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# METHOD OF IMPROVING AND SIMPLIFYING THE COLD MILLING OF SOAP AND PRODUCT OBTAINED THEREBY

Donald E. Marshall, Minneapolis, Minn., assignor to Micro Processing Equipment Co. Inc., Savage, Minn., a corporation of Minnesota

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This invention relates to the art of refining soap preparatory to formation thereof into bars and cakes, and has as its purpose to provide a better bar of soap.

The invention is predicated upon the discovery that a greatly improved bar of toilet soap with an unprecedented highly desirable waxy texture is obtained if the base material from which it is formed or pressed consists essentially of a mixture of fatty-acid potash soap and fatty-acid soda soap in proportions of between 5% and 30% potash soap, and between 95% and 70% soda soap, which mixture has been subjected in the solid state and at a temperature below the crystalline reversion point of the soap, to a mechanically produced internal shearing action great enough to convert the mixture to an ultramicrocrystalline state. This state is evidenced by a rubbery translucent waxy texture, good cold welding properties, a substantially non-swelling gel structure, freedom from objectionable soap dish jelly formation, high viscosity and excellent solubility and lathering action. These are the qualities which have always been sought in fine toilet soaps but heretofore could not be attained except by the ultramilling technique taught in the Marshall Patent No. 2,619,680, and the Marshall et al. Patent No. Re. 23,760. Cold roller milling, which had long been the conventional way of mechanically refining the crystalline structure of toilet soap prior to the invention of the ultramilling methods covered in Patents Nos. 2,619,680 and Re. 23,760, was incapable of achieving the internal shearing action needed to attain an ultramicrocrystalline state.

The ultramilling technique disclosed in the aforesaid patent enabled ordinary fatty-acid soda soap to be reduced to an ultramicrocrystalline state, but required the application of high speed shearing forces upon very thin films of high viscosity soap. The present invention not only yields a product which has the desired ultramicrocrystalline state without entailing ultramilling in the manner taught in these patents, but in addition, greatly expands the range of soap formulations and still obtains a satsifactory bar, because the invention achieves a soap having an unexpectedly high viscosity or firmness over a wide range of fat titers and moisture percentages. This increase in firmness or viscosity is quite contrary to the softening effect normally experienced when fatty-acid potash soap is admixed with soda fat acids.

Moreover, a toilet soap made in accordance with this invention and containing 20% fatty-acid potash soap and 80% fatty-acid soda soap, and 12% to 14% moisture has a substantially higher viscosity, i. e., is much firmer than if the same fats were saponified with sodium alone, other conditions being equal.

It is not known just why a mixture of potash soap with soda soap milled in the solid state at a temperature below the reversion point of the soap brings about all the desirable qualities that have been attained. It is possible that the potash soap when thus milled with the soda soap somehow softens the crystals of the soda soap



so that they are more easily subdivided, notwithstanding the fact that less speed and less pressure is employed in the milling operation than is required for the ultramilling of soda soap alone. On the other hand the remarkably high viscosity of the product, despite the presence of a considerable amount of potash soap, suggests that the step of milling the two soaps together in the solid state not only converts this soap mixture to an ultramicrocrystalline state but also brings the resulting sub-micron sized hard crystal particles closer together and perhaps even effects an interlocking engagement between them.

Whatever the explanation may be, there is unquestionably a highly advantageous and significant consequence which flows from the cold milling of mixtures of potash and soda soaps in the solidified state since this invention for the first time has made it possible to produce the much sought glassy or vitreous soap with its characteristic waxy texture by milling or extrusion processes conducted at shearing speeds and pressures far below those needed in the practice of the ultramilling techniques of Patents Nos. 2,619,680 and Re. 23,760.

While the best results are obtained by milling the potash soda soap mixture in a machine constructed in accordance with either of the aforesaid Patents Nos. 2,619,680 or Re. 23,760, excellent results are also obtained if the mixture is merely extruded through a suitably small orifice under sufficient pressure. Thus it has been found that a mixture of 15% potash soap and 85% soda soap at 13% moisture, will be satisfactorily converted to an ultramicrocrystalline state if extruded three or four times through a perforated plate having 1/16" diameter orifices, at a pressure of 500 to 1000 p. s. i., this having been done with the special gear pump extruder described in the copending application of Donald C. Marshall, Serial No. 271,059, filed February 11, 1952.

