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DETERGENT BAR

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This invention relates to a detergent bar containing water soluble soap and lesser amounts of certain synthetic detergents. The invented bar product has excellent washing properties, yields no undispersed curd in hard water and possesses the tactile properties, appearance, drying activity and processing characteristics of the ordinary higher fatty acid soaps.

Previous workers in the detergent art have disclosed that synthetic detergents may be manufactured in bar form. In some of the recommended formulations large amounts of non-detergent builders and fillers had to be employed to improve the processing qualities of the synthetic detergent. Sometimes these additives also made the detergent product harder and reduced its solubility in water. Other researchers have suggested that mixtures of synthetic detergents may be made so that the end product could possess the advantages of each component washing agent. A number of patents have been issued in which synthetic detergents and soaps were combined, often with other additives, to improve their properties and several of these products have met with some measure of commercial success. Although in certain types of formulations a degree of generalization is possible, those of greatest skill and experience in this art usually consider, with justification, that when the particular types of detergents are varied, new properties, often undesirable, will be observed. Because the purchaser of the average commercial toilet detergent bar or cake applies a high standard in evaluating detergent products of this type, and because the market conditions are so competitive, it is necessary that each detergent formulation intended for use in bar form must pass rigid tests, the ultimate of which is consumer acceptance. The changes of properties, observed in bars made from mixed detergents as variations are made in the nature of detergent constituents, have resulted in a general conclusion that each of these complex formulas is a problem within itself. The application of general principles, arrived at from experience with seemingly analogous detergents, can often be very misleading and might result in a product which fails the test of a discriminating consumer public.

In accordance with the present invention it has been discovered that a milled and plodded detergent bar forming no undispersed curd in use, having excellent detergency, tactile qualities, lathering and foaming ability and good solubility, sloughing and drying properties, as well as exceptionally good processing characteristics, consists essentially of: 8 to 20% alkali metal salt of substantially saturated higher fatty glyceryl sulfuric acid compound; 3 to 10% alkali metal alkyl aryl sulfonate in which the alkyl group is of 10 to 18 carbon atoms and the aryl radical is selected from the group consisting of benzene and its substitution compounds; 3 to 10% alkali metal salt of higher acyl amide of an amino lower aliphatic sulfonic acid of 2 to 4 carbon atoms; 45 to 65% soluble

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alkali metal soap with a major proportion thereof being sodium soap, more than 65% of the soap fatty acid content being saturated fatty acids, and having a predominant amount, over 75%, of the soap fatty acid of 12 to 18 carbon atoms, of which fatty acids 25 to 60% is of 12 to 14 carbon atoms and 75 to 40% is of 16 to 18 carbon atoms; 6 to 14% moisture; and less than 7% total content alkali metal sulfate and alkali metal chloride. In preferred formulations there are employed 10 to 17% of sodium salt of substantially saturated higher fatty acid monoglyceride sulfate; 4 to 8% sodium alkyl aryl sulfonate in which the alkyl group is a propylene tetramer or pentamer and the aryl radical is benzene; 4 to 8% sodium salt of higher acyl amide of N-methyl taurine; 50 to 60% soluble sodium soap having more than 70% of its fatty acid content of saturated fatty acids, over 85% of the soap fatty acid being of 12 to 18 carbon atoms, of which fatty acids 30 to 50% is of 12 to 14 carbon atoms and 70 to 50% is of 16 to 18 carbon atoms; 8 to 12% moisture; and less than 5% total content of sodium sulfate and sodium chloride.

