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(54) SOAP BAR MANUFACTURE

(71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

This invention relates to the manufacture of soap bars containing very high molecular weight poly (ethylene oxide).

The inclusion of such poly (ethylene oxide) in a toilet soap bar makes it possible to provide a hard tough bar which when wetted has a degree of slipperiness pleasant to the user, gives a lather which is creamy, pleasantly silky and effective, has good resistance to sloughing in use despite a high moisture pickup, is long lasting, flexible and tough even after much of the bar has been used up, and provides a beneficial effect on the hands (e.g. reduces chapping and flaking, and moisturizes the skin, particularly dry skin).

When one attempts to incorporate the high molecular weight poly (ethylene oxide), which is supplied as a dry powder, into a toilet soap bar using the methods by which powdered ingredients are conventionally added (e.g. by addition to the soap amalgamator along with other ingredients) it is found that the resulting toilet soap bars have spaced visible and palpable specks. These specks are sometimes observed on the surface of the final pressed bar, or they become evident when the bar is used in cold water. For instance, there may be some 50 to 500, or more, visible specks per bath size bar. Examination of these specks reveals that they are agglomerates or gels containing poly (ethylene oxide); typically, the volume of a speck is from about 0.005 mm^3 to about 0.3 mm^3.

The formation of such specks can be substantially avoided by the method according to the invention.

According to the invention a method of making soap bars containing, by weight, at least 60% of soap and from 0.5% to 10% of poly (ethylene oxide) comprises mixing the soap in the form of chips with the poly (ethylene oxide) in the form of powder while the surfaces of the soap chips are in powder-adherent condition with respect to the polyethylene oxide powder to produce soap chips having poly (ethylene oxide) bonded thereto, then adding other ingredients of the soap bar and mixing the other ingredients with the bonded chips, then forming the resulting mixture into a soap bar.

Two preferred forms of the method comprise:

(a) adding the powdered high molecular weight poly (ethylene oxide) to soap chips having a moisture content such that the powder adheres thereto (e.g. at least 11% water – this and other percentages and proportions given herein are by weight) and mixing before adding the other solid ingredients; and

(b) adding the powdered high molecular weight polyethylene oxide to soap chips having a lower moisture content than 11%, mixing, and then adding some water in a finely dispersed state (e.g. to bring the water content, based on soap, to a level sufficient to provide powder adhesion) before adding the other solid ingredients.

The reason why the method avoids the formation of specks is not understood, but it may be that the particles of high molecular weight poly (ethylene oxide) (whose moisture sorption is below 3% at a relative humidity of 60% at 25°C, according to the manufacturer's bulletins) take up sufficient moisture from the higher moisture content soap chips and become bonded, individually, to the surfaces of the chips so that these particles are thus prevented from agglomerating; if there is not sufficient moisture for this to occur before the subsequent addition of other solid ingredients (particularly powders of low moisture contents, e.g. below 8% water), the latter may compete for the limited amount of moisture available, and loose particles of high molecular weight polyethylene oxide may agglomerate in later stages.

The powder-adherent property of the soap chips may be tested in the manner illustrated in Example I below. Best and most consistent results are obtained when the moisture content of the surface is such that the powder "disappears" on remaining in contact with the surface for a short time (e.g. 1 to 2 minutes) as for the 15% moisture chip in Example I.

The soap constitutes at least 60%, preferably more than 70%, of the moisture-free weight of the bars. The soap may be of a conventional type consisting premominantly of 12 to 18 carbon atom molecules and may be produced by the saponification of fatty materials suitable for use in soap making, suitable fatty materials comprising, for example, fats, oils and waxes of animal, vegetable or marine origin and fatty acids derived therefrom, or of synthetic origin. More specifically, the fatty acids may be of mixed character such as are derived from natural or hydrogenated tallow, cottonseed oil, coconut oil, palm oil, palm kernel oil, babassu nut oil, grease, fish oils, and fatty acids derived therefrom by hydrolysis or saponification, or they may be pure materials such as lauric, myristic, palmitic, stearic and oleic acids. It is generally preferred to used the sodium salts of the mixed fatty acids derived from tallow and coco (coconut oil) and mixtures thereof. A desirable blend has a weight ratio of sodium coco soap to sodium tallow soap in the range from 50:50 to 10:90, a ratio below 30:70, e.g. a range from 25:75 to 17:83, being especially preferred. As is known in the art, the higher coco contents give faster, more copious lather but more irritation, in conventional soaps. It is permissible to use blends of the sodium soaps and the corresponding potassium soaps (e.g. in mole ratios of sodium:potassium of 90:10 or 75:25).

