3,055,837

SYNTHETIC DETERGENT CAKE AND PROCESS FOR MAKING THE SAME

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This invention relates to a soap-free detergent. More particularly it relates to a novel solid detergent composition in bar or cake form which has highly advantageous properties and has equally effective detergent properties in hard, soft, and salt water. This application is a continuation-in-part of my copending application Serial No. 603,229, filed August 10, 1956, which is a continuation-in-part of application Serial No. 369,505, filed July 21, 1953, which in turn is a continuation-in-part of application Serial No. 221,746, filed April 18, 1951, all now abandoned.

Commercial detergents prepared in cake or bar form heretofore have consisted principally of soaps derived from animal and vegetable fats as alkali metal salts of higher fatty acids. This conventional type of cake detergent is readily soluble, producing a rapid and copious lather when used in soft water. When used in hard water, however, the soluble fatty acid salts of the soap react with the mineral constituents of the hard water, producing undesired precipitation of insoluble fatty acid salts, and when used in sea water the phenomenon of curding is produced. Because of these adverse reactions in hard water and sea water, conventional soaps do not lather well in such water, and the full benefit of their otherwise good detergent properties is not realized.

Non-soap, or so-called synthetic detergents, are available in powder and other substantially solid form, such as flakes, which are readily soluble in all types of water and produce satisfactory lathers in hard and sea water. These synthetic detergents include the alkali metal salts of sulfonated and sulfated aliphatic alcohols, the sulfonated and sulfated aliphatic hydrocarbons, the alkylaryl sulfonic acids, particularly those of the benzene series, the fatty acid amide of methyl amino ethyl sulfonic acid, and the alkyl ethers of polyoxyethylene glycols. These and other sulfuric acid reaction products of high molecular weight organic compounds are characterized by their high solubility in water, their resistance to precipitation by the constituents of hard water, and their excellent detergent properties, particularly when used in a de-greasing operation.

It is difficult to form these non-soap synthetic detergents into satisfactory cake or bar shapes without the use of binding agents having undesirable properties which impart a gritty feel to the cake and generally impair its usefulness as a general purpose detergent. Such solid cake forms of these synthetic detergents as can be effected with known available binding agents also tend to slough off to a high degree and become softened at a rapid rate upon standing in the presence of moisture. They are generally of high solubility and have a higher degree of hydroscopicity than conventional soap, and, therefore, are subject to these defects to a higher degree than is conventional soap. Some attempts have been made to modify these defects of the soluble non-soap or synthetic detergents while retaining their good sudsing, lathering, and degreasing properties. One such suggestion is described in U.S.P. 2,175,285, where the addition of from 5–60% of a polyhydric alcohol, such as glycerine and ethylene glycol partially esterified with a saturated fatty acid containing 12 or more carbon atoms, is proposed. Other combinations which have been tried include mixtures of sodium diamyl sulfosuccinate, methyl cellulose and boric acid, as in U.S.P. 2,373,863, and a mixture of sodium lauryl sul-

foacetate and thiourea, as in U.S.P. 2,374,544. Such mixtures of synthetic detergents have generally been compounded with varying percentages of conventional soaps in order to insure the proper cake formation and its retention in use. To the extent that conventional soaps are contained in the mixture, they are subject to the same defects as the conventional soaps, themselves, when used in hard and sea water. They are also subject to more rapid deterioration in water and moisture than the conventional soap themselves.

I have now found that a satisfactory all-synthetic detergent cake can be made having excellent lasting properties and a pleasing feel, with no impairment to the inherent detergency, sudsing, and lathering properties of the synthetic detergent by combining alkylaryl synthetic detergent with the lauric acid ester of hydroxy ethane sodium sulfonate as the binder. This binder is a relatively insoluble compound having a solubility in the order of 0.2272%, or 2.27 parts per thousand in distilled water at 21° C. The lauric acid ester of hydroxy ethane sodium sulfonate produces some detergent action, and, when combined with the alkylaryl detergent in accordance with the process described below, not only effectively binds the alkylaryl detergent into a proper acceptable detergent cake, but contributes its detergency to the mixture in a synergistic manner to the end that the total available detergency exceeds the sum of the individual detergencies of the alkylaryl detergent and the lauric acid ester binder. This lauric acid ester contains no unsaturated hydrocarbon groups, amide linkages or hydroxy radicals common to surface active and sudsing agents of similar chemical structure which cannot provide effective binding action for the detergent. It is referred to chemically as sodium lauroyl isethionate, or sodium B-laurylethane[1] sulfonate. It can be prepared by esterification of lauric acid and isethionic acid with subsequent saponification as follows:

$$\underset{\text{Lauric acid}}{CH_3(CH_2)_{10}COOH} + \underset{\text{Isethionic acid}}{HOCH_2CH_2SO_3H} \xrightarrow{Na^+} \underset{\text{Sodium B-laurylethane sulfonate}}{CH_3(CH_2)_{10}\underset{\underset{O}{\|}}{C}OCH_2CH_2SO_3Na}$$

The sodium B-laurylethane sulfonate may be used as the only binder in the detergent cake, or may be combined with other binders such as the sodium B-stearylethane sulfonate more specifically described in my above-mentioned application Serial No. 603,229. When combined with B-stearyl ethane sulfonate, the sum of the amounts of B-lauryl ethane sulfonate and B-stearyl ethane sulfonate may comprise the minimum percentage of the binder required for the cake formation as set forth more particularly below.

The alkylaryl synthetic detergents used in the preparation of my synthetic detergent cakes are classified as anionic synthetic detergents, and chemically can be represented generally by the formula

$$R \cdot R' \cdot SO_3Na$$

where R is an alkyl radical or group of alkyl radicals having an average of at least 10 carbon atoms, and preferably from 12 to 18 carbon atoms, and R′ is an aryl radical, generally of the benzene series, which may be modified by additional short-chain alkyl radicals. In commercially available alkylaryl sulfonate detergents of such composition, the essential alkyl component is generally a straight chain radical having at least 10 carbon atoms, such as decyl benzene sodium sulfonate. How-

[1] Throughout the specification and claims, wherever "B" is used in a chemical name or formula, it is intended to designate "beta."

ever, the essential alkyl component need not be of uniform length for each molecule, but may consist of a mixture of different molecules, the average carbon content of the alkyl radical being above 10. This is particularly true in the case of dodecyl benzene. Some commercially available dodecyl benzene detergents contain uniformly straight chain dodecyl radicals. Others, such as those derived from kerosene fractions and referred to as keryl benzene detergents, contain a mixture of alkyl substituted benzene sulfonates wherein the alkyl radical averages C_{13}. These are nevertheless classified as dodecyl benzene compounds. Other compounds of the alkylaryl sulfonate class of detergents include compounds having modifying alkyl groups on the aryl radical, such as isoalkyls, or alkylated toluenes or poly alkyl benzenes. When such modifying alkyl groups are present, or if solubilizing substituent groups are present in the aryl radical, such as OH, COOH, and NH_2 groups, the alkyl side chain may contain more than the 18 carbon atom limit designated for the more common unsubstituted type. In the presence of such substituent groups for the aryl nucleus, the essential alkyl side chain may contain as many as 20 or more carbons in its radical. In the absence of such solubilizing groups, the essential alkyl radical preferably should contain a number of carbon atoms within the range of 10–18, as higher alkyl chains tend to decrease the solubility of the compound and impair its detergent properties.

Suitable commercial decyl and dodecyl benzene synthetic detergents, and other alkylaryl synthetic detergents within this class, are referred to in a publication entitled "Synthetic Detergents," compiled by J. W. McCutcheon, New York, 1950, at pages 120 and following.