The alkali metal salt of substantially saturated higher fatty glyceryl sulfuric acid compound is made by any of various known techniques in which a higher fatty radical is attached to a glyceryl stem converted to a corresponding sulfuric acid compound. The detergent contains only one sulfuric acid type group and only one higher fatty radical. The sulfuric acid compound may be either a sulfate or sulfonate and the fatty portion may be of 10 to 18 carbon atoms, preferably in straight line configuration, attached to the glyceryl stem through either a carbonyl or ether linkage. As examples of this specific type may be mentioned the sodium salt of coconut oil fatty acids monoglyceride sulfate, wherein the coconut oil may be hydrogenated if so desired, sodium lauryl ether glyceryl sulfonate, sodium and potassium hydrogenated tallow fatty acids monoglyceride sulfates, sodium myristyl monoglyceride sulfonate and sodium palmityl ether glyceryl sulfate, to name a few of these suitable detergents. These compounds may be used in mixtures if so desired. Some of this type of detergent, e.g., sodium and potassium lauryl ether glyceryl sulfonate, possess sufficiently good curd dispersion properties to allow replacement of some amide sulfonate constituent too.

The alkyl aryl sulfonate detergent is preferably the sodium salt of a polyalkylene derivative of benzene sulfonic acid in which the alkyl group is of 10 to 18 carbon atoms, e.g., propylene tetramer or pentamer. Other alkyl groupings obtained in alkylation of benzene or its derivatives with kerosene fractions, as well as comparatively straight chain alkyl radicals are also suitable. Instead of the benzene nucleus, suitable benzene substitution compounds having relatively small or lower radicals substituted for the hydrogen thereon may be employed, such as toluene and xylene.

The alkali metal salt of higher acyl amide of amino lower aliphatic sulfonic acid is one in which the acyl group is of 12 to 18 carbon atoms. The amino aliphatic sulfonic acid portion of the molecule may have a lower alkyl radical attached to the amino nitrogen. The total of carbon atoms in the lower aliphatic stem connecting the amino and sulfonic acid groups and in said lower alkyl radical may be from 2 to 4. The lower alkyl of the connecting alkyl stem is of 2 to 3 carbon atoms and

the lower alkyl which may be attached to the nitrogen may be of 1 to 2 carbon atoms. Among the compounds of this type which may be used in the disclosed detergent bars are sodium higher acyl amide of N-methyl taurine in which the acyl grouping is a mixture of palmitoyl and stearoyl, sodium oleic acid amide of N-methyl taurine and sodium hydrogenated coconut oil fatty acids amide of amino propane sulfonic acid.

As is seen from the above examples it is preferred to use those compounds having 3 carbon atoms in the lower amino sulfonic acid portion of the molecule.

The water soluble alkali metal soap of the invented compositions contains a major proportion of sodium soap, usually over 75%. The soap fatty acid content is 65% or more saturated. The soap also consists predominantly, of 12 to 18 carbon atom molecules, preferably 85% and more being of this chain length. These soaps comprise specified amounts of fatty acid soaps of 12 to 14 carbon atoms and of others of 16 to 18 carbon atoms. Such materials may be made by combining in proper proportions certain natural oils of known fatty acid analyses. For example, it has been found that coconut oil or hydrogenated coconut oil may be mixed with tallow in the soap kettle in such proportions as to result in soaps of the type needed in the present detergent bar. Thus, it is possible to make such a soap by mixing one part by weight of coconut oil with two parts by weight of commercial tallow, and similarly, a satisfactory soap can be produced from four parts coconut oil and one part tallow. Within the boundaries of such compositions are other satisfactory soap mixtures, the preferred embodiment of which is one made from equal parts of these oils. Instead of coconut oil and tallow, other suitable sources of fatty acids or glycerides may be substituted to obtain a soap mixture of the type described.