The high molecular weight poly (ethylene oxide) preferably has an average molecular weight of at least 100,000. Examples of such compounds are those sold by Union Carbide Company, U.S.A., under the trademark "Polyox". These polymers are nonionic and extremely soluble in water and their molecular weights range from about 100,000 to about 5,000,000 or more. It is preferred to employ polymers having average molecular weights below 1,000,000, more preferably not above 600,000 such as about 300,000 to about 400,000. The proportion of high molecular weight polymer of ethylene oxide in the soap bar is from 0.5% to 10% and is preferably at least 1% and less than 5%, more preferably below 4%. For the material having an average molecular weight of about 300,000 a proportion in the neighbourhood of 2% has given excellent results. This 300,000 molecular weight material (sold as Polyox WSR N-750) has a viscosity at 25°C for a 2% aqueous solution of about 40 centipoises (Brookfield Spindle No. 1 at 10 rpm); for a 5% solution the viscosity is about 600–1,000 centipoises. Use of, say, 2% of extremely high molecular weight poly (ethylene oxide), e.g. of 4,000,000 average molecular weight, causes the lather to be pituitous, which is less desirable. According to the manufacturer the Polyox materials typically have a pH of about 10 (e.g. in 5% solution). Soap typically has a pH in 1% aqueous solution of about 10 (e.g. 10.2).

The poly (ethylene oxide) is generally supplied as a powder and typically has the following particle size distribution when a sample thereof is screened through a series of sieves, expressed as weight percent retained of the indicated Sieve No. screen (U.S. Sieve Series): No. 20–5.2%: No. 40–31.2%: No. 60–20.7%; No. 100–16.7% and through No. 100–balance. It is often preferable to use a finer particle size poly (ethylene oxide) having the following distribution as measured above: No. 20–0.3%; No. 40–13%; No. 60–13%; No. 100–13.9% and through No. 100–balance.

The invention has found its greatest utility so far in the production of soap bars containing hydrolyzed protein. A particularly preferred hydrolyzed protein is Protein A sold by Croda Inc., New York, N.Y., U.S.A., and is a particularly enzymatically hydrolyzed protein derived from beef collagen and characterised by having a zero Bloom gram gel strength, a 10% weight/weight water solution having a viscosity range of about 16 to about 25 millipoises (mps), a pH of 5.5 to 6.5, and, in weight percent, a hydroxyproline content (mainly chemically combined hydroxyproline) of about 10% to about 12%, a nitrogen content of about 15% to about 18%, and a total nitrogen as amino nitrogen of about 5% to about 12%, and a molecular weight of about 1,000 to about 3,000, such as about 2,000. Its ash content is generally low (e.g. below 10%). Other hydrolyzed proteins which may be used include hydrolysis products comprising proteoses, peptones and/or polypeptides, typically having a molecular weight of at least 600 and below 12,000, preferably below 5,000, and including moieties of a plurality of amino acids. These hydrolysis products may be formed by partial enzymatic hydrolysis, such as by the action of typsin, erepsin or pancreatic enzymes on protein material (e.g. at about 35 to 50°C for about 12 to about 48 hours). The partially degraded protein may also be a product obtained by partial hydrolysis of protein by heat and/or alkali. Proteins partially degraded by heat may be prepared, for instance, by heating proteinaceous material such as bones, feet, or skin of pork or beef which has been reduced to small pieces and immersed in water, by autoclaving at about 2.8 to about 3,5 kg/cm 2 of saturated steam (i.e. at from 141.5 to 147.6°C) for about two hours; three phases including fat, the desired aqueous phase, and a residue may thus be obtained; the aqueous phase which may contain about 8% to about 10% solids may be concentrated *in vacuo* to about 50% to about 60% solids at 60–70°C to obtain a "solubilized collagen", a heat degraded protein, which may be employed in performing this invention.

Typical proteins which may be partially hydrolyzed for use in the soaps of this invention include casein, gelatin, collagen, albumin, zein, gliadin, keratin, fibroin, globulin and glutenin. Typical commerical partially enzymatically hydrolyzed proteins include Bacto-Proteose (sold by Difco Laboratories Detroit, Mich., U.S.A.), proteous-peptone, casein-peptone, gelatin-peptone, Bacto-Peptone (sold by Difco Laboratories), vegetable peptones, such as soybeans peptone, Proto-Peptone (sold by Wilson Co., U.S.A.), the peptone enzymatically derived from solubilized collagen using ground frozen pancreatic enzymes having a pH of 8, digestion being at about 49°C for about 12 to about 48 hours, the solubilized collagen being derived by heating bones, feet or skin of pork or beef). The preferred proteins are solubilized beef collagen and solubilized pork collagen which may be prepared as described and are generally characterised by a gel strength of about zero Bloom grams.

