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SYNTHETIC DETERGENT BAR

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2 Claims

ABSTRACT OF THE DISCLOSURE

A toilet bar which comprises as the essential and major ingredients 80 to 25% by weight of a salt of at least one fatty acid ester of a sulfonated phenol, said ester moiety being derived from a mixture of fatty acids having from 8 to 18 carbon atoms and said mixture having an average chain length of from 11 to 15 carbon atoms in the alkyl portion, 10 to 35% by weight of a mixture of a salt of said mixture of fatty acids and free fatty acid and 10 to 55% by weight of a salt of said sulfonated phenol.

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 yet which bar 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. In addition most synthetic as well as soap bars soften in "soap dishes" due to the presence of moisture in these dishes.

It is, therefore, an 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, do not scum and which leave the skin feeling pleasant, soft, smooth, and tack-free. It is a further object to provide a bar which remains hard and strong in the presence of moisture in "soap dishes."

It is also an object of the present invention to provide a synthetic detergent toilet bar composition which has the following desirable properties, to wit:

- (1) Good lathering properties in hard water.
- (2) Leaves no "bath-tub" ring.
- (3) Lather "breaks" after rinsing in lavatory.
- (4) Cleansing properties equal to or better than soap.

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(5) Compatible with the various constituents of other bars and imparts its good quality to these bars.

(6) Imparts a substantial non-drying feeling to the skin.

5 (7) Lathers well in presence of oil.

(8) Lathers well in presence of lanolin.

(9) Lathers well on hair.

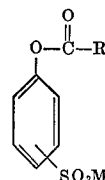
(10) Solubility rate less than soap and actual use rate is less than soap.

10 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 in accordance with the following invention.

15 There are three essential components that are present in the product as manufactured to wit: a fatty acid ester of a sulfonated phenol, a salt of the fatty acid, a salt of the sulfonated phenol. To maintain the excellent qualities of the toilet bar we have found that it is desirable that the proportion of each constituent be optimized in the bar in order to obtain superior lathering and anti-scrumming properties. If the toilet bar 20 is made of 100% fatty acid ester of the sulfonated phenol, the bar does not lather properly and scums as the water hardness increases. And, while a mixture of sodium salt of the fatty acid and free acid lathers profusely, it is too soft for toilet soap and scums badly whereas while sodium sulfophenol alone is not a surfactant, it imparts a degree of hardness to the bar structure.

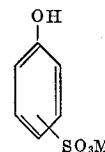
30 The synthetic organic anionic detergent systems suitable for use as a commercial toilet bar are those containing not more than 80% and not less than 25% by weight of a salt of a fatty acid ester of sulfonated phenol, e.g.,



40 wherein R represents an aliphatic moiety of a fatty acid having from 8 to 18 carbon atoms and mixtures thereof, and M represents a self-forming moiety selected from the group consisting of alkali metal and ammonium, not less than 10% nor more than 35% of a mixture of the salt and free acid of a fatty acid having the formula



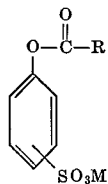
50 wherein R has the aforesaid significance and which may be the same or different from the R in the ester, and not less than 10% and not more than 55% by weight of a salt of sulfonated phenol having the formula



60 wherein M has the same significance as above and may be the same or different from the ester. It has been found preferable on the basis of laboratory tests to employ between about 35 and 65% by weight of the ester to obtain a desirable lathering property and to prevent the formation of even the dispersible scum. It 70 has also been found that the product most publicly accepted for use as an all purpose toilet bar is a compromise one containing about 50% sodium sulfophenyl

cocoate, about 25% sodium sulfophenol and 25% of a mixture of sodium cocoate and the coco acids. The bar may also contain up to 7.5% zinc stearate and up to 5% sodium ammonium α -sulfopalmitic acid to harden the bar and give even better antiscumming properties. Mixtures of ingredients within the ranges above set forth can be obtained by adding together each component or they can be prepared by neutralizing the product of the reaction between a sulfonated phenol and a fatty acid chloride and adding the zinc stearate and palmitic acids later. It is to be understood that other well known additives to improve slip and feel, and moisturizing those which prevent scumming and sloughing can also be added as well as perfumes and the like. For example, to obtain the best response of the toilet bar toward water hardness, a sulfonated fatty acid may be included in the formulation. Some that have been used are α -sulfopalmitic and α -sulfostearic acid as the sodium salts, ammonium salts or a combination of sodium ammonium salts, esters of the carboxyl portion, such as methyl, ethyl, isopropyl with the sulfonic acid as an alkali metal salt. These may be added from 1 to higher percentages but we prefer from 3 to 10%. Of course, the lower the amount, the more economical the toilet bar. Other detergents such as the alkylbenzene sulfonates and the alkyl sulfates have been tried but are not as effective in all respects in regard to bar characteristics as the α -sulfo fatty acid salts above set out.

