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3,442,812

DETERGENT BARS

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14 Claims

ABSTRACT OF THE DISCLOSURE

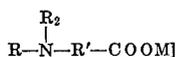
A detergent bar capable of yielding an acidic lather the active detergent components thereof consisting essentially of from about 30% to about 65% by weight of said bar of a non-soap anionic detergent selected from the group consisting of (1) alkane sulfonates, (2) alpha-sulfofatty esters and (3) mixtures of (1) with a minor proportion of a higher alkyl benzene sulfonate, and at least about 5% by weight of said bar of an amphoteric detergent selected from the group consisting of (1) N-long chain alkyl aminocarboxylic acids and (2) N-long chain alkyl iminocarboxylic acids (3) carboxymethyl dimethyl highly alkyl ammonium inner salts and (4) carboxymethyl dimethyl higher alkyl phosphonium inner salts.

This invention relates to detergent bars and relates particularly to novel detergent bars having desirable skin-conditioning effects.

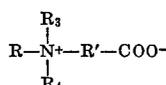
In accordance with one aspect of this invention, there is provided an acidic detergent bar containing an amphoteric detergent together with an anionic foam-producing detergent active under acidic conditions, the anionic detergent constituting at least half of the total detergent in the bar. The bar yields a lather which has an acidic pH.

We have found that washing with the bars of this invention acts to condition the skin of the user; for a considerable length of time after washing the skin retains a desirable high moisture content (which may be measured, for example, by determining the surface conductivity of the skin) and the skin is buffered against the harmful effects of alkaline agents. It is believed that the amphoteric surfactant is absorbed onto the skin during the washing operation and there acts as a reservoir of acidity on the skin to neutralize such alkaline agents (e.g. strong detergents or alkaline salts) as may thereafter come into contact with the skin. The presence of the anionic surfactant does not interfere with this action; surprisingly, very pleasant and healthful effects on the skin are obtained when there is a major amount of the added anionic detergent in admixture with the amphoteric surfactant.

The amphoteric detergent used contains both an anionic and a cationic group and a hydrophobic organic group, which is advantageously a higher aliphatic radical, e.g. of 10-20 carbon atoms. Compounds containing a carboxyl group and an amine group having a higher aliphatic hydrophobic substituent are particularly suitable. Among these are the N-long chain alkyl aminocarboxylic acids [e.g. of the formula



the N-long chain alkyl iminodicarboxylic acids [e.g. of the formula $RN(R'COOM)_2$] and the N-long chain alkyl betaines, e.g. of the formula



where R is a long chain alkyl group, e.g. of about 10-20 carbons, R' is a divalent radical joining the amino and carboxyl portions of an amino acid (e.g. an alkylene radical of 1-4 carbon atoms), M is hydrogen or a salt-forming metal, R² is a hydrogen or another monovalent substituent (e.g. methyl or other lower alkyl), and R³ and R⁴ are monovalent substituents joined to the nitrogen by carbon-to-nitrogen bonds (e.g. methyl or other lower alkyl substituents). Especially good results have been attained with compounds in which the cationic group is tertiary, e.g. trisubstituted compounds of nitrogen or phosphorus, particularly tertiary amines (the nitrogen or similar atom, e.g. phosphorus, of the cationic group becoming protonated in acid medium and thus serving as a reservoir of acidity), or in which the cationic group is quaternary (as in the betaines). These surfactants are advantageously of the type which foam readily in acidic medium.

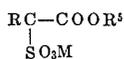
Examples of specific amphoteric detergents are N-alkyl-beta-aminopropionic acid; N-alkyl-beta-iminodipropionic acid, and N-alkyl, N,N-dimethyl glycine; the alkyl group may be, for example, that derived from coco fatty alcohol, lauryl alcohol, myristyl alcohol (or a lauryl myristyl mixture), hydrogenated tallow alcohol, cetyl, stearyl, or blends of such alcohols. The substituted amino-propionic and iminodipropionic acids are often supplied in the sodium or other salt forms, which may likewise be used in the practice of this invention.

