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DETERGENT COMPOSITION

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13 Claims. (Cl. 252—117)

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The present invention relates to novel detergent compositions and to a process for producing said compositions.

The use of soap in washing operations is very old, and in soft water (that is, water containing at most only a very small amount of mineral salts) soap is a very efficient and satisfactory cleansing agent. However, natural water usually contains salts, such as calcium and magnesium salts, which decompose water soluble soaps to form water-insoluble soaps. The formation of such water-insoluble soaps decreases the apparent efficiency of the soap used by requiring that a greater amount of soap be added to the solution to remove the salts and still have enough water-soluble soap present for an effective washing concentration.

The water-insoluble soaps formed, usually comprising calcium and magnesium soaps, have another disadvantage in that they appear in the wash water as curds or scum which settle upon the material being washed. A further difficulty is that they are often formed within the interstices of cloth during laundering and are extremely hard to remove. Moreover, even if all the soap is added to the water before introduction of the cloth, so that only the solution of soluble soap gets into the interstices during the washing operation, the insoluble soaps may still be formed therein during rinsing, as the soluble salts in the rinse water react with the soluble soap in the interstices to form these insoluble soaps. The presence of such curds or scum gives the cloth a grayish or yellowish cast in many cases, which is most undesirable, and frequently imparts an unpleasant rancid odor.

From time to time, various substances have been proposed for admixture with soaps in order to modify their properties and to render them more efficient for use in hard waters. Some of these substances have had limited success, in that curds and scums have largely been eliminated. However, in a large number of such instances the detersive efficiency has been considerably impaired.

It is an object of the present invention to provide a new composition of matter of high detersive efficiency in aqueous solution but with none of the undesirable scum-forming characteristics of soaps.

It is another object of this invention to provide a highly detergent composition capable of dispersing hard water scum. It is also an object of the invention to provide a soap-containing composition which effectively disperses curds in hard water without substantial impairment of the detersive efficiency of the soap.

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Another object of the present invention is the provision of a detergent composition which is very soluble in water and which has high detersive efficiency in hard water as well as soft.

This invention further provides a novel method for producing new compositions of high detergency.

Other objects and advantages of the invention will be apparent from the following description.

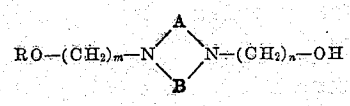
According to the present invention, it has now been found that the incorporation of a cationic surface-active agent of the type of aliphatic carboxylic acid monoester or monoether derivatives of a dialkanol piperazine with a fatty acid soap provides a composition of high detergency (even as compared with soaps alone) and of excellent lime soap dispersing characteristics.

The soaps comprised by the novel compositions of the invention are the so-called water-soluble soaps of the soap-making art and include sodium, potassium, ammonium and amine salts of the higher fatty acids, that is, those having about eight to about twenty carbon atoms per molecule. Such soaps may be represented by the following general formula:

$$RCOOM$$

where R is an alkyl radical containing from about eight to about twenty carbon atoms; and M is a monovalent radical e. g. alkali metal, ammonium or substituted ammonia group. These soaps are normally prepared from such naturally-occurring esters as coconut oil, palm oil, olive oil, cottonseed oil, tung oil, corn oil, castor oil, soya bean oil, wool fat, tallow, whale oil, menhaden oil, pilchard oil, sardine oil, herring oil, and the like, as well as mixtures of these.

The aliphatic carboxylic acid monoester or monoether derivatives of N,N'-dialkanol piperazines, which may be mixed with soaps to form the new detersive compositions of the invention and to achieve the desirable results described, are those represented by the general structural formula:



where R is an alkyl or acyl radical having about five to about twenty-three, preferably about eight to about eighteen, carbon atoms; A and B are ethylene radicals wherein any number of hydrogens (none, one or more) may be replaced by

alkyl radicals, preferably of not more than two carbon atoms; and *m* and *n* are small integers, say two to about five, preferably two. The carbon chain represented by R may be straight or branched, saturated or unsaturated, and may be either unsubstituted or substituted by substituents such as halogens, hydroxyls, acyl groups, acyloxy groups, alkoxy groups, aryl groups, etc., although it is generally preferred that substituent groups of hydrophilic character be located near or adjacent to the piperazyl alkoxy group. Where R is an alkyl or substituted alkyl group, the material mixed with the soap in accordance with the invention is an ether; and where R is an acyl or substituted acyl group, the compound thus employed is an ester.