For good detergent properties the synthetic detergent cake should contain at least 10% of the alkylaryl synthetic detergent. This may be compounded with various percentages of the lauric acid ester of hydroxy ethane sulfonate sodium salt binder in the range of from 10–90% of the cake, on a dry weight basis. As indicated above, the binder percentage may be all the lauric acid ester, or it may be a combination of the lauric acid and stearic acid esters in various proportions. The proportion of the alkylaryl sulfonate detergent accordingly will be in the range of from 90–10% of the cake, also on a dry weight basis. The remainder of the composition of the cake may consist of other and suitable binding materials, such as waxes and/or the B-stearylethane sulfonate mentioned above. It may also comprise fillers or diluents, particularly starches, such as cornstarch, and clays, such as china clay and fuller's earth, which add bulk without impairing the detergent properties or cohesiveness of the synthetic cake. Other materials may be included in the remainder of the cake composition for specific purposes. Sodium sulfate, which is often present as a diluent of the commercial alkylaryl synthetic detergent, may be present. Sodium chloride and aluminum sulfate may be included to control the foaming characteristics and improve the feel of the cake. Tetra sodium pyrophosphate or other alkaline or acid salts may be included in small amounts for producing a desired pH in the cake. Emollients, such as stearic acid, lanolin, lecithin, glyceryl monostearate, ethylene glycol stearate, propylene glycol monostearate, may be included and are generally preferred in percentages up to about 4% when making cakes for toilet use, since the synthetic alkylaryl detergent is characterized by a high degree of fat solubility which has a tendency to produce a harsh, drying action on the skin. Perfumes, antiseptics, coloring materials, and other special purpose ingredients may also be included. Small amounts of soaps (metallic salts of higher fatty acids) may also be included in the remainder of the cake composition for changing the lathering characteristics of the cake. Collectively, these materials constituting the remainder of the composition of the cake may be referred to as fillers and additives.

Although it is desirable to have varying amounts of

the fillers and additives incorporated into the cake composition for economic reasons, and for the purpose of producing special effects, satisfactory cakes having excellent detergent properties and good lasting properties can be made from combinations of the two essential components, that is, the synthetic detergent and the lauric acid ester binder, within the stated limits where the combination of the amounts of detergent and binder constitute 100% of the cake composition without the inclusion of any fillers or additives. Where fillers and additives are included, the combined proportions of the detergent and lauric acid ester binder will, of course, be less than 100%, and may be as little as 20%. Such a cake may include any one or all of the possible additives and fillers named above, or other materials commonly utilized in the compounding of detergent cakes in whatever proportions are needed to produce the desired effect.

It is believed that the relatively insoluble lauric acid ester binder of this invention becomes completely dispersed by the synthetic detergent during use of the detergent cake in washing operations. There is no precipitate or insoluble residue apparent such as is encountered when using conventional soaps in hard water, nor is there any excessive wasting away of the cake under moist conditions, such as to cause sliming and consequent loss of the detergent material. Apparently lauric acid ester binder substantially reduces or eliminates the tendency of the more soluble components of the detergent cake to dissolve selectively. This action permits of the use of large amounts of inert filler materials, such as those mentioned above, and sodium sulfate and sodium chloride in the cake without danger of adversely affecting its wash-stand life. Ordinarily, salts such as sodium sulfate and sodium chloride, when used as filler materials in a detergent cake, are selectively dissolved out in use and contribute to the sliming and deterioration of the detergent cake.

The foaming, lathering, and general detergency properties of a synthetic detergent cake made in accordance with the process hereof are good, and are independent of the type of water and the degree of its hardness. In the case of hard water, which contains varying proportions of calcium and magnesium compounds as a measure of the degree of hardness, it is not necessary to vary the composition of this detergent cake to accommodate higher degrees of hardness. The same cake can be used equally well with water of any degree of hardness. In the case of sea or salt water, the performance of a synthetic detergent cake made in accordance with the process hereof is superior to that of standard salt water soaps.

