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TOILET DETERGENT BAR AND PROCESS OF PREPARING SAME

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This invention relates to a new toilet detergent bar or cake characterized by a major proportion of water-soluble soaps and a minor proportion of certain mixed synthetic detergents, and to a novel process of preparing such a toilet combination bar.

It has been suggested that soap and a synthetic detergent may be compounded together such that certain desirable characteristics may be obtained, such as possible improvement in lime soap dispersion. More particularly, laundry bars composed of soap and a synthetic detergent, generally using an alkyl aryl sulphonate type, have been prepared for use in salt water. The production of toilet bars has also been proposed, usually with an inert diluent such as starch. In general, such products frequently form objectionable scum or curd in hard water with normal use. Furthermore, the presence of large amounts of synthetic detergents generally results in elimination of certain desirable physical properties attributable to the soap, in increased cost and difficulty of manufacture, etc. In view of the many basic chemical and physical differences between synthetic detergents and soap stocks, such mixtures have not attained any practical acceptance in the art.

The preparation of a suitable combination bar is a specialty problem and results generally in a "tailor-made" product. It is considered desirable to preserve and integrate in such a product the desirable characteristics of all-soap and all-synthetic detergent bars to a maximum beneficial degree which requires vital consideration as to the dynamic physico-chemical effects involved such as dispersion or deflocculation, solubilization, foaming, etc., the essential ingredients, their relative proportions and their mutual compatability, and the processing techniques necessarily interrelated therewith.

It has now been discovered that a suitable toilet combination bar may be prepared with comprises essentially a milled toilet bar or cake having a major amount of anhydrous water-soluble higher fatty acid soaps, and a minor amount of mixed water-soluble synthetic detergents comprising a mixture of higher fatty acid monoglyceride monosulphates and higher fatty acid amide of aminomethane sulphonates uniformly dispersed throughout said soap. As a preferred embodiment, the present invention relates to a milled and plodded toilet combination bar or cake consisting essentially of above about 50% of water-soluble higher fatty acid soaps by weight, and uniformly dispersed therein a minor proportion of a mixture of water-soluble synthetic detergents comprising alkyl aryl sulphonate, higher fatty acid monoglyceride monosulphate, and higher fatty amide of aminomethane sulphonate detergents, said alkyl aryl sulphonate being up to about 25% by weight, and said monoglyceride and said amide detergents totalling at least about 10% by weight. The ratio of the monoglyceride sulphate detergent to amide detergent is preferably from about 2:1 to about 1:2 by weight, and ordinarily will total from about 10–45%, usually about 10–35%, and preferably 10–25%, by weight of the total detergent composition containing a minor amount of moisture. These novel combination bars of the present invention are characterized by a soap-like workability, texture and feel, by substantial absence of scum or lime soaps effected by improved solubilization, dispersion and deflocculation, by excellent foaming power with respect to initial and sustained lather, mildness on skin, suitability for use in hard and soft water, etc.

The combination bar has as the major ingredient above about 50% of water-soluble anhydrous salts of higher fatty acids. These soaps may be produced by the saponification of fatty materials suitable for use in soap making. Among suitable fatty materials are the fats, oils, and waxes of animal, vegetable, and marine origin, and the fatty acids derived therefrom or of synthetic origin. More specifically, the fatty acids may be derived from tallow, cottonseed oil, coconut oil, palm oil, palm kernel oil, grease, fish oils, and their hydrogenated derivatives fatty acids, derived therefrom by hydrolysis, etc. It is preferred ordinarily to use in the present invention the sodium salts of the fatty acids derived from tallow, coconut oil and mixtures thereof.

