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DETERGENT COMPOSITION

Lester F. Hoyt, East Aurora, N. Y., assignor to
Allied Chemical & Dye Corporation, New York,
N. Y., a corporation of New York

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This invention relates to detergent compositions. It relates more particularly to detergent compositions in the form of solid cakes or similar formed solid masses adapted for use as a substitute for toilet soaps, especially by persons who are allergic to ordinary soaps.

The usual toilet soaps, as ordinarily marketed, are essentially mixtures of the sodium salts of higher fatty acids which, because they are salts of weak acids and strong bases, are easily hydrolyzed in water solution and lead to the presence of free fatty acids and alkali in their aqueous solutions and on the skins of persons using them. Many persons exhibit an allergic reaction to soaps, manifested by a dermatitis, or an eczematous condition, which some attribute to the free fatty acids and others regard as a hypersensitivity to alkali. In addition, persons who are required to wash their hands frequently and persons with delicate skins suffer from the harmful effects of the alkali on the skin.

One class of compounds which, by reason of certain of their advantageous properties, are of value for use as substitutes for ordinary soaps by persons exhibiting an allergic reaction to ordinary soaps is the class of non-aromatic soapless detergents (polar-nonpolar organic compounds having in their structure no radicals of the benzene series and having detergent properties) which are neutral, water-soluble salts of anion-active polar-nonpolar organic derivatives of sulfuric acid having a single higher open-chain hydrocarbon group of 12 to 14 carbon atoms in the nonpolar portion of the molecule. A number of such compounds have been introduced commercially as substitutes for the usual soaps in the textile and related industries because of their wetting, emulsifying and cleansing action on textile fibers. They include products containing, as the essential cleansing agent, alkyl sulfates containing 12 to 14 carbon atoms in the alkyl group, alkyl sulfonates having 12 to 14 carbon atoms in the alkyl group, sulfates and sulfonates of higher monoalkyl esters, amides and imides of lower mono- and polycarboxylic acids having 12 to 14 carbon atoms in the higher alkyl group and a sulfate or sulfonate group in the carboxylic acid radical or in the esterifying radical, sulfates of polyhydric alcohols (such as glycerin) partially esterified by fatty acids having 12 to 14 carbon atoms, and the like. They are water-soluble compounds which form substantially neutral aqueous solutions. Further, they do not hydrolyze in the objectionable manner of soaps and, being relatively stable in aqueous solution and

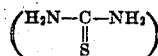
for the most part being free from higher fatty acid components, they do not introduce into their aqueous solutions the objectionable alkali and free fatty acids produced by the hydrolysis of ordinary soaps.

While the said soapless detergents can be prepared in the form of solid cakes of the type of ordinary soap cakes, such cakes possess a number of disadvantages. Because of the solubility of the soapless detergents, the cakes usually disintegrate rapidly in water; and when rubbed between the hands in the usual washing operation, an excessive amount of the detergent is removed from the cake, resulting in waste of the detergent and in a roughness and dryness of the hands after washing.

An object of the present invention is to provide a soap substitute for persons who are allergic to the ordinary soaps. More specific objects are to provide a cleansing composition which is non-allergenic to the human skin; which can be manufactured in the form of the usual soap-cakes, bars, and the like; which will possess cleansing and sudsing properties at least equal to the usual toilet soaps; which will leave the skin in a soft, smooth condition; and which will be economical to use.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

According to the present invention the objectionable effects of soaps upon the human skin are overcome and a non-allergenic cleansing agent which is adapted for personal toilet use in the same manner as ordinary soap cakes by persons showing an allergic reaction to ordinary soaps is provided while avoiding the objectionable properties of cakes of soapless detergents by replacing a large part of the said soapless detergent in a solid cake thereof by thiourea



I have discovered that thiourea has a number of advantageous properties which adapt it for use in combination with said soapless detergents, and that compositions which are composed essentially of one or more of said non-aromatic soapless detergents which are neutral, water-soluble salts of sulfuric acid derivatives containing a single higher open-chain hydrocarbon group of 12 to 14 carbon atoms, preferably joined to each other in a continuous chain, in intimate mixture with at least a substantially equal amount of thiourea and preferably an amount which is about 2 to about 6 times the weight of the soapless deter-

gent (on a pure basis), possess a number of advantageous properties which adapt them for use as non-allergenic substitutes for toilet soaps.

