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ALKALI METAL SALT OF HYDROGENATED ROSIN

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This invention relates to alkali metal salts of hydrogenated rosin, and to the method of preparation thereof. More particularly it relates to alkali metal salts of hydrogenated rosin in the form of soaps and sizes.

Heretofore alkali metal salts of rosin have been made by the saponification of rosin with a suitable alkali metal compound, basic in nature. These salts have found extensive commercial use in the sizing of paper and in the manufacture of soaps. Paper sizes have heretofore been used in the form of wet paste, and in the form of dry powder, known as dry size. It has been found that these alkali metal salts of rosin in dry form are more desirable than the same salts in paste form, primarily from the standpoint of economy in shipping. There is, however, a serious objection to the alkali metal salts of ordinary rosin when dry, in that they oxidize in the presence of air. This oxidation and the consequent heating are deleterious and undesirable where the material is to be kept for any length of time or shipped any considerable distance. The oxidation of these salts is not only deleterious to the salts themselves, but also to the paper sized with said salts, because such paper becomes brittle and discolored when it is exposed to light and air, and, hence, is objectionable for most uses where any degree of permanence is desired.

In the extensive use of rosin in the soap industry, the alkali metal salt of rosin is formed during the manufacture of the soap and is present as such in the finished soap. However, as in the case of sizes, oxidation is an important factor here and is evidenced by yellowing of the soap, which is, of course, an objectionable feature that has not heretofore been overcome to any satisfactory degree.

In the case of the alkali metal salts of rosin, when used as sizes for paper, attempts have been made to prevent oxidation of said salts by incorporating various antioxidants therewith prior to their application to paper. However, the use of an antioxidant in the dry size is attended with an appreciable cost, an undesirable tinge of color is imparted to the paper so sized, and, in addition, introduction of the antioxidants requires a separate, distinct operating and control feature. The effect of the antioxidant is also not permanent, so that the stability of the dry size containing antioxidant decreases with age, depending upon the amount of antioxidant originally used.

It is well known that rosins in general contain unsaturated rosin acids, such as abietic acid, pyroabietic acid, pimaric acid, sapinic acid, etc., as well as varying amounts of both visible and latent color bodies. The latter are evident in unrefined or partially refined wood rosin and rapidly darken under certain conditions, as when exposed to air in the presence of an alkali. The unsaturation of ordinary rosin, together with the various color bodies therein, tend to produce the undesirable results mentioned when such rosins are saponified with alkali metal compounds, basic in nature, and these alkali metal salts of rosin then used as soaps for example.

Now, I have found that an alkali metal salt of a rosin which has been saturated to the extent of at least 50% of theoretical for two double bonds of its rosin acids by treatment with hydrogen, avoids to a great extent the objections heretofore experienced with soaps and sizes comprising alkali metal salts of ordinary rosin.

More particularly, I have found that by the use of hydrogenated rosin, the double bonds of the rosin acids of which will be saturated with hydrogen to at least 50% of theoretical, preferably from about 60% to 95% and generally within about the range of 65% to 85% of theoretical, I am able to produce by treatment with alkali metal compounds, basic in nature, such as alkali metal hydroxides and alkali metal carbonates, alkali metal salts of hydrogenated rosin which have unique properties in soaps and in sizes.

The hydrogenated rosin which I utilize will contain hydrogenated rosin acids such as hydrogenated abietic acid, hydrogenated pyroabietic acid, hydrogenated pimaric acid, hydrogenated sapinic acid, etc., and will be distinguished from the hydrogenated rosin heretofore known by its high degree of saturation with hydrogen. The use of a hydrogenated rosin, the unsaturated rosin acids of which have been saturated to the extent of at least 50% of theoretical, in preparing my new product is necessary to overcome the disadvantages set forth above. The product in accordance with this invention will, therefore, comprise an alkali metal salt of a hydrogenated rosin which is saturated to an extent of at least 50% of theoretical for two double bonds of its unsaturated rosin acid radicals by combination with hydrogen.