If the milling methods and machines of Patents Nos. 2,619,680 and Re. 23,760 are employed, the desired conversion of the potash-soda soap mixture is achieved with shearing speeds of 500 to 1,000 feet per minute when the mixture has a moisture content of 11% and the percentages of the soda and potash soaps are 85 and 15 respectively. This compares with shearing speeds of 4,000 feet per minute required for such ultramilling of 100% soda soap of the same moisture content.

Numerous experiments made during the development of this invention have demonstrated that aside from the fact that the moisture content of the soap mixture at the time it is milled must be roughly inversely proportional to the percentage of potash soap in the mixture, the amount of moisture is not critical as long as the other factors affecting viscosity such as temperature and the titer of the fats used are satisfactory.

Thus it has been found that a mixture of 15% fatty-acid potash soap and 85% fatty-acid soda soap, with both soaps containing 80% tallow or the equivalent thereof and 20% coconut oil or a similar nut oil, if milled at a temperature on the order of 80° F. to 100° F. or at least below 100° F. will yield a bar which is firmer and of far superior texture than the finest toilet soap heretofore obtainable with conventional methods, even though the mixture has a moisture content of 18% at the time it is milled. Apparently, the exceptional crystal-to-crystal nearness attained by the milling of the potash-soda soap mixture in the solid state enables the product to hold far more water without objectionably decreasing the viscosity of the bar, than was heretofore possible.

Another very important and desirable consequence of this invention is the fact that the potash-soda soap combination permits the incorporation into the milled product of extraordinarily large percentages of non-detergent additives. Thus it has been found that such skin emollients

as petrolatum and lanolin, and hair conditioners such as petrolatum, lanolin and gums, may be incorporated in the product to a much greater extent than is possible with ordinary roller milled soaps. As much as 15% of such non-detergent skin emollients and hair conditioners are readily accommodated.

Until 10% or more of these emollients are added, their beneficial effects are very little, if any. On the other hand, when 10% petrolatum is added, the mildness of the soap is definitely improved so that over washing is prevented and the high activity of potassum soaps is moderated to the extent that the same mildness which characterizes shaving creams is attained.

The incorporation of 10% petrolatum also brings about an improvement in the durability of the cake in respect to long periods of submersion as when the bar is left in the bath tub. The oil barrier presented by the petrolatum seems to prevent penetration of the water and subsequent cake distintegration.

If lanolin is substituted for a portion of the petrolatum the bar will yield a lather which conditions the hair so as to make it curl after a shampoo. Other resins, glue and miscellaneous gums commonly used in hair creams may be substituted for the petrolatum to gain special hair behavior after shampooing.

A point of major importance in connection with the so-called super-fatting of bar soaps with petrolatum, etc., is the danger that the addition of such emollients may render the bar too soft or too poorly lathering. This danger is overcome by this invention because the higher viscosity and better lathering ability (solubility) it imparts to the soap enables the soap to accommodate more of these materials which retard lather formation than conventional soaps having a softer texture and less active lathering properties.

Many synthetic detergents also make desirable additives to bar soaps for boosting lathering ability and as an aid in rinsing. The term "synthetic detergent" is well understood in the soap making art and refers to any water-soluble surface active agent having a long chain organic radical which, unlike soap, has the property of dispersing or dissolving calcium or magnesium soaps instead of forming such insoluble alkaline earth soaps as is the case with ordinary fatty-acid soaps in hard water washing. In general, such synthetic detergents are much more effective for breaking the interface between oil and water than soap, and thus more effectively wet greasy surfaces and more effectively disperse oil and grease to enable its removal from surfaces being washed.

