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COMBINATION SOAP-SYNTHETIC DETERGENT BAR

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The present invention relates to a detergent bar comprising zinc soap, soluble soap and a particular sulfated anionic synthetic detergent. More particularly it relates to combinations of water soluble higher fatty monoglyceride monosulfate detergent, water soluble higher fatty acid soap and water insoluble higher fatty acid zinc soap in certain proportions which result in a combination detergent bar of excellent properties and suitable for toilet use in waters of varying degrees of hardness.

In accordance with the present invention a toilet bar detergent comprises 15 to 60% of water soluble higher fatty monoglyceride monosulfate detergent, 10 to 60% of a water soluble higher fatty acid soap and 5 to 40% of water insoluble zinc soap, the total of these three components amounting to at least 50%. Also in accord with the invention is the process of making such products comprising mixing into an aqueous slurry water soluble higher fatty monoglyceride monosulfate detergent, water soluble higher fatty acid soap and water soluble zinc salt, drying the mix and converting the dried product into bar or cake form.

The monoglyceride sulfate detergent is a water soluble salt of the monosulfuric acid ester of a higher fatty monoglyceride. These compounds may be made from fatty acids having 12 to 18 carbon atoms, mixtures of higher fatty acids averaging 12 to 18 carbon atoms and from fats and oils having an average acyl chain length within that range. The degree of unsaturation should be low. Products having more than one carbon-carbon double bond are unsatisfactory and those of complete saturation are preferred. Among the detergents most satisfactory in the present bar products are those made from fatty acids such as lauric, myristic, palmitic, oleic and stearic acids and glyceride fats and oils such as coconut oil, tallow, hydrogenated coconut oil and hydrogenated tallow. Mixtures of the various detergents or fatty raw materials may be employed.

The monoglyceride monosulfuric acid ester detergents in water soluble form normally include an alkali metal at the sulfuric group to form a salt which improves water solubility and other properties. Of the alkali metals sodium is most commonly employed due to its economy, solidifying action and generally favorable characteristics. Potassium salts are useful in the formula if their incorporation results in a firm bar and minor amounts of potassium detergent are sometimes blended with sodium compounds. The alkali metal monoglyceride sulfate detergents possess certain unique favorable properties in combination bar compositions among which are excellent soap curd-dispersion power, mild action on human skin, excellent lathering, foaming and cleaning activity, good coherence, a waxy soap-like character and feel unlike that of most synthetic detergents which are often either not cohesive or tacky, compatibility with a wide variety of adjuvants and good processability. Amine and ammonium salts of detergents are excellent washing agents and perform satisfactorily in many specialized applications but are not generally suitable for use in detergent-soap bar products in more than minor proportions.

The water soluble soaps in the present compositions are usually and preferably the alkali metal salts of higher fatty acids, e.g. sodium stearate, sodium laurate, sodium oleate. Potassium salts may be employed providing that the finished bar is of suitable hardness and acceptable solubility. Amine and ammonium soaps may find limited application as minor constituents of a soap mixture. The fatty acid portion of the soap may be a mixture of saturated and unsaturated acids obtained from the usual soap-making fats such as coconut oil and tallow or may be a relatively pure fatty acid or mixture such as commercial stearic acid. In either case poly-unsaturated acids will be held to a minimum.

The water insoluble zinc soaps may be made from the same fatty materials suitable for manufacturing the soluble soaps described above. They may be admixed with the other essential and adjuvant components in the dry state or in aqueous dispersion such as the reaction mixture of soluble soap and soluble zinc salt.