Other amphoteric surfactants are the fatty imidazolines such as those made by reacting a long chain fatty acid (e.g. of 10 to 20 carbon atoms) with diethylene triamine and monohalocarboxylic acids having 2 to 6 carbon atoms, e.g. 1-coco-5-hydroxyethyl-5-carboxymethylimidazoline; betaines containing a sulfonic group instead of the carboxylic group; betaines in which the long chain substituent is joined to the carboxylic group without an intervening nitrogen atom, e.g. inner salts of 2-trimethylamino fatty acids such as 2-trimethylaminolauric acid, and compounds of any of the previously mentioned types but in which the nitrogen atom is replaced by phosphorus.

When the amphoteric surfactant is not itself sufficiently acidic to impart a pH of about 5 or less to the lather formed during the use of the bar, or when the amphoteric surfactant is supplied in its non-acidic or weakly acidic salt form, it is advantageous to include in the bar-forming composition a suitable acidifying agent. This may, for example, be a monobasic acid such as hydrochloric, acetic, sulfonic, halogenated acetic (e.g. chloroacetic) dialkylphosphoric (e.g. diethyl ester of phosphoric acid), alkylsulfuric (e.g. monoethyl ester of sulfuric acid) ethanesulfonic or other alkanesulfonic acid, or a polybasic acid such as citric, sulfuric, phosphoric, malonic, tartaric, fumaric or maleic acid. Phosphoric acid is particularly preferred as an additive to a composition containing a basic detergent since in neutralizing the latter the phosphoric acid becomes converted to the mono- and dibasic phosphates. These latter salts help to buffer the product during its shelf life and to buffer the skin at healthy skin pH as the product is used. Also, when basic surfactants or other basic materials are used as the feed and the materials are mixed in relatively dry condition, the addition of the acid helps to heat up the mixture (owing to the exothermic heat of neutralization) thus softening the detergent and aiding the mixing process. Another acidic phosphate buffering agent is acidified pentasodium tripolyphosphate.

Suitable anionic detergents which form foam at acid pH usually contain an $-SO_3M$ radical (where M, as previously indicated, is hydrogen or a salt-forming metal). Surfactants of the primary alkanesulfonate type (e.g. of

the formula $R\text{SO}_3M$) and α -sulfofatty esters (e.g. of the formula



where R^5 is the residue of an alcohol of the formula $R^5\text{OH}$, e.g. a lower alkanol) have been found to be especially useful. The primary alkanesulfonates are generally supplied with mixed chain lengths; a sulfonate of a blend of C_{15} - C_{20} has been found very suitable; when a C_{10} - C_{20} blend was used, the sloughing properties were less desirable. Bars made with alpha-sulfofatty esters, such as the methyl ester of α -sulfomyristic acid or α -sulfotallow acid, tended to be soft when first formed but hardened on standing. We have also found that at acidic pHs these types of aliphatic materials (the alkanesulfonates and the sulfofatty esters) yield slippery and copious foam on lathering. In addition, when they are used in the preferred bars of this invention, the acidic bar compositions can be plodded easily on a soap plodder (a screw extruder), and otherwise processed without undesirable sticking to the steel processing machinery.

Ordinary soap is not suitable for use as the chief anionic detergent, because it is largely converted to free fatty acid at the acidic pH of the product.

Another anionic surfactant which is advantageously employed, in minor proportions relative to the aliphatic sulfonic acid materials, is a higher alkyl arylsulfonic acid having, for example, an alkyl radical of about 10 to 16 carbon atoms on the arylsulfonic group. We have found that the presence of this type of material is advantageous in inhibiting the cracking of the bars which may occur when the bars dry out after use. When the proportion of alkylbenzenesulfonate is relatively high (e.g. in the range of about 15 to 20%, based on the total weight of the bar) it is advantageous to include in the composition an inorganic salt that reduces the tendency to stickiness of this type of sulfonate; sodium chloride (generally in amount less than 10%, e.g. 5%) is particularly suitable for this purpose. The salt has also been found to effectively reduce the sloughing of the bar.