In the case of the compound's being an ester, the acyl group may be the residue of any suitable carboxylic acid, including lauric acid, myristic acid, palmitic acid, stearic acid, hydroxystearic acid, oleic acid, linoleic acid, linolenic acid, ricinoleic acid, caproic acid, isocaprylic acid, α-aminocapric acid, undecylenic acid, lignoceric acid, erucic acid, lauryl succinic acid, chloropalmitic acid, mixed coconut oil fatty acids, mixed tallow fatty acids, mixtures of any of these acids, etc. Where the compound is an ether, the alkyl group may be any corresponding to a suitable carboxylic acid, such as the above-mentioned, including lauryl, myristyl, palmityl, stearyl, hydroxystearyl, oleyl, linoleyl, linolenyl, ricinoleyl, hexyl, isoctyl, β-aminodecyl, etc.

The dialkanol piperazine residue of the ester or ether employed may be symmetrical or mixed. That is, *m* and *n* may be the same number or they may be different numbers. In general, it is preferred to employ symmetrical dialkanol piperazines such as diethanol piperazine, dipropanol piperazine, diisopropanol piperazine, etc., and especially the symmetrical dialkanol piperazines having both hydroxyl groups in omega position with respect to the piperazyl radical. However, mixed piperazines of the type of β-propanol-4-β-ethanol piperazine, 1-β-ethanol-4-γ-butanol piperazine, etc. can also be used.

Suitable esters for use in the compositions of this invention include diethanol piperazine monolaurate, ricinoleic acid monoester of diethanol piperazine, di-ω-butanol piperazine monostearate, coconut oil fatty acid monoesters of diethanol piperazine, etc. Ethers suitable for employment in the novel compositions include 1-(2-lauroxyethyl) -4-(2- hydroxyethyl) - piperazine, 3,6 - dimethyl - 1 - (2 - myristoxypropyl) - 4-(2-hydroxypropyl) -piperazine.

The relative proportions of the dialkanol piperazine monoester or monoether and the soap in the new compositions vary greatly, depending largely upon the use intended for the composition. Again, given any specific characteristics desired for a particular use, the optimum proportions employed will also vary with the particular active ingredients (both soap and piperazine derivative) or mixtures of ingredients used; with the proportion of other ingredients present, if any; and to some degree with the strength or concentration of solution to be formed in use. While useful solubilizing, wetting and emulsifying compositions of high detergency can be formed by mixing small proportions of soap with large proportions of a dialkanol piperazine monoester or monoether (as will be pointed out more fully hereinafter), so that the compositions of the invention comprises mixtures of these ingredients in all proportions, it is contemplated that the greatest value and usefulness of the present invention lie in compositions having less than 90% of the dialkanol piperazine derivative based on the total weight of the composition. In general, it is preferred to incorporate about 5% to about 75%, and more preferably about 10% to about 50% by weight of the monoester based upon the total weight of the soap and the dialkanol piperazine derivative.

The dialkanol piperazine monoester or monoether may be incorporated with the soap to form the novel composition of the invention at any point during the soap manufacturing process at which subsequent operations will not destroy or objectionably modify the piperazine derivative or cause a deleterious reaction between the piperazine derivative and any other material in the composition. In general, it is preferred to add the piperazine derivative at a point in the manufacturing subsequent to the saponifying or neutralizing step. This may be accomplished by adding the piperazine derivative in solid form or in solution to molten soap in the soap kettles, by mixing or milling the piperazine derivative with solid soap in comminuted form, or by adding the piperazine derivative to a soap solution and thereafter subjecting the solution containing soap and piperazine derivative to spray-drying, roll-drying, etc., to form a solid composition.

The novel compositions, if desired, may be made up in solutions, preferably concentrated, or a dry or partially hydrated solid product or a paste may be formed. The product may be made in a more or less finely divided condition, which permits its ready transformation into flakes or other physical forms, for example by passing between a pair of properly spaced rolls, or by milling or pressing into cakes, or by other means, with or without addition of modifying agents. Also the dialkanol piperazine ester and soap or ether derivative may be added separately to washing solutions.