The zinc soaps contribute many desirable characteristics to the present combination bars. Among the most important of these properties is that of improving the curd dispersion of a soluble soap-monoglyceride sulfate combination bar when the zinc soap is substituted for soluble soap. Additionally, it has been established that such a replacement significantly improves the foaming and lathering properties of these combination bars. Zinc soap aids in adjusting processing characteristics of such bars. It decreases sloughing and helps to control the degree of solubility of these products. Finally, the presence of zinc soap in the formula contributes its fungicidal activity and mild antiseptic properties to the bar, aiding in the prevention of fungus and bacterial growth on the bar as well as on surfaces to which the zinc soap-containing bar or lather obtained therefrom is applied. The employment of zinc soap to increase foam lather and curd dispersing activity makes unnecessary the use of additional synthetic detergent and thereby avoids problems associated therewith such as poorer rinsability, increased sloughing, greater solubility and a somewhat increased defatting action on the skin. It is evident that the zinc soap, in addition to contributing its own desirable properties to the combination toilet detergent bar also acts as a balancing component of such formulations enabling the use of soluble soap and monoglyceride sulfate detergent in the most desirable proportions. The three-component system gives a fomulator the ability to combine any of a variety of monoglyceride sulfate detergents with a number of soluble soaps to make an acceptable detergent bar for toilet use.

The amount of monoglyceride sulfate detergent in the present combination detergent bars should be within the range of 15–60% of the total bar weight. If less than 15% is employed the improvement in curd dispersion and foaming power is insufficient to be worthwhile, while if more than 60% synthetic detergent is included in the formula the product resulting is essentially a synthetic detergent bar and the incorporation of soaps, soluble or insoluble does not improve the tactile and other properties enough to satisfy the consumer.

The soluble soap employed should be within the range of 10 to 60% for reasons similar to those given above in the case of the monoglyceride sulfate. At less than 10% soluble soap the product does not benefit from the inclusion thereof and at over 60% it may be considered to be essentially a soap bar with the balance amount of synthetic detergent insufficient satisfactorily to disperse curd and improve foam in very hard water.

If less than 5% of zinc soap is included in the formula no appreciable effect on the properties of the bar will be obtained. At a concentration of 5% the zinc soap will measurably improve the properties of many soap-monoglyceride sulfate bar compositions. More than 40% will cause the final product to be too hard and of unpleasant tactile characteristics which would offend the esthetic sensibilities of consumers.

The preferred ranges of the essential components are about 25 to 45% soluble monoglyceride sulfate synthetic detergent, 10 to 35% soluble soap and 15 to 30% insoluble zinc soap. Within the ranges given it is advantageous to maintain the ratio of soluble monoglyceride sulfate to the sum of soluble soap and zinc soap at from 0.25 to 4. It is also best to keep the proportion of soluble soap to insoluble soap between the same limits. Within these ranges excellent combination detergent bars of balanced properties are obtained.

Combination bars within the percentage and proportioned limitations given in the paragraph immediately preceding have essentially complete soap curd dispersing characteristics. They do not produce a sticky agglomerative insoluble soap in hard waters and leave no "bathtub ring" type of residue. If the amount of monoglyceride sulfate detergent is decreased below about 25% some undispersed curd appears in extremely hard waters and foam and lather are diminished. Although the amount of agglomerating curd may not be sufficient detrimentally to affect most consumer acceptances of the product, nevertheless, the bar will no longer be one which deposits absolutely no curd. It has been found that if the amount of monoglyceride sulfate is in the range of 25–35% of the bar the presence of stearic acid soap will improve foam and lather advantageously. Thus, instead of making such a bar from an ordinary settled white soap base made from 85% tallow and 15% coconut oil, this soap may advantageously be partially replaced (up to 70%) by a soap made from commercial stearic acid. A more saturated soap is obtained and it improves the particular combination detergent product.

The total weight of the 3 essential components of the present detergent bars should be at least 50% of the final product and, in the absence of large amounts of emollient or superfatting additives, preferably should be over 70%. The balance of the composition may comprise water soluble higher alkyl aryl sulfonate detergent, water soluble inorganic salts, insoluble fillers and plasticizers, as well as the usual adjuvants such as perfumes, pigments, sequestering agents, colorants, brighteners, bactericides, emollients, antioxidants and other stabilizers. Inert substances and unobjectionable impurities found with the other components may also be tolerated.