The partially hydrolyzed protein may have a relatively broad spectrum of molecular weights and may contain some (usually small amounts of) almost completely degraded polypeptides, such as dipeptides and tripeptides, and even some amino acids, as a result of the degradation process. If desired, these may be removed by dialysis, e.g. by placing the partially degraded protein in a cellophane bag which is then closed at both ends and is lowered into a tank into which deionized water continuously enters and from which it continuously leaves; products such as the tripeptides, dipeptides and amino acids pass out through the cellophane by dialysis to mix with the deionized water and leave the partially degraded protein. When employed, dialysis procedure has the additional advantage of removing the odours of the more completely hydrolyzed material.

The proportion of protein ingredient in the soap bar is generally at least 0.1% and below 10%. Amounts in the range from 1% to 5% are preferred, a level of about 3% being especially preferred. For the preferred protein material the 1% to 5% range provides a hydroxyproline content of about 0.1% to about 0.5%, preferably about 0.3%.

In addition to, or in place of, the protein, super-fatting agents may be included. It is found that acetylated lanolin (such as Modulan sold by American Cholesterol, U.S.A.; see U.S. Patent No. 2,725,334) gives especially good results. Other superfatting agents are hydroxylated lanolin, (e.g. OH Lan sold by American Cholesterol), higher (C_{10}–C_{20}) fatty acids such as stearic acid or coconut oil fatty acid, higher fatty alcohols and petrolatum. Amounts of superfatting agents less than 10% total are generally employed, preferably from 1% to 5% e.g. 2% to 3%.

The bars may also contain a synthetic surfactant of high foaming characteristics in hard water, such as alkali metal salts of organic sulphuric reaction products having in their molecular structure an alkyl radical of from 8 to 22 carbon atoms, e.g. alkyl benzene sulphonates, coconut oil fatty acid monoglyceride sulphonates and sulphates, and alkali metal fatty acid (C_{10}–C_{16}) isethionates. A particularly preferred ester is sodium coco isethionate sold as Igepon AC–78 by the General Aniline and Film Corporation, U.S.A. The proportion of synthetic surfactant is generally in the range from 0.5% to 5%, preferably from 1% to 3%, e.g. about 2%. Preferably the weight ratio of synthetic surfactant to high molecular weight poly (ethylene oxide) is in the range from 2:1 to 1:2. such as about 1:1.

In addition to the components mentioned above, the soap bars may contain other additives in small proportions, including those usually in soap bars, such as fillers, perfumes, dyes, fungicides, humectants (e.g. 0.2% to 1% of glycerine) and bactericides.

Toilet soap bars generally range in size from the relatively small hotel size (weighing from about 20 to about 30 grams) through the regular size (about 100 grams) and the bath size (about 150g) to the extra large size(about 200 g). The soap bars of this invention may be of such sizes, particularly in the range of from 100 to 200 grams. The soap may also be aerated, in a manner well known in the art, to give lower density (floating) soaps, such as those having a specific gravity of about 0.8.

The invention is particularly suitable for making milled and plodded toilet soap bars. Bars of this type are well known in the art; see for instance the description thereof in U.S. Patent No. 3,179,596. Also see 'Encyclopedia of Chemical Technology, Volume 12, edited by Kirk and Othmer, pages 573–598 and 'Industrial Oil and Fat Products,' Alton E. Bailey, Second Edition, 1951, pages 365–386 and 840–865. Thus one may take a kettle soap, form it into dried chips (as described in the foregoing references) and blend it with the various ingredients before milling and plodding.

The moisture contents of the soap bars of this invention are such as to provide a solid, non-tacky bar, preferably they are well below 30%. For a milled, plodded bar they are generally less than 20%, preferably in the range from 10 to 17%, such as about 13%.

Milled, plodded soaps typically are made up of fine crystals of hydrated fatty acid salt. The high molecular weight poly (ethylene oxide) appears to have an affinity for the moisture in the soap as shown by the experiment described in Example I, but the physical state of this material in relation to the soap crystals is not presently known.

The following Examples illustrate the invention.