Thus I have found, in accordance with the present invention, that a composition consisting of an intimate admixture of as little as 10 parts of commercial sodium lauryl sulfoacetate and 90 parts of thiourea (by weight) constitutes a composition having desirable properties as a non-allergenic toilet soap substitute: it leaves the skin with a soft smooth feel and a silky texture; it has a healing effect on the skin; its cleansing action is superior to ordinary soap; it can be readily formed into cakes similar in appearance to cakes of toilet soap and, when used for personal toilet purposes, forms a suds similarly to soap; and it does not produce the harmful effects upon the skin caused by ordinary soaps. Further the compositions, especially in a form resembling conventional cakes of soap, are economical in use and can be stored with little or no deterioration or disintegration through absorption of moisture. A tablet of said admixture gained only 2.1% in weight after seven weeks exposure to an atmosphere at 91% relative humidity at 25° C.

The non-aromatic soapless detergent component of the compositions of the present invention may be any one or a mixture of such compounds which are solid, neutral, water-soluble salts of anion-active polar-nonpolar non-aromatic sulfates or sulfonates having a single higher open-chain hydrocarbon group of 12 to 14 carbon atoms, preferably joined to each other in a continuous chain, in the nonpolar portion of the molecule. They are preferably compounds which do not decompose to give higher fatty acids under conditions of toilet use. They include salts of the following types of compounds:

A. Open-chain hydrocarbon sulfates and sulfonates derived from aliphatic hydrocarbons, olefines or alcohols containing 12 to 14 carbon atoms. Those which are primary normal (straight-chain) sulfates and sulfonates are preferred. A commercial product of this type containing sodium lauryl sulfate as its essential detergent constituent is sold in the market under the name of "Gardinol." Sodium myristyl sulfonate is another compound of this type.

B. Sulfates and sulfonates of higher monoalkyl esters of lower mono- and polycarboxylic acids containing 12 to 14 carbon atoms in the higher alkyl group and a sulfate or sulfonate group in the carboxylic acid radical or in the esterifying radical. Lauryl sulfoacetate and disodium monolauryl sulfosuccinate, particularly in the form of commercial products derived from mixtures of alcohols obtained by the hydrogenation of coconut oil (fat), are compounds of this type.

C. Sulfates and sulfonates of polyhydric lower alcohol partial esters of fatty acids containing 12 to 14 carbon atoms which contain only one higher fatty acid radical in the molecule. The sodium salt of lauric acid monoester of glycerin sulfate is a compound of this type.

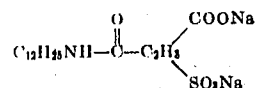
D. Sulfates and sulfonates of lower alkyl ethers of aliphatic alcohols containing 12 to 14 carbon atoms. Compounds of the type



in which R is an open-chain hydrocarbon group of 12 to 14 carbon atoms, are examples of such compounds.

E. Sulfates and sulfonates of monoalkyl amides

and imides of polycarboxylic acids containing a single higher open-chain hydrocarbon group of 12 to 14 carbon atoms as an N-substituent. Disodium monolauryl amide of sulfo-succinic acid, having the formula



is a compound of this type. It can be prepared by reacting equimolar proportions of maleic anhydride and laurylamine (or a commercial laurylamine containing a mixture of higher alkylamines) to produce the monolauryl amide of maleic acid, and reacting the resulting amide with aqueous sodium sulfite.

The said sulfates and sulfonates are employed in accordance with the present invention in the form of their solid, water-soluble, neutral salts, more particularly the alkali metal (including ammonium) salts. Ordinarily the sodium or potassium salts are employed, the sodium salts being preferred because of their superior detergency. In particular cases it may be desirable to use the ammonium or magnesium salts in whole or in part. Further, in some cases it may be desirable to employ the mono-, di- or triethanolamine salts. As obtained commercially, the non-aromatic soapless detergents employed in accordance with the present invention frequently contain substantial amounts of water-soluble inorganic salts, such as sodium sulfate, sodium chloride, and the like. Such commercial products are useful in accordance with the present invention and in many cases the presence of the inorganic salts assists the deterging action of the soapless detergent. If desired, the soapless detergent may be employed in the salt-free form, however.