To increase the slip of the present combination bars it has been found useful to add a minor proportion of higher alkyl aryl sulfonate detergent to the composition. The higher alkyl group is of 12–18 carbon atoms. The aryl radical is most often that of benzene and the sulfonic acid group, usually located para to the alkyl, is neutralized with alkali metal base. Preferred compounds of this class are the sodium alkyl benzene sulfonates in which the alkyl group is propylene tetramer or polymer. The alkyl aryl sulfonate is preferably employed in amount about 10% of that of the monoglyceride sulfate but 5–20% of such content is useful. The alkyl aryl compound appreciably increases the slippery soap-like feel of the bar in use and also improves detergency against many types of non-fatty soil.

The total of unessential components in the present bars must be limited to prevent the finished product from having a predominance of chaacteristics typical of the adjuvants rather than the detergent components. This limit is 50%. Those skilled in the art will realize that as a practical matter within this limit the amounts of individual constituents are also often necessarily further restricted. For example a bar containing as much as 50% of any single material mentioned above would be unsatisfactory.

As was previously mentioned only the monoglyceride sulfate detergent, soluble soap and insoluble zinc soap are essential components of the present combination soap-synthetic detergent bars. Plasticizers such as partial esters of polyhydric alcohol, e.g., diglycol laurate, diglycol stearate, carbowaxes (polyoxyethylene derivatives) and higher fatty acids may be used if desirable but are not necessary in the present invention. Often the synthetic detergent material, derived as it is from higher fatty acid compounds, has with it some ether soluble impurities, among which are included free fatty acid and unreacted glyceride or derivative thereof. These compounds often possess plasticizing properties. Water soluble inorganic salt such as sodium sulfate is sometimes found as an impurity with the monoglyceride sulfate detergent and so may find its way into the present formulations. In addition, water soluble salts, e.g., sodium chloride, sodium sulfate, may sometimees be present with the insoluble zinc soaps. Water soluble inorganic salt may be tolerated in the formula but should be kept low enough so as not to cause development of an efflorescence or blooming of salt, which would result in an unsightly or rough surface on the bar.

In the preceding disclosure of the invention certain limits on the amounts of three essential components of satisfactory combination synthetic detergent-soap toilet bars have been given and optional adjuvants have been mentioned. To one of skill in the detergent art it is evident, as related in the disclosure, that the claimed combination bars should possess a balance of desirable properties to satisfy the requirements of a critical consuming public.

It is not usually enough for a toilet detergent merely to clean satisfactorily. It should also be of pleasing appearance, should have the feel and lustre of a good soap, should not become jellied or too soft on standing wet, as in a soap dish, and should be of pleasing fragrance. Such a product should foam and clean satisfactorily whether the water supply is very hard, such as 300 or more parts per million or as soft as rain water. The product should be compatible with the water supply whether the hardness is either mostly calcium of magnesium, temporary or permanent. In hard water areas the presence of soap in a detergent product often results in the production of a slimy, sticky curd which adheres to surfaces contacted and which results in an undesirable film on the skin as well as unsightly bathtub ring on the washing receptacle. In a satisfactory combination bar it is important that the soap curd be eliminated or else rendered non-adherent or dispersed. The elimination of soluble soap from a formula solves this problem but creates another because of the loss of the contribution of the soap to detergency, tactile properties, decreased solubility, limitation of drying effect of synthetic detergent on human skin and promotion of easy rinsability.

In producing an acceptable toilet detergent bar satisfactory in all important respects, minor differences between individual monoglyceride sulfate detergents or the several higher fatty acid soaps or the zinc soaps will suggest to one skilled in the art that to obtain optimum results adjustments should usually be made, within the ranges given, when changes are made in the components of the formulation. For example, if it is desired to improve sloughing characteristics of a particular product a decrease in synthetic detergent accompanied by an increase in zinc soap is indicated. If curd-dispersing properties are unsatisfactory an increase in synthetic detergent content and/or replacement of alkali metal soap with zinc soap is helpful. With the guidance and teaching of the present specification and with the same desiderata a skilled formulator will have no difficulty in manufacturing superior combination detergent bars within the ranges of constituents disclosed.

