacuum system 107. The steam and non-condensible gases are exhausted from the vacuum system by way of discharge pipe 108.

The esters condensed in the entrainment separator 104 and in partial condenser 102 drain into split flow box 111 by means of pipes 109 and 110 respectively and a fixed portion of this condensate is recycled as reflux to fractionating column 98 by way of pipe 112. The remainder flows from split flow box 111 into the methyl esters storage vessel 114 by means of pipe 113.

The bottoms overflow continuously from fractionating column 88 and pass by means of pipe 115 into a second fractionating system 116 which is similar to the one just described. In this system the bottoms are subjected to vacuum steam distillation at an absolute pressure of from 10 mm. to 50 mm. of mercury and at a temperature of from 250° C. to 300° C. The resulting intermediate ester fraction is recycled at a predetermined rate to the esterification tank 73 by means of pipes 71 and 69 respectively and the steam and non-condensible gases flow out of the fractionating system by means of pipes 117 and 118 for ultimate disposal by the vacuum system 107.

The bottoms from the distillation carried out in the fractionating system 116 are discharged through pipe 119 into stripping column 120. Steam is introduced by pipe 121 and it passes up the column countercurrently to the flow of the bottoms being fed into the top of the column. The resin oil thus obtained, together with steam and non-condensible gases, passes into a partial condenser (not shown) wherein the resin oil is condensed and discharged into suitable evacuated storage vessel 123 by pipe 122. The steam and non-condensible gases flow through an entrainment separator (not shown) and are finally conveyed via pipe 118 to vacuum system 107 for disposal.

The residue from the stripping operation which consists of a high boiling pitch flows continuously out of stripping column 120 into storage vessels 125 by means of pipe 124.

The conditions of operation of the more important steps of the process will now be discussed in detail.

Tall oil drying step

The crude oil is preferably dried by distilling it under reduced pressure at a temperature of from 120° C. to 280° C., but the invention is not restricted thereto as other known methods of achieving this result may be employed.

Tall oil refining step

As hereinbefore indicated, the tall oil may be refined in any desired manner, but the most effective way to accomplish this is to subject the tall oil to straight vacuum distillation or vacuum steam distillation at a temperature of from 240° C. to 285° C. and at an absolute pressure of from 10 to 25 millimeters of mercury. The distillation may also be executed with satisfactory results at a temperature of from 145° to 300° C. and at an absolute pressure of from 10 to 50 millimeters of mercury.

Initial abietic acid crystallization step

In this step of the process, the distilled tall oil is cooled to about 23° C., but lower temperatures may be employed if desired. As indicated earlier in the present specification, this step may be omitted but when carrying out the process batchwise, we prefer to include it as by doing so the yield of the product is substantially increased.

Esterification step

This reaction is carried out in the presence of a mineral acid catalyst, preferably HCl, and at a temperature which falls substantially within the range of from 40° C. to 60° C., but higher or slightly lower temperatures may also be used.

The amount of acid catalyst added does not appear to be critical but for economic reasons and to facilitate its removal from the esterified mixture, it is preferably limited to about 3% to 5% by weight of the distilled tall oil treated.

Methyl, ethyl, propl, isopropyl, butyl, isobutyl, amyl or isoamyl and mixtures thereof may be selectively reacted with the fatty acids of tall oil to form the corresponding esters. The amount of alcohol required for substantially complete esterification varies with the composition of the tall oil and also with the particular alcohol and catalyst used. In general, we prefer to use alcohol in an amount equivalent to about 50% by weight of the distilled tall oil, but it should be clearly understood that the invention is not restricted thereto.

Washing step

This operation is designed to remove the excess alcohol and acid so that the esterified mixture will be more adapted for distillation. Moreover, it has as its purpose the recovery of the unreacted alcohol so that it can be reused in the process. Although it is desirable to remove the alcohol and acid as completely as possible, there is nothing particularly critical about this step so that any suitable means for achieving this end may be employed.

Fractionation step

The distillation of the methyl esters is carried out at a temperature of from 220° C. to 250° C. and at an absolute pressure of from 10 to 50 millimeters of mercury or preferably from 18 to 30 millimeters of mercury. After the desired methyl esters fraction has been recovered, the distillation is continued at a temperature of from 250° C. to 300° C. and at an absolute pressure within the above range. An intermediate fraction is thus separated consisting of abietic acid and a relatively small amount of methyl esters.

In the separation of the esters of other alcohols, the optimum distillation temperature and pressure will vary with the alcohol used in the esterification step.

