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SYNTHETIC DETERGENT TOILET BAR

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This invention relates to synthetic detergent compositions having superior properties which can be shaped into bars, cakes or other forms. More particularly, this invention relates to a synthetic detergent toilet bar in which an anionic-type detergent is the major component and which has a "soapy" or slippery feel, good sudsing and rinsibility characteristics, and leaves the skin feeling soft and smooth with no tacky sensation.

Synthetic detergents, particularly alkyl aryl sulfonate detergents, have rapidly replaced soap as a general cleaning agent for laundry, dishwashing, and similar purposes both in industry and in the home. These synthetic detergents have been prepared and marketed in powdered, granular, and liquid forms for the consumer. However, in spite of their great popularity and superiority over soap, synthetic detergents in the form of toilet bars have not met with any substantial commercial success. In an attempt to find more outlets for the sale of synthetic detergents, considerable research has been directed to the development of a synthetic detergent toilet bar which would be acceptable to the consumer.

Synthetic detergent toilet bars thus far developed have had a number of undesirable characteristics. Some have left an unpleasant tacky sensation on the skin immediately after washing with the bar; others have had an objectionable "defatting" action on human skin. Some do not suds well, while others become soft and slushy in use and waste away rapidly when wet. Furthermore, in general, they do not have the "soapy" feel desired in a toilet bar.

It is, therefore, an object of this invention to provide synthetic detergent compositions capable of being formed into a toilet bar.

It is another object of this invention to provide synthetic detergent toilet bars which have a "soapy" feel, good rinsibility and sudsing properties, are non-hygroscopic, do not become soft and slushy in use, and leave the skin feeling soft, smooth, and tack-free.

Other objects will become apparent from the following description of this invention.

These and other objects of this invention are attained by compounding a synthetic detergent toilet bar of the following composition.

Component:	Percent by weight
Synthetic organic anionic detergent.....	50 to 75
Long chain alcohol.....	5 to 35
Wax	1 to 25
Alkanolamide	2 to 25
Water	1 to 8

The synthetic organic anionic detergent used in this invention is selected from the group consisting of water soluble alkali metal and alkanol amine salts of higher aliphatic sulfates and sulfonates containing a hydrocarbon radical of at least 11 to about 30 carbon atoms in a straight chain and alkyl aryl sulfates and sulfonates containing at least one alkyl side chain radical of at least 8 to about 18 carbon atoms. Examples of synthetic organic anionic detergents suitable for use in this invention include the alkali metal, ammonium, and alkaline earth metal long chain alkyl aryl sulfonates, such as the sodium, potassium, and magnesium octyl-, nonyl-, decyl-, dodecyl-, tridecyl-, pentadecyl- and octadecyl benzene or toluene sulfonates; N-long chain acyl N-alkyl taurates, such as

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sodium oleoyl methyl taurate, sodium palmitoyl methyl taurate, sodium lauroyl methyl taurate, and the corresponding acyl ethyl taurates; long chain alkyl oxyethylene sulfates, such as sodium or potassium laurylpolyoxyethylene sulfate, sodium laurylmonoxoethylene sulfate, sodium octadecylpolyoxyethylene sulfate, and sodium cetylpolyoxyethylene sulfate; long chain alkyl aryl oxyethylene sulfates, such as ammonium, sodium, or potassium nonyl-, octyl-, and tridecylphenol mono- and polyoxyethylene sulfates; long chain alkyl sulfates such as sodium lauryl- and stearyl sulfates; long chain alkyl isothionates, such as sodium oleic isothionate, sodium lauric isothionate, and the like.

The preferred synthetic organic anionic detergents to be used in accordance with this invention are the alkali metal or alkanol amine long-chain (C_8 to C_{18}) alkyl aryl sulfonates, particularly sodium or potassium or mono-, di-, or triethanolamine, dodecyl, tridecyl-, or pentadecyl benzene sulfonate or mixtures thereof.

The synthetic organic anionic detergents used in this invention may be prepared by any one of a number of well-known commercial methods; for example, benzene is alkylated by treating an excess of benzene with a halogenated aliphatic hydrocarbon of 8 to 18 carbon atoms in the presence of a suitable alkylation catalyst of the Friedel-Crafts type, i.e., $AlCl_3$, to obtain substantial yields of mono-alkylated benzenes. These mono-alkylated benzenes may also be prepared by alkylating benzene with an alcohol or mono-olefin of 8 to 18 carbon atoms using either sulfuric acid or a Friedel-Crafts catalyst.