Various fillers or diluents are advantageously used in the composition to lower its cost. Clay, hydrogenated tallow, powdered polyvinyl chloride resin, paraffin wax, starch, and stearic acid are examples of such materials. These, of course, are preferably used in limited amounts to avoid affecting substantially the properties of the bar, such as lathering power and surface slipperiness. Limited amounts (e.g. below 10%) of certain fillers or diluents such as starch and stearic acid actually enhance the surface slipperiness of the bar. Some fillers, such as glycerine, polyglycerine (e.g. of degree of polymerization of about 6), sugar, pectin, gelatin, finely divided silica, in limited amounts (e.g. less than 15%) inhibit the cracking of the bars which may occur when the bars dry out after use.

It is advantageous to have present above about 30% and preferably at least 40% (e.g. 40-65%) of the additional foam-producing detergent to promote the cleansing action, lathering and slipperiness of the bar in use. While proportions above about 65% of this material may be employed, the increase in the amount above about 65% does not yield corresponding improvement in the cleansing and lathering properties and does increase the cost of the bar. It is also advantageous to use more than 5%, preferably at least 10%, of the amphoteric detergent, the most pleasant and healthful effects on the skin being attained when the amount of the amphoteric detergent is about $\frac{1}{10}$ to $\frac{1}{4}$ the total weight of the bar. The ratio of the amount of the foam-boosting detergent to the amount of amphoteric detergent is advantageously in the range of about 12:1 to 1:1, preferably at least about $1\frac{1}{2}$:1 and most preferably in the range of about 5:1 to 2:1. The amount of acidic material, to give the bar an acidic pH, is advantageously sufficient to produce a pH (measured on a mixture of 10% of the bar material and 90% of

water, at room temperature, e.g. 25° C.) below 6, preferably, in the range of about 4 to 5. Typically the pH of the lather (formed by rubbing the wet bar against the hands in the usual manner employed in washing the hands) will also be in the range of about 4 to 5. The amount of acid used for this purpose will usually be about 5-10% of the weight of the bar, when the acid is phosphoric acid and the detergents are supplied as their sodium salts, but when more neutral starting materials are employed, considerably smaller amounts of the acid are effective to reduce the pH to the desired level. The total amounts of inert fillers or diluents and anti-cracking agents are advantageously within the range of, say, about 5 to 55%, preferably about 10 to 35%.

The use of the formulations of this invention makes it possible to produce bars that bathe the skin in mild acidity, restoring the skin's natural pH and preserving that pH for several hours. The amount of moisture retained in the outer layers of the skin is also increased, which also makes for a healthier skin, even for pathologically dry skins. The use of the bars delays the onset of the skin irritation caused when the hands are habitually thereafter subjected to strong detergent solutions, and hastens the recovery of the skin from chapping. Also, the skin is left in a smooth, silky condition; it is found that at least a portion of the amphoteric detergent is substantive to the skin. Another desirable effect of the bars of this invention is their protein-substantive antimicrobial effect (e.g. against *S. aureus*). Also, the preferred bars of this invention give a copious lather and excellent cleaning with only modest sloughing. The lathering is unaffected by hard water and "bath tub ring" is avoided.

The following examples are given to illustrate the invention further.