EXAMPLE I

In this Example there are employed soap chips of various moisture contents (3%, 9%, 11%, 13% and 15%). 100 grams of soap chips are placed in a 400 cc beaker and 2% of poly (ethylene oxide) powder is added thereto and mixed (tumbled) therewith by hand with a 1 inch wide spatula, for one minute. The poly (ethylene oxide) employed has a fine particle size as indicated by the preferable particle size referred to above. The contents of the beaker are then spread on black paper. The paper is inspected with the naked eye to see the amount of powder left thereon and the chips are inspected under a 30-power microscope. When the chips contain 3% and 9% moisture substantially none of the powder adheres thereto and the black paper has a distinct layer of white powder. When the chips containing 11% moisture are stirred (with the spatula) the chips on the paper cause a noticeable release of powder (e.g. about 40% of the total powder) onto the paper; under the microscope the powder particles are seen to be distinct and resting on the surface of the soap chips and loosely adhering thereto. When the chips contain 13% moisture the powder is found to be more tightly held (e.g. about 20% to 30% is released when the chips are stirred on the paper); under the microscope one can see distinct powder particles on the chips' surfaces. When the chips contain 15% moisture substantially none of the powder is released onto the paper; microscopic examination, almost immediately, shows substantially no powder particles resting on the chip surfaces; the surfaces look substantially the same as if no powder had been added.

EXAMPLE II

A soap bar of the following composition is prepared by adding the ingredients in the order listed, to a conventional soap amalgamator (while the blades thereof are moving) operating at room temperature.

When added to the soap chips in the amalgamator, the individual particles of the homopolymer of ethylene oxide stick to the chips, especially when the water is then sprinkled onto the moving chips. The other ingredients

Component	Weight %
Soap chips (17 sodium coco soap/83 sodium tallow soap)[1]	88.50
50% aqueous solution of stannic chloride (a preservative)	0.15
Poly (ethylene oxide)[2]	2.00
Water	1.00
Titanium dioxide-powder (substantially moisture-free, a pigment)	0.60
Protein A-powder (containing up to 6% moisture)	3.00
Sodium coco isethionate-powder (containing 1% to 2% moisture)	2.00
Glycerine	0.50
Acetylated lanolin[3]	1.00
Perfume	1.25
	100.00

[1] Moisture is about 11.5%; bar moisture 10.5% 10.5%; measured by weight loss at 105°C.

[2] Polyox WSR N-750 in the form of powder, of size such that less than 5% by weight (e.g. 0.3%) is retained on a 20 mesh screen (U.S. Standard).

[3] Modulan-added in molten state (temperature about 120°F).

are then added in the order indicated, while mixing is continued for a total of about 2 minutes. At this time the mixture is not clumped together, but is still flowable, in chip form.

The blend is then milled on a conventional five-roll mill to a thickness of about 0.05 to about 0.1mm, the resulting milled chips having a temperature of about 34 to about 37°C. The chips are fed directly into a jacketed soap plodder and extruded to form a continuous bar ('plodder bar'). The plodding is controlled in one run to produce a plodder bar whose core temperature measured directly after extrusion is about 34 to about 38°C; in a second run the temperature is controlled to give a plodder bar core temperature of about 40 to about 43°C. The plodder used is a Doelger-Kirsten eight inch doubel barrel Vacuum Plodder, Schwantes Design. The plodder bars are cut in conventional fashion to give units whose volumes are suitable for a toilet bar (e.g. about 140g for a bath size bar and about 100 g for a regular size bar) pressed in conventional metal soap-pressing dies to the final rounded shape of the toilet bar. The units made from the higher temperature plodder bars are more difficult to press, without sticking to the die, but when the same plodder bar is cooled to about 38°C the pressing is much better.

Examination and use of the bars show a smooth surface, similar to that of normal soap bars. They are hard, tough and shiny, have a degree of slipperiness when wetted which is especially pleasant to the user, give a lather which is creamy, pleasantly silky and effective, have good resistance to sloughing in use despite a high moisture pickup, are long lasting and are flexible and tough even after much of the bar has been used up, and provide a beneficial effect on the hands (e.g. reduce chapping and flaking, and moisturize the skin, particularly dry skin).

EXAMPLE III

Example II is repeated except that the sodium coco isethionate is omitted from the formulation and the soap content is correspondingly increased.

EXAMPLE IV

Example II is repeated except that the acetylated lanolin is omitted from the formulation and the soap content is correspondingly increased.

EXAMPLE V

Example II is repeated, except that the coco and tallow soap ratio is 25/75, the soap chips have a higher moisture content (about 14% moisture), and there is no separate addition of water (and the bar moisture content is thus about 13%), and higher plodder temperatures are used so as to produce a bar having a core temperature of about 50°C. The bar surface is then cooled (with cool air), and a film of pressing lubricant (e.g. an aqueous solution containing 16% sodium chloride and 25% glycerol) is directly applied to the pressing dies before each pressing operation.

