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(54) **Detergent composition.**

(57) This invention relates to detergent compositions for use in washing textiles containing an essential three component surfactant system consisting of specific alkyl sulfate, specific sulfonate and cationic detergent surfactants. Such three component surfactant system provides excellent detergency, especially on organic soils such as lipid, greasy and oily soils. Also, such compositions provide unusually low levels of soil redeposition.

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DETERGENT COMPOSITION

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TECHNICAL FIELD

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10 This invention relates to detergent compositions containing specific alkyl sulfate, specific sulfonate and cationic detergent surfactants for use in washing textiles. The compositions can be in any form, such as granules, liquids, tablets or pastes. In preferred
15 embodiments the detergent compositions within the invention contain a detergency builder and/or a nonionic surfactant and/or a fatty acid soap and/or enzymes.

BACKGROUND ART

Cationic surfactants have been incorporated in
20 detergent compositions for purposes other than cleaning; for example, for a germicidal or sanitization benefit, a fabric softening benefit or a static control benefit. More recently it has been disclosed that cationic surfactants in combination with anionic and/or nonionic
25 surfactants are effective for cleaning purposes. U.S. Patent 4,235,759, Ohbre et al (November 25, 1980), discloses liquid detergent compositions that are superior in detergency containing an alkyl polyoxyalkylene ether sulfate anionic surfactant and a mono- long chain
30 alkyl quaternary ammonium cationic surfactant wherein the molar ratio of anionic surfactant:cationic surfactant is from 8:1 to 1:1.

U.S. Patent 4,321,165, Smith et al (March 23, 1982), discloses solid detergent compositions containing
35 from 2% to 60% of a surfactant system consisting of a water-soluble anionic surfactant, an alkoxylated alcohol

nonionic surfactant and a water-soluble quaternary ammonium cationic surfactant wherein the ratio of anionic surfactant:cationic surfactant is from 5:1 to 1:3 and the ratio of nonionic surfactant:cationic surfactant is from 100:1 to 2:3. It is disclosed that such compositions have improved greasy soil removal capabilities.

European Patent Application 0,026,529, Spadini et al (published August 4, 1981), discloses detergent compositions containing from 3% to 40% of an anionic surfactant, from 0.5% to 15% of a mono- long chain alkyl quaternary ammonium compound or an aliphatic amine and from 1.5% to 45% of an impalpable smectite-type clay wherein the molar ratio of the nitrogenous compound: anionic surfactant is less than 1. It is stated that such compositions clean well and also act as textile softeners.

U.S. Patent 4,333,862, Smith et al (June 8, 1982), discloses liquid detergent compositions containing from about 10% to about 82% of an anionic surfactant, from about 10% to about 82% of an alkoxylated alcohol nonionic surfactant and from about 4% to about 35% of a water-soluble quaternary salt cationic surfactant. It is disclosed that such combinations exhibit improved cleaning performance on greasy and oily soils.

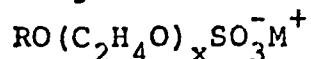
It is an object of the present invention to provide detergent compositions for washing textiles that provide excellent soil removal, especially organic soil removal, with an unusually low level of soil redeposition onto the surface of the textiles.

Another object of the present invention is to provide detergent compositions that provide such benefits over a wide range of washing temperatures.

SUMMARY OF THE INVENTION

The present invention comprises a detergent composition containing, by weight:

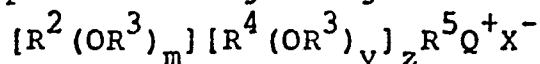
- (a) from 2% to 50% of a water-soluble alkyl sulfate detergent surfactant having the formula:



wherein R is an alkyl chain having from 8 to 18 carbon atoms saturated or unsaturated, wherein the longest linear alkyl portion of the chain extending from the head group is no more than 15 carbon atoms on the average; M is any compatible cation and x is from 0 to 4;

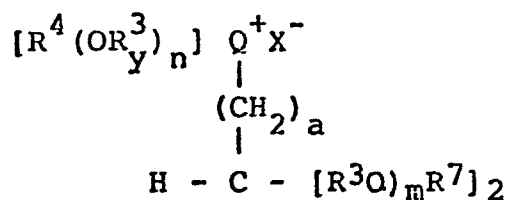
- (b) from 1/4% to 12% of a cationic surfactant selected from:

- (i) compounds having the general formula:



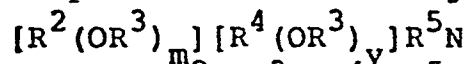
wherein Q is N, P or S; z is 1 if Q is S and 2 if Q is N or P; R^2 is selected from alkyl and alkyl benzyl groups having from 6 to 16 carbon atoms excluding the benzyl group; each R^3 is selected from $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2-\text{CH}(\text{CH}_3)-$, $-\text{CH}_2\text{CH}(\text{CH}_2\text{OH})-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, and mixtures thereof; each R^4 is selected from H when y is not 0, C_{1-4} alkyl, C_{1-4} hydroxyalkyl, benzyl groups, ring structures formed by joining the two R^4 groups, and $-\text{CH}_2\text{CHOHCHOHCHOR}^6\text{CHOHCH}_2\text{OR}^6$ wherein each R^6 is H or any hexose wherein at least one R^6 is H; R^5 is selected from $[\text{R}^2(\text{OR}^3)_m]$, $[\text{R}^4(\text{OR}^3)_y]$ and ring structures formed by joining any of the carbon atoms of R^2 and R^5 wherein the total number of carbon atoms of R^2 plus R^5 is not more than 18, a benzene ring being treated as equivalent to 2 carbon atoms and wherein, if R^4 is less than 4 carbon atoms then R^2 contains from 8 to 16 carbon atoms excluding the benzyl group; each y is from 0 to 3, m is from 0 to 3 and X is any compatible anion; and

(ii) compounds having the general formula:



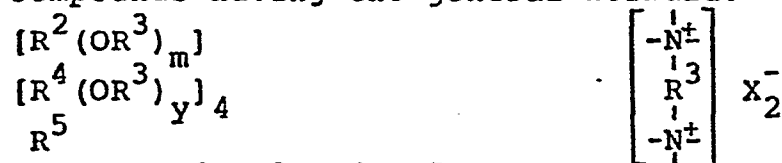
wherein Q, R³, R⁴, y, m and X are as defined above; n is 2 if Q is S and 3 if Q is N or P; each R⁷ is selected from an alkyl or alkyl benzyl group containing at least 1 carbon atom excluding the benzyl group and said R⁷ groups can be joined to form 5 or 6 membered ring structures, and wherein the sum of the carbon atoms of [(R³O)_mR⁷]₂ is from 9 carbon atoms to 16 carbon atoms when m is 0 and from 10 carbon atoms to 18 carbon atoms when m is from 1 to 3, a benzene ring being treated as equivalent to 2 carbon atoms; and a is from 0 to 3;

(iii) aliphatic amines having the general formula:



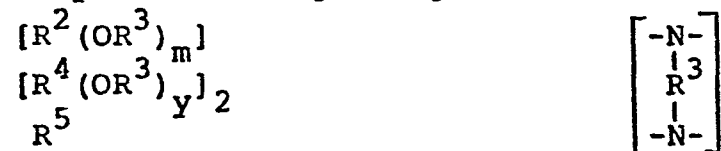
wherein R², R³, R⁴, R⁵, m and y are as defined above and the pKa is at least 1/2 unit above the initial pH of the wash liquor;

(iv) compounds having the general formula:



wherein R², R³, R⁴, R⁵, m, y and X are as defined above;

v) compounds having the general formula:



wherein R^2 , R^3 , R^4 , R^5 , m and y are as defined above and the pKa is at least 1/2 unit above the initial pH of the wash liquor; and mixtures thereof;

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- (c) from 1/2% to 50% of a sulfonate detergent surfactant selected from the water soluble salts of C_{9-15} alkyl benzene sulfonates, C_{8-24} paraffin sulfonates, C_{8-24} alkyl glyceryl ether sulfonates and esters of alpha-sulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group, and C_{1-6} alkyl or aryl sulfonates containing an ether, ester or amide linkage to a C_{7-15} alkyl chain;
 - (d) from 0% to 50% of a nonionic detergent surfactant; and
 - (e) from 0% to 70% of a detergency builder;
- wherein the molar ratio of (b):(c) is less than 1.5.
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DETAILED DESCRIPTION OF THE INVENTION

This invention comprises detergent compositions containing an essential three component detergent surfactant system consisting of specific alkyl sulfate, specific sulfonate and cationic detergent surfactants. This specific three component surfactant system is an extremely effective detergent. It is particularly effective on organic soils, for example, lipid, greasy and oily soils. Also, the use of such system results in an unusually low level of soil redeposition. Soil redeposition results when soil that is removed from the textiles into the wash liquor during the wash process is redeposited onto the textiles.

The detergent compositions within the invention provide the desired superior performance over a broad range of wash water conditions. The wash water temperature can range from 5°C. to 95°C. It is preferred that the initial pH of the wash liquor; i.e., the detergent composition and wash water mixture, be greater than 8 and most preferably from 9 to 11.

The detergent compositions within the invention can be in any form, such as granules, liquids, tablets or pastes, but the granular compositions are preferred. The granules can range in density from .15 grams/cubic centimeter to .8 grams/cubic centimeter.

Without being bound by theory, it is believed that the detergent compositions within the invention provide the desired superior performance on organic soils because the alkyl sulfate detergent surfactant and the

sulfonate detergent surfactant each form an electro-neutral complex with the cationic surfactant. The mechanism of organic soil removal is believed to be based upon the surfactant adsorbing to the soil surface to reduce the soil/water interfacial tension to such an extent that the mechanical action of the washing process removes soil from the textile surface. Since the complexes formed are electrically neutral and, therefore, do not repel each other, they can pack densely when they adsorb onto the soil surface. This results in a much lower soil/water interfacial tension and thereby extremely effective soil removal. It should be noted that in order to obtain the desired superior performance of the present invention both the alkyl sulfate detergent surfactant and the sulfonate detergent surfactant must be present. However, experimental evidence indicates that it is essential that the molar ratio of cationic surfactant to sulfonate detergent surfactant be less than 1.5. Otherwise, the desired superior performance is not obtained.

Additionally, it is preferred that there be a molar excess of the sum of the alkyl sulfate detergent surfactant and the sulfonate detergent surfactant with respect to the cationic surfactant to ensure proteinaceous and particulate soil removal and the suspension in the wash liquor of the soil removed from the textiles. Such soil suspension prevents soil redeposition.

The following is a detailed description of the essential and the optional components of the detergent compositions within the invention. All percentages, parts and ratios are by weight unless otherwise indicated.

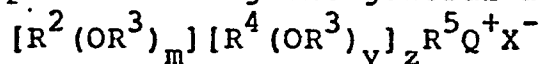
THE CATIONIC SURFACTANT

The cationic surfactant is an essential component of the compositions within the invention. Without the cationic surfactant, the electro-neutral complex cannot

be formed with the alkyl sulfate detergent surfactant and/or the sulfonate detergent surfactant and, therefore, the desired superior performance is not obtained. Though, theoretically, essentially any cationic surfactant can be utilized to provide such benefit, nitrogenous surfactants that are cationic or capable of existing in cationic form are the most practicable. Also, the cationic surfactants within the invention can be saturated or unsaturated.