A further method for producing the alkylated benzenes or mixtures of alkylated benzenes having 8 to 18 carbon atoms in the alkyl group is to polymerize an olefin such as propylene, or a gas stream containing propylene, with an acid catalyst such as a supported phosphoric acid catalyst or boron trifluoride catalyst, at elevated temperatures and pressures according to well-known methods thereby obtaining a mixture of propylene polymers which are fractionated to produce polymers of from 8 to 18 carbon atoms or intermediate fractions of a narrower molecular weight range. The benzene is then alkylated with the propylene polymer fraction in the presence of a Friedel-Crafts catalyst or with a sulfuric acid catalyst to produce the alkylated benzene or mixture of alkylated benzenes.

The alkylated benzene having an alkyl group of from 8 to 18 carbon atoms, or a mixture of alkylated benzenes within this range, is subjected to sulfonation with sulfuric acid of 98 to 100 percent concentration at temperatures of 150° F. to 160° F. using about one volume of acid to one volume of the alkylated benzene mixture or, more preferably, it is subjected to sulfonation with 20 percent fuming sulfuric acid at somewhat lower temperatures, i.e., 135° F. with about the same ratio of acid to hydrocarbon. When the sulfonation reaction is completed the reaction mixture is diluted with a solvent such as benzene or hexane or mixtures thereof and the spent sulfuric acid is settled out, leaving the alkylated benzene sulfonic acids in solution in the immiscible benzene layer. The benzene solution of the sulfonic acids is then extracted with a mixture of water and methanol or other lower alcohol to dissolve and remove the sulfonic acids from the benzene. The aqueous alcohol solution, after separation from the benzene, is neutralized with an alkali metal hydroxide such as sodium or potassium hydroxide or an alkanolamine such as mono-, di-, or triethanolamine or a slurry of an alkaline earth metal oxide such as a slurry of magnesium oxide. The resulting neutralized sulfonate solution is then further processed by either evaporation to obtain a purified sulfonate product or the crude sulfonate solution may be desalted with a water miscible solvent such as acetone or isopropyl

alcohol and further purified to produce a concentrated salt-free sulfonate product.

The synthetic organic anionic detergent is the major component of the synthetic detergent bar of this invention and is present in the bar in an amount ranging between about 50 percent to about 75 percent by weight. Preferably the synthetic organic anionic detergent is present in the toilet bar in an amount ranging between about 60 percent to about 70 percent by weight. It has been found that if the amount of synthetic organic anionic detergent is less than about 50 percent by weight the amount of suds produced by the bar is unsatisfactory and, that if it is present in the bar in an amount in excess of 75 percent by weight the tack and hygroscopicity is markedly increased.

The long chain alcohols used in this invention are those having from at least 12 carbon atoms to about 27 carbon atoms. Examples of suitable alcohols are lauryl-, tridecyl-, myristyl-, pentadecyl-, cetyl-, margaryl-, stearyl-, nonadecyl- and arachidyl alcohols. These alcohols are available commercially.

It has been found that the alcohol component of the toilet bar of this invention must contain at least 12 carbon atoms, otherwise the bar will not be sufficiently hard. A mixture of long chain alcohols may also be used. If a mixture of alcohols is used, no alcohol component of the mixture may contain less than 12 carbon atoms for the reasons stated above. Examples of mixtures of alcohols which may be used in this invention are lauryl- and stearyl alcohols; cetyl- and stearyl-alcohols; tridecyl- and nonadecyl-alcohols; myristyl- and stearyl alcohols, etc. Any combination of two or more alcohols each of which has at least 12 carbon atoms may be used.

The total alcohol content of the synthetic detergent toilet bars of this invention ranges between about 5 percent by weight to about 35 percent by weight, preferably about 5 percent by weight to about 15 percent by weight. It has been found that if the total alcohol content is less than about 5 percent by weight the toilet bar leaves an objectionable tacky sensation on the skin, whereas if the total alcohol content is greater than about 35 percent by weight the sudsing properties of the bar are substantially reduced or eliminated.

The wax used in this invention may be an animal, vegetable, mineral, or synthetic wax or mixtures thereof. Examples of waxes which may be used in this invention are beeswax, carnauba, palm, ouricuri, raffia, candleilla, Madagascar, sugar cane wax, bamboo leaf wax, esparto, Japan, Parafint, cranberry wax, ozocerite, montan, and ceresin; petroleum waxes, i.e., paraffin and microcrystalline waxes are preferred, paraffin waxes being most preferred. It will be understood, however, that any wax which has a melting point lower than ambient temperatures cannot be used for obvious reasons. The wax, therefore, should melt at a temperature not less than about 120° F. nor should it exhibit any appreciable cold flow properties at temperatures less than about 120° F. It is most preferred in this invention to use a n-paraffin wax having a melting point of from about 125° F. to about 170° F.