In preparing my synthetic detergent cakes containing the sodium B-laurylethane sulfonate binder and the sodium alkaryl sulfonate detergent, it has been found that the ingredients must be melted together in the mixing process at a fairly high temperature in order to insure that a homogeneous mixture of the ingredients in fused combination shall be obtained. Otherwise, the mixture will not be satisfactory and the finished cake will not be smooth. The cakes produced from a mixture of the ingredients which has not been properly fused together will be gritty and sandy, and in use the lastability and uniform dissolution of the binder and detergent will be affected. In order to effect the necessary homogeneous mixing and fusion of the ingredients, I first prepare a mixture of the sodium alkaryl sulfonate detergent, the sodium B-laurylethane sulfonate binder in the solid state, and submit this mixture to a roller mixing operation. Additives, such as alkaline or acid salts which may be added in the solid state, are also incorporated into this dry mix. I then place this mixture in a rotary blade mixer equipped with a steam jacket or other suitable means of heating. Water is added to the mixture in the rotary mixer in an amount of from 15–20% by weight, in order to effect blending of the ingredients. The temperature is raised to from 80–100° C. and maintained at that level during the mixing of the resulting slurry. The mixing is continued at the elevated temperatures until a homogeneous mass has been formed. During this mixing procedure the relatively insoluble sodium B-laurylethane sulfonate binder becomes fused with the more soluble alkaryl detergent and the additives, and the water which has been added for proper blending is slowly reduced by evaporation. Vigorous agitation of the rotary blade mixer should be continued during the heating and mixing process, and the temperature level and agitation should be maintained until the water content has been reduced to a minimum determined by the hydroscopicity of the detergent ingredients and generally not over 5% is retained.

Coloring materials, perfumes, and other such additives soluble in water may be incorporated by mixing the coloring agent or such other additive with the water which is added for blending purposes in the mixing operation of the rotary blade mixer. Also, if starch is added as the filled or diluent, it may be pre-mixed with heated water to which alkali may have been added for the purpose of gelatinizing the starch and that mixture used as the blending water for the binder and detergent.

When the mass has been thoroughly mixed and the water evaporated to the minimum level, the mixture is transferred to a soap plodder for extrusion under pressure into large bars. Smaller cakes can be made from the bars by pressure molding of the latter.

The following examples will serve to further illustrate representative compositions of my new synthetic detergent cake. The process of mixing and fusing the binder and detergent described above is used in the compounding of each of the compositions set forth in the tables containing the illustrative examples, it being understood that during the compounding, in addition to the parts of the ingredients enumerated in the tables, water in the amount of from 15–20% has been added during the mixing procedure, and has been evaporated down to the minimum of about 5% while fusion of the components has been effected during the drying stage. Since the parts given in the tables are on a dry weight basis, the amount of water in the order of not over 5% retained in the cake is not included.

TABLE OF COMPOSITIONS I

Component	Dry Weight Parts				
Example No.	1	2	3	4	5
Na B-lauryl ethane sulfonate	65	35	104	156	113.75
Na B-stearyl ethane sulfonate		30			113.75
Na dodecyl benzene sulfonate	455	455	403		286.00
Na keryl benzene sulfonate				351	
Corn Starch	104	104	117	117	110.50
Tetra-Na-pyrophosphate	13	13	13	13	13.00
Aluminum sulfate	13	13	13	13	13.00
Total Dry Weight Parts	650	650	650	650	650.00

TABLE OF COMPOSITIONS II

Component	Dry Weight Parts				
Example No.	6	7	8	9	10
Na B-lauryl ethane sulfonate	227.5	260	97.5	130	65
Na B-stearyl ethane sulfonate			27.0		20
Na dodecyl benzene sulfonate		260	97.5		65
Na decyl benzene sulfonate	279.5			130	
Na lauryl sulfate			12.0		19
Corn starch	117.0	117	390.0	364	455
Tetra Na pyrophosphate	13.0	13	13.0	13	13
Aluminum sulfate	13.0		13.0	13	13
Total Dry Weight Parts	650.0	650	650.0	650	650

TABLE OF COMPOSITIONS III

Component	Dry Weight Parts				
Example No.	11	12	13	14	15
Na B-lauryl ethane sulfonate	260	113.75	37.5	130	60
Na B-stearyl ethane sulfonate		113.75	37.5	130	70
Na dodecyl benzene sulfonate	130	116.00	299.0	260	130
Na lauryl sulfate	130	287.00	130.0		
Corn starch	117		120.0	117	364
Tetra Na pyrophosphate	13	13.00	13.0	13	13
Aluminum sulfate		13.00	13.0		13
Total Dry Weight Parts	650	650.00	650.0	650	650

TABLE OF COMPOSITIONS IV

Component	Dry Weight Parts					
Example No.	16	17	18	19	20	21
Na B-lauryl ethane sulfonate	325	24	42	36	48	54
Na dodecyl benzene sulfonate	325	36	18	24	12	6
Total Parts	650	60	60	60	60	60