Adjuvant materials may be admixed with the novel compositions by mixing such materials with the fatty compounds (whether glycerides, alkyl esters or fatty acids) and/or the neutralizing or saponifying agents before neutralization or flashing, by simultaneously flashing a second solution containing such adjuvant materials, and/or by mixing the final product herewith. When added after neutralization or saponification, the adjuvant materials may be added before, after or simultaneously with the piperazine derivative. Such adjuvant materials may include any of the substances employed by the art in admixture with soaps generally, such as the common inorganic builders of the type of carbonates, phosphates, silicates, etc., and including certain of the sulphated and/or sulphonated organic surface-active agents known to the detergent art. In employing such adjuvant materials, care is exercised to avoid the use of any material which would remove or otherwise substantially diminish the effectiveness of the dialkanol piperazine monoester or monoether incorporated. The type of addition agent will depend upon the ultimate use of the new composition.

The novel and improved detersive, dispersing and emulsifying agents of this invention, comprising fatty acid soaps (with or without adjuvant materials) and a proportion of the dialkanol-piperazine monoester and/or monoether described, produce solutions which are efficient

in dispersing hard water scum without substantial impairment of the detersive efficiency of the soap. Similarly, addition of a small proportion of soap to the piperazine derivative raises the detersive efficiency above that of soap under certain conditions.

The following examples, described hereinafter, are merely illustrative of the present invention, and it will be understood that the invention is not limited thereto.

Example I

Hot molten tallow soap is pumped to a mixing vessel, and there one part by weight of the oleic acid monoester of diethanol piperazine is admixed with about three parts of the tallow soap. The resulting composition is then dissolved in water containing 300 parts per million of calcium and magnesium hardness (calculated as calcium carbonate) to form a 0.55% aqueous solution, and the detersive efficiency of this solution is tested in a multiple swatch (General Electric) washer test on cotton soil at 115° C. over a twenty-minute period. Compared with the tallow soap alone as tested in this washer at this concentration and under these conditions, the solution of the new detergent composition has a detersive efficiency of about 97%, and, moreover, complete dispersion of the lime soap is effected.

Example II

Tallow soap is added to coconut oil fatty acid monoester of diethanol piperazine in the proportion of about 20% soap to 80% of the monoester. Using the multiple swatch washer test, as in Example I, and the standard for comparison of an arbitrary 100% detersive efficiency for a 0.55% aqueous solution of tallow soap, the detersive efficiency of a 0.25% aqueous solution of the new composition according to this invention is 102%. This unexpectedly high figure is all the more surprising when it is compared with the detersive efficiency of a 0.25% aqueous solution of the diethanol piperazine monoester employed in the composition, as this solution gives an efficiency under similar conditions of only 94%.

Example III

About 40 parts by weight of coconut oil fatty acids monoester of diethanol piperazine is mixed with 60 parts of sodium coconut oil soap. The detersive efficiency of a 0.25% aqueous solution of the resulting composition is 97% with complete dispersion of scum or curds in the rinse water.

Example IV

One part by weight of the mono-lauryl ether of N-N'-diethanol piperazine is added to about six parts of coconut oil fatty acid sodium soap and about one part of sodium abietate. The materials are thoroughly mixed, and the resulting mixture provides a solution of high detersive efficiency with excellent dispersing characteristics.

Example V

A soap composition comprising about 50 parts of a mixture of palm oil and olive oil soaps and about 35 parts of alkaline soap builders including tetrasodium pyrophosphate and sodium silicate is mixed with 15 parts of tallow fatty acid monoesters of N-N'-diethanol piperazine to form a novel composition according to the present invention. The composition thus produced provides solutions of excellent detergent and dispersing properties.

Example VI

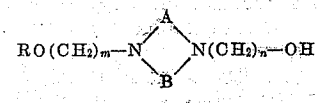
Instead of employing the fatty acid esters or ethers of diethanol piperazine admixed with soaps, e. g. alkali metal fatty oil soaps, the "non fatty" acid derivatives may be used such as the esters and ethers of diethanol piperazine derived from abietic acid or the like, for example abietinic, abietinolic, etc.

The present application is a continuation-in-part of applicant's copending application 638,470 filed December 29, 1945, and now Patent 2,491,992 issued on December 20, 1949.

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 of this invention can be made and that equivalents can be substituted therefore without departing from the principles and true spirit of the invention.