The synthetic detergents contemplated in this invention are only the solid organic non-soap type, that is, such synthetic detergents as will form a solid particle capable of being attached to a particle of ultramicrocrystalline cold milled fatty-acid soap. More specifically, the synthetic detergents contemplated by the present invention are usually sodium salts of long chain organic compounds containing sulfate or sulfonate groups and ordinarily referred to as organic sulfated and sulfonated anionic detergents. As is well known in the art, such synthetic detergents may also contain an aryl group. Also, instead of being sodium salts of the compounds mentioned above, they may be ammonium salts or salts or other alkali metals such as potassium. As is also well known in the art, groups other than sulfates or sulfonates may be employed to produce water soluble synthetic detergents, for example, a series of hydroxyl or other groups.

These synthetic detergents may be added to the potash-soda soap mixture in quantities such that their active ingredients comprise from 5% to 20% of the total ingredients of the finished product. Despite the fact that these synthetic detergents alone may provide all the suds boosting needed, the addition of potash soap is still necessary in order to obtain economically a soap having all of the other desirable attributes, the attainment of which is the object of this invention, and this is of course because potash soap aids so effectively in bringing the admixture to the ultramicrocrystalline state.

Examples of synthetic detergents usable in the present invention are as follows:

| Chemical Name | Typical Formula |
|---|---|
| Sodium Lauryl Sulfate | $C_{11}H_{23}CH_2O\,S\,O_3Na$ |
| Sodium Lauric Monoglyceride Sulfate | $C_{11}H_{23}C\,O\,O\,CH(CH_2)O\,S\,O_3Na$ |
| Sodium Hydroxyethane Sulfonate | $C_{17}H_{33}C\,O\,O\,CH_2CH_2S\,O_3Na$ |
| Sodium Alkyl Benzene Sulfonate | $C_{12}H_{23}$ (C6H4) $S\,O_3Na$ |
| Sodium Alkyl Benzene Sulfonate | $C_9H_{19}$ (C6H4) $S\,O_3Na$ |
| Sodium Alkyl Sulfonate | $C_{20}H_{41}S\,O_3Na$ |
| Sodium Dihexyl Sulfosuccinate | $C_6H_{13}O\,C\,O-CH_2$ / $C_6H_{13}O\,C\,O-CH-S\,O_3Na$ |
| Sodium Secondary Tridecyl Sulfate | $O\,S\,O_3Na$ / $C_5H_{11}-C-C_7H_{15}$ |

As noted hereinbefore, the viscosity of the product of this invention is well above that of conventional roller milled fatty-acid soap of equivalent moisture content and fat titer, despite the presence of a substantial percentage of potash soap. This has been clearly demonstrated with the Harrington viscosity engine described in the Marshall et al. Patent No. 23,760. That machine provides an accurate way of making viscosity comparisons by depicting the viscosity of a substance tested by a definite numerical value or index number. Thus on this Harrington viscosity engine conventional roller milled soaps will be found to have a viscosity of about 100, whereas the product of this invention containing as much as 30% potash soap will show a viscosity as high as 400.

Very briefly, the Harrington viscosity measuring engine consists of a pneumatic power cylinder acting through a leverage system to drive a ram though a close-fitting collar and into a cylindrical chamber containing the mass to be tested. For the ram to enter the cylinder, the material therein of course, must be displaced. Hence, as the ram is forced into the cylinder, the material is extruded through the clearance between the ram and its close-fitting collar.

The pertinent dimensions of an embodiment of this viscosity engine used in the development of this invention are as follows:

Power cylinder—piston area of 28.2 square inches.
Ram—the area of face is .11045 square inches.
Leverage—6 to 1.
Clearance—.001 inch clearance between ram and its collar.
Pressure developed—for every pound of pressure on the driving cylinder the pressure on the soap sample being tested is 1,538 p. s. i.

By measuring the time required to extrude a given amount of the sample through the .001 inch clearance and multiplying that time factor by the pressure in the pneumatic driving cylinder, an arbitrary viscosity index number is obtained. The numerical viscosity indications 100 and 400 used hereinbefore are such viscosity index numbers.

The superior lathering ability of bars made of the product of this invention, was accurately determined by the Toof method described in Patent No. 2,674,889. This method tests the solubility (lathering ability) of a bar of soap by measuring the rate of migration of a precipitate cloud formed in a shallow quiet pool of hard water in consequence of the immersion of the bar in the water.