The compositions of the present invention can be prepared in a number of ways. One method found to be satisfactory is to grind the components together, if desired with the addition of a small amount of water or alcohol, and press the resulting mixture into formed solid masses, such as cakes or bars similar to the usual soap cakes.

The amounts of soapless detergent and thiourea employed in preparing the compositions of the present invention are variable, depending upon a number of factors. From the standpoint of cost, a maximum amount of thiourea is desirable consistent with washing action. From the standpoint of lathering and other soap-like effects a greater amount of the soapless detergent is desirable. Other factors are the solubility in water of the resulting compositions and their hygroscopicity. Thiourea is soluble in water to the extent of approximately 10 parts in 100 parts of water at 25° C. (by weight). I have found that as I increase the content of thiourea in my compositions, the latter become less soluble in water. In general, an amount by weight of thiourea is employed which is at least substantially equal to, and preferably a multiple of, the amount by weight of the soapless detergent (on the basis solely of the sulfuric acid derivative containing 12 to 14 carbon atoms in a higher alkyl group, in the soapless detergent; that is, exclusive of other substances which may be present in the soapless detergent in commercial form, such as small amounts of sulfuric acid derivatives of higher and/or lower alkyl compounds and/or inorganic salts—herein referred to as "on a pure basis").

While the invention includes compositions containing about 95 parts of thiourea to about 3.5

parts of soapless detergent (about 5 parts of soapless detergent in commercial form containing about 30 per cent of inorganic salts) by weight, such as the composition of Example 6, a larger amount of soapless detergent is preferably used. Even when the compositions contain 42 parts of soapless detergent (about 60 parts of the detergent in commercial form containing about 30 per cent of inorganic salts) to about 40 parts of thiourea by weight, the compositions are satisfactory for use. This is because the particles of thiourea, by their lesser solubility, serve to protect the particles of soapless detergent in a cake of a mixture of them, and prevent the particles of soapless detergent from going into solution or being removed by rubbing of the cake between the hands when the composition is used; only the exposed particles of the soapless detergent are dissolved.

Accordingly, compositions having a commercially acceptable standard of detergent and lathering qualities may contain an amount of thiourea varying from about 93 to about 50 parts by weight per 100 parts by weight of the mixture of thiourea and soapless detergent (on a pure basis). Such compositions are stable, and can be stored for long periods of time without unsightly or otherwise undesirable changes due to absorption of moisture. Preferred compositions, particularly in the form of tablets resembling cakes of milled soap, contain 68 to 85 parts by weight of thiourea per 100 parts by weight of mixture of thiourea and soapless detergent (on a pure basis). Such preferred compositions have superior lathering, foaming and cleansing properties, and in these respects closely simulate the properties of a milled soap.

The invention will be illustrated by the following specific examples in which the parts are by weight. Commercial sodium lauryl sulfoacetate, as employed in the examples, was in the form of a powder and was prepared by esterifying chloroacetic acid with commercial lauryl alcohol derived from coconut oil and reacting the resulting ester with sodium sulfite. In addition to sodium lauryl sulfoacetate and sodium myristyl sulfoacetate, it contained about 12 per cent of higher and lower alkyl sulfoacetates; it also contained approximately 30 per cent of its weight of inorganic salts, chiefly sodium chloride.

Example 1

Commercial thiourea was micropulverized. The comminuted material, about 97 per cent of which passed through a 200 mesh screen, and commercial sodium lauryl sulfoacetate (containing about 30 per cent inorganic salts, chiefly common salt) substantially all of which passed through a 200 mesh screen were intimately mixed in the following proportions:

	Parts
Commercial sodium lauryl sulfoacetate.....	10
Thiourea	90

The mixture was moistened with 1 per cent of its weight of water, and was then pressed into cake form in a steel mold in a hydraulic press under a pressure of 10,000 lbs. per square inch.