Example 1

18 parts of sodium hydrogen N-lauryl- β -iminodipropionate (supplied in 30% solution in water as Deriphath 160C), 44.5 parts of a primary paraffin sulfonate (supplied as a 34% slurry in water), 16.3 parts of flakes of hydrogenated tallow (a triglyceride), 4.5 parts of 85% phosphoric acid, 4.5 parts of a sodium linear alkylbenzene sulfonate, 2.2 parts of finely divided commercial stearic acid were mixed to form a thick slurry and thoroughly blended together in slurry form and then dried to a moisture content of about 2%. Thereafter, an additional 8 parts of water was added together with 1 part of perfume and 1 part of finely divided titanium dioxide, after which the mixture was thoroughly milled (on a three-roll soap mill) and plodded at a temperature such that the extruded rod continuously emerging from the plodder had a temperature of about 110° F., this temperature being low enough to avoid melting of the hydrogenated tallow (with agglomeration and hardening of the latter on cooling, giving a gritty bar) and being high enough to yield a rod having high cohesion. The extruded rod was then cut transversely to form bars of standard toilet soap size and then pressed in conventional manner.

The primary paraffin sulfonate used in this Example 1 was a sodium sulfonate of a C_{15} - C_{20} alkane mixture and was made by reaction of the corresponding alpha-olefine mixture with sodium bisulfate. Its average molecular weight was 364, corresponding to an average of about C_{18} in the molecule and it was made from an olefine cut in which the proportions of C_{15} , C_{16} , C_{17} , C_{18} , C_{19} , and C_{20} olefines were each in the range of 13-18%, the proportion of C_{14} olefine being about 1% and the proportion of C_{21} olefine being about 5%. The alkylbenzene sulfonate had an average of 13 carbon atoms in its alkyl substituent (about 15 mole percent C_{12} , 55 mole percent C_{13} and 30 mole percent C_{14}); the alkyl substituent contained about 20% of alkyl groups whose benzene attachment is on the 2-carbon of the alkyl group, the remainder of its alkyl groups having the benzene attachment on the 3-,

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or higher, carbon atom (e.g. 45% on the 5- or 6-carbon atom).

Example 2

20.5 parts of sodium hydrogen N-lauryl- β -iminodipropionate (supplied in 30% solution in water as Deriphath 160C), 46.1 parts of a primary paraffin sulfonate (as in Ex. 1 and supplied as a 34% slurry in water), 17.5 parts of flakes of hydrogenated tallow, 5.1 parts of tapioca starch, 5.1 parts of the sodium alkylbenzene sulfonate of Ex. 1, 5.1 parts of 85% phosphoric acid were mixed and heated to form a thick slurry and thoroughly blended together in slurry form and then dried to a moisture content of about 2%. Thereafter, there was added 0.5 part of perfume and 0.004 parts of pigment, after which the mixture was thoroughly worked (in a Read mixer) while warming. The mixture was then thoroughly milled (on a three-roll soap mill), plodded as in Example 1 and then pressed.

Example 3

10 parts of disodium N-coco-B- β -iminodipropionate, 4 parts of sodium N-coco- β -aminopropionate, 43 parts of a primary paraffin sulfonate (as in Ex. 1), 14 parts of flakes of hydrogenated tallow, 5 parts of 85% phosphoric acid, 5 parts of sodium chloride and 19 parts of a sodium linear alkylbenzene sulfonate (as in Ex. 1) together with a total of 93 parts of water were mixed to form a thick slurry and thoroughly blended together in slurry form and then dried to a moisture content of about 2%. Thereafter, the mixture was worked, milled, plodded and pressed (all as in Example 2).

The following examples illustrate other satisfactory bars which do not, however, have all the desirable features of the bars of Examples 1-3.

Example 4

The following ingredients in finely divided form were mixed by stirring: 15 parts "Deriphath 160" (Disodium N-lauryl- β -iminodipropionate), 30 parts of a primary paraffin sulfonate (as in Ex. 1), 15 parts of paraffin wax, 15 parts of hydrogenated tallow and 15 parts of NaH_2PO_4 . Then 5 parts of water were added while stirring continued, and thereafter 5 parts of 85% phosphoric acid were added. The mixture, soft because of its heated condition, was mixed further, then cooled, milled thoroughly and formed into bars, by plodding and pressing or simply by pressing.