By this test it was found that soap bars made from the product of this invention and containing as little as 2% moisture and no coconut oil soap, will lather three times as well as conventional roller milled soap containing 15% to 20% coconut oil and having a moisture content of 8% plus.

By this test, it was also found that non-floating bars made with the product of this invention and containing 15% potash soap have a solubility twice as great as that of "Swan" soap (the floating soap made according to the Bodman Patent No. 2,215,539) containing 10% moisture and 17% potash soap, but of course, not converted to the ultramicrocrystalline state as is the product of this invention; and twice as great as that of "Ivory" soap (the floating soap made according to the Mills Patent No. 2,295,594) which has no potash content but contains 10% coconut oil soaps and 17% moisture.

Although the foregoing description is no doubt sufficient to enable those skilled in the soap making art to fully understand and practice this invention, the following examples of specific embodiments of the invention may be helpful, and in any event will serve to graphically illustrate the scope of its achievement.

*Example A*

Soda soap chips were dry mixed with potash soap chips in the proportions of 95% and 5% respectively. Both soaps had a fat base of 85% tallow and 15% coconut oil. The moisture content of this mixture was a fraction above 11%. In its solidified state the soda-potash soap mixture was ultramilled on the band mill of the Marshall et al. Patent No. 2,619,680 with the band traveling 1,000 feet per minute and the temperature of the mixture between 100° F. and 120° F. so that there was no danger of crystalline reversion. This ultramilling subjected the soap mixture to an internal shearing action which reduced it to the ultramicrocrystalline state.

The resultant product which was in the form of very thin flakes and had a viscosity of 150 on the Harrington viscosity engine, was then pulverized and compacted into bars in the manner taught in the Marshall Patent No. 2,594,956. The bars had a moisture content of 11% and possessed all the characteristics typical only of soap in the ultramicrocrystalline phase, namely, a rubbery translucent waxy texture, substantially non-swelling gel structure, freedom from objectionable soap dish jelly formation, high viscosity and excellent solubility and lathering action.

In explanation of the slightly indefinite 11% plus definition of the moisture content of the mixture at the time it was ultramilled, it is pointed out that the determination of moisture content was made after the product had been formed into a bar, and that at the temperatures involved, i. e., less than 120° F. (the crystalline reversion point) the loss of moisture during milling is inconsequential ranging from one tenth of one per cent to one-half of one per cent.

All percentages given are by weight.

A recapitulation or brief formula of this example is as follows:

| | Per cent |
|---|---|
| Soda soap (85% tallow, 15% CNO) | 95 |
| Potash soap (85% tallow, 15% CNO) | 5 |

This mixture at 11% plus moisture content was bandmilled at temperatures between 100° F. and 120° F.

The product was pulverized and then compacted into bars. The finished bars had 11% moisture and a viscosity of 150.

*Example B*

The same procedure as described for the preceding example was followed, but the percentages of the ingredients were as follows:



| | |
|---|---|
| Soda soap (85% tallow, 15% CNO)_____per cent | 85 |
| Potash soap (100% tallow) _____do____ | 15 |
| Moisture content of mixture at time of bandmilling _____ | 10% plus |
| Finished bar: | |
| Moisture content _____per cent__ | 10 |
| Viscosity _____ | 300 |

*Example C*

Again the same procedure described for Example A was used, but on the following formula:

| | |
|---|---|
| Soda soap (100% tallow)_____per cent__ | 70 |
| Potash soap (100% tallow)_____do____ | 30 |
| Moisture content of mixture at time of bandmilling _____ | 8% plus |
| Finished bar: | |
| Moisture content _____per cent__ | 8 |
| Viscosity _____ | 400 |

*Example D*

In this example the ratio of potash to soda soap was the same as in Example C, but a higher moisture content was used, and in lieu of bandmilling, the mixture was extruded four times through a perforated plate having 1/16" diameter orifices under a pressure of 1000 p. s. i., at a temperature of 80° F. The formula for this example was:

| | |
|---|---|
| Soda soap (100% tallow)_____per cent__ | 70 |
| Potash soap (100% tallow)_____do____ | 30 |
| Moisture content of mixture at time of extrusion _____ | 18% plus |
| Finished bar (made by compacting the final product of the multiple extrusion into a mass and extruding the mass into a bar which was cut and stamped to size): | |
| Moisture content _____per cent__ | 18 |
| Viscosity _____ | 100 |