The combination of three synthetic detergents and the soap in the proportions disclosed, together with the proper amount of moisture and minimum content of sodium sulfate and sodium chloride, less than 5%, results in a composition which can be made into bar form in substantially the manner employed to make soap cakes and which possesses excellent performance characteristics. If 5 to 7% total content of sodium chloride and sodium sulfate is present, more synthetic detergents should be employed than is used for the preferred compositions, containing less than 5% of such salts. Although the constituents of the present composition do have properties which distinguish them, one from the other, it is found that when made into a bar there is an interrelationship and interaction of the various components to produce a product which cannot be considered as merely the sum of the individual properties of its ingredients. Thus, it has been found that the detergent bar made according to the formulas given does not slough excessively although a combination of alkyl aryl sulfonate and sodium salt of higher fatty glyceryl sulfuric acid compound tends to cause ordinary soap bars to slough when added thereto in amounts sufficient to give other acceptable performance characteristics. The present detergent bar is excellent insofar as curd dispersion or scum formation in hard water is concerned although similar formulations made from different soaps and detergents do cause objectionable curd production. The present composition dries relatively fast to an exceptionally attractive glossy appearance. This rapid drying in normal use occurs while otherwise substantially satisfactory bars containing monoglyceride sulfate, alkyl aryl sulfonate and ordinary soap dry slowly, leading to rejection by the consumer.

As was said above, the present detergent bars are the products of interacting detergent components present in the proportions specified. Although each component affects the properties of the others, within the formulas disclosed it is possible to set forth a set of principles to assist one skilled in the detergent art in manufacturing the best detergent bars. The monoglyceride sulfate or other suitable sulfuric acid compound aids in the production of

a bar having excellent foaming properties. This type compound also exhibits curd dispersing activity, but in itself, in the quantities employed, is not sufficiently effective in this respect. The alkyl aryl sulfonate improves the hard water foaming ability of the formulation and also contributes a desirable slip or lubricity to the detergent bar. The amide of amino sulfonic acid is a most excellent curd disperser in these formulas and has foaming powers. The soap employed in the present compositions has been found to result in producing much less soap curd in water containing calcium and magnesium ions than soaps of lesser saturation and greater content of 16 and 18 carbon atoms. Because of this behavior it is possible to make a bar of the relatively low synthetic detergent content range given and still obtain a degree of foaming and curd dispersion formerly associated principally with products of higher synthetic detergent: soap ratios. The present soaps also produce more foam than does ordinary soap in bars containing the disclosed mixture of synthetic detergents, yielding a quicker, richer and creamier lather. As the moisture content is increased, the bar becomes softer, more soluble and tends to slough more readily, while below a minimum amount the composition is very difficult or impossible to mill and plod. The presence of sodium sulfate and sodium chloride in amounts in excess of the limit given tends to cause crystallization and sometimes produces in the detergent bar a graininess which is objectionable to the user.

In formulating detergent bars according to the teaching of this specification, amounts of components may be adjusted within the ranges given but best results are obtained by selection of proportions in accordance with the following principles. If the amount of amide sulfonate compound is near the maximum, that of glyceryl sulfuric salt may be decreased, allowing use of an amount thereof sufficient to yield a good foaming product in conjunction with the formula amounts of other detergents employed. On the other hand, if a maximum of glyceryl sulfuric salt is used, less amide is needed for satisfactory curd dispersion. The amide compound is a more effective curd dispersant and the glyceryl sulfuric salt is a better foaming agent in these compositions. A decrease in total synthetic detergent concentration permits use of more lower molecular weight soap (made from fatty acids of 12 and 14 carbon atoms) and an increase of such detergents indicates that more of the higher soaps can be used and should be added to improve bar hardness and decrease any excessive solubility. The alkali metal of the detergents and soaps is preferably sodium but potassium compounds are also useful. The amounts of sodium and potassium soaps and detergents should be chosen to obtain a bar of satisfactory hardness and solubility. Other considerations in formulations, similar to those recited above, will be apparent to one of skill in the art from the disclosure.

Although good foaming, curd dispersion, slip, appearance and detergency are desirable, even very important properties of detergent bars, those products intended for personal use should also possess other attributes to make them acceptable to the consumer. Among the more important of these properties are those of speedy drying and, associated therewith, aesthetically pleasing appearance and tactile properties of a wetted bar. The ordinary fatty acid soaps, being water soluble, dissolve to some extent when in contact with water in the soap dish or on the wash stand. In addition to dissolving some of the soap at the surface of the bar, water contacting the bar is absorbed by the soap and forms with it a soft gel-like surface layer which is easily removed and deposited on the soap dish or hands of the user. Although the soap gel described is undesirable, soap dries and hardens fairly quickly and therefore a cake of soap is normally of acceptable hardness in ordinary usage, provided that it is not stored continuously in water and if it is given sufficient time to drain and dry between washings.