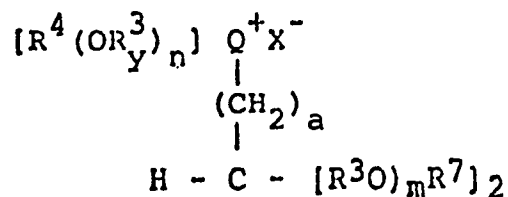
The cationic surfactants within the invention are selected from

(i) compounds having the general formula:



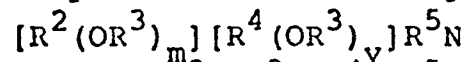
wherein Q is N, P or S; z is 1 if Q is S and 2 if Q is N or P; R² is selected from alkyl and alkyl benzyl groups having from 6 to 16 carbon atoms excluding the benzyl group; each R³ is selected from -CH₂CH₂-, -CH₂-CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from H when y is not 0, C₁₋₄ alkyl, C₁₋₄ hydroxyalkyl, benzyl groups, ring structures formed by joining the two R⁴ groups, and -CH₂CHOHCHOHCHOR⁶CHOHCH₂OR⁶ wherein each R⁶ is H or any hexose wherein at least one R⁶ is H; R⁵ is selected from [R²(OR³)_m], [R⁴(OR³)_y] and ring structures formed by joining any of the carbon atoms of R² and R⁵ wherein the total number of carbon atoms of R² plus R⁵ is not more than 18, a benzene ring being treated as equivalent to 2 carbon atoms and wherein, if R⁴ is less than 4 carbon atoms then R² contains from 8 to 16 carbon atoms excluding the benzyl group; each y is from 0 to 3, m is from 0 to 3 and X is any compatible anion; and

(ii) compounds having the general formula:



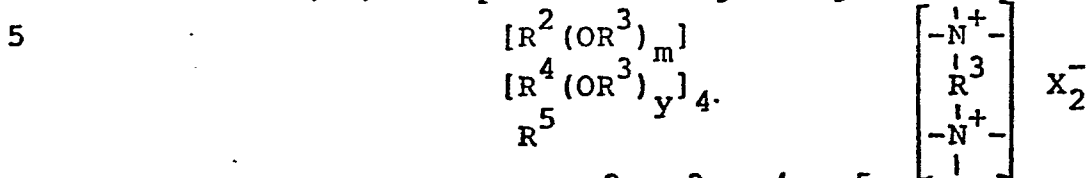
wherein Q, R³, R⁴, y, m and X are as defined above; n is 2 if Q is S and 3 if Q is N or P; each R⁷ is selected from an alkyl or alkyl benzyl group containing at least 1 carbon atom excluding the benzyl group and said R⁷ groups can be joined to form 5 or 6 membered ring structures, and wherein the sum of the carbon atoms of [(R³O)_mR⁷]₂ is from 9 carbon atoms to 16 carbon atoms when m is 0 and from 10 carbon atoms to 18 carbon atoms when m is from 1 to 3, a benzene ring being treated as equivalent to 2 carbon atoms; and a is from 0 to 3;

(iii) aliphatic amines having the general formula:



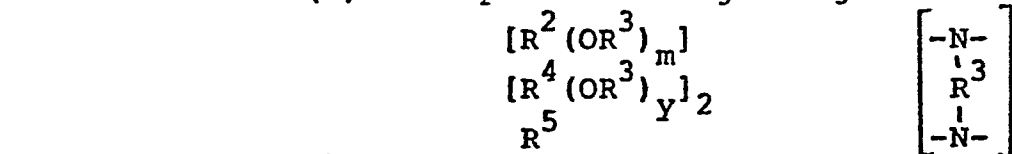
wherein R², R³, R⁴, R⁵, m and y are as defined above and the pKa is at least 1/2 unit above the initial pH of the wash liquor;

(iv) compounds having the general formula:



wherein R^2 , R^3 , R^4 , R^5 , m , y and X are as defined above;

(v) compounds having the general formula:

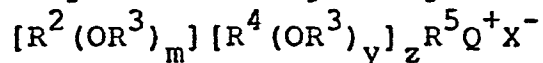


wherein R^2 , R^3 , R^4 , R^5 , m and y are as defined above and the pK_a is at least about 1/2 unit above the initial pH of the wash liquor;

and mixtures thereof.

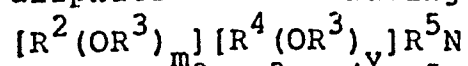
Preferred cationic surfactants are:

(i) compounds having the general formula:



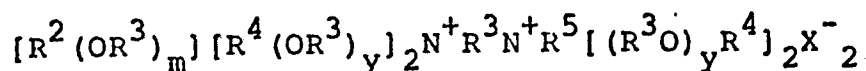
wherein Q is N, P or S; z is 1 if Q is S and 2 if Q is N or P; R^2 is an alkyl or alkyl benzyl group having from 8 to 16 carbon atoms in the alkyl chain; each R^3 is selected from $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from H when y is not 0, C_{1-4} alkyl, C_{1-4} hydroxyalkyl, benzyl groups, ring structures formed by joining the two R^4 groups, and $-CH_2CHOHCHOHCOR^6CHOHCH_2OH$ wherein R^6 is H or any hexose; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than 18; each y is from 0 to 3, m is from 0 to 3 and X is any compatible anion; and

(ii) aliphatic amines having the formula:



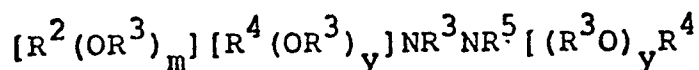
wherein R^2 , R^3 , R^4 , R^5 , m and y are the same as defined above and the pK_a is at least 1/2 unit above the initial pH of the wash water;

(iii) compounds having the general formula:



wherein R^2 , R^3 , R^4 , R^5 , m , y and X are as defined above;

(iv) compounds having the general formula:



wherein R^2 , R^3 , R^4 , R^5 , m and y are as defined above and the pK_a is at least 1/2 unit above the initial pH of the wash water;

and mixtures thereof.

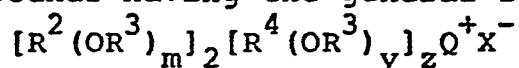
Because of their practicability, nitrogenous surfactants, which are described in (i) when Q is N , (ii), (iii) and (iv) are the preferred cationic surfactants. In this discussion (i), (ii), (iii), and (iv) refer to the compounds in the Summary of the Invention. Especially preferred are the alkyl quaternary ammonium surfactants which are described in (i), and, in particular, the mono- long chain alkyl and alkoxy quaternary ammonium surfactants, which are described in (i) when R^5 is selected from the same groups as R^4 . The most preferred

cationic surfactants are the chloride, bromide and methylsulfate salts of C₈₋₁₂ alkyltrimethyl ammonium surfactants, C₈₋₁₂ alkylhydroxyethyldimethyl ammonium surfactants, C₈₋₁₂ alkylmethyldihydroxyethyl ammonium surfactants, C₁₀₋₁₄ alkoxytrimethyl ammonium surfactants, C₁₀₋₁₄ alkoxydihydroxyethylmethyl ammonium surfactants and C₁₀₋₁₄ alkoxyhydroxyethyldimethyl ammonium surfactants.