*Example E*

In this example the procedure followed was the same as in Example A, but the formula was as follows:

| | |
|---|---|
| Soda soap (100% tallow)_____per cent__ | 80 |
| Potash soap (100% tallow)_____do____ | 20 |
| Moisture content of mixture at time of bandmilling _____ | 5% plus |
| Finished bar: | |
| Moisture content _____per cent__ | 5 |
| Viscosity _____ | 600 |

*Example F*

This example incorporated an emollient. The procedure was the same as in Example A but the formula was as follows:

| | |
|---|---|
| Soda soap (85% tallow, 15% CNO)____per cent__ | 85 |
| Potash soap (100% tallow)_____do____ | 15 |
| Emollient (petrolatum) added to soap mixture before bandmilling _____per cent__ | 5 |
| Moisture in mixture at time of bandmilling___ | 10% plus |
| Finished bar: | |
| Soda-potash soap mixture_____per cent__ | 85 |
| Moisture _____do____ | 10 |
| Emollient _____do____ | 5 |
| Viscosity _____ | 200 |

*Example G*

This example was the same in all respects as Example F except that the percentage of emollient to soap was greater, and as a result, the viscosity was lower, as will be seen from the following analysis of the finished bar:

| | |
|---|---|
| Soda-potash soap mixture_____per cent__ | 80 |
| Emollient _____do____ | 10 |
| Moisture _____do____ | 10 |
| Viscosity _____ | 100 |

*Example H*

This was another example incorporating an emollient, and like the preceding example, was the same as Example F, but in this case even a greater percentage of emollient was accommodated. The finished bar analysis was as follows:

| | | |
|---|---|---|
| Soda-potash soap mixture | per cent | 80 |
| Emollient | do | 15 |
| Moisture | do | 5 |
| Viscosity | | 100 |

*Example I*

In this example a synthetic detergent was added to the formula. The procedure was the same as in Example F, but the analysis of the bar was as follows:

| | | |
|---|---|---|
| Soda-potash soap mixture | per cent | 82 |
| Emollient (petrolatum) | do | 5 |
| Moisture | do | 7.5 |
| Synthetic: | | |
| Salt | do | .5 |
| Active ingredient | do | 5 |
| Viscosity | | 100 |

*Example J*

This example was the same as the preceding one but the ratio of synthetic detergent to soap was higher. The analysis of the resulting bars was as follows:

| | | |
|---|---|---|
| Soda-potash soap mixture | per cent | 63 |
| Emollient (petrolatum) | do | 10 |
| Moisture | do | 5 |
| Synthetic: | | |
| Salt | do | 2 |
| Active ingredient | do | 20 |
| Viscosity | | 100 |

*Example K*

This was another example to test the effect of the synthetic detergent. The general procedure was the same as in the previous two examples, but no emollient was used, and the percentage of synthetic detergent used was reduced. A notable increase in viscosity was noted. The analysis of the finished bars of this example follows:

| | | |
|---|---|---|
| Soda-potash soap mixture | per cent | 79 |
| Moisture | do | 10 |
| Synthetic: | | |
| Salt | do | 1 |
| Active ingredient | do | 10 |
| Viscosity | | 200 |

The last three examples were made with sodium lauryl sulfate for the synthetic detergent and were repeated with sodium alkyl benzine sulfonate as the synthetic detergent.

In some of the examples given, the potash soap was added to or mixed with the soda soap while both components were in the form of dry chips or pellets, i. e., discreet and independent of one another; in others the potash soap had been combined with part of the soda soap content of the total mixture while both were in the liquid state.

Experience indicated that neither the manner in which the mixture was effected, nor the state of the soap (liquid or dry) at the time of mixture, had any bearing upon the results. The important factor was that the mixture had to be in the solidified state at the time it was reduced to an ultramicrocrystalline state by milling. "Solidified state" is understood to mean that the mixture had a moisture content substantially no greater than 18% and was at a temperature less than 120° F. The lower limits of moisture and temperature depend only upon the capabilities of the apparatus. Thus, while the examples given show no moisture content less than 5%, the apparatus of Patents Nos. 2,619,680 and Re. 23,760 (especially the latter) is capable of handling soap mixtures of less moisture content; and in one instance, in order to more effectively demonstrate the exceptional solubility of the product, the moisture content was reduced to 2%.