In the same manner, cakes were prepared from the same ingredients in the following proportions:

Example 2

	Parts
Commercial sodium lauryl sulfoacetate.....	15
Thiourea	85

Example 3

	Parts
Commercial sodium lauryl sulfoacetate.....	20
Thiourea	80

Example 4

	Parts
Commercial sodium lauryl sulfoacetate.....	30
Thiourea	70

Example 5

	Parts
Commercial sodium lauryl sulfoacetate.....	50
Thiourea	50

The resulting cakes were hard, firm tablets which in use for personal cleansing behaved like an ordinary cake of milled soap, but without its irritating effect on skins allergic to ordinary soap. In addition, the cakes of Examples 3, 4 and 5 were more economical in use than milled soap, especially in hard water, due to the high lathering properties of the soapless detergent.

Example 6

An intimate mixture of 5 parts of the commercial sodium lauryl sulfoacetate and 95 parts of finely ground (100 mesh) thiourea was made by grinding in a mortar. To this mixture, 1 part water was added. The resulting mass was made into cakes by pressing in steel molds in a hydraulic press under a pressure of 10,000 lbs. per square inch.

The approximate ratios by weight of the thiourea and soapless detergent (sodium alkyl sulfoacetates having 12 and 14 carbon atoms in the alkyl group, but exclusive of the other substances present) in the above examples are as follows:

	Example No.					
	1	2	3	4	5	6
Thiourea.....	93	89	85	77	59	96.4
Sodium alkyl sulfoacetates (on a pure basis).....	7	11	15	23	41	3.6

Compositions containing proportions by weight of the above commercial (salt containing) sodium lauryl sulfoacetate and thiourea ranging from 20:80 to 40:60, and especially those ranging from 25:75 to 30:70, are particularly valuable forms of the invention, in view of their stability against softening and disintegration when left standing in the atmosphere, their superior lathering, foaming and cleansing properties and soap-like feel.

It will be realized by those skilled in the art that the invention is not limited to the above examples and that changes can be made without departing from the scope of the invention. Thus, instead of the specific soapless detergents employed in the above examples, others of the soapless detergents herein disclosed may be substituted in the same amounts. Instead of a single soapless detergent, a mixture of two or more may be employed. Accordingly, where in the claims a single soapless detergent is referred to, it is intended that such mixtures shall also be included.

The compositions of the present invention furthermore are not limited to those consisting solely of the soapless detergent and thiourea, but, as above indicated, the compositions may also contain minor amounts of other usually innocuous materials; such as inorganic salts, therapeutic agents, antiseptic agents, coloring matter, per-

fume, and the like. Inorganic salts may be carried into the compositions of the present invention by the use of commercial forms of soapless detergents which usually contain them. Additional diluents of a non-detergent character are sugar, starch, methyl cellulose and mild abrasives (for example, clay). If desired, small amounts of higher alcohols (for example, lauryl alcohol) may be included as supplementary binder so as to obtain a more coherent cake on molding. Ordinarily such supplementary binder is not required inasmuch as the compositions herein disclosed can be easily molded by pressure into cakes which simulate ordinary soap in appearance.

To persons who are allergic to soap, the compositions of the present invention are especially useful as harmless and non-irritating detergents for personal toilet use. The compositions are excellent cleaning agents for removing dirt and soil; they produce cleansing and sudsing similarly to soap, and they are not precipitated by hard water.

It is not intended to suggest, by the above description of the compositions of this invention as non-allergenic soap substitutes, that they are usable universally in place of soap, without producing an allergic response, by all persons who are allergic to soap. As used herein, the term "non-allergenic" signifies that generally the compositions do not produce an allergic response when used by such persons.

I claim:

1. A detergent composition in the form of a solid mass adapted for toilet purposes and possessing cleansing and sudsing properties similar to those of ordinary soap, comprising as its essential components a solid non-aromatic soapless detergent which is a neutral, alkali metal salt of an anion-active polar-nonpolar organic derivative of sulfuric acid selected from the group consisting of sulfates and sulfonates of higher aliphatic hydrocarbons, sulfates and sulfonates of higher monoalkyl esters of lower mono- and polycarboxylic acids, sulfates and sulfonates of polyhydric alcohol partial esters of fatty acids, sulfates and sulfonates of lower alkyl ethers of aliphatic alcohols, and sulfates and sulfonates of monoalkyl amides and imides of polycarboxylic acids, said derivatives having a single higher open-chain hydrocarbon group of 12 to 14 carbon atoms in the nonpolar portion of the molecule, in intimate mixture with at least a substantially equal weight of thiourea, said thiourea serving to protect said soapless detergent from the dissolving action of water and to protect the composition from disintegration, during toilet use.

