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ROSIN-CONTAINING SOAPS

Irvin W. Humphrey, Wilmington, Del., assignor to Hercules Powder Company, Wilmington, Del., a corporation of Delaware

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12 Claims. (Cl. 252—369)

This invention relates to soaps, for example, laundry and toilet soaps, and more particularly relates to rosin-containing soaps having improved aging characteristics.

For many years it has been common practice in the soap industry to replace a part of the saponified fatty acids, which form the essential component of washing soaps, with saponified rosin. The latter not only acts as an inexpensive filling ingredient but has detergent properties of its own which contribute to the cleansing and lathering characteristics of the finished soap. Such use of saponified rosin in soap-making, however, has been limited almost entirely to the manufacture of cheap soaps, such as yellow laundry soap, since the saponified rosin is of a yellow or tan color and gradually oxidizes and darkens upon aging.

It is accordingly an object of this invention to provide an improved rosin-containing fatty acid soap which is initially of a light color and which is more stable to yellowing or darkening upon aging than the rosin-containing soaps heretofore known.

A further object is to provide a light-colored rosin-containing fatty acid soap suitable for use as a high-grade laundry or toilet soap.

Other objects will be apparent from the following detailed description of the invention, and many advantages other than those referred to herein will occur to those skilled in the art upon employment of the invention in practice.

I have found that the above objects and attendant advantages may be realized in rosin-containing fatty acid soaps in which the saponified rosin constituent has been prepared from rosin which has been hydrogenated to an extent greater than 50 per cent, generally from about 60 to about 95 per cent and preferably from about 65 to about 80 per cent, of the theoretical for two double bonds of its unsaturated rosin acids. Rosin which has been hydrogenated to such an extent will contain hydrogenated rosin acids, such as hydrogenated abietic acid, hydrogenated pyroabietic acid, hydrogenated pimaric acid, hydrogenated sapinic acid, etc., as well as hydrogenated neutral bodies, and is distinguished from the hydrogenated rosin previously known by its high degree of saturation with hydrogen and its resistance to oxidation. The saponification products, i. e. the alkali-metal salts, of such hydrogenated rosin also have increased resistance to oxidation, and accordingly fatty acid soaps containing such saponified hydrogenated rosin display improved resistance to oxidation and consequently less yellowing or darkening upon aging as compared with soaps containing saponified rosin which has not been subjected to hydrogenation. Furthermore, the soaps provided by the present invention have initial color which is lighter than that of similar soaps containing saponified rosin which has not been hydrogenated or which has not been hydrogenated to such a high degree.

The rosin employed in preparing the new and improved soaps is prepared by subjecting either gum rosin, such as obtained from living pine trees, or wood rosin, such as is obtained by extraction from dead pine stump wood, to hydrogenation under such conditions that more than 50 per cent, and preferably from about 65 to about 80 per cent, of the double bonds of the rosin are saturated with hydrogen. Such treatment effects an improvement in the color of the rosin by reason of the fact that the hydrogen combines with the visible color bodies thereof to produce colorless, or at least lighter colored, hydrogenation products. In the case of partially refined wood rosin, not only is the visible color of the rosin improved, but the latent color bodies are also combined with hydrogen, and yellowing or darkening upon aging is decreased.

The hydrogenation treatment is preferably carried out by contacting the rosin in a fluid state with hydrogen in the presence of an activated base metal hydrogenation catalyst, such as activated nickel, under 200–15,000 pounds per square inch pressure and at a temperature of 125°–225° C. Procedure under a pressure less than about 200 pounds per square inch will not be productive of the desired reduction of the double bonds of the unsaturated rosin acids and it is essential that the reaction be carried out above this pressure, preferably at 2,000–5,000 pounds per square inch. The time required to secure the desired degree of hydrogenation depends upon the particular condition of temperature and pressure employed, the degree of activity of the catalyst, the type of rosin being treated, and other less influential factors, but is generally between about 0.5 and about 5 hours. A highly activated platinum or platinum oxide catalyst may also be employed, in which case the reaction is usually carried out at room temperature under relatively low pressure and in the presence of an inert reaction medium such as acetic acid.

Many variations in the procedure described above will occur to those skilled in the art. For example, if desired, the rosin may be dissolved

in an inert reaction solvent, such as gasoline, light mineral naphtha, ethanol, ether, etc., before being subjected to the hydrogenation reaction. Also, other suitable hydrogenation catalysts may be employed, either in a finely divided state or supported on pumice, kieselguhr, Filtercel or the like. Similarly, if desired, the rosin may be subjected to distillation under reduced pressure, heat-treatment at 250°–325° C., solvent refining as with furfural or phenol, or treatment with fuller's earth, activated carbon, or the like before hydrogenation, and the hydrogenated product may likewise be fractionally distilled under reduced pressure, heat-treated, or refined with selective solvents. All of these and many other variations are known in the art and are described in detail in U. S. Patent 2,113,808. The hydrogenation treatment may also be carried out as described in U. S. Patent 2,174,651.