As indicated, one of the specific synthetic detergents suitable for the manufacture of the combination bar of the present invention is the water soluble salts of the monosulfuric acid esters of higher fatty acid monoglycerides such as the alkali metal (e. g. sodium, potassium), ammonium and amine salts. The higher fatty acid radicals are also derived from natural fats, oils, and waxes or fatty acids of natural or synthetic origin. These water-soluble monoglyceride sulphates may also be derived from hydrogenated fatty materials. These products may be prepared in any convenient manner. A suitable process cited by way of illustration only involves the interaction of such components as glycerine, fatty oils or fatty acids, and a substantial excess of a strong sulphonating agent. The resulting acidic products may be neutralized with a neutralizing agent and may be dried in any conventional manner. Such procedures and the like are well known in the art, as illustrated by Muncie, U. S. Patent Nos. 2,130,361, 2,130,362, 2,242,979, etc.

As a result of such processing, the final reaction mass comprises primarily about 30 to 35% of the organic sulphate salt, and the remaining per cent of sulphates (about 65 to 70%) being inorganic salts such as sodium sulphate. It is preferred that the bulk of these inorganic salts be separated from the synthetic detergent base. This result may be accomplished in any suitable manner, preferably by solvent extraction processes, such as illustrated by Russell et al., U. S. Patent No. 2,303,582; Russell, U. S. Patent No. 2,316,719, etc., which have been developed for such purposes primarily. It is not necessary that the synthetic detergent base be completely free of these inorganic salts, since the presence of minor amounts of inorganic salts which do not substantially adversely affect the desired characteristics for the combination bar may be tolerated herein. After purification of the synthetic detergent base by the solvent extraction process indicated above, the base will contain generally about 80 to 95% synthetic detergent with the remainder being sodium sulphate. This material is highly suitable for use in manufacture of the combination bar. The minor amounts of sodium sulphate and the like are not detrimental to the product. Generally excessive amounts of sodium sulphate and similar inorganic salts in the bar should be avoided since adverse effects may result on the properties of the combination bar.

Another active specific ingredient is the higher fatty acid amides of aminomethane sulphonates. The higher fatty acyl radicals may be derived from the fatty acids or fats, fatty oils, etc. similarly to the monoglyceride sulphates above described, and this aminosulphonate de-

tergent may also be employed in the form of its water-soluble salts, such as sodium, potassium, etc., though the sodium salt is preferred for optimum results.

The alkyl aryl sulphonate detergents are well known in the art. The aromatic nucleus may be derived from benzene, toluene, xylene, phenols, etc. The alkyl substituent will usually be higher alkyl such as decyl, dodecyl, keryl, mixed long-chain alkyls from polymeric lower monoolefins such as propylene tetramers. It is preferred to use the high alkyl mononuclear aromatic sulphonates wherein the alkyl group has about 8 to 18, and usually about 12 to 18 carbon atoms. Optimum results are obtained with the higher alkyl benzene sulphonates having about 12 to 16 carbons in the alkyl group. These compounds are also to be used in the form of their water-soluble detergent salts, such as the alkali metal and amine salts. The sodium and potassium salts, particularly the former, is preferred for use in the combination bar.

The total amount of the monoglyceride sulphate and aminomethane sulphonate detergents should be sufficient to substantially prevent lime soap and/or scum formation or its presence under normal conditions of use of the combination bar. In this respect, it has been found that an amount at least about 10% will be adequate with excellent results achieved within the range of about 10–45%, and preferably about 10–25%. The ratio of monoglyceride sulphate to aminosulphonate detergent is usually about 4:1 to 1:4 and preferably from about 2:1 to about 1:2. Under such conditions, the desirable attributes of the soap are essentially preserved and complemented with other desirable characteristics produced by the conjoint action of these two synthetic detergents.

Scum or lime soaps produced by soap in the presence of calcium or magnesium hardness in water may be at least partially eliminated by several different means or effects, such as dispersion, solubilization, etc. The monoglyceride sulphate detergent is an excellent dispersing or deflocculating agent for lime soaps such that only minor amounts will effect a substantial degree of dispersion, in comparison to other synthetic detergents such as the alkyl aryl sulphonate type. Whereas with soap a large, dense, coarse and flocculent precipitate is generally obtained in hard water, the presence of the monoglyceride detergent substantially decreases the amount of curd, prevents any rapid settling of the same and results in a high degree of fineness of particle size of any possible precipitable material. The incorporation of the aminosulphonate detergent with the monoglyceride produces marked beneficial unitary action. The presence of lime soaps in hard water is substantially completely avoided, with a high degree of dispersion such that very little scum results even after the solution has been permitted to age for several days. The bulk solution of soap in hard water is ordinarily very turbid, and a mixture of soap and monoglyceride detergent still possesses some turbidity in solution. With the added effect of the aminosulphonate detergent, a very clear solution is obtained however. While the invention is not limited to any particular theory, it is considered that in the latter case marked solubilization occurs with resulting increased clarity of solution.