2. A detergent composition in cake form adapted for toilet purposes and possessing cleansing and sudsing properties similar to those of ordinary soap, comprising as its essential components a solid, neutral, water-soluble salt of an alkyl sulfoacetate having an open-chain hydrocarbon group of 12 to 14 carbon atoms, in intimate mixture with at least a substantially equal weight of thiourea.

3. A detergent composition in cake form adapted for toilet purposes and possessing cleansing and sudsing properties similar to those of ordinary soap, comprising as its essential components a solid, neutral, water-soluble salt of an alkyl sulfate having an open-chain hydrocarbon group of 12 to 14 carbon atoms, in intimate mixture with at least a substantially equal weight of thiourea, said thiourea serving to protect said alkyl sulfate from the dissolving action of water and to protect

said cake from disintegration, during toilet use.

4. A detergent composition in cake form adapted for toilet purposes and possessing cleansing and sudsing properties similar to those of ordinary soap, comprising as its essential components a solid non-aromatic soapless detergent which is a neutral, water-soluble salt of an anion-active polar-nonpolar organic derivative of sulfuric acid selected from the group consisting of sulfates and sulfonates of higher aliphatic hydrocarbons, sulfates and sulfonates of higher monoalkyl esters of lower mono- and polycarboxylic acids, sulfates and sulfonates of polyhydric alcohol partial esters of fatty acids, sulfates and sulfonates of lower alkyl ethers of aliphatic alcohols, and sulfates and sulfonates of monoalkyl amides and imides of polycarboxylic acids, said derivatives having a single higher open-chain hydrocarbon group of 12 to 14 carbon atoms in the non-polar portion of the molecule, in intimate mixture with thiourea, the amount of thiourea being about 65 to 85 parts per 100 parts by weight of its mixture with the soapless detergent, said thiourea serving to protect said soapless detergent from the dissolving action of water and to protect said cake from disintegration, during toilet use.

5. A detergent composition in cake form adapted for toilet purposes and possessing cleansing and sudsing properties similar to those of ordinary soap, comprising as its essential components an alkali metal salt of a higher alkyl sulfoacetate having 12 to 14 carbon atoms in an open-chain hydrocarbon group, in intimate mixture with thiourea, the amount by weight of thiourea being about 50 to about 93 parts per 100 parts by weight of its mixture with said salt.

6. A detergent composition in cake form adapted for toilet purposes and possessing cleansing and sudsing properties similar to those of ordinary soap, comprising as its essential components a sodium salt of a higher alkyl sulfoacetate having 12 to 14 carbon atoms in an open-chain hydrocarbon group, in intimate mixture with thiourea, the amount of thiourea being about 2 to about 6 times the weight of the salt of the alkyl sulfoacetate.

7. A detergent composition in cake form adapted for toilet purposes and possessing cleansing and sudsing properties similar to those of ordinary soap, comprising as its essential components commercial sodium lauryl sulfoacetate in intimate mixture with thiourea in proportions by weight ranging from 20:80 to 40:60.

8. A detergent composition in cake form adapted for toilet purposes and possessing cleansing and sudsing properties similar to those of ordinary soap, comprising as its essential components commercial sodium lauryl sulfoacetate in intimate mixture with thiourea in proportions by weight ranging from 25:75 to 30:70.

9. A detergent composition in cake form adapted for toilet purposes and possessing cleansing and sudsing properties similar to those of ordinary soap, comprising as its essential components an alkali metal salt of a higher alkyl sulfate having 12 to 14 carbon atoms in an open-chain hydrocarbon group, in intimate mixture with thiourea, the amount by weight of thiourea being about 50 to about 93 parts per 100 parts by weight of its mixture with said salt, said thiourea serving to protect said alkyl sulfate from the dissolving action of water and to protect said cake from disintegration, during toilet use.

LESTER F. HOYT.