As an option, the salts of the cationic surfactants can be prepared by precomplexing the cationic surfactant directly with an anionic detergent surfactant within the invention rather than having such complex be formed in the wash liquor.

Under cold water washing conditions, i.e., below 45°C, the preferred cationic surfactants are:

(i) compounds having the general formula:



wherein Q is N, P or S; z is 1 if Q is S and 2 if Q is N or P; each R² is selected from an alkyl or alkyl benzyl group containing from 4 to 10 carbon atoms excluding the benzyl group; each R³ is selected from

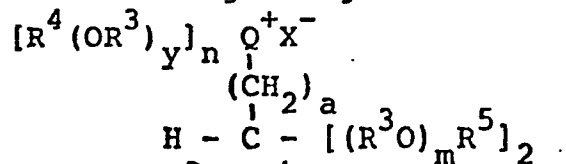
-CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; and wherein the sum of the carbon atoms of [R²(OR³)_m]₂ is from 10 carbon atoms to 16 carbon atoms when m is 0 and from 10 carbon atoms to 18 carbon atoms when m is from 1 to 3, a benzene ring is treated as equivalent to 2 carbon atoms; each R⁴ is selected from

H when y is not 0, C₁₋₃ alkyl, C₁₋₄

hydroxyalkyl, benzyl groups, ring structures formed by joining the two R^4 groups, and $-\text{CH}_2\text{CHOHCHOHCHOR}^6\text{CHOHCH}_2\text{OR}^6$ wherein R^6 is H or any hexose wherein at least one R^6 is H; each y is from 0 to 3, each m is from 0 to 3 wherein m is 1 when R^3 is $-\text{CH}_2\text{CH}_2-$; and X is any compatible anion, particularly one selected from

halide, hydroxide, methylsulfate and acetate anions and mixtures thereof;

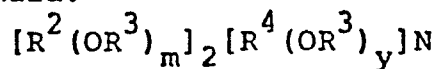
(ii) compounds having the general formula:



wherein Q , R^3 , R^4 , y , m and X are as defined above; n is 2 if Q is S and 3 if Q is N or P; each R^5 is selected from

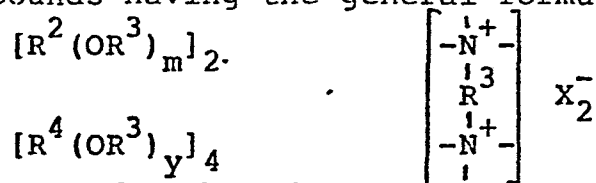
an alkyl or alkyl benzyl group containing at least 1 carbon atom excluding the benzyl group and said R^5 groups can be joined to form 5 or 6 membered ring structures, and wherein the sum of the carbon atoms of $[(\text{R}^3\text{O})_m \text{R}^5]_2$ is from 9 carbon atoms to 16 carbon atoms when m is 0 and from 10 carbon atoms to 18 carbon atoms when m is from 1 to 3, a benzene ring being treated as equivalent to 2 carbon atoms; and a is from 0 to 3;

(iii) aliphatic amines having the general formula:



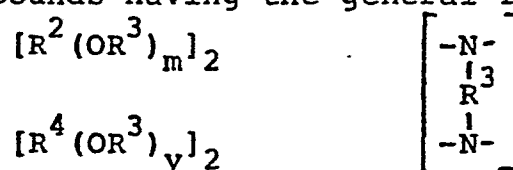
wherein R^2 , R^3 , R^4 , m and y are as defined above and the pK_a is at least $1/2$ unit above the initial pH of the wash liquor;

5 (iv) compounds having the general formula:



10 wherein R^2 , R^3 , R^4 , m , y and X are as defined above; and

(v) compounds having the general formula:



15 wherein R^2 , R^3 , R^4 , m and y are as defined above and the pK_a is at least $1/2$ unit above the initial pH of the wash liquor;

and mixtures thereof.

20 Such cationic surfactants are preferred under cold water washing conditions because when they are utilized in combination with the alkyl sulfate detergent surfactant and the sulfonate detergent surfactant the electro-neutral complex formed does not crystallize or become
25 highly viscous. It has been observed that the electro-neutral complex formed under cold water washing conditions with a cationic surfactant such as C_{12} trimethyl ammonium chloride results in such complex being crystalline or highly viscous and, thereby, is rendered less
30 effective.

Once again, because of their practicability, nitrogenous surfactants, which are described in (i) and (ii) when Q is N , (iii), (iv) and (v) are the preferred cationic surfactants for use under cold water washing
35 conditions. Especially preferred are the alkyl quaternary ammonium surfactants which are described in (i) and

(ii). The most preferred cationic surfactants are the chloride, bromide and methylsulfate salts of the alkyl quaternary ammonium surfactants which are described in (i) when each R^2 is an alkyl group containing from 4 to

10 carbon atoms wherein the sum of the carbon atoms of $[R^2(OR^3)_m]_2$ is from 10 carbon atoms and to 14 carbon atoms and preferably from 10 to 12 carbon atoms; each m and y are 1 or 0, preferably 0; and each R^4 is selected from

methyl and hydroxyethyl. Also, most preferred are the chloride, bromide and methylsulfate salts of the alkyl quaternary ammonium surfactants which are described in (ii) when each R^5 is selected from

an alkyl group containing at least one carbon atom and ring structures formed by joining each R^5 containing five or six carbon atoms wherein the sum of the carbon atoms of $[(R^3O)_mR^5]_2$ is from 10 to 16 carbon atoms and preferably from 10 to 14 carbon atoms; each m and y are 1 or 0, preferably 0; and each R^4 is selected from methyl and hydroxyethyl.