In the case of a size, for example, I have found that by saponification of hydrogenated rosin, with characteristics above shown, and the desiccation of the alkali metal salt of rosin so formed as by spraying or atomizing into the air, I am able to make a dry size which does not oxidize in the air to any appreciable extent, even though it contains no antioxidant and which has a per-

manent stability superior to that of ordinary dry rosin size containing an antioxidant. Consequently, my size made from hydrogenated rosin eliminates the necessity of using antioxidants and, therefore, eliminates the unsatisfactory features introduced by antioxidants as hereinbefore noted. Thus, by the use of my hydrogenated rosin, I produce a satisfactory and commercially practical dry rosin size which is resistant to oxidation and which, when incorporated in paper, initially produces a paper sized therewith of paler color and greater brightness, and one which subsequently aged or exposed to sun light, etc. is less subject to discolorization than the dry size of prior art.

Similarly, in the case of a soap, as in a laundry soap, I have found that the alkali metal salt of my hydrogenated rosin is superior to the same salt of ordinary rosin. The advantages of using my hydrogenated rosin in this case are that the soap so made has improved original color, it has better aging properties, and it is more resistant to oxidation.

The rosin which I use in producing my improved alkali metal salts of rosin is prepared by subjecting either gum rosin or wood rosin to a hydrogenation treatment. I may subject gum rosin, such as is obtained from living pine trees, and also wood rosin, such as is obtained by extraction from dead pine stump wood, down wood and the like, to a hydrogenation treatment. Hydrogenation will be effective to produce a high degree of saturation with hydrogen of the unsaturated rosin acids contained in rosins and, at the same time, will be effective to improve the color of rosins by combination of hydrogen with visible color bodies contained by rosins. In the case of wood rosin, not only will the visible color of the rosin be improved but the latent color bodies will be combined with hydrogen and the darkening under certain conditions will be lessened or inhibited.

Hydrogenated rosins suitable for uses in accordance with this invention may be made, for example, by contacting a fluid rosin with hydrogen in the presence of an activated base metal hydrogenation catalyst under a pressure within the range of about 200 to 15,000 pounds per square inch, and at a temperature within the range of about 125° C. to about 225° C. Procedure under a pressure of less than about 200 pounds per square inch will not be productive of the desired reduction in the unsaturation of the double bonds of the rosin acid, and it will be essential that the contact of the rosin with hydrogen and the base metal catalyst be carried out under hydrogen pressure within about the range 200 to 15,000 pounds per square inch, or within the narrower range of about 1,000 to about 8,000 pounds per square inch, and generally, in the average case, the treatment will be carried out under a pressure within about the range of 2,000 to 5,000 pounds per square inch.

The time of treatment of rosin with an activated base metal hydrogenation catalyst, and with hydrogen under a pressure within the limits above given, and also at an elevated temperature within the range of about 125° C. to about 225° C. will depend to an extent upon conditions such as pressure, the particular rosin treated, temperature of contacting the reagents, solvent, degree of activity of the catalyst, and the extent of hydrogenation desired. As a whole, however, the time of treatment will range from 0.5 to about 5 hours, and generally it will range from about 1 to 2 hours.

Hydrogenated rosin may be made with the aid of any suitable activated base metal hydrogenation catalyst supported or unsupported such as nickel, cobalt, etc. and activated mixtures of nickel with cobalt, etc. These catalysts in an activated state may be prepared by any well-known method. The base metal hydrogenation catalyst will be used in suitable form or suitably supported, thus, for example, the reduced base metal hydrogenation catalysts pure or admixed with their oxides may be agitated in finely divided state in admixture with hydrogen under pressure and the rosin under treatment, or the base metal catalyst may be supported on any suitable support, such as pumice, kieselguhr, or the like. The rosin for treatment will be in a fluid state, to which it may be brought by the application of a suitable temperature, or where hydrogenation is effected at a temperature below that at which the rosin is desirably fluid, by dissolving it in any suitable solvent such as for example, certain petroleum hydrocarbon cuts, for example, gasoline, light mineral naphtha, etc., a suitable alcohol, as ethyl alcohol or in solution in ether, acetic acid, etc., or other suitable solvent from which the hydrogenated products may be recovered, or the rosin may be rendered fluid by use of both heat and solvent.