Representative of the fatty acid ester aryl sulfonates which are useful in accordance with the present invention are the alkali and ammonium salts of fatty acid esters of sulfonated phenol



Percent by weight						
(A)	(B)	(C)				
NaSO ₃ φOH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{NaO}-\text{C}-\text{C}_{7-17}^1+ \\ \text{HOC}-\text{C}_{7-17} \\ \parallel \\ \text{O} \end{array}$	NaSO ₃ φO-	$\begin{array}{c} \text{O} \\ \parallel \\ \text{O}-\text{C}-\text{C}_{7-17}^1 \end{array}$	Lather ²	Scum ³	Notes
23.4	26.6		50	G	N	
28.6	31.4		40	E	N	
34.0	36.0		30	E	M	
39.3	40.7		20	G	B	Probably too high in cocoate, insufficient ester to balance Na sulfophenol.
18.7	41.3		40	E	M	Do.
14.0	56.0		30	E	B	Do.
9.3	70.7		20	E	B	Do.
38.7	21.3		40	F	N	
54.0	16.0		30	G	N	

¹ NaO-C(=O)-C₁₇-Neofat 265 analyzed as containing about C₈, 5%; C₁₀, 6%; C₁₂, 52%; C₁₄, 19%; C₁₆, 9.0%; C₁₈, 9%.

² E—excellent, G—good, F—fair, P—poor.

³ N—none, M—medium, B—bad.

wherein



is the residue of a long fatty acid having from 8 to 18 carbon atoms such as caprylic, capric, lauric, myristic, palmitic, stearic, oleic and linoleic, as well as mixtures, of the acids. The symbol M can be selected from the group consisting of the salt-forming moieties alkali metal, such as sodium, lithium, potassium, cesium and the nitrogen compound ammonia. The preferred compounds falling within the formula are the mixed fatty acid esters (said acids having been derived from C₈₋₁₈ fatty acids having 1-5% C₈, 1-7% C₁₀, 40-60% C₁₂, 10-30% C₁₄,

5-15% C₁₆, and 2-15% C₁₈ acids) of sulfonated phenol neutralized, i.e., to pH of about 7 to 9, with an alkali or ammonium base. When the sulfonic acid is neutralized, some of the ester is saponified, and there is then produced a mixture of the salts of the sulfonated phenolic ester, the sulfonated phenol and the fatty acid containing some free fatty acid. The various mixtures produced under different conditions of pH result in very satisfactory toilet bars.

The principal ingredients of the toilet bar of the present invention can be obtained in their commercially available form and mixed together or they can be obtained by a three-step process to wit:

(1) Phenol is sulfonated, suitably with SO₃ in an inert solvent such as methylene chloride;

(2) The sulfonated phenol is esterified, suitably with a fatty acid chloride or a mixture of fatty acid chlorides obtained by the reaction of PCl₃ and the fatty acids; and

(3) Finally the ester so derived is neutralized with alkaline material, such as sodium hydroxide, to pH of from about 6.5 to 9 and preferably from about 7.2 to 8.5 to produce a mixture which consists of some 50 to 80% of fatty acid ester of sodium sulfophenol, equimolar amounts of 10-25% each of sodium sulfophenol and a mixture of the free acid and sodium salt of the fatty acids. As would be expected, the amount of each ingredient is substantially affected by the temperature of neutralization, the concentration of the neutralizing agent and the pH of the final product mixture. If it is desirable to increase the amount of any ingredient other than the ester of the sulfonated phenol, these may be added separately since all are readily available commercially but not sodium sulfophenyl cocoate or the like.

The data in the following table illustrates the effect various ratios of components have on the properties of the toilet bar. It is to be understood that the properties listed can be improved in all instances by the addition of a salt of α -sulfopalmitic acid. Thus, all bars wherein the scumming is indicated B will improve to medium by adding a small percent of a salt of α -sulfopalmitic acid.