It is essential that cationic surfactants derived from aliphatic amines have a pK_a at least $1/2$ unit above the initial pH of the wash liquor. Otherwise, the desired superior performance is not achieved. It is believed that such a pK_a and pH limitation ensures that a substantial portion of such amines are protonated and, thus, exist in cationic form and, therefore, are able to complex with the alkyl sulfate detergent surfactant and sulfonate detergent surfactant.

The level of cationic surfactant within the invention is related to the level of sulfonate detergent surfactant. The molar ratio of cationic surfactant: sulfonate detergent surfactant is at most 1.5 and preferably less than 1. It is desirable to have some molar excess sulfonate detergent surfactant present

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because it is effective at stripping fabric softeners that have been deposited on the textile surface in previous wash cycles. The sum of the equimolar levels of cationic surfactant and sulfonate detergent surfac-
5 tant is preferably at least 2%, more preferably above 5% and most preferably above 10% of the total level of anionic detergent surfactant present. Such excess of anionic detergent surfactant is preferred to ensure proteinaceous and particulate soil removal and
10 the suspension in the wash liquor of the soil removed from the textiles.

The level of cationic surfactant within the invention is from 1/4% to 12%, preferably from 1/2% to 8% and most preferably from
15 1/2% to 6%.

THE ALKYL SULFATE DETERGENT SURFACTANT

The alkyl sulfate detergent surfactant is an essential component of the detergent compositions within the invention. Detergent compositions without the alkyl
20 sulfate detergent surfactant do not provide the desired superior performance. Such compositions provide poor particulate soil removal and increased soil redeposition. It is believed that the alkyl sulfate detergent surfactant, in addition to forming the electro-neutral
25 complex with the cationic surfactant, is particularly efficacious for such purposes. Furthermore, only specific alkyl sulfate detergent surfactants provide the desired superior performance. Performance is quite poor with an alkyl sulfate detergent surfactant in which the
30 alkyl chain contains more than 15 carbon atoms in a linear portion of the chain extending from the head group and/or more than four ethoxy groups.

The alkyl sulfate detergent surfactants of the present invention are of the general formula:



wherein R is an alkyl chain having from 8 to 18 carbon atoms, saturated or unsaturated, wherein the longest linear portion of the alkyl chain extending from the head group is 15 carbon atoms or less on the average, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation and x is from 0 to about 4. The preferred substituted ammonium cations are the mono- and diethanol ammonium cations.

Preferably, the alkyl sulfate detergent surfactants are not ethoxylated. The preferred alkyl sulfate detergent surfactants are the sodium and potassium salts of C₁₂₋₁₅ primary and C₁₂₋₁₈ secondary alkyl sulfates. The most preferred alkyl sulfate detergent surfactants are the sodium and potassium salts of C₁₂₋₁₅ linear and methyl branched alkyl sulfates.

Under cold water wash conditions, i.e., below 45°C, the preferred alkyl sulfate detergent surfactants are the secondary and shorter alkyl chain alkyl sulfate detergent surfactants within the invention.

The level of alkyl sulfate detergent surfactant within the present invention is from 2% to 50%, preferably from 3% to 30% and most preferably from 5% to 20%.

THE SULFONATE DETERGENT SURFACTANT

A sulfonate detergent surfactant is an essential component of the compositions within the invention. Compositions without the sulfonate detergent surfactants within the invention do not give the desired superior performance.

A very wide range of sulfonate detergent surfactants can be used in the compositions of the invention. However, it is believed that the alkyl chain portion of such surfactants should be saturated. For example, α -olefin sulfonates, which have an unsaturated carbon bond, do not provide the desired superior performance.

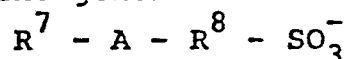
Suitable sulfonate detergent surfactants are C₉₋₁₅ alkyl benzene sulfonates, C₈₋₂₄ paraffin sulfonates, C₈₋₁₈ alkyl glyceryl ether sulfonates, esters of α-sulfonated fatty acids containing from 6 to

5 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group and C₁₋₆ alkyl or aryl sulfonates containing an ether, ester or amide linkage to a C₇₋₁₅ alkyl chain.

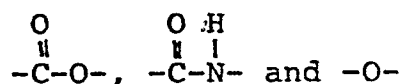
The preferred sulfonate detergent surfactants are 10 the secondary alkyl benzene sulfonates having from 9 to 15, preferably from 11 to 13 carbon atoms in the alkyl chain.

Suitable paraffin sulfonates contain from 8 to 24 carbon atoms and preferably from 12 to 15 18 carbon atoms. The alkyl glyceryl ether sulfonates are those ethers of C₈₋₁₈ alcohols, e.g., those derived from tallow and coconut oil. Suitable esters of α-sulfonated fatty acids contain from 6 to 20 carbon atoms in the fatty acid group and from 1 to 20 10 carbon atoms in the ester group.

Suitable alkyl sulfonates with an ether, ester or amide linkage have the general formula:



wherein R⁷ is an alkyl chain having 7 to 15 25 carbon atoms, R⁸ is an alkyl chain having from 1 to 6 carbon atoms or a benzyl group and A is selected from



30 Under cold wash water conditions, i.e., below 45°C, the shorter alkyl chain sulfonate detergent surfactants are preferred.

The level of sulfonate detergent surfactant within the invention is such that the molar ratio of cationic 35 surfactant:sulfonate detergent surfactant is less than 1.5 and preferably less than 1. The sum of

the equimolar levels of cationic surfactant and sulfonate detergent surfactant is preferably at least above 2%, more preferably above 5% and most preferably above 10% of the total anionic surfactant present.

5 The level of sulfonate detergent surfactant of the detergent compositions within the present invention is from .5% to 50%, preferably from 2% to 30% and most preferably from 3% to 20%.

10

THE DETERGENCY BUILDER

In a highly preferred embodiment the detergent compositions within the invention contain a detergency builder. The level of detergency builder of the detergent compositions is from 0% to 70%, preferably from 10% to 60% and most preferably from 20% to 50% of a detergency builder.