Rosins as such, comprising largely abietic, pimaric, sapinic, and the like rosin acids or mixtures thereof, resenes, and also including appreciable amounts of visible color bodies, resin acids, high in oxygen, and in the case of wood rosin also latent color bodies, etc., and other ingredients normally found in rosins, such as, wood and gum rosin, may be directly subjected to the hydrogenation treatment. Again the rosin may first be subjected to a refining treatment, such as distillation under reduced pressure, say 5 to 30 mm. of mercury or under reduced pressure with the injection of steam or an inert gas; extraction with a selective color body solvent, as furfural, phenol, etc.; filtration as through fuller's earth, activated carbon; crystallization, etc., or combinations of the foregoing and the fraction or fractions subjected to treatment with hydrogen. Again the rosin before treatment with hydrogen may be subjected to distillation under vacuum for the removal of light ends with treatment of the residue, or an intermediate fraction. Likewise, if so desired, the rosin after treatment with hydrogen as above shown may be subjected to distillation under a reduced pressure say 5 to 30 mm. of mercury or under reduced pressure with injection of steam or inert gas, and a hydrogenated fractionated residue or fractions obtained, or the hydrogenated rosin may be refined with a selective solvent for color bodies, as furfural, phenol, or an absorbent as fuller's earth, activated carbon, etc., or crystallization as from alcohol, etc., or combinations of the foregoing.

Rosin, before or after hydrogenation, may also be subjected to a heat treatment. This heat treatment, either before or after hydrogenation, may be given irrespective of other treatments, as refining, fractional distillation, etc., to which the rosin or hydrogenated product may be subjected as herein described. Heat treatment of the rosin either before or after hydrogenation will generally comprise heating of the rosin or hydrogenated rosin product at a temperature of, for example, from about 275° C. to about 325° C. for a period, for example,

from about 0.2 hour to about 3 hours, under atmospheric or higher pressure. The heating will desirably be carried out in an inert atmosphere, as, for example, an atmosphere of carbon dioxide. It will be appreciated that the rosin may be heat treated before or after refinement, or before or after fractional distillation and then hydrogenated, or the hydrogenated product may be heat treated after hydrogenation, and either before or after fractional distillation.

In hydrogenating wood rosin as such, or fractionated or pre-treated in any manner indicated before, a quantity of molten rosin is mixed with about 2% of active nickel hydrogenation catalyst supported on kieselguhr. Hyrogen is then contacted with the molten rosin for a period of about 5 hours, the rosin being agitated by shaking the reaction vessel at a temperature of about 200° C. and under hydrogen pressure of about 200 pounds. During the treatment the molten rosin and catalyst are agitated. On completion of the treatment, the catalyst is filtered from the rosin or separated by dissolving the rosin with a solvent such as ether and filtering, by distillation under reduced pressure, by combinations of filtering, dissolving and distilling, or in any other convenient manner.

Following the above procedure under the conditions of temperature and pressures indicated and using a nickel hydrogenation catalyst, the rosin will be found to have about 54% saturation of hydrogen required by theory for the double bonds of abietic acid, and to be of substantially improved color by virtue of the conversion of visible color bodies into colorless color body-hydrogen combination products.

The following is another example of making hydrogenated rosin. 200 parts of "I" grade wood rosin procured by refining ordinary FF wood rosin with furfural according to the procedure described in U. S. Pat. No. 1,715,088, is agitated with 2% of an active, suitably supported nickel-hydrogenation catalyst at about 180° to about 190° C. in an atmosphere of hydrogen under 1,800 to 2,200 pounds per square inch hydrogen pressure for a period of 1.5 hours. The rosin when filtered from the catalyst will grade "N" in color and will be saturated to 61% of theory required for two double bonds of the abietic acid. By hydrogenating at 3,000 to 5,000 pounds per square inch, hydrogen pressure, a saturation of 70 to 75% will be attained when using a highly active nickel catalyst. If the catalyst is not of high activity, considerably higher pressures will be required to attain the stated degrees of hydrogenation.