EXAMPLE VI

(a) Example II is repeated with the following formulation:

Component	Weight %
Soap chips (25 sodium coco/75 sodium tallow)	89.25
50% aqueous solution of stannic chloride	0.15
50% aqueous solution of citric acid (to react with any excess alkali)	0.25
Poly (ethylene oxide)[1]	2.00
Titanium dioxide	0.60
Protein A	3.00
Sodium coco isethionate	2.00
Hydroxylated lanolin	1.00
Glycerine	0.50
Perfume	1.25
	100.00

(1) Added as Polyox WSR N-750

(b) Example VI (a) is repeated except that the proportion of poly (ethylene oxide) is reduced to 1% and the soap content is raised by 1%. Users prefer the product of Example V (a).

(c) Example VI (a) is repeated but a second poly (ethylene oxide), 0.5% Polyox WSR-N-3000 (molecular weight 400,000), is also included and the soap content is correspondingly lowered to 88.75%.

EXAMPLE VII

Example VI is repeated except that the sodium coco isethionate is omitted (the soap chips being increased to 91.25%) and the polyethylene oxide has an average molecular weight of about 400,000 (Polyox WSR-N-3000).

EXAMPLE VIII

A series of soap bars are prepared as in Example II having the following composition:

Component	Weight %
Soap (25 sodium coco soap/ 75 sodium tallow soap)	88.9
Stearic acid	4.7
Poly (ethylene oxide) (Polyox WSR N-750)	1.8
Water	2.4
Titanium dioxide	0.7
Perfume	1.5
	100.00

The stearic acid is added to a hot kettle soap, in a crutcher, and the resulting blend is then dried and formed into soap chips having a moisture content of 10.6% (measured by weight loss at 105°C). The other ingredients are added in the amalgamator in the order listed. The moisture content of the bars is about 13%.

When these bars were evaluated by a hand-washing panel against a commercial beauty soap, these bars were preferred in terms of overall preference, lather, amount of lather, creaminess and richness of lather, and skin-feel. In contrast, when the same formulation, except for omission of poly (ethylene oxide) was similarly tested, the commercial beauty soap was preferred.

EXAMPLE IX

Example VIII is repeated using (a) coconut oil fatty acids or (b) palm fatty acids in place of the stearic acid.

EXAMPLE X

Example II is repeated except that 0.25% of a 50% aqueous solution of citric acid is added, the sodium coco isethionate is omitted (the soap chips being increased to 91.25%) and the polyethylene oxide has a molecular weight of about 400,000 (Polyox WSR-N-3000).

The invention includes soap bars which have been made by the method of the invention.

The invention also includes a soap bar containing from 1% to 10% of poly (ethylene oxide) having a molecular weight of at least 100,000, the bar being substantially free from visible specks.

WHAT WE CLAIM IS:–

1. A method of making soap bars containing, by weight, at least 60% of soap and from

0.5 to 10% of poly (ethylene oxide) which comprises mixing the soap in the form of chips with the poly (ethylene oxide) in the form of powder while the surfaces of the soap chips are in powder-adherent condition with respect to the polyethylene oxide powder to produce soap chips having polyethylene oxide bonded thereto, then adding other ingredients of the soap bar and mixing the other ingredients with the bonded chips, then forming the resulting mixture into a soap bar.

2. A method as claimed in Claim 1 or Claim 2 wherein the poly (ethylene oxide) has a molecular weight of at least 100,000.

3. A method as claimed in any of the preceding Claims wherein the moisture content of the soap chips is at least 11% by weight.

4. A method as claimed in any of Claim 1 or Claim 2 wherein the moisture content of the soap chips is less than 11% by weight and sufficient water is added to the initial mixture of soap chips and poly (ethylene oxide) to provide the said powder-adherent condition.

5. A method as claimed in any of the preceding Claims wherein the other ingredients are selected from hydrolysed protein, superfatting agents, synthetic surfactants of high foaming characteristics, and mixtures thereof.

6. A method as claimed in any of the preceding Claims wherein from 0.5% to 5% by weight of the bar of synthetic surfactant is included with the other ingredients.

7. A method of making soap bars substantially as described in any of Examples II to X.

8. Soap bars which have been made by a method as claimed in any of the preceding Claims.

9. A soap bar containing from, 0.5% to 10% of poly(ethylene oxide) having a molecular weight of at least 100,000, and at least 60% by weight of soap, the bar being substantially free from visible specks caused by the poly (ethylene oxide).

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