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TALL OIL TREATMENT

Ernest Segessemann, Wood-Ridge, N. J., and Nicholas M. Molnar, New York, N. Y.

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This invention relates to a treatment of tall oil, and, more particularly, to the manufacture of saturated fatty acids of lower carbon content and a more stable form of rosin from tall oil.

Tall oil is obtained in large quantities as a by-product in the production of paper pulp from rosin bearing woods by the so-called sulphate process. It could advantageously be used in the manufacture of soap and like materials. However, on account of its content in highly unsaturated fatty acids soaps made from tall oil are of soft consistency which has up to the present time prevented any important industrial application thereof.

The object of the invention is to convert tall oil into a new material for soap.

Another object of the invention is to provide an improved process for converting the unsaturated fatty acids of tall oil into saturated fatty acids of lower carbon content.

A further object is to provide a process for converting the rosin contained in the tall oil into a more stable form by reducing its degree of unsaturation.

These objects, and other objects which will appear hereafter, are accomplished, in general, by heating the alkali soap of tall oil with an alkali hydroxide at an elevated temperature. This causes the migration of the double bonds towards the alpha carbon of the fatty acid with a subsequent cracking of the fatty acid at the new position of the double bond. The resulting product is a saturated fatty acid of lower carbon content. As a by-product of the reaction acetic acid and hydrogen are formed. For every double bond in the unsaturated fatty acid one molecule of acetic acid is split off and the newly formed saturated fatty acid is shorter by two carbon atoms.

Thus the unsaturated fatty acids contained in tall oil are degraded mainly into palmitic and myristic acids. These new substances are excellent raw materials for the manufacture of hard soaps. Furthermore, the newly formed saturated fatty acids of lower carbon content have a vapor pressure appreciably higher than the unsaturated acids originally present in tall oil and, for this reason, are more easily separated from the rosin by means of fractional distillation. The new substance recovered as the still residue, which may conveniently be designated as stabilized rosin, is very hard and brittle and has an iodine number only two-thirds to one-half of that of the commonly known rosin which is present in untreated tall oil.

When an alkali soap of tall oil is heated with

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alkali hydroxide the shifting of the double bond sets in at about 180° C. but any appreciable cracking of the isomerized unsaturated fatty acids into saturated fatty acids of lower carbon content does not start until a temperature of about 230° C. is reached. For full completion of the cracking operation the temperature has to be raised to about 280° C. As soon as the evolution of hydrogen has ceased the reaction is completed which usually requires from four to six hours.

In carrying out the process of the invention the alkali soap for tall oil is mixed with an amount of alkali hydroxide from one to two times the amount which is already present as combined alkali in the soap. The mixture is heated to about 230° C. at which temperature a copious evolution of hydrogen begins. The temperature is then gradually raised to 280° C.

The process of the reaction can conveniently be followed by collecting and measuring the hydrogen or by passing the evolved hydrogen through a bubble counter. If potassium hydroxide is used as the alkali hydroxide the reaction may be carried out in an open vessel, or the vessel may be covered and provided with a vent pipe allowing the hydrogen to escape. If sodium hydroxide is used it is preferable to carry out the reaction in an autoclave.

Upon completion of the reaction which usually requires from four to six hours, the mixture is allowed to cool to below 100° C. and is thereafter dissolved in water. The soap may then be salted out and used as such or the soap solution may be acidified to recover the mixture of saturated fatty acids and stabilized rosin.

If a soap stock for pure white soaps is desired, this mixture of saturated fatty acids and stabilized rosin may be distilled. If desired the saturated fatty acids may be separated from the stabilized rosin by fractional distillation under reduced pressure.

An alternative method of separating the saturated fatty acids from the stabilized rosin consists in dissolving the product after acidification in a suitable solvent which permits the fatty acids to precipitate out at a low temperature while retaining the rosin in solution. Suitable solvents are, among others, petroleum hydrocarbons, such as gasoline, kerosine, heptane; aromatic hydrocarbons, such as benzene, toluene, xylene; alcohols, such as methyl alcohol, ethyl alcohol, isopropyl alcohol; ketones, such as acetone, ethyl methyl ketone, cyclohexanone; chlorinated hydrocarbons, such as ethylene dichloride, and trichloroethylene.

Precipitation of the saturated fatty acids can be effected within a temperature range from about 5° C. to minus 70° C., varying with the kind of solvent used. The precipitated fatty acids are removed from the solvent solution by any suitable means including centrifuging and filtration. The stabilized rosin is then recovered from the mother liquor by distilling off the solvent.