Second abietic acid crystallization step

The abietic acid content of the intermediate fraction is preferably crystallized from its mother liquor by cooling the fraction to room temperature. Lower temperatures may also be utilized provided the intermediate fraction is not cooled to the point where the resulting slurry is too viscous for efficient handling in the centrifuge.

Separation of abietic acid crystals from mother liquor and purification thereof

The abietic acid crystals are separated from their mother liquor by centrifuging (or in any other suitable manner) and then purified by washing while in the centrifuge with hot water, alcohol, or a water soluble organic solvent. This method of separation and purification is also applied to the abietic crystals which are recovered from the distilled tall oil.

Mother liquor treatment after separation of abietic acid crystals

As indicated above the abietic acid mother liquor may be mixed with refined tall oil of reduced abietic acid content, and then reworked, or the mother liquor may be accumulated and reprocessed separately to yield additional quantities of abietic acid and fatty acid esters. The latter procedure yields a final mother liquor which may be heat treated to produce a viscous resin oil. This treatment involves heating the

mother liquor at a temperature of from 250° C. to 300° C. for a period of from about 8 hours to about ½ an hour with simultaneous steaming or partial distillation under reduced pressure, the time of heating varying inversely with the temperature. Within these limits we prefer to carry out the heat treatment at a temperature of about 280° C. for a period of about 2 hours. As an alternative to the foregoing procedure, the treatment may be carried out in steps, that is, the mother liquor may be heated to a temperature within the above range and then subjected to partial steam or vacuum distillation. The resulting undistilled product consisting of a viscous resin oil is then cooled in an inert atmosphere to room temperature.

Abietic acid heat treatment

This operation is carried out at a temperature substantially within the range of from 250° C. to 350° C. and preferably within the range of from 280° C. to 290° C. The heating is accompanied or followed by steaming or vacuum distillation, the time of heating varying inversely with the temperature. The heat treatment with steam or with vacuum distillation removes small amounts of rosin oils, fatty acids, methyl esters and other volatile impurities and at the same time converts the crystalline abietic acid into a brittle glassy product simulating commercial rosin in appearance and chemical properties.

The heat treatment is preferably carried out in such a manner that about 20% by weight of the abietic acid treated is distilled. The invention, however, is not limited thereto as greater or smaller amounts may be distilled, the extent of distillation being controlled by the properties desired in the final product.

Where abietic acid is used in the specification and claims, it is to be understood that this expression covers tall oil resin acids, that is, abietic acid, abietic acid anhydride, abietic acid isomers and mixtures of these materials. Also, where the expression aliphatic alcohol is used in the claims, it is to be understood that an aliphatic alcohol having from 1 to 5 carbon atoms is intended.

As many widely different embodiments of this invention may be made without departing from the spirit and the scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. As a new product, a heat treated tall oil abietic acid having substantially the following properties:

Acid No.	173.9
Rosin acid No.	171.6
Saponification No.	175.7
Unsaponifiables ——per cent—	3.1
Softening point (A. S. T. M. ball and ring method) ——° C—	86
Color	X

2. As a new product, a heat treated tall oil abietic acid in the form of non-tacky, free flowing flakes, said flakes being further characterized by the following properties:

Acid No.	173.9
Rosin acid No.	171.6
Saponification No.	175.7
Unsaponifiables ——per cent—	3.1
Softening point (A. S. T. M. ball and ring method) ——° C—	86
Color	X

3. As a new product, a heat treated tall oil abietic acid in the form of non-tacky, free flowing flakes varying in thickness from 0.001 to 0.5 of an inch, said flakes being further characterized by the following properties:

Acid No.	173.9
Rosin acid No.	171.6
Saponification No.	175.7
Unsaponifiables ——per cent—	3.1
Softening point (A. S. T. M. ball and ring method) ——° C—	86
Color	X

4. As a new product, a heat treated tall oil abietic acid simulating commercial rosin having the following properties:

Acid number	172.5–178
Softening point (ASTM ball and ring method) ——° C—	85–87
Unsaponifiable content ——per cent—	2.6–4.4

5. As a new product, a heat treated tall oil abietic acid simulating commercial rosin having the following properties:

Acid number	175
Softening point (ASTM ball and ring method) ——° C—	87
Unsaponifiable content ——per cent—	2.3

6. A process of producing valuable products from crude tall oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said refined tall oil into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid therefrom and thereupon recovering said crystallized abietic acid.