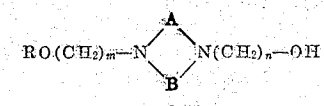
I claim:

1. A detergent composition comprising essentially a water-soluble soap represented by the structural formula: RCOOM, where R is an alkyl radical containing from about 8 to about 20 carbon atoms and M is a monovalent radical selected from the class consisting of alkali metal, ammonium and substituted ammonia groups, and an amount of a piperazine derivative equivalent to about 5% to about 75% by weight of the total composition, said piperazine derivative being represented by the structural formula:



where R is a member of the group consisting of alkyl and acyl radicals having about 5 to about 23 carbon atoms, A and B are members of the group consisting of an ethylene radical and alkyl derivatives thereof wherein any number of hydrogens in the ethylene radical are replaced by alkyl radicals of not more than 2 carbon atoms, and m and n are integers of 2 to about 5.

2. A detergent composition comprising essentially a water-soluble soap represented by the structural formula: RCOOM, where R is an alkyl radical containing from about 8 to about 20 carbon atoms and M is a monovalent radical selected from the class consisting of alkali metal, ammonium and substituted ammonia groups, and an amount of a piperazine derivative equivalent to about 10% to about 50% by weight of the total composition, said piperazine derivative being represented by the structural formula:



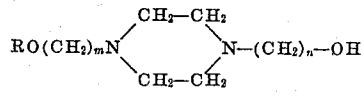
where R is a member of the group consisting of alkyl and acyl radicals having about 8 to 18 carbon atoms, A and B are members of the group consisting of an ethylene radical and alkyl derivatives thereof wherein any number of hydrogens in the ethylene radical are replaced by alkyl radicals of not more than two carbon atoms, and m and n are integers of 2 to about 5.

3. A detergent composition comprising essentially a water-soluble soap represented by the structural formula:

RCOOM

where R is an alkyl radical containing from about 8 to about 20 carbon atoms and M is a monovalent radical selected from the class con-

sisting of alkali metal, ammonium and substituted ammonia groups, and an amount of a piperazine derivative equivalent to about 5% to about 75% by weight of the total composition, said piperazine derivative being represented by the structural formula:

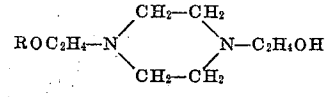


where R is a member of the group consisting of alkyl and acyl radicals having about 8 to about 18 carbon atoms, and m and n are integers of 2 to about 5.

4. A detergent composition comprising essentially a water-soluble soap represented by the structural formula:

RCOOM

where R is an alkyl radical containing from about 8 to about 20 carbon atoms and M is a monovalent radical selected from the class consisting of alkali metal, ammonium and substituted ammonia groups, and an amount of a derivative of N,N'-diethanol piperazine equivalent to about 5% to about 75% by weight of the total composition, said derivative being represented by the structural formula:



where R is a member of the group consisting of alkyl and acyl radicals having about 5 to about 23 carbon atoms.

5. A detergent composition comprising essentially a water-soluble salt of higher fatty acids containing from about 8 to about 20 carbon atoms per molecule with an alkali metal, and an amount of a fatty acid monoester of 1,4-di(β-hydroxy ethyl) piperazine equivalent to about 5% to about 75% by weight of said detergent composition and wherein the fatty acid residue of said piperazine contains about 5 to about 23 carbon atoms.

6. A detergent composition comprising essentially a water-soluble salt of higher fatty acids containing from about 8 to about 20 carbon atoms per molecule with ammonium and an amount of a fatty acid monoester of 1,4-di(β-hydroxy ethyl) piperazine equivalent to about 5% to about 75% by weight of said detergent composition and wherein the fatty acid residue of said piperazine contains about 5 to about 23 carbon atoms.

7. A detergent composition comprising essentially a water-soluble salt of higher fatty acids containing from about 8 to about 20 carbon atoms per molecule with an alkali metal, and an amount of a fatty acid monoether of 1,4-di(β-hydroxy ethyl) piperazine equivalent to about 5% to about 75% by weight of said detergent composition and wherein the fatty acid residue of said piperazine contains about 5 to about 23 carbon atoms.

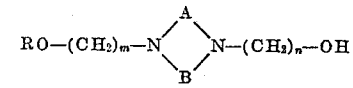
8. A detergent composition comprising essentially a water-soluble salt of higher fatty acids containing from about 8 to about 20 carbon atoms per molecule with ammonium, and an amount of a fatty acid monoether of 1,4-di(β-hydroxy ethyl) piperazine equivalent to about 5% to about 75% by weight of said detergent composition and wherein the fatty acid residue of said piperazine contains about 5 to about 23 carbon atoms.