Under normal conditions of use, such as in bath-tub bathing and the like, the total concentration of active ingredients in solution is of an extremely small order, probably of the order of about 0.01%. In view of the relatively minute amount of synthetic detergents in solution during bathing using a combination bar, it is required that its scum prevention power be of the highest possible order. The desired effects may be achieved by the combination bar of the present invention. The amount of the monoglyceride sulphate and aminosulphonate detergents previously set forth is usually in excess of the theoretical amount of synthetic detergent in solution required to achieve necessary scum dispersion in hard water. In actual practice, however, such excess is required in the bar in order to achieve the desired effects since in natural use of the toilet bar some curd or scum may form prior to solution of the necessary amounts of synthetic detergents.

It is known that the monoglyceride sulphate detergent is particularly liable to hydrolysis upon the alkaline side. This effect is evident to some degree upon aging of a solution of soap and this synthetic detergent since the soap has a high pH in aqueous solution, such as about 10.5. In the combination bar, however, hydrolysis of this synthetic detergent is not encountered to any significant degree. Furthermore, the C—N—C bond of the aminosulphonate detergent is much stronger than the C—O—C bond of the ester detergent, and therefore is not liable to hydrolysis by the soap to any significant extent. In addition, these synthetic detergents are substantially neutral in character, and therefore have a reduced tendency to change the normal pH of the skin in comparison to the use of more alkaline cleansing agents. In commercial manufacture of the combination bar, it will usually be found that the pH value of a solution to the combination bar is below the normal value of an equivalent all-soap solution. In general, the pH of the combination bar in 0.5% concentration in hard water is usually less than 9.5. Thus, a high degree of alkalinity is avoided which is believed to have a deleterious effect on the skin of some individuals. It appears that the emollient properties of soap, however, are retained to a marked degree with the improved detersive and dispersal power of the toilet bar.

The combination of the monoglyceride sulphate and aminosulphonate detergents yield in the combination bar good foaming characteristics. A good initial and sustained lather, both in respect to volume and creaminess, is obtained with such a bar.

A minor amount of alkyl aryl sulphonate detergent in the combination bar yields certain added beneficial effects in combination with the other specified synthetic detergents. In general, the alkyl aryl sulphonates per se are not highly effective dispersing agents for lime soaps, the monoglyceride sulphates for example being many times superior. The presence of the alkyl aryl sulphonates, however, does increase the ratio of synthetic detergents to soap, lends good bulk and cohesiveness to the product, etc. Its primary contribution is the activation of the foaming properties in the relationship set forth. With its inclusion in the combination bar, excellent lathering properties are obtained with a high volume and creaminess of foam both initially and for a sustained period. The alkyl aryl sulphonate detergent will ordinarily be employed in up to about 25% by weight, e. g. about 1–25%, and preferably from about 5–20% with optimum results achieved usually with about 10 to 20%. Excessive amounts of this detergent adversely affect the workability of the mixture in the manufacture of the bar, particularly its plasticity and flow during plodding, since the alkyl aryl sulphonates are usually very hygroscopic, and rubbery or tacky in the plodder. In addition, such excessive amounts also tend to destroy the soap-like "feel" of the bar and have a defatting tendency on the skin during use. With proper usage, however, these adverse effects are largely minimized and a combination bar containing desired characteristics is obtained.