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The large majority of synthetic detergents is considerably more soluble than soap and usually such products dissolve too rapidly to be useful toilet bar detergents by themselves. When mixed with soap in amounts sufficient to yield a curd-free washing solution of satisfactory foaming power and detergency they aggravate the tendency of the bar to dissolve and increase the amount of surface softening and gelation. Sometimes this leads to unacceptable degrees of sloughing and unsightly deposits of gel in the soap dish. In some formulas the synthetic detergent decreases the drying rate of the soap, giving a product that appears wet and jellyfied at the surface for comparatively long periods after usage. The present detergent bar is exceptional in that it is of sufficient solubility and excellent performance characteristics but does not exhibit either excessive sloughing and gel formation nor does it dry slowly, as might have been expected. In comparative tests against a large number of other detergent bar formulations, after an extended period of immersion in water the invented product dried more quickly than any other formula tested, being as good in this respect as commercial toilet soap cakes. Possibly as important as the improved drying rate of this product is the fact that the bar not only dries to an attractive surface but also appears to the consumer to be dry.

In the composition of this invention there may be incorporated in minor amounts various adjuvant materials designed to contribute specific properties to the bar. Included among this group of materials are: bactericides, e.g., hexachlorophene, trichlorcarbanilide, halosalicyl haloanilides, mercurials; perfumes; pigments and opacifying agents, e.g., titanium dioxide; dyes and colorants; brighteners, e.g., aminostilbenes; sequestrants, e.g., tetrasodium ethylene diamine tetraacetate; antioxidants and stabilizers, e.g., sequestrants for metal impurity catalysts, stannic chloride, stannous chloride, di-tertiary-butyl para cresol; emollients, e.g., lanolin. The amount of adjuvant should be sufficient to impart the desired activity but not to substantially adversely affect the bar properties. Also present in these bars there will sometimes be found small quantities of so-called ether solubles, which are usually unreacted oils or fats or by-product oils, fatty acids or other compounds from the manufacture of the detergents and soaps. As with some of the adjuvants it is preferred to hold this ingredient to a practical minimum consistent with detergent manufacturing considerations but small amounts, e.g., 1-4%, do not interfere with production of a satisfactory bar.

The bars of this invention may be made according to the usual methods employed in the manufacture of corresponding soap products with only minor adjustments known to those skilled in the art of making combination soap-detergent bars. The constituents of the formula may be mixed in the crutcher and dried to proper moisture content, or alternatively, may be blended in the amalgamator. If desired, neutralization or other reactions may be effected in the crutcher. For example, the acylated amino sulfonic acid, together with unreacted or excess fatty acid, may be crutcher neutralized. Drying of the crutched detergent mixture may be by known tunnel-, flash-, spray- or film-drying techniques. In the amalgamation step the desired moisture content of the final product may be adjusted by any of various known methods. Water may be added to the formula constituents, if needed, or one or more of the components may be added in water solution or slurry. Usually the minor adjuvants of the bar composition are blended with the detergents in the amalgamator. The formula is then milled to form a homogeneous chip which is compacted and extruded, usually by a soap plodder. After plodding the extruded bar is cut to lengths and pressed in a conventional soap press, such as a standard high speed, duplex press in which opposed dies form the soap cake in a rotatable die box.

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The following examples are given to illustrate the invention but are not to be regarded as limiting. All amounts and percentages in the specification and claims will be by weight unless otherwise indicated.