In preparing the new and improved soaps of the present invention, the hydrogenated rosin may first be saponified by treatment with an alkali and the saponified product thereafter added to the fatty acids, saponifiable oils or fats, etc. employed in preparing the soap either before, during, or after the actual soap-making operation. Alternatively, the hydrogenated rosin itself may be added to the fatty acids and saponifiable oils or fats, and saponified in situ and simultaneously therewith during the soap-making process.

In the first instance, the saponification of the hydrogenated rosin may be carried out according to the known procedure for the saponification of ordinary rosin. In general, such procedure consists simply in heating a mixture of molten hydrogenated rosin and an aqueous alkali, e. g., sodium hydroxide, sodium carbonate, potassium hydroxide, etc., at a suitable reaction temperature, e. g. 100–150° C., until the reaction is complete. The proportion of alkali may be just sufficient to saponify all of the hydrogenated rosin acids present, or a small excess or deficiency may be employed to obtain a saponified product containing an excess of free alkali or free hydrogenated rosin. The proportion of water employed depends upon whether the product is to be employed in the form of a solution or paste or whether it is to be dried and employed in solid form. In some cases it may be desirable to employ a relatively large proportion of water, e. g. 8 parts by weight of water per part of hydrogenated rosin, to obtain the saponified product in relatively dilute solution from which it may be salted out with sodium chloride or other suitable salt.

Regardless of the exact details of the saponification treatment, the saponified hydrogenated rosin may be incorporated with the fatty acid soaps in the same manner heretofore employed for saponified rosin. Thus, for example, in preparing soaps by the full-boiled process with several brine wash changes, a strong change, and a finishing change, the saponified hydrogenated rosin may be added immediately following the strong change, and the soap finished as usual. The saponified hydrogenated rosin may also be added at any previous point in the soap-making process, particularly if it contains a substantial proportion of free hydrogenated rosin, or it may be mixed with the finished soap during the filling operation. The saponified hydrogenated rosin may also be added to soaps before, during, or after their preparation by other processes, for example, the semi-boiled, cold-made, or carbonate processes.

In employing the hydrogenated rosin itself in preparing soaps, it may be added at any point during the soap-making operation as described above. Likewise, it may be mixed with fats, fatty acids, and/or saponifiable oils, e. g., fish oil, cottonseed oil, coconut oil, hardened fish oil, lard oil, hydrogenated cottonseed oil, tallow, stearic acid, oleic acid, and the like, or mixtures thereof, and the mixture saponified in one step with a suitable aqueous alkali. For example, a mixture of equal parts of rosin which has been hydrogenated to an extent of about 60 per cent of the theoretical, palm oil, and olive oil may be heated to a temperature of about 100° C., after which an aqueous solution of sodium hydroxide is added and the mixture stirred until it has thickened properly. The partially saponified product may then be molded and cured for about 24 hours, during which time the saponification reaction continues to completion to form the desired soap.

The hydrogenated rosin may be used in varying proportions, alone or together with ordinary rosin, with any of a wide variety of fats, fatty acids, or saponifiable oils to prepare a wide variety of soaps. In general, however, the saponified hydrogenated rosin will comprise from about 1 to about 65 per cent, preferably from about 5 to about 50 per cent, by weight of the total saponified material present in the finished soap.

Various builders and fillers, such as sodium carbonate, sodium silicate, sodium phosphate, etc., may be added to the soap upon completion of the saponification reaction. In addition, oils, such as petroleum naphtha, kerosene, pine oil, etc., perfumes, scents, pigments, etc., may be added to impart additional properties desired in some types of soaps.

The following example is illustrative of the preparation of a hydrogenated rosin-containing soap typical of those provided by the invention, but is not to be construed as limiting the invention:

Two hundred parts of I wood rosin prepared by refining FF wood rosin with furfural according to the procedure described in U. S. Patent 1,715,088 is stirred with 2 per cent by weight of an activated nickel hydrogenation catalyst at a temperature of 180°–190° C. in a hydrogen atmosphere under a pressure of 1,800–1,200 lbs./sq. in. for about 1.5 hours. When filtered from the catalyst, the rosin grades "N" in color and is hydrogenated to an extent of about 61 per cent of the theoretical for two double bonds of the rosin acids. One hundred and eighty-two parts of the hydrogenated rosin so prepared is then mixed with 726 parts by weight of coconut oil and placed in a soap kettle and heated to a temperature of about 100° C. To this molten mixture 492 parts by weight of a 32 per cent aqueous sodium hydroxide solution is added gradually with stirring. Stirring is continued until the mixture acquires the consistency of whipped cream, after which it is poured into molds and allowed to cure for at least 24 hours. The soap so prepared is light in color and does not readily darken upon aging as determined by exposure to ultra-violet light.