15

The preferred detergency builders are the water-soluble sequestrants such as tripolyphosphates, hexametaphosphates and higher polymerization species, citrates, nitrilotriacetates and water-soluble polyacetals as disclosed in U.S. Patents 4,144,266 and 4,246,495, and mixtures thereof. The most preferred detergency builders are tripolyphosphates, nitrilotriacetates and water-soluble polyacetals and mixtures thereof.

20

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Water-soluble inorganic or organic electrolytes are suitable builders. The electrolytes have an equivalent weight of less than 210, especially less than 100 and include the common alkaline polyvalent calcium ion sequestering agents. The builder can also be water-insoluble calcium ion exchange materials; however, nonlimiting examples of suitable water-soluble, inorganic detergent builders include: alkali metal carbonates, borates, phosphates, bicarbonates, silicates, sulfates and chlorides. Specific examples of such salts include sodium and potassium tetraborates, perborates,

30

35

bicarbonates, carbonates, percarbonates, orthophosphates, pyrophosphates and sulfates.

Examples of suitable organic alkaline detergency builders include: (1) water-soluble aminocarboxylates and aminopolyacetates, for example, sodium and potassium glycinate, ethylenediaminetetraacetates and N-(2-hydroxyethyl)nitrlodiacetates and diethylenetriamine-pentaacetates; (2) water-soluble salts of phytic acid; for example, sodium and potassium phytates; (3) water-soluble polyphosphonates, including sodium, potassium, and lithium salts of ethane-1-hydroxy-1, 1-diphosphonic acid; sodium, potassium, and lithium salts of ethylene diphosphonic acid; and the like; (4) water-soluble polycarboxylates such as the salts of lactic acid, succinic acid, malonic acid, maleic acid, citric acid, carboxymethyloxysuccinic acid, 2-oxa-1,1,3-propane tricarboxylic acid, 1,1,2,2-ethane tetracarboxylic acid, cyclopentane-cis, cis, cis - tetracarboxylic acid, mellitic acid and pyromellitic acid; (5) water-soluble organic amines and amine salts such as monoethanolamine, diethanolamine and triethanolamine and salts thereof; (6) water soluble polyacetals as disclosed in U.S. Patents 4,144,266 and 4,246,495

and (7) water soluble salts of fatty acids; for example, C₁₂₋₁₈ fatty acids.

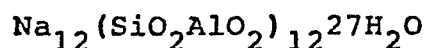
Another type of detergency builder material useful in the present compositions comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations preferably in combination with a crystallization seed which is capable of providing growth sites for said reaction product. Such "seeded builder" compositions are fully disclosed in British Patent Specification No. 1,424,406.

A further class of detergency builder materials useful in the present invention are insoluble sodium aluminosilicates, particularly those described in

Belgian Patent 814,874, issued November 12, 1974.

This patent discloses and claims detergent compositions containing sodium aluminosilicates having the formula:

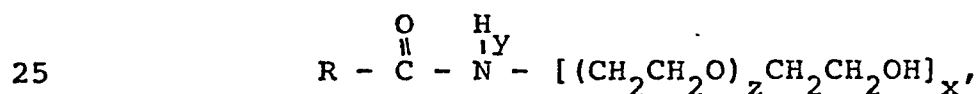
5
$$\text{Na}_z(\text{AlO}_2)_z(\text{SiO}_2)_y \cdot \text{XH}_2\text{O}$$
 wherein z and y are integers equal to at least 6, the molar ratio of z to y is in the range of from 1.0:1 to about 0.5:1, and X is an integer from 15 to 264, said aluminosilicates having a calcium ion exchange capacity of at least 200 milligrams equivalent/gram and
10 a calcium ion exchange rate of at least 2 grains/minute/gram. A preferred material is:



THE NONIONIC SURFACTANT

15 As an option, the compositions of the invention can contain a nonionic surfactant. Such surfactants for use herein comprise those typical nonionic surfactants well known in the detergency arts. The preferred nonionic surfactants are fatty acid amide surfactants, amine
20 oxide surfactants and ethoxylated alcohols.

Suitable fatty acid amide surfactants are ammonia amides, monoethanol amides, diethanol amides and ethoxylated amides. The preferred amides have the formula



wherein R is a C_{8-20} alkyl group, $x + y = 2$ and z is from 0 to 5. Particularly preferred amides are those where the alkyl group contains from 10 to 16 carbon atoms, such as coconut alkyl monoethanol
30 or diethanol amide. Such compounds are commercially available under the tradenames Super-Amide L-9 and GR, from Onyx Chemical Company, Jersey City, NJ; Super-Amide F-3 from Ryco, Inc., Conshohocken, PA and Gafamide CDD-518, available from GAF Corp., New York, NY.

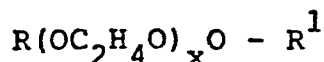
The amine oxide surfactants of the present invention comprise compounds and mixtures of compounds having the formula



wherein R^1 is an alkyl, hydroxyalkyl, alkoxyhydroxypropyl radical, alkoxyhydroxyethyl, alkyl amido or alkyl carboxylate in which the alkyl and alkoxy, respectively, contain from 8 to 18 carbon atoms, R^2 and R^3 are methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, or together are a heterocyclic, e.g., morpholino structure in which the nitrogen is part of the heterocyclic ring and n is from 0 to 10.

Specific examples of amine oxide surfactants include: dimethyldodecylamine oxide, dimethyltetradecylamine oxide, ethylmethyltetradecylamine oxide, cetyldimethylamine oxide, dimethylstearylamine oxide, cetylethylpropylamine oxide, diethyldodecylamine oxide, diethyltetradecylamine oxide, dipropyldodecylamine oxide, bix-(2-hydroxyethyl)dodecylamine oxide, bis(2-hydroxyethyl)-3-dodecoxy-2-hydroxypropylamine oxide, (2-hydroxypropyl)methyltetradecylamine oxide, dimethyloleamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, C_{8-20} alkyl(alpha-dimethylamine oxide) carboxylate, and the corresponding decyl, hexadecyl and octadecyl homologs of the above compounds. A particularly preferred material is dimethyl C_{12-16} alkyl amine oxide.