Example I

	Percent
Sodium hydrogenated coconut oil fatty acids monoglyceride sulfate-----	15
Sodium dodecyl benzene sulfonate (alkyl group being principally propylene tetramer)-----	5
Sodium higher fatty (mixed C ₁₆ , C ₁₈) acid amide of N-methyl taurine-----	5
Sodium soap (1:1 coconut oil:tallow ratio)-----	55
Sodium sulfate-----	1.4
Sodium chloride-----	1.6
Moisture -----	12
Other ingredients (bactericide, perfume, pigment, opacifier, color solution, unreacted and by-product ether soluble oils, fatty acids, etc.)-----	5
	100.0

The synthetic detergents and soap are crutched together (with accompanying sodium salts and ether solubles) and are dried in a film drier to the indicated moisture content after which they are mixed in an amalgamator with desired adjuvants. The amalgamated composition is then milled three times to homogeneity, plodded in a vacuum plodder, cut and pressed in essentially the same manner employed for making soap.

Bars made were tested for various properties indicative of utility of the product in hard and soft water, among which were lather and foam, hand washing, curd dispersion, drying characteristics, slough and appearance. They produced essentially no undispersed curd, gave a copious, creamy lather, dried even faster than ordinary soap alone, and were rated as excellent bar detergents.

In the formula given, either all or part of the sodium hydrogenated coco-monoglyceride sulfate may be replaced by others of the higher fatty glyceryl sulfuric acid products described elsewhere, in accordance with the teachings of this specification. The resulting products will also be excellent bar detergents.

Example II

	Percent
Sodium higher fatty acids monoglyceride sulfate--	11
Sodium dodecyl benzene sulfonate-----	6
Sodium soap ¹ -----	59
Total alkali metal sulfate and sodium chloride----	2.8
Moisture -----	11
Other ingredients-----	5.2
Sodium higher fatty acid amide of N-methyl taurine	5
	100.0

¹ 71% saturated fatty acid soap of which 94% is of 12 to 18 carbon atoms, 38% of which is of 12 to 14 carbon atoms and 62% of which is of 16 to 18 carbon atoms.

Example III

	Percent
Sodium higher fatty acid monoglyceride sulfate----	12
Sodium higher alkyl benzene sulfonate-----	6
Sodium higher fatty acid amide of N-methyl taurine (Igepon TE-42)-----	5
Alkali metal (sodium) soap (3:1 coconut oil:tallow ratio)-----	59
Total sodium sulfate and sodium chloride-----	3
Moisture -----	11
Other ingredients-----	4
	100

Example IV

	Percent
Sodium coconut oil fatty acids monoglyceride sulfate-----	12
Sodium dodecyl benzene sulfonate-----	6 5
Sodium higher fatty acid amide of N-methyl taurine	6
Sodium soap ¹ -----	60
Total alkali metal sulfate and chloride (sodium salts)-----	3
Moisture-----	10 10
Other ingredients-----	3
	100

¹ 81% saturated fatty acid soap of which 91% is of 12 to 18 carbon atoms, 56% of which is of 12 to 14 carbon atoms and 44% of which is of 16 to 18 carbon atoms.

The N-methyl tauride of this formula may be replaced either wholly or in part by other amides of amino lower aliphatic sulfonic acids previously mentioned. When such substitution is made and the teachings of this specification are followed the bar resulting will produce little or no undispersed curd and will have the other desired qualities of the above compositions.

The formulas of Examples II, III and IV were made into bars by amalgamation with adjuvants and amounts of water which would yield good products of satisfactory processing characteristics. The compositions were milled, plodded and pressed.

The bars made were subjected to rigid tests similar to those described after Example I. They were found to give a wash water free of objectionable curd, even at very dilute concentrations of the composition in hard water. They foamed very well in hard and soft water and made a rich, creamy lather. The bars dried rapidly to an attractive glossy appearance and possessed comparatively little jellied material on their surfaces after immersion in water. They passed other evaluation tests with excellent ratings and were found to be exceptionally fine toilet detergent products.

The above invention has been described in conjunction with illustrative examples thereof. It will be obvious to those skilled in the art who read this specification that other variations and modifications of the invention can be made and various equivalents substituted therein without departing from the principles disclosed or going outside the scope of the specification or purview of the claims.