Percent by weight						
(A)	(B)	(C)				
NaSO ₃ φOH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{NaO}-\text{C}-\text{C}_{7-17}^1+ \\ \text{HOC}-\text{C}_{7-17} \\ \parallel \\ \text{O} \end{array}$	NaSO ₃ φO-	$\begin{array}{c} \text{O} \\ \parallel \\ \text{O}-\text{C}-\text{C}_{7-17}^1 \end{array}$	Lather ²	Scum ³	Notes
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18.7	41.3		40	E	M	Do.
14.0	56.0		30	E	B	Do.
9.3	70.7		20	E	B	Do.
38.7	21.3		40	F	N	
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² E—excellent, G—good, F—fair, P—poor.

³ N—none, M—medium, B—bad.

The active ingredients of the toilet bar can be prepared according to the following techniques.

PREPARATION I

Preparation of fatty acid ester of sulfophenol

Phenol is dissolved in an inert organic solvent such as methylene chloride, and at least one molar equivalent of SO₃ dissolved in the same solvent added portionwise. Upon completion of the addition of the SO₃, a vacuum is drawn and the fatty acid chloride prepared in the usual way with PCl₃, is slowly added in a portionwise manner so as to maintain the temperature between about 25° to 30° C. Upon completion of the addition the reactor

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and reaction mixture are sparged with nitrogen until all HCl of the reaction is removed.

Neutralization

When all evidence that HCl is removed, the reaction mixture is neutralized to a pH between about 6.5 to 8.5 or 9.0. The neutralization is carried out in a stepwise manner with cooling and stirring to prevent overheating.

Control of ester content of neutralized surfactant is accomplished by careful neutralization techniques including using dilute caustic, cooling and good agitation as well as following the neutralization to control the final pH to between about 6.5 and about 9.0.

The following example illustrates the present invention but is not to be construed as limiting.

EXAMPLE 1

Preparation of phenol sulfonate

Five (5.0) moles of phenol was placed in a 5 liter flask containing 1 liter of methylene chloride and fitted with a stirrer. Five and one-quarter moles of sulfur trioxide in 750 ml. of methylene chloride was added to the phenol mixture through a dropping funnel over a 1 hour period with stirring. Thereafter, five (5.0) moles of cocoyl chloride derived from a commercially available mixture of coco fatty acid was added over a 53 minute period while maintaining the reaction mixture at 25° to 30° C. A partial vacuum was maintained over the surface of the reaction mixture to help remove hydrogen chloride of reaction. The resulting mixture was sparged with nitrogen to remove the HCl. One third of reaction mixture was neutralized to pH 8.5 by slowly adding 25% NaOH, then dried in a vacuum oven at 90° C. Another third of the product was neutralized with 25% NaOH to pH 8.5 and dried on a steam drum drier. The final one-third portion was neutralized to pH 8.0 and dried on a steam drum drier. A total of 930 grams of 25% NaOH was used to neutralize the product.

Each of the above neutralized one-third portions of product was pressed into soap bars and tested for sudsing, scum, slime, etc. Each portion produced a bar which was rated good on all accounts by 5 persons who used the bars.

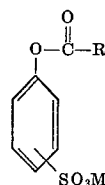
In accordance with the present invention a number of bars were tested by over 100 persons selected by an independent testing laboratory. A typical composition of a representative toilet bar used in this testing was:

	Percent
Sodium sulfophenyl cocoate	43.5
Coco acid	13.8
Sodium coco acid	9.2
Sodium sulfophenol	20.5
Slip agent (zinc stearate)	7.5
Anti-scum assistant (α -sulfopalmitic acid, Na salt) ..	5.0
Polyoxyethylene glycol having an average molecular weight of about 600 (moisturizer)	0.25
Perfume	0.25

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We claim:

1. A toilet bar consisting essentially of from about 25 to about 80 percent by weight based on total composition of a fatty acid ester of a sulfonated phenol having the generic formula



wherein R represents a mixture of alkyl radicals of from 7 to 17 carbon atoms and having an average of from 11 to 15 carbon atoms and M represents a salt-forming moiety selected from the group consisting of alkali metals and ammonium radicals; 10 to 55 percent by weight of an alkali metal or ammonium salt of a sulfonated phenol; 10 to 35 percent by weight of a mixture of free fatty acids and their alkali metal or ammonium salts; 0 to 7.5% zinc stearate; 0 to 5% salt of α -sulfopalmitic acid; 0 to 1% moisturizers and 0 to 1% perfumes.

2. A toilet bar consisting essentially of about 43.5% by weight sodium sulfophenyl cocoate; 13.8% coco acid, 9.2% sodium coco acid; 20.5% sodium sulfophenol; about 7.5% zinc stearate, about 5.0% sodium salt of α -sulfopalmitic acid; about 0.25% polyoxyethylene glycol having an average molecular weight of about 600, and, about 0.25% perfume.

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