The present compositions may be made by forming dry mixes of the essential components and adjuvant materials and then further treating these mixtures to form homogeneous solid masses of detergent in cake form. Usually a dry mix is milled or otherwise compressed and forced into relatively thin films, after which it is plodded and extruded into bar form. The plodded bars are then cut and pressed to final shape. If the dry mix components

resist blending into a homogeneous mass it may be desirable initially to treat those ingredients which fuse but slowly into the composition mass with softening or plasticizing agents. Thus diglycol laurate, water, perfume or other ingredients may be used for this purpose.

Although it is possible to make the present products as described above it is often simpler and more economical to mix together, in the process of formulating in the crutcher, compounds which will react to form one or more of the essential components of the present bar product. In the detergent art it is conventional to utilize the crutcher for blending and reacting various components of the desired product. In making the present bars by this preferred technique one may mix together in the crutcher in aqueous slurry soluble synthetic detergent, soluble soap and soluble zinc salt. These should be added in amounts sufficient to result in the desired proportions of monoglyceride sulfate detergent, soluble soap and zinc soap. Although in some circumstances the reactants or part thereof may be in solid form initially, usually they will be in solution or dispersion in water or aqueous solvent. In a typical commercial process synthetic detergent solution is crutched gently with soluble kettle soap at an elevated temperature between 120° F. and 170° F. To this is added a solution of soluble zinc salt. Usually zinc chloride and zinc sulfate are favored because of their comparatively great solubility and relatively low cost but other suitable soluble zinc compounds may be utilized instead. Crutching is continued for 5–20 minutes at about 120–170° F. and the reaction mix is then dried.

During the crutching and drying operations it is believed that zinc soap is made, it being the least soluble of the possible reaction products. Instead of making the product by the method outlined above it has been found feasible first to prepare the zinc soap in the crutcher by any suitable method and then to add the other ingredients. For example one may react zinc oxide or hydroxide with fatty acid at elevated temperature and then admix soluble soap and synthetic detergent. It is also sometimes desirable to add commercial zinc soaps to the crutcher mix of other essential components but this gives rise to the problem of dispersing a large mass of fine powder in the rather viscous crutcher mixture and is usually avoided.

Although analyses of the dried combination soap-synthetic detergent have been made and have indicated that the zinc compounds in the present formulas are there as insoluble zinc soaps, theoretically, due to the possibly destructive action of solvents during separation processes it is not definitely established that all the zinc is actually in insoluble soap form. This is so because, during the separation of water insolubles from other bar or chip components, theoretically at least, zinc compounds could be broken down into insoluble soaps or the presence of an excess of water might promote metathesis which would not take place in the more concentrated slurries.

This application has been drawn to the three member composition for the sake of simplicity and because, according to sound chemical principles the insoluble zinc soap is present. However, due to the lack of complete certainty mentioned above, in the present application and claims when the term insoluble zinc soap is used it should be interpreted to include the zinc and fatty acid components thereof whatever their actual form in the detergents. The drying of these crutcher mixes may be effected by any standard method. They may be spray dried, drum dried, tunnel dried and flash dried but it is preferred to dry them to near the desired bar moisture content in film-type evaporators such as that known as the 'Turbafilm." Alternatively they may be partially dried by one method, e.g., the Turbafilm, and then reduced further in moisture by another, e.g., tunnel drying. The crutcher mixes may also be handled like kettle soap in many instances, especially after partial moisture reduction and so can be spread on a chill roll, cut into ribbons and reduced to milling moisture content in the conventional soap apparatus known as the tunnel drier. It has been found that the presence of zinc soap in the crutcher mix often aids in producing a good strong ribbon from the chill roll and thus facilitates the drying operation.