7. A process of producing valuable products from crude tall oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said refined tall oil into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters; and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid therefrom; separating said crystallized abietic acid and heating it to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while subjecting the molten product during at least the final stages of said heat treatment to partial distillation and thereby producing a brittle glassy residue simulating commercial rosin and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product.

8. The process defined in claim 7, wherein the partial distillation is carried out under reduced pressure.

9. The process defined in claim 7, wherein the partial distillation is accomplished with the aid of steam.

10. The process defined in claim 7, wherein the partial distillation is carried out in the final stages of the heat treatment.

11. The process defined in claim 7, wherein the separated abietic acid is washed to remove impurities prior to being subjected to heat treatment and partial distillation.

12. A process of producing valuable products from crude tall oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said refined tall oil into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid contained therein; separating and purifying said abietic acid by washing; and heating the purified abietic acid to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while passing steam through the molten product and thereby producing a brittle glassy residue simulating commercial rosin, and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product.

13. A process of producing valuable products from crude tall oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said refined tall oil into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid contained therein; separating and purifying said abietic acid by washing; and heating the purified abietic acid to a temperature of about 285° C. for a period of about ½ hour while passing steam into the molten product and thereby producing a brittle glassy residue simulating commercial rosin and a distillate in an amount equivalent to about 12% by weight of said molten product.

14. The process of producing valuable products from crude tall oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said tall oil into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid contained therein; separating and purifying said abietic acid by washing; and heating the purified abietic acid to a temperature of about 285° C. for a period of about 3 hours while passing steam into the molten product and thereby producing a residue which upon cooling yields a brittle glassy solid simulating commercial rosin, and a distillate in an amount equivalent to about 41% by weight of said molten product.

15. The process of producing valuable products from crude tall oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said tall oil into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid contained therein; separating and purifying said abietic acid by washing; and heating the purified abietic acid to a temperature of about 285° C. for a period of about 4 hours while passing steam into the molten product and thereby producing a residue which upon cooling yields a brittle glassy solid simulating commercial rosin, and a distillate in an amount equivalent to about 23% by weight of said molten product.

16. The process of producing valuable products from crude tall oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said tall oil into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid contained therein; separating and purifying said abietic acid by washing; and heating the purified abietic acid to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while passing steam into the molten product and thereby producing a residue which upon cooling yields a brittle glassy solid simulating commercial rosin, and a distillate in an amount equivalent to about 20% by weight of said molten product.

17. The process of producing valuable products from crude tall oil, which comprise refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said tall oil into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid contained therein; separating and purifying said abietic acid by washing; and heating the purified abietic acid to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while subjecting the purified product to vacuum distillation and thereby producing a residue which upon cooling yields a brittle glassy solid simulating commercial rosin, and a distillate in an amount equivalent to about 20% by weight of said product.

18. The process of producing valuable products from crude tall oil, which comprises refining said

tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said refined tall oil into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize said abietic acid therefrom; centrifuging the resulting abietic acid slurry to separate the mother liquor therefrom; purifying said abietic acid by washing with hot water; heating said purified abietic acid to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while passing steam through the molten product and thereby producing a molten residue and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product; and thereupon flaking said molten residue by rapidly chilling same in thin layers.

19. A process of producing valuable products from crude oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said refined tall oil into methyl esters by selective esterification with methanol; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said methyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said methyl esters, and a final fraction comprising resinous pitch; cooling said intermediate fraction to form a crystalline slurry of abietic acid; centrifuging said slurry to separate the abietic acid from its mother liquor; purifying said abietic acid by washing with methanol; and then heating said purified abietic acid to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while passing steam through the molten product and thereby producing a brittle glassy residue simulating commercial rosin and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product.

20. The process of producing valuable products from crude tall oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; converting the fatty acids in said refined tall oil into methyl esters by selective esterification with methanol; removing the excess methanol from the resulting ester mixture by washing with water; fractionally distilling the washed ester mixture to produce a fraction consisting essentially of said methyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said methyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to form a crystalline slurry of abietic acid; separating the abietic acid from its mother liquor by centrifuging said slurry; purifying the separated abietic acid by wishing with methanol; and thereupon heating said purified abietic acid to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while passing steam through the molten product and thereby producing a brittle glassy residue simulating commercial rosin and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product, said crude tall oil being refined by vacuum steam distillation at a temperature of from 240° C. to 300° C.