Various adjuvant materials may be employed in the manufacture of the combination bar. It will usually be preferred to keep the amount of inorganic salts to a minimum, e. g. up to about 10% as indicated supra. The addition of minor amounts of coloring agents, whitening agent (e. g. titanium dioxide), perfumes, preservatives, super-fatting agents, antiseptics, and the like may, and usually are, to be added to the combination mix for their individual effects. Certain agents such as guanidine carbonate may be added to the mixture to decrease the hygroscopicity of the alkyl aryl sulphonate during plodding.

Other agents such as wetting agents, anionic sulphated or sulphonated or non-ionic detergents may also be added provided the essential characteristics of the bar are not substantially adversely affected.

The combination bar of the present invention may be made by a modified soap milling and plodding process. In the manufacture of soap bars there are two methods in wide commercial use, namely, the framing method and the milling method.

In the framing method, molten kettle soap is crutched with various addition agents and cast while still molten into frames or molds for cooling and settling. After setting, the solidified mass may be cut into bars or cakes of desired size and shape. Cakes of soap may by this process have a high moisture content (at least about 30% moisture) and in general are unsuitable for manufacture of the combination toilet bar. Combination bars made by this framing technique are quite soft because of the relatively high moisture content and wear away comparatively rapidly in use. They are subject to warping and distortion on aging, due to evaporation of the moisture content. It is difficult to incorporate perfume into the mix satisfactorily in view of the high temperatures established prior to framing. Moreover, by this procedure the combination bar does not have uniform composition and fine texture.

In the milling process, however, kettle soap is cooled and dried to chip or granular form. The soap particles are then mechanically mixed with various addition agents such as perfume, coloring materials, whitening agents, etc., and then milled to produce chips of homogeneous composition. The milled particles are compacted under pressure in a plodder from which the soap is extruded as a continuous bar having a cross section approximating that of the finished cake. The continuous bar is then cut into individual cakes which usually are pressed to give a smooth and polished appearance to the finished cake, and, when desired, to impress upon the cake a trade name, trade mark, etc.

The combination bars of the present invention may be made by the milling process provided the moisture content of the mix is kept within rather narrow and critical limits and correlated with the temperature of the mixture during plodding. Generally speaking, the process comprises milling a mixture of the water soluble soap and synthetic detergents, plodding the resulting chips and serving the bar extruded from the plodder into convenient lengths for use. The moisture content of the mixture is to be maintained within the rather critical limits of 5 to 15%. This moisture content refers to the free moisture i. e., the moisture which is not combined as water of crystallization.

If the moisture content is below about 5%, it cannot be plodded satisfactorily. The internal friction is so great that the temperature of the mixture rises so high that the extruded bar cannot be handled satisfactorily. If the moisture content exceeds about 15%, apart from the moisture present as water of crystallization, the material cannot be plodded to produce an extruded bar capable of maintaining its shape.

The temperature of the material being plodded must be correlated with the moisture content and the temperature of the extruded bar will vary within the range of about 100 to 135° F. With a moisture content of about 10%, the temperature of the extruded bar for best results should be about 120° F. If the moisture content is lower than 10%, a higher temperature should be used for satisfactory operation. Thus, with a water content approximating 5%, the temperature of the extruded bar should be about 135° for best results. If the moisture content is higher than about 10%, the temperature of the extruded bar should be less than 120° for best results.

The loss in moisture content in manufacture generally is nil, or in any event not in excess of more than a few per cent, such that the final composite bar product does not have a moisture content in excess of about 15%, and usually within the range of about 5–15%.

The finished bars and cakes have a fine texture, firmness, appearance, shape stability, and wearing qualities requisite to a high grade toilet soap. The most striking improvements appear in better lathering qualities, significant and substantial scum dispersion, clarity of solutions, and greater mildness. With regard to the latter factor, the emollient properties of soap are retained with the improved detersive and dispersive power of the toilet bar in soft and hard water.