The hydrogenated rosin produced in the manner illustrated above may, as has been indicated, be subjected to further treatment as by distillation at reduced pressure, fractionation under reduced pressure, extraction with a latent color body solvent, crystallization from alcohol, treatment with activated carbon, fuller's earth, and the like, or various combinations of the foregoing for the production of products of desired characteristics or improved purity.

In proceeding in accordance with my invention I take a hydrogenated rosin having a saturation of at least 50% of the theoretical for the two double bonds of an unsaturated rosin acid, such as abietic, prepared in the manner before indicated and saponify this with an alkali metal compound, basic in nature, thereby producing an alkali metal salt of hydrogenated rosin suitable for soaps and sizes. Among the alkali compounds, basic in nature, which I have found suitable for reacting with my hydrogenated rosin, are, for example, sodium hydroxide, potassium hydroxide, sodium carbonate, and potassium carbonate. The alkali metal salt of hydrogenated rosin may be made in situ, in the case of ordinary soap to be used, for example, for laundry purposes, or it may be made as such, for sizes to be applied to paper. In the latter case, it may be in the form of a paste, that is, containing sufficient water to form a paste or after formation in aqueous solution it may be recovered therefrom by suitable means of drying, thereby producing what is commonly referred to as dry size. When in the form of a paste it may contain from about 50% to about 80% of dry material, and if so desired, it may contain as high as 90%, the remainder being water.

For the manufacture of an alkali metal salt of hydrogenated rosin, suitable for use as a sizing agent, for example, I may proceed in the following manner: A quantity of hydrogenated rosin, prepared in the way before shown, is introduced into a tank or other suitable reaction vessel, an aqueous solution of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate or other suitable alkali metal compound, basic in nature, is added and the mixture heated to saponify the hydrogenated rosin. The quantity of the basic alkali metal compound added, should generally be sufficient to completely saponify the hydrogenated rosin, although I may add a small excess or a small deficiency of the alkali metal compound, thereby forming a size containing an excess of free alkali metal compound or an excess of free hydrogenated rosin respectively. The quantity of water added to the mixture in the saponification vessel should be so chosen that when spraying or atomizing the saponified rosin into a chamber through which air is circulated, substantially all the water in the sprayed or atomized size will be evaporated before the particles settle to the bottom of the chamber.

The drying of the alkali metal salt of hydrogenated rosin may be done in a variety of ways. The saponified rosin prepared as indicated above may be sprayed or atomized into a gaseous medium, e. g., air, the temperature of which is higher than that of the sprayed rosin size in order to evaporate the water from the size, or the aqueous rosin size may be superheated and sprayed or atomized into a gaseous absorbent medium, e. g., air, which is at a temperature below that of the sprayed or atomized material or the aqueous size may be dried by passing it over heated drums, thereby producing a dry size substantially free of water.

Paper sized with the alkali metal salt of my hydrogenated rosin is better in color and has a higher brightness than paper sized with similar materials made from ordinary rosin or from similar materials made from ordinary rosin and containing an antioxidant. A further advantage of my material is that the paper sized therewith is not as subject to yellowing or discoloration when aged or exposed to sunlight, ultraviolet rays, etc.

I have found that the alkali metal salts of my hydrogenated rosin are particularly applicable to the sizing of photographic papers, wherein the oxidation, with age, of any of the components is a serious objection, because of reactions with the sensitive, active components of the pho-

tographic emulsion. For this purpose I have found that rosin hydrogenated to an extent in excess of about 70% of theoretical is particularly effective.

I have further found that if ordinary rosin and my hydrogenated rosin are saponified together, that the alkali metal salt of hydrogenated rosin so produced exerts an antioxidant effect upon the alkali metal salt of ordinary rosin. For example, by the use in saponification of a mixture of about 75% or more of my hydrogenated rosin and 25% of natural gum rosin, thereby producing a mixed alkali metal salt of hydrogenated and ordinary rosin, I have found that oxygen absorption of the dry size is so reduced that the dry size does not heat in storage or transportation, does not darken by slow oxidation and does not decrease markedly the color or brightness of paper sized therewith.