The alkali hydroxides may be employed in the dry powder or flake form, but it is preferable to use their concentrated aqueous solutions. The course of the reaction may be accelerated if it is carried out at a higher temperature, e. g., at about 300° C. to 400° C., but for good quality and light color of the fatty acids and of the stabilized rosin it is preferable to work at a lower temperature, e. g., below 300° C., but above 230° C.

The vessel used for the reaction may be a kettle made of iron or any other material which is resistant to hot alkalies.

In order to effect the cracking of the unsaturated acids into saturated acids of lower carbon content and acetic acid, the amount of alkali hydroxide employed must be at least equal to the combined alkali in the soap. To insure completion of saturation and degradation, however, it is preferable to use an amount of alkali hydroxide from one and one-half to twice that amount.

If a neutral tall oil soap without addition of any excess alkali hydroxide is heated to temperature of about 200° C. to 300° C., some isomerization involving the change in position of the double bonds will take place as shown by Dreger (U. S. Patent No. 2,240,365); however, no cracking into saturated fatty acids of lower carbon content occurs.

If the temperature during the alkali treatment is kept below 225° C. apparently a rearrangement of the double bonds of the polyunsaturated fatty acids is the main reaction taking place, as is shown by British Patent 558,881. For an extensive cracking of the isomerized fatty acids into saturated fatty acids of lower carbon content, however, temperatures above 225° C. are required.

If the reaction is carried out in an autoclave, pressures of 10 to 20 atmospheres and temperatures of 230° C. to 280° C. have been found suitable, but higher pressure and temperatures may also be used.

A hydrogenation catalyst may also be added to the reaction mass and the hydrogen evolved may be utilized directly for hydrogenating a part of the unsaturated fatty acids and rosin. The product will then consist of a mixture of palmitic, myristic and stearic acids and partly hydrogenated rosin. However, to effect hydrogenation in this way, it is necessary to work at considerable higher pressures than are required for simple degradation to palmitic and myristic acids.

For a fuller understanding of the nature and the objects of the invention, reference should be had to the following examples, which are given merely to illustrate the invention and are not to be construed in a limiting sense.

Example #1

1400 grams of a neutral potassium soap containing 30% moisture made from solvent refined tall oil are mixed in an open cast iron kettle together with 685 grams of potassium hydroxide solution of 41% strength. The mixture is then heated between 100° to 150° C. until all the water has been boiled off. The kettle is thereupon

closed with a cover which is provided with a vent pipe and the temperature is raised to 230° C. At this temperature hydrogen starts to escape through the vent pipe. The temperature is then gradually increased until at the end of six hours it has reached 290° C. At this time the evolution of hydrogen ceases. The substance is allowed to cool to 95° C. and is dissolved in 5,000 ml. of water. The soap is finally salted out by the addition of sodium chloride. The resulting product is a soap of brown color, practically odorless and can be milled into a good firm cake or dried and converted into chips or powder according to known processes.

Example #2

The substance obtained according to the process described in Example #1 is dissolved in water and thereafter acidified by the addition of 670 ml. of hydrochloric acid of 37% strength. The aqueous bottom layer is drawn off and the fatty layer is washed repeatedly with hot water until it has been freed of hydrochloric acid. The product is then distilled at a pressure of 15 mm. mercury. The light yellow distillate which consists chiefly of myristic and palmitic acids and stabilized rosin gives upon saponification a pure white hard soap.

Example #3

The crude mixture of fatty acids and stabilized rosin obtained in accordance with the process described in Example #1 is separated into a fatty acid fraction and a stabilized rosin fraction by fractional distillation at 15 mm. mercury. 580 grams of the solid fatty acid fraction consist chiefly of palmitic and myristic acids and of 8.6% rosin. The fraction is a pure white solid having melting point of 48° C. and an iodine number of 10.2. The still residue consists of a hard and brittle stabilized rosin fraction having an iodine number of 63.0.

Example #4

200 grams of crude tall oil are saponified with 50 grams of a 50% sodium hydroxide solution. The soap is then mixed with an additional 100 g. of 50% sodium hydroxide and heated in a steel autoclave with agitation at 230° C. to 290° C. for five hours. The pressure in the autoclave is kept at 12 to 14 atmospheres. The substance is allowed to cool and then dissolved in 1500 ml. of hot water. Thereafter, it is acidified with 55 ml. of sulphuric acid of 66° Bé. The fatty layer is then washed free from sulphuric acid with hot water dissolved in 1500 ml. of acetone, cooled to minus 20° C. and allowed to stand at that temperature for 6 hours. The precipitated fatty acids, after being filtered off and washed three times with 100 ml. portions of cold acetone, yield 100 grams of solid fatty acids.