The wax is present in the novel detergent bar of this invention in an amount ranging between about 1 percent to about 25 percent by weight, preferably from about 5 percent to about 10 percent by weight. If the wax is present in an amount less than about 1 percent by weight, the bar tends to be soft and slushy whereas if the wax is present in an amount greater than about 25 percent by weight, the skin will not feel smooth after having been washed with the bar.

The alkanolamides used in this invention are the mono- or dialkanolamides of saturated aliphatic carboxylic acids. The saturated aliphatic carboxylic acids contain from at least 12 carbon atoms to about 27 carbon atoms. Examples of suitable alkanolamides useful in this invention are mono- or diethanolamides of lauric, tridecanoic,

myristic, pentadecanoic, palmitic, margaric, stearic, nonadecanoic or arachidic acids; mono- or dibutanolamides of lauric, tridecanoic, myristic, pentadecanoic, palmitic, margaric, stearic, nonadecanoic or arachidic acids, etc.

It is most preferred in the practice of this invention to use a monoethanolamide of palmitic, margaric, or stearic acid.

The alkanolamides of saturated aliphatic carboxylic acids may be prepared in any suitable manner and numerous processes for their production are well-known in the art. They are also available commercially. A convenient and economical mode of synthesis involves the condensation of a higher acylating compound, (e.g., lauric acid, myristic acid, palmitic acid, margaric acid, stearic acid, etc.) with a suitable alkanol amino compound to produce a material having the desired alkanolamide structure. The higher acylating substances may be derived from either pure or commercial grades of saturated aliphatic carboxylic acids and the like.

Alkanolamines suitable for condensation with these higher acylating substances are mono- and di-ethanolamine, N-N-bis(2,3-dihydroxypropyl) amine, mono- or dipropanol amine, N - N - bis(2-hydroxypropyl) amine, mono- or dibutanol amine, etc. These alkanolamines may be utilized in pure or impure form and are available commercially.

It has been found that an excellent toilet bar may be prepared using an amount of alkanolamide ranging between about 2 percent by weight to about 25 percent by weight. While amounts of alkanolamide in excess of 25 percent by weight do not adversely affect the properties of the toilet bar, for reasons of economy and practicality an upper limit of 25 percent by weight is preferred. It is most preferred to use from 5 to 15 percent by weight of the alkanolamide. If the amount of alkanolamide used is less than about 2 percent by weight, after washing with the toilet bar, the skin feels dry and harsh.

The amount of water incorporated in the toilet bar may range between about 1 percent by weight to about 8 percent by weight, preferably from about 1 percent by weight to about 5 percent by weight. It has been found that if the amount of water used is in excess of about 8 percent by weight, it is not possible to form a solid toilet bar of sufficient hardness.

In a specific embodiment of this invention, a number of synthetic detergent toilet bars were prepared using the following ingredients in weight percent based on the total weight of the bar:

Sodium dodecyl benzene sulfonate.....	68.0
Stearyl alcohol.....	6.3
Cetyl alcohol.....	3.4
Monoethanolamide of stearic acid.....	9.7
Wax (n-paraffin, M.P. 131° F.).....	9.7
Water	2.9

These toilet bars were evaluated qualitatively by a testing panel. The testing panel was asked to evaluate the bars with regard to suds, slippery feel, rinsibility, lack of a harsh or dry feel to the skin after washing (after-feel), hardness of the bar, lack of slushiness, and longevity as compared to commercial bars. The results of this test are reported in Table I below.

TABLE I

Property:	Percent of panel rating satisfactory
Suds	75
Slippery feel.....	70
Rinsibility	100
Afterfeel	60
Hardness	85
Lack of slushiness.....	73
Longevity	81

The data presented in Table I clearly demonstrate that a synthetic detergent toilet bar compounded in accord-

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ance with this invention is more than satisfactory with regard to all properties desirable in a toilet bar.

The following examples will illustrate further preferred modes of this invention, but it will be understood that this invention is not limited thereto. All amounts are in percent by weight unless otherwise specified.

Example I

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium dodecyl benzene sulfonate.....	45
Stearyl alcohol.....	20
Wax (n-paraffin, M.P. 131° F.).....	15
Monoethanolamide of stearic acid.....	15
Water	5

It will be noted that the amount of synthetic organic anionic detergent used in preparing the toilet bar of Example I was less than 50 percent by weight. This bar when tested was found to have an extremely poor sudsing action.