TABLE OF COMPOSITIONS V

Component	Dry Weight Parts					
Example No.	22	23	24	25	26	27
Na B-lauryl ethane sulfonate	18	12	6	18	27	6
Na B-stearyl ethane sulfonate				18	27	6
Na dodecyl benzene sulfonate	42	48	54	24	6	48
Total parts	60	60	60	60	60	60

As stated above, the lauric acid ester binder prevents the selective dissolution of the more soluble components of the detergent cake, and particularly the alkylaryl sulfonate detergent. It has also been discovered that the solubility of the sodium B-lauryl ethane sulfonate binder is unexpectedly increased when combined according to the process of this application with the alkylaryl sulfonate detergent. The following table shows the multiple by which the solubility of the sodium B-lauryl ethane sulfonate is increased by addition of the selected increments of the alkylaryl detergent. All determinations are at 21° C. The detergent in the test cakes is sodium dodecylbenzene sulfonate. The binder is sodium B-lauryl ethane sulfonate. The dissolved binder was determined as cocoanut free fatty acids (FFA). The molecular ratio factor of 1.60 converts the cocoanut free fatty acids parts per hundred to sodium B-lauryl ethane sulfonate parts per hundred. The dry weight percentages of the binder and detergent in the test cakes range from 28.6% to 61.5% for the detergent, and from 38.5% to 71.4% for the binder. Since the test cakes contain only binder and detergent the dry weights of the respective components can be derived from the solution percentages given in the table.

TABLE VI

Binder Solubility Increase

Cake No.	Binder, Percent	Detergent, Percent	H_2O, Percent	Dissolved FFA, Percent	Dissolved Binder, Percent	Binder Solubility Increase Multiple
Control	4.762	0.000	95.238	0.142	0.2272	0.00
1	4.762	1.905	93.333	0.639	1.0224	4.50
2	4.762	3.809	91.429	0.831	1.3296	5.85
3	4.762	5.714	89.524	0.950	1.5200	6.69
4	4.762	7.619	87.619	0.961	1.5376	6.77

These results provide a clear indication that there is a complementary action of the two principal ingredients homogeneously fused in the detergent cake. Thus, the highly insoluble binder is solubilized by the detergent and dispersed during use of the cake in washing operations, and the highly soluble detergent is thereby discharged with the binder, so as effectively to prevent selective dissolution of the detergent.

Having thus described my invention, what I claim as new and useful and desire to secure by Letters Patent is:

1. A solid detergent bar consisting essentially of a homogeneous mixture of a compound taken from the class consisting of sodium laurylisethionate and mixtures of sodium lauryl isethionate with sodium stearyl isethionate, with an alkyl aryl sulfonate having detergent properties, the alkyl radical of said sulfonate averaging at least 10 carbon atoms, said sulfonate comprising 10% to 90% of said bar on a dry weight basis and said compound comprises 90% to 10% of said bar on a dry weight basis.

2. A solid detergent bar according to claim 1 wherein said compound and said sulfonate together comprise at least 20% of said bar on a dry weight basis.

3. A solid detergent bar according to claim 1 wherein said sulfonate is taken from the class consisting of dodecyl benzene sodium sulfonate, decyl benzene sodium sulfonate and keryl benzene sodium sulfonate.

4. A solid detergent bar according to claim 1 wherein said compound is composed of 50% sodium lauryl isethionate and 50% sodium stearyl isethionate by weight.

5. A method of making a solid detergent cake which comprises mixing a compound taken from the class consisting of sodium lauryl isethionate and mixtures of sodium lauryl isethionate with sodium stearyl isethionate, with an alkyl aryl sulfonate detergent having an average alkyl radical length of at least 10 carbon atoms, in such amounts as to produce a mixture containing 10–90% of said detergent by dry weight and 90–10% of said isethionate by dry weight, adding 15–20% by weight of water, heating the slurry thus produced to 80–100° C., agitating said slurry until a homogeneous fused mixture is achieved, continuing the heating of said mixture until the water content has been reduced to not more than about 5% and forming the resultant fused mixture into bars.

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