It is preferred to control the evaporation of moisture from the crutcher mixture so that the final 'drying" chip, bead or particle will have a moisture content slightly higher than that desired in the finished bar. Usually the finished bar moisture will be between 5 and 15% and therefore the crutcher mix will normally be dried to between 6 and 17% moisture.

Adjuvants or essential components not added in the crutcher may be mixed with the dried crutcher batch in an amalgamator. After amalgamation the mixture is milled, usually to a chip thickness of .003 to .015 inch which is sufficient to work the amalgamator mixture into a homogeneous chip. After milling the product is plodded in a conventional Schwantes-type double barrelled vacuum plodder, cut into lengths and pressed into cake form. It is preferred to employ the soap making equipment and the procedures outlined above but other forming apparatuses adapted to compress homogeneous particles of the present formulas may also be employed providing only that the bar obtained is of uniform composition and structure.

Plodding, milling, and drying temperatures should be regulated for optimum performance in the manner well known to those skilled in the art. Plodding temperatures will be between 120° F. and 160° F. Milling temperatures (chip temperature) will be between 60° F. and 115° F., preferably 90° F. to 105° F. The temperature of drying medium, be it gaseous or solid will preferably be between 120° F. and 300° F. but may rise as high as 550° F. if the product is kept at that temperature for only a very short time.

The following examples are given to illustrate the invention but are not to be regarded as limitations thereof. All amounts and percentages in the specification and claims will be by weight unless otherwise indicated. The given weights, percentages and proportions of the three essential components are exclusive of impurities and by-products often present in the commercially available substances.

Example I

The following materials were crutched together, addition being in the order given, at a temperature of about 160° F. for about 15 minutes.

	Parts
Sodium monoglyceride sulfate extract [1]	61.0
Alkyl aryl sulfonate base [2]	3.8
Tallow kettle soap [3]	29.0
Zinc chloride solution (50% $ZnCl_2$, 50% H_2O)	6.0
Water (@140° F.)	50.0

[1] This detergent is the sodium salt of the monosulfuric acid ester of a monoglyceride of hydrogenated coconut oil fatty acids. The extract used is 29% solids of which 89.9% is monoglyceride sulfate.

[2] This detergent is the sodium salt of tetra propyl benzene sulfonate. The slurry contains 52% solids of which 88.8% is active detergent.

[3] 67% tallow soap of iodine value 30.

After crutching the mix was dried to about 6% moisture in a Turbafilm thin film-type evaporator.

The dry product was of the formula:

	Parts
Sodium monoglyceride sulfate	40.1
Alkyl aryl sulfonate	4.5
Sodium tallow soap	17.8
Zinc tallow soap	26.8
Sodium chloride	5.7
Sodium sulfate	2.2
Ether soluble material (glycerides, fatty acids)	2.9
	100.0
Moisture	6.0

The dried combination bar composition was mixed with about 2 parts adjuvants such as perfume, dye, germicide, stabilizer, antioxidant and pigment and 3 parts water. After milling three times at 100° F. it was plodded in a vacuum plodder at 115° F. with the nozzle plate at 130° F. and was pressed into bars of 8% moisture. The product processed easily.

The finished bar tested excellent in slough, foam, lather, slip, appearance, curd dispersion and stability. It was superior to a similar bar containing no zinc soap (sodium soap used instead) in foam, lather and curd dispersion. The combination bar containing zinc leaves no bathtub ring when used in hard water.

Example II

A combination bar similar to that of Example I was made by using a settled white soap (made from 85% tallow, 15% coconut oil). This was of formula:

Sodium monoglyceride sulfate	34.2
Alkyl aryl sulfonate	3.8
Sodium soap	15.2
Zinc soap	24.8
Sodium chloride	5.2
Sodium sulfate	2.4
Ethyl ether solubles	2.6
Adjuvants	3.1
Water	8.7
	100.0

This bar was easily processed, of attractive appearance and tactile characteristics, good slip and slough properties, excellent foam, lather and curd dispersion and of satisfactory storage stability.