Example II

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium dodecyl benzene sulfonate.....	80
Stearyl alcohol.....	8
Wax (n-paraffin, M.P. 131° F.).....	5
Monoethanolamide of stearic acid.....	5
Water	2

It will be noted that the amount of synthetic organic anionic detergent used in preparing the toilet bar of Example II was greater than 75 percent by weight. This bar when tested was found to be extremely hygroscopic, and left the skin feeling harsh and tacky.

Example III

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium dodecyl benzene sulfonate.....	68
Stearyl alcohol.....	3
Wax (n-paraffin, M.P. 131° F.).....	9
Monoethanolamide of stearic acid.....	15
Water	5

It will be noted that the amount of long chain alcohol used in preparing the toilet bar of Example III was less than 5 percent by weight. This bar when tested was found to leave the skin tacky.

Example IV

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium dodecyl benzene sulfonate.....	50
Stearyl alcohol.....	40
Wax (n-paraffin, M.P. 131° F.).....	3
Monoethanolamide of stearic acid.....	5
Water	2

It will be noted that the amount of long chain alcohol used in preparing the toilet bar of Example IV was greater than 35 percent by weight. This bar when tested was found to have an extremely poor sudsing action.

Example V

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium dodecyl benzene sulfonate.....	68
Stearyl alcohol.....	15
Wax	0
Monoethanolamide of stearic acid.....	15
Water	2

It will be noted that the amount of wax used in preparing the toilet bar of Example V was less than 1 percent

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by weight. This bar when tested was found to be soft and slushy.

Example VI

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium dodecyl benzene sulfonate.....	56
Stearyl alcohol.....	6
Wax (n-paraffin, M.P. 131° F.).....	30
Monoethanolamide of stearic acid.....	6
Water	2

It will be noted that the amount of wax used in preparing the toilet bar of Example VI was greater than 25 percent by weight. This bar when tested left the skin feeling rough.

Example VII

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium dodecyl benzene sulfonate.....	70
Stearyl alcohol.....	13
Wax (n-paraffin, M.P. 131° F.).....	12
Monoethanolamide of stearic acid.....	0
Water	5

It will be noted that the amount of monoalkanolamide of a saturated aliphatic carboxylic acid used in preparing the toilet bar of Example VII was less than 2 percent by weight. This bar, when tested, left the skin feeling harsh and dry.

Example VIII

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium dodecyl benzene sulfonate.....	60
Stearyl alcohol.....	8
Wax (n-paraffin, M.P. 131° F.).....	1
Monoethanolamide of stearic acid.....	30
Water	1

It will be noted that the amount of monoalkanolamide of a saturated carboxylic acid used in preparing the toilet bar of Example VIII was in excess of 25 percent by weight. This bar when tested was found to be quite satisfactory as a toilet bar. No additional benefits were noted however over a bar containing a maximum of 15 percent by weight of the alkanolamide of a saturated aliphatic carboxylic acid.

Example IX

An attempt was made to prepare a synthetic detergent toilet bar using the following ingredients:

Sodium dodecyl benzene sulfonate.....	60
Stearyl alcohol.....	10
Wax (n-paraffin, M.P. 131° F.).....	5
Monoethanolamide of stearic acid.....	10
Water	15

It will be noted that the amount of water used in an attempt to prepare the toilet bar of Example IX was in excess of 8 percent by weight. It was not possible to prepare a solid bar.

Example X

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium tridecyl benzene sulfonate.....	68.0
Stearyl alcohol.....	6.3
Cetyl alcohol.....	3.4
Wax (n-paraffin, M.P. 131° F.).....	9.7
Monoethanolamide of stearic acid.....	9.7
Water	2.9

Example XI

A synthetic detergent toilet bar was prepared using the following ingredients:

Sodium pentadecyl benzene sulfonate.....	68.0
Stearyl alcohol.....	6.3
Cetyl alcohol.....	3.4
Wax (n-paraffin, M.P. 131° F.).....	9.7
Monoethanolamide of stearic acid.....	9.7
Water	2.9

The detergent bars prepared in accordance with Examples X and XI when tested were found to be quite satisfactory as toilet bars.

Thus, the foregoing Examples I to XI, inclusive, not only show the advantages of the synthetic detergent toilet bar of this invention, but also show the criticality of the amounts of each component used in formulating the toilet bars of this invention.

The synthetic detergent toilet bars of this invention may be prepared in any conventional manner known to those skilled in the art such as framing, milling, pressing and similar processes.

In making frame bars, all the ingredients are mixed at elevated temperatures in a crutcher to permit easy stirring. The mass is then poured into wooden frames to cool, solidify and partially dry after which the frame is removed, and the soap block cut into pieces and stamped in a soap press. In the milling process all of the materials for making the bar are mixed in an amalgamator, preferably passed through a roller mill one or more times to assure a thorough mixing, and the milled mass is then compressed and extruded from a plodder into long bars which are cut into suitable lengths and stamped into the desired shape and size.