The ethoxylated alcohols for use herein have the formula



wherein R is an alkyl, hydroxy alkyl, alkylene, hydroxy alkylene acyl, or hydroxy acyl group containing from 8 to 22 carbon atoms or an alkylbenzene group wherein the alkyl group contains from 6 to

15 carbon atoms or mixtures thereof; X is a number from 2 to 30; and R¹ is selected from

H, alkyl groups containing from 2 to 4 carbon atoms, acyl groups containing from 2 to 4 carbon atoms and mixtures thereof. The HLB Of these nonionic surfactants is preferably from 5 to 20, most preferably from 8 to 14.

Other suitable nonionic surfactants are: (1) the condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide and propylene glycol, and (2) the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. These surfactants are marketed by BASF Wyandotte under the tradenames Pluronic and Tetronic respectively.

The level of nonionic surfactant that can be present is from 0% to 50%, preferably from .5% to 10% and most preferably from 1% to 5%.

MISCELLANEOUS INGREDIENTS

In addition to the above named ingredients, the compositions of this invention can contain all of the usual components of detergent compositions including the ingredients set forth in U.S. Patent 3,936,537, Baskerville et al.

Such components include color speckles, bleaching agents, bleach activators, suds boosters, suds suppressors, antitarnish and/or anticorrosion agents, soil-suspending agents, soil-release agents, dyes, fillers, optical brighteners, germicides, pH adjusting agents, alkalinity sources, hydrotropes, antioxidants, enzymes, enzyme stabilizing agents, perfumes, etc.

In addition to being able to function as a detergency builder, water soluble salts of fatty acids can be added as part of the surfactant system. Surprisingly,

they are most effective under cold water wash conditions. Suitable water soluble salts of fatty acids have from 8 to 18 carbon atoms. The preferred water soluble salts of fatty acids are the sodium, potassium and magnesium salts of C₁₂₋₁₄ fatty acids. They can be present at levels up to 10%.

Enzymes are believed to be particularly effective in the detergent compositions of this invention. The enzyme-containing detergent compositions are particularly effective on enzyme sensitive stains such as grass and blood while maintaining greasy and oily soil detergency. Suitable enzymes are those, for example, disclosed in U.S. Patent 4,176,079, Guerry et al (November 27, 1979).

The enzymes are included at a level of from .02% to 3%, preferably from .1% to 1%.

Nonlimiting examples of bleaching agents are sodium perborate (as the monohydrate or tetrahydrate), sodium percarbonate and other perhydrates, at levels from 5% to 35% by weight of the composition, and activators therefor, such as tetraacetylenediamine, tetraacetylglucouril and others known in the art, and stabilizers therefor, such as magnesium silicate, and ethylenediaminetetraacetate. Peroxy carboxylic acids, for example, such as those disclosed in U.S. Patent 4,091,544, Hutchins (May 30, 1975), are especially useful.

Preferred optional ingredients include suds modifiers particularly those of suds suppressing types, exemplified by silicones, and silica-silicone mixtures.

U.S. Patents 3,933,672, issued January 20, 1976 to Bartolotta et al, and 4,136,045, issued January 23, 1979 to Gault et al, disclose silicone suds controlling agents. The silicone material can be represented by alkylated polysiloxane materials such as silica aerogels and xerogels and

hydrophobic silicas of various types. The silicone material can be described as siloxane having the formula:



wherein x is from 20 to 2,000 and R and R¹ are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl and phenyl. The polydimethylsiloxanes (R and R¹ are methyl) having a molecular weight within the range of from 200 to 2,000,000, and higher, are all useful as suds controlling agents. Additional suitable silicone materials wherein the side chain groups R and R¹ are alkyl, aryl, or mixed alkyl or aryl hydrocarbyl groups exhibit useful suds controlling properties. Examples of the like ingredients include diethyl-, dipropyl-, dibutyl-, methyl-, ethyl-, phenyl-methylpoly-siloxanes and the like. Additional useful silicone suds controlling agents can be represented by a mixture of an alkylated siloxane, as referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethylsilanated) silica having a particle size in the range from 10 millimicrons to 20 millimicrons and a specific surface area above 50 m²/gm. intimately admixed with dimethyl silicone fluid having a molecular weight in the range from 500 to 200,000 at a weight ratio of silicone to silanated silica of from 19:1 to 1:2. The silicone suds suppressing agent is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier.

Particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in U.S.

Patent 4,073,118, Gault et al, issued February 21, 1978.

An example of such a compound is DB-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

5 Suds modifiers as described above are used at levels of up to approximately 2%, preferably from 0.1 to 1% by weight of the surfactant.

10 Microcrystalline waxes having a melting point in the range from 35°C-115°C and a saponification value of less than 100 represent additional examples of preferred suds control components for use in the subject compositions, and are described in detail in U.S. Patent 4,056,481, Tate, issued November 1, 1977.

15 The microcrystalline waxes are substantially water-insoluble, but are water-dispersible in the presence of organic surfactants. Preferred microcrystalline waxes have a melting point from 65°C to 100°C, a molecular weight in the range from 400-1,000; and a penetration value of at least 6, measured at 77°F by ASTM-D1321. Suitable examples of the above waxes include: microcrystalline and oxidized microcrystalline petroleum waxes; Fischer-Tropsch and oxidized Fischer-Tropsch waxes; ozokerite; ceresin; montan wax; beeswax; candelilla; and carbauba wax.

25 Alkyl phosphate esters represent an additional preferred suds control agent for use herein. These preferred phosphate esters are predominantly monostearyl phosphate which, in addition thereto, can contain di- and tristearyl phosphates and monooleyl phosphate, which can contain di- and trioleyl phosphate.

30 The alkyl phosphate esters frequently contain some trialkyl phosphate. Accordingly, a preferred phosphate ester can contain, in addition to the monoalkyl ester, e.g., monostearyl phosphate, up to 50 mole percent of dialkyl phosphate and up to 5 mole percent of trialkyl phosphate.

Small amounts of zwitterionic and/or ampholytic surfactants can be present, but because of the outstanding performance characteristics of the compositions within the present invention, surfactants additional to the essential components will not generally be necessary.

The following examples are given to illustrate the parameters of and compositions within the invention. All of the compositions are stated in percent by weight.