The following examples are additionally illustrative of the present invention and it is to be understood that the invention is not restricted thereto:

Example I

A suitable combination bar is prepared from the following formulation:

8.0%—Sodium N-higher fatty acid aminomethane sulphonate [1](96.5% purity) (fatty acids derived from coconut oil)
10.0%—Sodium fatty acid monoglyceride monosulphate [1](91% purity) (derived from hydrogenated coconut oil)
15.0%—Sodium dodecyl benzene sulphonate [1](82% purity)
63.4%—Sodium soap chips with 10% moisture (derived from 3:1 tallow, coconut oil)
2.0%—Guanidine carbonate
0.2%—Preservative
0.4%—Titanium dioxide
1.0%—Perfume

The above ingredients are thoroughly mixed in an amalgamator mixer until a uniform mixture is obtained. This mixer is milled over a standard toilet soap mill to obtain a homogeneous ribbon, water added to adjust the moisture content to 10% and the mix is remilled twice. The milled material is then fed in the form of chips into a soap plodder having an extrusion nozzle temperature of 120–125° F. where it is compacted and extruded as a finished bar characterized by its toughness, workability, and uniform color and texture. The bar is cut and pressed in dies to cake form suitable for individual use.

If desired, the additional water may be added in the mixing stage prior to milling, with appropriate adjustment of the extrusion temperature.

The combination bar prepared above and tested under normal conditions of use exhibits markedly improved properties over a high grade toilet soap. The combination bar exhibits a high degree of initial and sustained lather, soil removal and scum or curd prevention, mildness on skin, etc., in both hard and soft water.

Example II

As in Example I, a combination bar is prepared using about 70% soap chips, 10% alkyl aryl sulphonate, 10% aminosulphonate, and 8% monoglyceride sulphate detergents with minor amounts of perfume, preservative, etc. After mixing the ingredients in a soap amalgamator, adding water until the mixture possesses about 15% moisture, milling and extruding it from a plodder at about 100–110° F., the toilet bars are prepared for individual use. These toilet combination bars are also highly satisfactory.

Example III

An improved combination bar is prepared from:

10.0%—Sodium N-cocyl aminomethane sulphonate
15.0%—Sodium fatty acid monoglyceride monosulphates (derived from 2:1 hydrogenated tallow and coconut oil)
73.5%—Sodium soap chips having 10% moisture (derived from 3:1 tallow and babassu nut oil)
1.0%—Perfume
0.3%—Titanium dioxide
0.2%—Preservative

[1] Remainder essentially inorganic salts.

The ingredients are mixed in an amalgamator, the moisture content is adjusted to 14% and the mixture milled and plodded with an extrusion temperature of about 125° F. A highly satisfactory toilet bar is obtained also.

The term "consisting essentially of" as used in the definition of the ingredients present in the composition claimed is intended to exclude the presence of other materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to permit the presence of other materials in such amounts as not substantially to affect said properties and characteristics adversely.

Having described the invention, what is desired to be secured by Letters Patent is:

1. An improved milled toilet detergent in the form of bars or cakes consisting essentially of at least about 50% of anhydrous water-soluble higher fatty acid soaps, and a minor amount of mixed water-soluble synthetic detergents comprising a mixture of higher fatty acid monoglyceride monosulphates and higher fatty acid amide of aminomethane sulphonates in an amount from about 10 to about 45% by weight uniformly dispersed throughout said soap and effective to substantially prevent lime soap precipitation during use as a toilet bar, the ratio of said sulphate to aminosulphonate detergent being from about 4:1 to about 1:4, and about 5 to about 15% moisture.

2. An improved milled toilet detergent in the form of bars or cakes consisting essentially of from about 50 to about 75% of anhydrous water-soluble higher fatty acid soaps, and about 10 to about 45% of mixed water-soluble synthetic detergents comprising a mixture of higher fatty acid monoglyceride monosulphates and higher fatty acid amide of aminomethane sulphonates uniformly dispersed throughout said soap and effective to substantially prevent lime soap precipitation during use as a toilet bar, the ratio of said sulphate to aminosulphonate detergent being from about 2:1 to 1:2, and about 5 to about 15% moisture.