Example 5

The following ingredients in finely divided form were mixed by stirring: 14.2 parts of the iminodipropionate of Example 4, 27.4 parts of a primary paraffin sulfonate, 25.4 parts of hydrogenated tallow and 21.3 parts of NaH_2PO_4 (unhydrated). Then 6.1 parts of water were added while stirring continued, and thereafter 5.6 parts of 85% phosphoric acid were added, followed by the addition of small amounts of dye and perfume. The mixture was then processed further as in Example 4.

In this Example 5, the primary paraffin sulfonate was a sodium salt made in the same way as that of Example 1, but from a broader cut of olefins, namely, a C_{10} - C_{20} cut.

Example 6

The following ingredients in finely divided form were mixed by stirring: 14.2 parts of the iminodipropionate of Example 4, 27.4 parts of a primary paraffin sulfonate (as in Ex. 5), 25.4 parts of very finely powdered polyvinyl chloride resin (Geon Type 121), and 21.3 parts of NaH_2PO_4 (unhydrated). Then 5.6 parts of water were added while stirring continued, and thereafter 5.6 parts of 85% phosphoric acid were added, followed by addition of a trace of FD & C Blue #1. The mixture was then processed further as in Example 4. The particles of polyvinyl chloride powder were not visible (to the naked eye) in the bar. The bar had a hydrophilic surface, unlike the

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more hydrophobic surface of bars made with hydrogenated tallow as the filler.

Example 7

The following ingredients in finely divided form were mixed by stirring: 10 parts of the iminodipropionate of Example 4, 10 parts of "Bioterg MMS" (sodium salt of the methyl ester of α -sulfomyristic acid), 10 parts of "Culveram CDG" (a betaine: carboxymethyl dimethyl laurylammonium inner salt), 55 parts of NaH_2PO_4 (unhydrated) and 10 parts of sodium tallow alcohol sulfate (supplied in a 30% aqueous paste). Then 5 parts of 85% phosphoric acid were added. The mixture was then processed further as in Example 4. A considerable portion of the water in the composition was evaporated during the milling step.

Example 8

The following ingredients in finely divided form were mixed by stirring: 14 parts of the iminodipropionate of Example 4, 14 parts of a primary paraffin sulfonate (as in Ex. 5) and 65 parts of NaH_2PO_4 (unhydrated). 7 parts of water were added and the resulting mixture was milled repeatedly on a three-roll soap mill until homogeneous, then formed into a bar by pressing, or plodding and pressing.

Example 9

The following ingredients in finely divided form were mixed by stirring: 15 parts of the iminodipropionate of Example 4, 15 parts of the sulfomyristate of Example 7, 60 parts of NaH_2PO_4 (unhydrated), 5 parts of sodium tallow alcohol sulfate (supplied in a 30% aqueous paste), 5 parts of glyceryl monostearate. 0.25 part of a perfume were then added and the mixture was processed as in Example 8.

Additional examples of the production of detergent bars are given below.

Example 10

14 parts of the betaine of Ex. 7, 43 parts of primary paraffin sulfonate (as in Ex. 1), 14 parts of hydrogenated tallow, 19 parts of the linear alkylbenzenesulfonate (as in Ex. 1), 5 parts of sodium chloride were blended together as an aqueous slurry and then dried to a moisture content of about 2%, milled and pressed into bars. During the process the pH of the mixture was adjusted so that the pH of the bar (measured on a mixture of 10% of the bar material and 90% of water, as previously mentioned) was about 5.