In addition to the components listed above, it will be understood that the detergent bars of this invention may contain conventional additives such as perfumes, dyes, fillers, binders, salts, fungicides, germicides, antiseptics or bactericides.

It will be understood that the term "detergent bar" or "toilet bar" as used in the foregoing description of this invention and appended claims shall mean a detergent composition in a solid cohesive state regardless of size or shape.

It will further be understood that various modifications and variations of the toilet bars of this invention will be obvious to one skilled in this art without departing from the spirit and scope of this invention and such modifications and variations are to be included within the purview of this description and appended claims.

I claim:

1. Synthetic detergent toilet bar consisting essentially of the following ingredients in weight percent based on the total weight of the bar:

Sodium alkyl benzene sulfonate.....	50-75
Stearyl alcohol.....	5-35
n-Paraffin wax, M.P. 125° F.-170° F.....	1-25
Monoethanolamide of saturated aliphatic carboxylic acid containing from 16 to 18 carbon atoms	2-25
Water	1-8

said sodium alkyl benzene sulfonate having from 12 to 15 carbon atoms in the alkyl group and having been prepared by alkylating benzene with a polypropylene fraction, sulfonating the thus produced alkylated benzene and neutralizing the sulfonated, alkylated benzene with sodium hydroxide.

2. Synthetic detergent toilet bar consisting essentially of the following ingredients in weight percent based on the total weight of the bar:

Sodium dodecyl benzene sulfonate.....	60-70
Stearyl alcohol.....	5-15
n-Paraffin wax, M.P. 125° F.-170° F.....	5-10

Monoethanolamide of saturated aliphatic carboxylic acid containing from 16 to 18 carbon atoms	5-15
Water	1-5

said sodium dodecyl benzene sulfonate having been prepared by alkylating benzene with a polypropylene fraction, sulfonating the thus produced alkylated benzene and neutralizing the sulfonated, alkylated benzene with sodium hydroxide.

3. Synthetic detergent toilet bar consisting essentially of the following ingredients in weight percent based on the total weight of the bar:

Sodium dodecyl benzene sulfonate.....	60-70
Stearyl alcohol.....	3.25-9.75
Cetyl alcohol.....	1.75-5.25
n-Paraffin wax, M.P. 131° F.....	5-10
Monoethanolamide of stearic acid.....	5-15
Water.....	1-5

said sodium dodecyl benzene sulfonate having been prepared by alkylating benzene with a polypropylene fraction, sulfonating the thus produced alkylated benzene and neutralizing the sulfonated, alkylated benzene with sodium hydroxide.

4. Synthetic detergent toilet bar consisting essentially of the following ingredients in weight percent based on the total weight of the bar:

Sodium dodecyl benzene sulfonate.....	68.0
Stearyl alcohol.....	6.3
Cetyl alcohol.....	3.4
n-Paraffin wax, M.P. 131° F.....	9.7
Monoethanolamide of stearic acid.....	9.7
Water	2.9

said sodium dodecyl benzene sulfonate having been prepared by alkylating benzene with a polypropylene fraction, sulfonating the thus produced alkylated benzene and neutralizing the sulfonated, alkylated benzene with sodium hydroxide.

5. Synthetic detergent toilet bar consisting essentially of the following ingredients in weight percent based on the total weight of the bar:

Sodium tridecyl benzene sulfonate.....	68.0
Stearyl alcohol.....	6.3
Cetyl alcohol.....	3.4
n-Paraffin wax, M.P. 131° F.....	9.7
Monoethanolamide of stearic acid.....	9.7
Water	2.9

said sodium tridecyl benzene sulfonate having been prepared by alkylating benzene with a polypropylene fraction, sulfonating the thus produced alkylated benzene and neutralizing the sulfonated, alkylated benzene with sodium hydroxide.

6. Synthetic detergent toilet bar consisting essentially of the following ingredients in weight percent based on the total weight of the bar:

Sodium pentadecyl benzene sulfonate.....	68.0
Stearyl alcohol.....	6.3
Cetyl alcohol.....	3.4
n-Paraffin wax, M.P. 131° F.....	9.7
Monoethanolamide of stearic acid.....	9.7
Water	2.9

said sodium pentadecyl benzene sulfonate having been prepared by alkylating benzene with a polypropylene fraction, sulfonating the thus produced alkylated benzene and neutralizing the sulfonated, alkylated benzene with sodium hydroxide.

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