It should also be noted that since the conversion to ultramicrocrystalline state is done at a temperature below the crystalline reversion point (120° F.) the product is stable against crystal enlargement and/or crystal separation or reorientation, which, if it occurred, would destroy the properties sought.

Comparison of the several examples given provides a graphic illustration of the fact that the milling of the soda-potash soap mixture in the solidified state achieves a remarkable result which is of utmost importance to the soap making art. Because of the aid which the presence of the potash soap affords in attaining the ultramicrocrystalline state, the highest quality bars now can be produced at a fraction of the cost in time and power consumption required for the attainment of such quality from soda soap alone, and in view of the unexpectedly high viscosity of the product even when the potash soap content of the soap component is as high as 30% (Example C), and the percentage of moisture in the bar is as high as 18% (Example D), the desired fine waxy textured soap is obtainable over a wide range of soap formulations.

This application is a continuation-in-part of the copending application Serial No. 271,060, filed February 11, 1952, and now abandoned.

What is claimed as my invention is:

1. In the process of milling solidified fatty acid soda soap to an ultramicrocrystalline state by subjecting said soap, at a temperature below its crystalline reversion point, to a mechanically produced shearing action, the characterizing step of introducing a milling promotion agent to the soda soap to be milled so that the transformation of the structure of the soda soap to the ultramicrocrystalline state is facilitated to such an extent that conventional soap extruders can be employed for such transformation, said milling promotion agent being a fatty acid potash soap which is mixed with the soda soap in proportions such that the potash soap constitutes from 5 per cent to 30 per cent by weight of the mixture, considered on an anhydrous basis.

2. In the process of milling a solidified soap base material which has fatty acid soda soap as its principal component, to an ultramicrocrystalline state, and which process involves subjecting said soap base material, at a temperature below the crystalline reversion point of the soda soap, to a mechanically produced shearing action, the characterizing step of incorporating in the base material to be milled a milling promotion agent by which the transformation of the structure of the soda soap component to the ultramicrocrystalline state is facilitated to such an extent that conventional soap extruders can be employed to effect such transformation, said milling promotion agent being a fatty acid potash soap which is mixed with the base material in proportions such that the potash soap constitutes from 5 per cent to 30 per cent by weight of the soda-potash soap combination, considered on an anhydrous basis.

3. A cake of milled toilet soap characterized by the fact that the soap base material from which the cake is formed consists essentially of a homogeneous and thoroughly coalesced milled mixture of fatty acid potash soap and fatty acid soda soap in the ultramicrocrystalline state which results from subjecting the mixture of potash and soda soap while in the solidified state, and at a temperature below the crystalline reversion point of the soaps to a mechanically produced shearing action, and which state is evidenced by a rubbery translucent waxy texture, good cold welding properties, a substantially non-swelling gel structure, freedom from objectionable soap dish jelly formation, high viscosity and excellent solubility and lathering action; the percentage of fatty acid potash soap in said milled mixture being 5 per cent to 30 per cent thereof, and the balance being fatty acid soda soap, considering the mixture in the anhydrous state.

4. The product of claim 3 further characterized by the fact that the milled soap base material from which the cake is formed has oily emollient, such as petrolatum and lanolin, coalesced therein in an amount such that the emollient constitutes 5 per cent to 15 per cent by weight of the whole coalesced mixture.

5. The product of claim 3 further characterized by the fact that the milled soap base material from which the cake is formed has the active ingredient of solid anionic non-soap organic type synthetic detergent coalesced therein in an amount such that the synthetic detergent constitutes 5 per cent to 20 per cent by weight of the resulting base material.

6. The product of claim 5 further characterized by the fact that the base material defined in claim 5 has oily



emollient, such as petrolatum and lanolin, coalesced therein in an amount such that the emollient constitutes 5 per cent to 15 per cent by weight of the total coalesced mixture.

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