In order to demonstrate the superiority of the soaps provided by the present invention over soaps containing unhydrogenated or less highly hydrogenated rosin, three soaps were prepared by a method similar to that described above.

Comparative tests on the three soaps revealed that:

(1) The soap containing rosin which had been hydrogenated to an extent of about 60 per cent of the theoretical was by far the lightest in color, and the soap containing rosin which had been hydrogenated to an extent of about 40 per cent of the theoretical was somewhat lighter than the soap containing ordinary rosin. Furthermore, the soap containing the 60 per cent hydrogenated rosin showed the least discoloration upon exposure either to ultra-violet or diffused light.

(2) The soap containing the 60 per cent hydrogenated rosin had a penetration hardness of about 11.5° as compared to 14.5° for the soap containing ordinary I wood rosin.

(3) If 2 per cent of pine oil be incorporated in the soaps during manufacture, the soap containing the 60 per cent hydrogenated rosin has sudsing properties superior to those of the similar containing ordinary I wood rosin.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the ingredients or methods disclosed, provided the product stated by the following claims, or the equivalent of such stated product, be obtained.

This application is a continuation-in-part of my co-pending application, Serial No. 193,915, filed February 28, 1938, now U. S. Patent 2,249,766, issued July 22, 1941, which application is in turn a continuation-in-part of application Serial No. 27,579, filed June 20, 1935, now U. S. Patent 2,113,808.

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

1. A soap comprising saponified 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 and a saponified fatty acid.

2. A soap comprising a saponified 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 and a saponified material selected from the class consisting of fats, fatty acids, and saponifiable oils.

3. A soap comprising an alkali-metal hydroxide saponification product of hydrogenated rosin which is saturated by combination with hydrogen to an extent from about 65 to about 80 per cent of the theoretical for two double bonds of its unsaturated rosin acid radicals and an alkali-metal hydroxide saponification product of a material selected from the class consisting of fats, fatty acids, and saponifiable oils.

4. A soap comprising a saponified hydrogenated wood rosin substantially free from latent color bodies and 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, and a saponified material selected from the class consisting of fats, fatty acids, and saponifiable oils.

5. A soap comprising saponified hydrogenated rosin which is saturated by combination with hydrogen to an extent of about 60 per cent of the theoretical for two double bonds of its unsaturated rosin acid radicals and saponified coconut oil.

6. A soap comprising saponified hydrogenated rosin which is saturated by combination with hydrogen to an extent from about 65 to about 80 per cent of the theoretical for two double bonds of its unsaturated rosin acid radicals and a saponified material selected from the class consisting of fats, fatty acids, and saponifiable oils, said saponified hydrogenated rosin being present in an amount representing from about 5 to about 40 per cent by weight of the total saponified material.

7. The method of preparing a soap which comprises saponifying a mixture of 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 and a material selected from the class consisting of fats, fatty acids, saponifiable oils, and the partial saponification products thereof.

8. The method of preparing a soap which comprises saponifying with an aqueous alkali a mixture of 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 and a material selected from the class consisting of fats, fatty acids, saponifiable oils, and the partial saponification products thereof.

9. In a process for the preparation of soap wherein a material selected from the class consisting of fats, fatty acids, and saponifiable oils is saponified with an aqueous alkali, the step which consists in adding to the saponification mixture prior to completion of the saponification reaction saponified 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.

10. A soap comprising the sodium salt of hydrogenated rosin which is saturated 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 and a saponified fatty acid.

11. A soap comprising the potassium salt of hydrogenated rosin which is saturated 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 and a saponified fatty acid.

12. A soap comprising a saponified hydrogenated rosin which is saturated by combination with hydrogen to an extent from about 60 to about 95% of the theoretical for two double bonds of its unsaturated rosin acid radicals and a saponified material selected from the class consisting of fats, fatty acids and saponifiable oils, said saponified hydrogenated rosin being present in an amount representing between about 1 and about 65% by weight of the total saponified material.

IRVIN W. HUMPHREY.

CERTIFICATE OF CORRECTION.

Patent No. 2,285,333. June 2, 1942.

IRVIN W. HUMPHREY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 31, for "50 per cent" read --40 per cent--; page 3, first column, line 21, for the words "containing ordinary I wood rosin" read --soap containing ordinary rosin--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of July, A. D. 1942.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)