In other formulas of the above type settled white soap is partially replaced with stearic acid soap. Alternatively zinc soap is made from zinc salt and fatty acid or zinc oxide and sodium soap.

Example III

	Parts
Sodium monoglyceride sulfate [1]	70
Sodium soap [2]	20
Zinc stearate	7.5
Titanium dioxide	1
Perfume	1.5
	100.0

[1] Made from mixed coconut oil and tallow acids (1:1 ratio). Contains 10% sodium sulfate, 10% ether solubles.
[2] Made from coconut oil and tallow (1:3 ratio). Contains 11% water.

The above materials were mixed dry, milled to homogeneity, plodded, cut and pressed into cakes. The product milled and plodded well and was satisfactory according to usual tests. It gave a very quick lather.

Example IV

Sodium coco-monoglyceride sulfate	25.0
Sodium soap chips [1]	31.2
NaCl	20.0
Zinc stearate	7.5
Diglycol stearate	3.0
Adjuvants	2.1
Sodium sulfate	3.1
Ether solubles	3.1
Water	5.0

[1] Made from coconut oil and tallow (1:3 ratio). Chips contain 11% H_2O.

These components were dry mixed, milled and plodded (140° F nozzle plate temperature) and pressed into cakes which combined in a satisfactory product the best properties of soap and synthetic detergent, being excellent detersive, foaming and lathering products while still being easy to process and of satisfactory tactile properties, hardness and appearance.

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 detergent composition in bar form comprising about 15 to 60% of a sodium higher fatty monoglyceride sulfate detergent in which the fatty acid ester group is of an average of about 12 to 18 carbon atoms, 10 to 60% of a sodium soap of a higher fatty acid of 12 to 18 carbon atoms and 5 to 40% of a water insoluble zinc soap of a higher fatty acid of about 12 to 18 carbon atoms, the sum of the aforesaid three components being at least 50% by weight of the detergent bar.

2. A detergent composition in bar form comprising about 15 to 60% of a sodium higher fatty monoglyceride sulfate detergent in which the fatty acid ester group is of an average of 12 to 18 carbon atoms, 10 to 60% of a water soluble sodium soap of a fatty acid of 12 to 18 carbon atoms and 5 to 40% of a water insoluble zinc soap of a fatty acid of 12 to 18 carbon atoms, the total of the aforementioned three constituents being at least 50% by weight of the detergent bar, and the ratios of sodium monoglyceride sulfate to total sodium and zinc soap and of sodium soap to zinc soap being within the range 0.25 to 4.0.

3. A toilet detergent bar comprising 25 to 45% of a water soluble sodium higher fatty monoglyceride sulfate detergent in which the fatty acid ester group is of an average of 12 to 18 carbon atoms, 10 to 35% of a water soluble sodium soap of a fatty acid of 12 to 18 carbon atoms and 15 to 30% of a water insoluble zinc soap of a fatty acid of 12 to 18 carbon atoms, the total of the aforementioned three constituents being at least 50% by weight of the detergent bar, and the ratios of sodium monoglyceride sulfate to total sodium and zinc soap and of sodium soap to zinc soap being within the range 0.25 to 4.0.

4. A toilet detergent bar comprising 25 to 45% of a water soluble sodium hydrogenated coco-monoglyceride sulfate detergent, 10 to 35% of a sodium soap of a fatty acid of 12 to 18 carbon atoms and 15 to 30% of a water insoluble zinc soap of a fatty acid of 12 to 18 carbon atoms, the total of the aforementioned three constituents being at least 70% by weight of the detergent bar and the ratios of sodium monoglyceride sulfate to total sodium and zinc soap and of sodium soap to zinc soap being within the range 0.25 to 4.0.

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