21. A process of producing valuable products from refined tall oil containing substantial amounts of unsaponifiable organic material; which comprises converting the fatty acids contained in said refined tall oil into alkyl esters by selective esterifictaion with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; washing the resulting ester mixture with water to remove excess alcohol; fractionally distilling the washed ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to form a slurry of crystallized abietic acid; separating said abietic acid from its mother liquor; purifying said abietic acid by washing; and heating the purified abietic acid to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while passing steam through the molten product and thereby producing a brittle glassy residue simulating commercial rosin and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product.

22. A process of producing valuable products from crude tall oil, which comprises refining said tall oil without substantial removal of unsaponifiable organic material; cooling said refined tall oil to crystallize abietic acid therefrom; separating said crystallized abietic acid from the resulting mother liquor; converting the fatty acids of said mother liquor into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid and recovering said crystallized abietic acid.

23. The process of producing valuable products from crude tall oil, which comprises refining said tall oil by vacuum steam distillation without substantial removal of unsaponifiable organic material: cooling said refined tall oil to crystallize abietic acid therefrom; separating said crystallized abietic acid from the resulting mother liquor; converting the fatty acids of said mother liquor into alkyl esters by selective esterification with a monohydric aliphatic alcohol having from 1 to 5 carbon atoms; fractionally distilling the resulting ester mixture to produce a fraction consisting essentially of said alkyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said alkyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid and recovering said crystallized abietic acid.

24. The process of producing valuable products from crude tall oil, which comprises refining said tall oil by vacuum steam distillation without substantial removal of unsaponifiable organic material; cooling said refined tall oil to crystallize abietic acid therefrom; separating said crystallized abietic acid from the resulting mother liquor; converting the fatty acids of said mother liquor into methyl esters by selective esterification with methanol; fractionally distilling the re-

sulting ester mixture to produce a fraction consisting essentially of said methyl esters, an intermediate fraction comprising abietic acid and a relatively small proportion of said methyl esters, and a final fraction comprising a resinous pitch; cooling said intermediate fraction to crystallize abietic acid and recovering said crystallized abietic acid.

25. The process defined in claim 24 wherein the recovered abietic acid is heated to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while subjecting the molten product during at least the final stages of said heat treatment to partial distillation and thereby producing a brittle glassy residue simulating commercial rosin and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product.

26. A continuous process of producing valuable products from crude tall oil, which comprises subjecting said tall oil to continuous flash distillation to remove moisture therefrom; refining said dried tall oil without substantial removal of unsaponifiable organic material by continuous vacuum steam distillation; condensing and mixing said refined tall oil with methanal and an abietic acid fraction comprising abietic acid and a relatively small proportion of methyl tall oil fatty acid esters; selectively esterifying the fatty acids of said refined tall oil by reaction with said methanol; cooling the resulting reaction product to produce a slurry of crystallized abietic acid; recovering said crystallized abietic acid from its mother liquor and continuously fractionally distilling said mother liquor to produce a fraction consisting of methyl tall oil fatty acid esters, an abietic acid fraction comprising abietic acid and a relatively small proportion of methyl tall oil fatty acid esters and a final fraction comprising a viscous resin oil, said abietic acid fraction being continuously recycled for reuse in the esterification step of the process.

27. The process defined in claim 26, wherein the recovered abietic acid is continuously heated to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while subjecting the molten product during at least the final stages of said heat treatment to partial distillation and thereby continuously producing a brittle glassy residue simulating commercial rosin and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product.

28. The process defined in claim 26, wherein the recovered abietic acid is continuously heated to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while passing steam into the molten product and thereby continuously producing a brittle glassy residue simulating commercial rosin and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product.

29. The process defined in claim 26, wherein the abietic acid recovered is continuously heated to a temperature of from 250° C. to 350° C. for a period of about 8 hours to about ½ hour while subjecting said molten product to vacuum distillation and thereby continuously producing a brittle glassy residue simulating commercial rosin and a distillate in an amount equivalent to about 11% to about 41% by weight of said molten product.

30. The process defined in claim 28, wherein the steam is passed into the molten product at a rate such that about 20% by weight of the molten product is continuously distilled.

31. The process defined in claim 29, wherein the vacuum distillation is so controlled that about 20% by weight of the molten product is continuously distilled.

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Certificate of Correction

Patent No. 2,487,000 November 1, 1949

GEORGE E. TAYLOR ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 7, line 27, and column 8, line 39, for the numeral "12.2" read *+12.2*; column 7, line 48, for "41" read *+41*; columns 9 and 10, in the table, sixth column thereof, sixth line under the heading, for "178.2" read *168.2*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of March, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.