From the mother liquor the stabilized rosin is recovered by distilling off the acetone.

Example #5

330 grams of crude "sulphate soap" having 60% solids are mixed with 140 grams of a 50% sodium hydroxide solution and heated in a steel autoclave with agitation at 280° C. for six hours, keeping the pressure at 15 to 20 atmospheres. The substance is allowed to cool and then dissolved in hot water and acidified with sulfuric acid to liberate the stabilized rosin and fatty acids. After washing free from sulphuric acid and drying, the substance is dissolved in 1500 ml.

of light kerosene. The solution is filtered off from any insoluble impurities and 15 ml. of concentrated sulphuric acid are added with rapid agitation. The product is allowed to stand over night and is then filtered off from the dark colored sludge which contains most of the coloring matter.

After distilling off the kerosene under reduced pressure, a light brown product of grease-like consistency is obtained which has an iodine number of 47.6 and can be converted into a soda soap of light color and hard consistency.

Example #6

The changes brought about in the rosin fraction of tall oil when autoclaved with an excess of sodium hydroxide can be ascertained by the following experiment on a technical grade of abietic acid.

An autoclave is charged with 200 grams of commercial abietic acid and 200 grams of sodium hydroxide solution of 50% strength. The autoclave is then heated with agitation to 230° C. At this temperature hydrogen starts to evolve and is sampled by means of a test vent pipe provided with a valve. The temperature is gradually raised at such a rate that at the end of 5 hours it has reached 260° C. At this time, the hydrogen evolution, which has been quite copious during the first few hours of the reaction, has ceased. The pressure in the autoclave is kept at 13 atmospheres. The product is then dissolved in hot water, acidified with sulphuric acid and washed with hot water. The acid and iodine numbers of the treated abietic acid in comparison with those of the untreated material are:

	Acid Number	Iodine Number
Untreated abietic acid	166	112.4
Autoclaved abietic acid	123.4	67.8

While in the above examples the procedure is carried out by the batch process, it is understood that it can also be readily adapted to a continuous process.

The application is a continuation in part of a copending U. S. application Serial No. 608,090, filed July 21, 1945, now abandoned.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A treatment of tall oil which comprises the steps of heating the alkali soap of tall oil with an amount of alkali at least 100% in excess of the combined alkali in the soap to a temperature of from 230° C. to 300° C. for at least four hours in order to effect isomerization and subsequent degradation of the unsaturated fatty acids into saturated fatty acids of a lower carbon content and to convert the rosin present in the original tall oil into a more saturated form, liberating the fatty acids and the stabilized rosin by acidification with a strong acid and separating the fatty acid fraction from the stabilized rosin by fractional distillation.

2. A treatment of tall oil which comprises heating the alkali soap of tall oil with an amount of alkali hydroxide one to two times that present as combined alkali in the soap to a temperature in the range of from 230° C. to 300° C. for at least four hours so as to effect isomerization with subsequent degradation of the unsaturated fatty acids into saturated fatty acids of a lower carbon content and to convert the rosin fraction into a more stable form by reducing its degree of unsaturation.

3. A treatment of tall oil which comprises the steps of heating the potassium soap of tall oil at atmospheric pressure with an equal weight of potassium hydroxide solution of 30% strength at a temperature of 230° C. to 290° C. for six hours, liberating the saturated fatty acids and the stabilized rosin by acidification with a mineral acid and distilling the product.

4. A treatment of tall oil which comprises the steps of heating the soda soap of tall oil in an autoclave with at least one quarter of its weight of sodium hydroxide in the form of a 50% solution at a temperature ranging from 230° C. to 290° C. for six hours, at a pressure from 5 to 20 atmospheres, acidifying the product with a mineral acid and purifying the product by solvent refining.

5. A treatment of tall oil which comprises the steps of heating the soda soap of tall oil in an autoclave with at least one-quarter of its weight of sodium hydroxide at a temperature ranging from 230° C. to 290° C. and at a pressure from 5 to 20 atmospheres for four to six hours, acidifying the product with a mineral acid and separating the saturated fatty acid fraction from the stabilized rosin fraction by fractional distillation.

6. A process for the modification of the rosin content of tall oil to convert said rosin into a more stable form, which comprises the steps of heating tall oil soap with alkali hydroxide at least 100 percent in excess of the alkali combined in the soap, to a temperature of from 230° to 300° C. and for at least four hours thereby effecting a reduction in the degree of unsaturation of the rosin fraction contained in said tall oil, reducing the iodine number below 80, and conversion of the unsaturated fatty acids of the soap into saturated acids.

ERNEST SEGESSEMANN.
NICHOLAS M. MOLNAR.

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