Example 11

14 parts of carboxymethyl dimethyl dodecyl-phosphonium inner salt, 43 parts of primary paraffin sulfonate (as in Ex. 1), 14 parts of hydrogenated tallow, 5 parts of sodium chloride and 19 parts of sodium linear alkylbenzene sulfonate (as in Ex. 1) were blended together as an aqueous slurry, and then dried to a moisture content of about 2%, milled and pressed into bars. During the process the pH of the mixture was adjusted so that the pH of the bar (measured on a mixture of 10% of the bar material and 90% of water, as previously mentioned) was about 5. In one case, the phosphonium inner salt was supplied in a relatively high acidic chloride form making the whole mixture acidic, and the pH adjustment was made by adding a small amount of a base, such as NaOH.

Our preferred bars have good resistance to sloughing, having slough numbers less than 10, preferably less than about 8. The slough number is determined by allowing a weighed bar 77 mm. x 49 mm. in area and at least 12 mm. thick to stand flat for 17 hours at room temperature in a standard Petri dish lid (100 mm. diameter and 15 mm. high) with 35 ml. of water; the bar is then removed from the water and the pasty "slough" is removed from the underside and edges of the bar with the side of the fore-

finger. Then, after drying on edge for 48 hours in air, the bar is weighed. The slough number is the difference between the weight of the dried bar before and after soaking and removal of slough, expressed in grams lost.

Best results, in terms of overall quality and performance of the bars, have thus far been obtained using the N-higher alkyl β -iminodipropionate, the carboxymethyl dimethyl higher alkyl ammonium inner salt, or the carboxymethyl dimethyl higher alkyl phosphonium inner salt (all mentioned in the foregoing examples) as the amphoteric detergent component and the primary paraffin sulfonate or the methyl α -sulfofatty ester (both mentioned in the foregoing examples) as the principal anionic detergent component.

Another aspect of this invention relates broadly to the provision of a bar having a pH of about 4-5 and containing a mixture of an acidic buffer salt of a weak polybasic acid (e.g. phosphoric, citric, tricarballic, tartaric or fumaric acid) and the amphoteric surfactant, and particularly an amphoteric surfactant which is an N-long chain alkyl iminodicarboxylic acid or is an N-long chain alkyl betaine. The presence of the buffering agent helps to keep the bar at the best pH during its shelf life and to buffer the skin at a healthy pH when the product is used. Formulations of this type without the anionic agent include the following: (a) A mixture of 63 parts of the amphoteric agent of Example 4 and 16.5 parts of monobasic sodium phosphate monohydrate, blended together dry and then mixed with 20 parts of 85% phosphoric acid and further mixed, milled and formed into bars; (b) A mixture of 50 parts of the betaine of Example 7, 48 parts of NaH_2PO_4 (anhydrous) and 2 parts of Na_2PO_4 (anhydrous) mixed, milled and formed into bars. However, particularly advantageous bars are obtained when the anionic detergent is present, as previously described.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications can be substituted therefor without departing from the principles and true spirit of the invention.

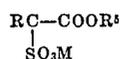
Having thus described the invention, what is claimed is:

1. A detergent bar capable of yielding a lather having an acidic pH the active detergent components thereof consisting essentially of from about 30% to about 65% by weight of said bar of a non-soap anionic detergent selected from the group consisting of

(1) alkane sulfonates of the formula:



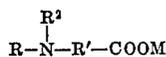
(2) alpha-sulfofatty esters of the formula:



and

(3) mixtures of (1) with a minor proportion relative to said alkane sulfonate of a higher alkyl benzene sulfonate said higher alkyl containing from 10 to 16 carbon atoms and at least 5% of an amphoteric detergent selected from the group consisting of

(1) N-long chain alkyl aminocarboxylic acids of the formula:



(2) N-long chain alkyl iminocarboxylic acids of the formula:



(3) carboxymethyl dimethyl higher alkyl ammonium inner salts said alkyl containing 10 to 20 carbon atoms and

(4) carboxymethyl dimethyl higher alkyl phosphonium inner salts said higher alkyl containing from 10 to 20 carbon atoms and wherein R

represents an alkyl group containing from 10 to 20 carbon atoms, R' represents alkylene of 1 to 4 carbon atoms R² represents hydrogen or lower alkyl R^s represents the residue of a lower alcohol and wherein the ratio of anionic detergent to amphoteric detergent is in the range of about 12:1 to about 1:1 by weight and the pH of the bar is acidic and at least about 4 as measured on a mixture of 10% by weight bar constituents and 90% by weight water.