In preparing soap the procedure is analogous to that used for making a size, only in this case some saponifiable oil, or fat or fatty acid is also present. I may, for example, prepare a soap in the following manner. Hydrogenated rosin, with the characteristics above shown and a fat, or fatty acid or a saponifiable oil such as, fish oil, cottonseed oil, cocoanut oil, lard oil, etc., or their hydrogenated counter parts are heated to a temperature of about 100° C. To this molten mixture there is added, while stirring, an aqueous solution of an alkali metal compound, basic in nature, and after all this has been added, stirring is continued until a whipped cream consistency is obtained. The resulting mixture is then allowed to stand in a mold for about 24 hours, during which time the saponification completes itself.

Hydrogenated rosin may be used in varying quantities in preparing soaps, depending upon the type of soap desired, and will vary from about 1% to about 65%, preferably from about 1 to about 20%.

Various fillers may also be added to the soap such as sodium carbonate, sodium phosphate, water glass, etc. In addition, various oils, such as kerosene, pine oil, etc., perfumes or scents may also be added to impart additional desirable properties, for some purposes.

Having indicated the procedure in accordance with my invention in general terms, I will now proceed to a more detailed description thereof with reference to the following example.

Example

This example is illustrative of the manufacture of an alkali metal salt of hydrogenated rosin in the form of a sizing agent for paper.

40 pounds of hydrogenated rosin, prepared as indicated before, is broken into small lumps and charged into an autoclave, the temperature of which is raised to 149° C. to 150° C. to melt the rosin. 4 pounds 15 ounces of sodium hydroxide, which is 12.35% of the weight of rosin, is dissolved in 7 pounds 11.7 ounces of water, thereby producing a 39% aqueous solution of sodium hydroxide. This caustic solution is then heated to 132° C. to 133° C. in the alkali injection blowcase, and when this temperature has been attained, the aqueous alkali solution is injected into the autoclave, which is being agitated and is under a gauge pressure of about 40 pounds. The time of injection is about 30 seconds. The alkali injection blowcase is washed out with a small amount of water to insure a complete caustic injection. After injection the pressure rises to about 80 pounds gauge and is maintained there, by venting, until the completion of the first and most vigorous reaction. Thereafter the vent is closed, and the reaction mass is allowed to cook for about 20 minutes, at a pressure from about 80–105 pounds gauge, the temperature rising during this period to about 176° C. At the end of this time the alkali metal salt of hydrogenated rosin is ejected in about 2 minutes at a pressure of about 120 pounds gauge and is recovered in the form of particles, substantially dry.

This application is a continuation-in-part of my application, Serial No. 27,579, filed June 20, 1935 which in turn is a continuation-in-part of my application, Serial No. 419,748, filed January 9, 1930.

No claim is made in this application to the method of making hydrogenated rosin nor to the product so made since such is claimed by me in my above application.

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

1. A dry rosin size in powder form and substantially free of water comprising an alkali-metal salt of an hydrogenated rosin which is saturated by combination with hydrogen to an extent greater than 50 per cent of the theoretical for two double bonds of its unsaturated rosin acid radicals.

2. A dry rosin size in powder form and substantially free of water comprising an alkali-metal salt of an hydrogenated rosin which is saturated by combination with hydrogen to an extent from about 60 to about 95 per cent of the theoretical for two double bonds of its unsaturated rosin acid radicals.

3. A dry rosin size in powder form and substantially free of water comprising an hydrogenated wood rosin which is saturated by combination with hydrogen to an extent from about 60 to about 95 per cent of the theoretical for two double bonds of its unsaturated rosin acid radical and an alkali-metal salt of said hydrogenated wood rosin.

4. A dry rosin size in powder form and substantially free of water comprising an alkali-metal salt of an hydrogenated wood rosin which is saturated to an extent greater than 50 per cent of the theoretical for two double bonds of its unsaturated rosin radicals, and saponified wood rosin, said alkali metal-salt acting as an anti-oxidant for the saponified wood rosin.

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