What is claimed is:

1. A milled and plodded detergent bar consisting essentially, by weight, of 8 to 20% alkali metal salt of substantially saturated higher fatty glyceryl sulfuric acid compound selected from the group consisting of sodium and potassium salt thereof; 3 to 10% alkali metal alkyl aryl sulfonate in which the alkyl group is of 10 to 18 carbon atoms and the aryl radical is selected from the group consisting of benzene, toluene and xylene; 3 to 10% alkali metal salt of higher acyl amide of an amino lower aliphatic sulfonic acid of 2 to 4 carbon atoms in which the higher acyl radical is of 12 to 18 carbon atoms and the alkali metal salt is selected from the group consisting of sodium and potassium salts thereof; 45 to 65% soluble alkali metal soap with a major proportion thereof being sodium soap, more than 65% of the soap fatty acid content being saturated fatty acids, and having a predominant amount, over 75% of the soap fatty acid of 12 to 18 carbon atoms, of which fatty acids 25 to 60%

is of 12 to 14 carbon atoms and 75 to 40% is of 16 to 18 carbon atoms; 6 to 14% moisture; and having less than 7% total content of alkali metal sulfate and alkali metal chloride.

2. A milled and plodded detergent bar consisting essentially, by weight, of 8 to 20% sodium salt of substantially saturated higher fatty acid monoglyceride sulfate; 3 to 10% sodium alkyl aryl sulfonate in which the alkyl is a propylene polymer in which the number of propylene constituents is from 4 to 5 and the aryl radical is benzene; 3 to 10% sodium salt of higher acyl amide of N-methyl taurine in which the higher acyl radical is of 12 to 18 carbon atoms; 45 to 65% soluble sodium soap, having more than 65% of its fatty acid content of saturated fatty acids and having substantially all of the soap fatty acid of 12 to 18 carbon atoms, of which fatty acids 25 to 60% is of 12 to 14 carbon atoms and 75 to 40% is of 16 to 18 carbon atoms; 6 to 14% moisture; and having less than 5% total content of sodium sulfate and sodium chloride.

3. A milled and plodded detergent bar consisting essentially, by weight, of 10 to 17% of sodium salt of substantially saturated higher fatty acids monoglyceride sulfate in which the higher fatty acids group is of 8 to 18 carbon atoms; 4 to 8% sodium alkyl benzene sulfonate in which the alkyl group is a propylene polymer in which the number of propylene constituents is from 4 to 5; 4 to 8% sodium salt of higher acyl amide of N-methyl taurine in which the acyl group is of 12 to 18 carbon atoms; 50 to 60% soluble sodium soap, having more than 70% of its fatty acid content of saturated fatty acids and having substantially all, over 85% of the soap fatty acid of 12 to 18 carbon atoms, of which fatty acids 30 to 50% is of 12 to 14 carbon atoms and 70 to 50% is of 16 to 18 carbon atoms; 8 to 12% moisture; and having less than 5% total content of sodium sulfate and sodium chloride.

4. A milled and plodded detergent bar consisting essentially, by weight, of 10 to 17% of sodium salt of substantially saturated higher fatty acids monoglyceride sulfate in which the higher fatty acids group is of 8 to 18 carbon atoms and is derived from coconut oil; 4 to 8% sodium dodecyl benzene sulfonate in which the dodecyl group is a propylene tetramer; 4 to 8% sodium salt of higher acyl amide of N-methyl taurine in which the acyl group is substantially all of 16 to 18 carbon atoms; 50 to 60% soluble sodium soap derived from a mixture of tallow and coconut oil, having more than 70% of its fatty acid content of saturated fatty acids and having substantially all, over 85% of the soap fatty acid of 12 to 18 carbon atoms, of which fatty acids 30 to 50% is of 12 to 14 carbon atoms and 70 to 50% is of 16 to 18 carbon atoms; 8 to 12% moisture; and having less than 5% total content of sodium sulfate and sodium chloride.

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