2. A detergent bar according to claim 1 wherein said amphoteric detergent comprises sodium, hydrogen, N-lauryl-beta-imino-dipropionate.

3. A detergent according to claim 1 wherein said amphoteric detergent comprises a mixture of disodium, N-coco-beta-imino dipropionate and N-coco-beta-amino-propionate.

4. A detergent bar according to claim 1 wherein said amphoteric detergent comprises disodium N-lauryl-beta-imino dipropionate.

5. A detergent bar according to claim 1 wherein said amphoteric detergent comprises a mixture of disodium-N-lauryl-beta-imino dipropionate and carboxymethyl dimethyl lauryl ammonium inner salt.

6. A detergent bar according to claim 1 wherein said amphoteric detergent comprises carboxymethyl dimethyl dodecyl phosphonium inner salt.

7. A detergent bar according to claim 1 wherein said amphoteric detergent comprises carboxymethyl dimethyl lauryl ammonium inner salt.

8. A detergent bar according to claim 1 wherein said anionic detergent comprises a sodium sulfonate of a C₁₅-C₂₀ alkane mixture.

9. A detergent bar according to claim 1 wherein said anionic detergent comprises a sodium sulfonate of a C₁₀-C₂₀ alkane mixture.

10. A detergent bar according to claim 1 wherein said anionic detergent comprises a mixture of a sodium sulfonate of a C₁₅-C₂₀ alkane mixture and a higher alkyl benzene sulfonate said higher alkyl containing from 10 to 16 carbon atoms.

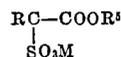
11. A detergent bar according to claim 1 wherein said anionic detergent comprises alpha-sulfofatty acid methyl ester, sodium salt.

12. A detergent bar capable of yielding a lather having an acidic pH the active detergent components thereof consisting essentially of from about 30% to about 65% by weight of said bar of a non-soap anionic detergent selected from the group consisting of

(1) alkane sulfonates of the formula:



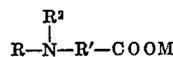
(2) alpha-sulfofatty esters of the formula:



and

(3) mixtures of (1) with a minor proportion relative to said alkane sulfonate of a higher alkyl benzene sulfonate said higher alkyl containing from 10 to 16 carbon atoms and at least 5% of an amphoteric detergent selected from the group consisting of

(1) N-long chain alkyl aminocarboxylic acids of the formula:



(2) N-long chain alkyl iminocarboxylic acids of the formula:



(3) carboxymethyl dimethyl higher alkyl ammonium inner salts said alkyl containing 10 to 20 carbon atoms and

(4) carboxymethyl dimethyl higher alkyl phosphonium inner salts said higher alkyl containing

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from 10 to 20 carbon atoms and wherein R represents an alkyl group containing from 10 to 20 carbon atoms, R' represents alkylene of 1 to 4 carbon atoms R² represents hydrogen or lower alkyl R⁵ represents the residue of a lower alcohol and wherein the ratio of anionic detergent to amphoteric detergent is in the range of about 12:1 to about 1:1 by weight and the pH of the bar is acidic and at least about 4 as measured on a mixture of 10% by weight bar constituents and 90% by weight water said detergent bar containing an acidic buffer salt of a weak polybasic acid.

13. The detergent bar defined in claim 1 wherein the pH is about 4 to less than 6.

14. The detergent bar defined in claim 13 wherein the anionic detergent is present in an amount of about 40 to 65% by weight of the bar and the ratio of anionic detergent to amphoteric detergent is in the range of about 5:1 to 2:1.

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U.S. Cl. X.R.

20 260—606.5; 252—138, 137, 136