3. An improved milled toilet detergent in the form of bars or cakes consisting essentially of from about 50 to about 75% of anhydrous water-soluble sodium higher fatty acid soaps, from about 5 to about 15% moisture, and about 10 to about 45% of mixed water-soluble synthetic detergents comprising a mixture of sodium higher fatty acid monoglyceride monosulphates and sodium higher fatty acid amide of aminomethane sulphonates uniformly dispersed throughout said soap and effective to substantially prevent lime soap precipitation during use as a toilet bar, the ratio of said sulphate to aminosulphonate detergent being from about 2:1 to 1:2.

4. An improved milled toilet combination bar or cake consisting essentially of at least about 50% water-soluble higher fatty acid soaps, and uniformly dispersed therein a minor proportion of a mixture of water-soluble synthetic detergents comprising higher alkyl aryl sulphonate, higher fatty acid monoglyceride monosulphate, and higher fatty acid amide of aminomethane sulphonate detergents, said aryl sulphonate detergents being up to about 25% by weight, and said monoglyceride and said amide detergents totalling about 10% to about 45% by weight, in a ratio from about 4:1 to about 1:4 by weight, and about 5 to about 15% moisture.

5. An improved milled toilet combination bar or cake consisting essentially of about 50% to about 75% water-soluble higher fatty acid soaps, from about 5 to about 15% moisture, and uniformly dispersed therein a minor proportion of a mixture of water-soluble synthetic detergents comprising higher alkyl aryl sulphonate, higher fatty acid monoglyceride monosulphate, and higher fatty acid amide of aminomethane sulphonate detergents, said aryl sulphonate detergent being from about 5 to about 25% by weight, and the ratio of said monoglyceride to said amide detergent being from about 4:1 to 1:4 and totalling about 10% to about 45% by weight.

6. An improved toilet combination bar or cake consisting essentially of about:

50–75% higher acid sodium soaps
1–25% higher alkyl aryl sulphonates
10–35% mixed higher fatty acid monoglyceride sulphates and higher fatty acid amide of aminomethane sulphonates in a ratio of about 4:1 to about 1:4
5–15% moisture

7. A process of making an improved toilet detergent in the form of bars or cakes which comprises forming a mixture of at least about 50% anhydrous water-soluble higher fatty acid soaps, about 5 to about 15% moisture, and a minor amount of mixed water-soluble synthetic detergents comprising a mixture in an amount from about 10 to about 45% by weight of higher fatty acid monoglyceride monosulphates and higher fatty acid amide of aminomethane sulphonates in a ratio from about 4:1 to about 1:4, milling said mixture to uniformly disperse said synthetic detergents therein and form homogeneous particles thereby, plodding the resulting milled mixture and extruding the same as a bar, and forming the resulting extruded bar into bar or cake form suitable for individual toilet use.

8. A process of making an improved toilet detergent in the form of bars or cakes which comprises forming a mixture of from about 50 to 75% anhydrous water-soluble higher fatty acid soaps, about 5 to 15% moisture, and a minor amount of mixed water-soluble synthetic detergents comprising a mixture of up to about 25% higher alkyl aryl sulphonates, and a total of about 10% to about 45% by weight of higher fatty acid monoglyceride monosulphates and higher fatty acid amide of aminomethane sulphonates in a ratio from about 4:1 to about 1:4 by weight, milling said mixture to uniformly disperse said synthetic detergents therein and form homogeneous particles thereby, plodding the resulting milled mixture and extruding the same as a bar, and forming the resulting extruded bar into bar or cake form suitable for individual toilet use.

9. An improved milled toilet detergent in the form of bars or cakes consisting essentially of at least about 50% of anhydrous higher fatty acid sodium soaps, and a minor amount of mixed synthetic detergents comprising about 10 to about 45% by weight of a mixture of sodium higher fatty acid monoglyceride monosulfate salt and sodium higher fatty acid amide of aminomethane sulfonate salt uniformly dispersed throughout said soap, the ratio of said sulfate to aminomethane sulfonate detergent being from about 4:1 to about 1:4, and about 5 to about 15% moisture.

10. A product in accordance with claim 9 which contains in addition sodium alkyl aryl sulfonate in an amount up to about 25% by weight.

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