9. A detergent composition comprising essentially a water-soluble soap of the formula:

RCOOM

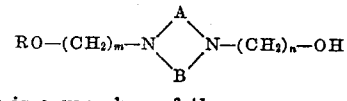
where R is an alkyl radical containing from about 8 to about 20 carbon atoms, M is selected from the class consisting of alkali metal, ammonium and substituted ammonia groups, and an amount of 1-(β-lauroxy ethyl)-4(β-hydroxy ethyl) piperazine equivalent to about 10% to about 50% by weight based upon the total weight of the soap and the piperazine material.

10. A process for preparing surface active compositions of high detersive efficiency which comprises incorporating in a water soluble soap which consists essentially of the salt of fatty acids containing at least about 8 carbon atoms per molecule and a material selected from the class consisting of alkali metal, ammonium, and substituted ammonia groups, an amount of a piperazine derivative equivalent to about 5% to about 75% by weight based upon the total weight of the soap and the piperazine derivative, said piperazine derivative being represented by the structural formula:



where R is a member of the group consisting of alkyl and acyl radicals having about 5 to about 23 carbon atoms, A and B are members of the group consisting of an ethylene radical and alkyl derivatives thereof wherein any number of hydrogens in the ethylene radical are replaced by alkyl radicals of not more than 2 carbon atoms, and m and n are integers of 2 to about 5.

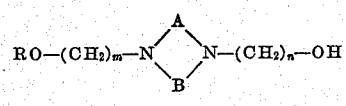
11. A process of preparing surface active compositions in solid form which compositions have improved detersive efficiency in aqueous solutions comprising wet mixing a water soluble soap which consists essentially of the salt of fatty acids containing at least about 8 carbon atoms per molecule and a material selected from the group consisting of alkali metal, ammonium and ammonia groups, with an amount of an aliphatic carboxylic fatty acid ester derivative of N,N'-diethanolamine piperazine equivalent to about 5% to about 75% by weight based upon the total weight of the soap and the piperazine derivative, said piperazine being represented by the structural formula:



where R is a member of the group consisting of acyl and substituted acyl radicals having about 8 to 20 carbon atoms per molecule, A and B are members of the group consisting of an ethylene radical and alkyl derivatives thereof wherein any number of hydrogens in the ethylene radical are replaced by alkyl radicals of not more than 2 carbon atoms, and m and n are integers of 2 to about 5, and subjecting said soap and piperazine derivative mixture to a drying operation to produce the surface active composition in solid form.

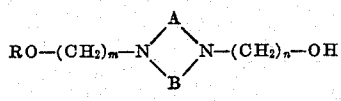
12. A detergent composition comprising a mixture of water soluble soaps which form water insoluble scums in hard water, said soaps consisting essentially of the salts of fatty acids containing from about 8 to about 20 carbon atoms per molecule and a material selected from the class

consisting of alkali metal, ammonium and substituted ammonia groups, and an aliphatic carboxylic acid ether derivative of N,N'-dialkanol piperazine in an amount equivalent to about 5% to about 75% by weight based upon the total weight of the soaps and the piperazine derivative, said piperazine derivative being represented by the structural formula:



where R is a member of the group consisting of alkyl and substituted alkyl radicals having about 5 to 23 carbon atoms, A and B are members of the group consisting of an ethylene radical and alkyl derivatives thereof wherein any number of hydrogens in the ethylene radical are replaced by alkyl radicals of not more than 2 carbon atoms, and m and n are integers of 2 to about 5.

13. A detergent composition comprising a mixture of water soluble soaps which form water insoluble lime soaps in hard water, said water soluble soaps consisting essentially of the salts of fatty acids containing at least about 8 carbon atoms per molecule and a material selected from the class consisting of alkali metal, ammonium and substituted ammonia groups, and a lime soap dispersing agent consisting of an aliphatic carboxylic acid ester derivative of N,N'-diethanol piperazine in an amount equivalent to about 5% to about 75% by weight based upon the total weight of the soaps and the piperazine derivative, said piperazine derivative being represented by the structural formula:



where R is a member of the class consisting of acyl and substituted acyl radicals having about 5 to about 23 carbon atoms, A and B are members of the group consisting of an ethylene radical and alkyl derivatives thereof wherein any number of hydrogens in the ethylene radical are replaced by alkyl radicals of not more than 2 carbon atoms, and m and n are integers of 2 to about 5.

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