EXAMPLE I

Wash water solutions were prepared that represented the following compositions:

	<u>A</u>	<u>B</u>	<u>C</u>
C ₈ alkyltrimethylammonium chloride	0	0	3.0
C ₁₂ alkyltrimethylammonium chloride	3.3	0	0
Sodium C ₁₃ linear alkylbenzene sulfonate (C ₁₃ LAS)	4.9	5.1	4.9
Sodium C ₁₄₋₁₅ methyl branched alkyl sulfate (C ₄₅ AS)	12.6	13.5	12.6
C ₉₋₁₁ alkyl polyethoxylate _{2.5T} * (C ₉₁ AE _{2.5T})	3.3	3.4	3.3
Sodium carbonate	24.6	25.4	24.7
Sodium tripolyphosphate	28.1	29.1	28.2
Sodium nitrilotriacetate	8.6	8.9	8.6
Sodium sulfate	12.3	12.7	12.3
Sodium silicate (1.6 r)	2.0	2.0	2.0
Optical brightener	.29	.30	.29

*Stripped of lower ethoxylated fractions and fatty alcohol.

Three sets of four 3"x3" swatches consisting of standard textiles stained with standard soils were prepared.

A laundry load consisting of one set of the swatches along with six clean terry cloth towels and one

terry cloth towel soiled with a mixture of particulate soil and oily soil was placed in a mini-wash system. The load was then washed with a quantity of Composition A that corresponds to detergent concentrations utilized in conventional automatic wash processes. The mini-wash system with such a load simulates a conventional automatic washing process. The wash water had a temperature of 95°F and contained 5 grains/gallon water hardness.

This wash process was repeated two more times, once with the second set of swatches and Composition B and once with the third set of swatches and Composition C.

Each of the four swatch types was then comparison graded against its identical counterpart that had been washed with a different detergent composition to determine relative soil removal. A grading scale of -4 to 4 was used, with -4 indicating much less soil removal, 0 indicating no difference and 4 indicating much more soil removal.

The entire above procedure, consisting of preparing three sets of four swatches and three wash cycles, was repeated four more times. Therefore, each swatch type of each detergent composition was graded a total of four times. Such four grades were then averaged. Finally, the average of such averages for each detergent composition was calculated. This average is known as the Cleaning Index.

The results were as follows:

	<u>A</u>	<u>B</u>	<u>C</u>
Cleaning Index	0	-.56	+.38
Least Significant Difference (.05)	.41	.41	.41

Compositions A and C provided significantly more soil removal than Composition B, which did not contain the essential cationic surfactant.

EXAMPLE II

Wash water solutions were prepared that represented the following compositions:

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Sodium C ₁₆ alkyl-4-sulfate	0	0	0	0	5.1	0
5 Sodium α-olefin sulfonate	0	0	0	5.5	0	0
α-sulfonated coconut fatty acid hexyl ester	0	0	6.4	0	0	0
10 Sodium C ₁₆ alkyl paraffin sulfonate	0	5.4	0	0	0	0
C ₁₃ LAS	5.4	0	0	0	0	5.4
C ₄₅ AS	11.7	11.7	11.6	11.7	11.7	11.7
15 C ₁₂ alkyltrimethyl-ammonium chloride	3.1	3.1	3.0	3.1	3.1	3.1
C ₉₁ AE _{2.5T}	3.1	3.1	3.0	3.1	3.1	3.1
Sodium carbonate	22.4	22.5	22.3	22.4	23.0	22.4
Sodium tripolyphosphate	36.3	36.4	36.1	36.3	36.6	36.3
20 Sodium nitrilotriacetate	5.7	5.7	5.6	5.7	5.7	5.7
Sodium sulfate	9.9	9.9	9.8	9.9	9.9	9.9
Sodium silicate (1.6r)	1.8	1.8	1.8	1.8	1.8	1.8
25 Optical brightener	.27	.27	.27	.27	.27	.27

Soil removal capabilities of Compositions were A-D then compared by determining the Cleaning Index by the same procedure as described in Example I. Such comparison was also made with Compositions E and F. The results were as follows:

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Cleaning Index	0	-.3	-.4	-.9	-.48	0
Least Significant Difference (.05)	.46	.46	.46	.46	.31	.31

Compositions A, B and C provided significantly more soil removal than Composition D which did not contain a sulfonate detergent surfactant within the invention. Composition F provided significantly more soil removal
 5 than Composition E. Thus, it appears that sodium C₁₆ alkyl-4-sulfate cannot "substitute" for a sulfonate detergent surfactant within the invention.

EXAMPLE III

Wash water solutions were prepared that represented
 10 the following compositions:

	<u>A</u>	<u>B</u>	<u>C</u>
C ₁₃ LAS	5.3	10.6	17.6
C ₄₅ AS	12.3	7	0
C ₁₂ alkyltrimethylammonium			
15 chloride	3.1	3.1	3.1
C ₉₁ AE _{2.5T}	3.1	3.1	3.1
Sodium carbonate	22.4	22.4	22.4
Sodium tripolyphosphate	36.3	36.3	36.3
Sodium nitrilotriacetate	5.7	5.7	5.7
20 Sodium sulfate	9.9	9.9	9.9
Sodium silicate (1.6 r)	1.8	1.8	1.8
Optical brightener	.27	.27	.27

Six 3"x3" clean swatches of various textile types were made. The six swatches and six clean terry cloth
 25 towels were placed in a mini-wash system. The load was then washed in wash water containing lipid soil and organic and inorganic particulate soil with a quantity of Composition A that corresponds to detergent concentrations utilized in conventional automatic wash pro-
 30 cesses. The textiles were then dried. The same swatches and terry cloth towels were washed in such process five more cycles.

After the sixth cycle the six swatches were measured to obtain the difference in Hunter Whiteness Units
 35 Filtered (Δ HWUF). This measurement corresponds to the amount of soil deposited onto the swatches, with the

lower number signifying greater soil redeposition. The average ΔHWUF grades for the six swatches, Δ-HWUF avg., was calculated.

The entire above procedure was repeated two more times, once with Compositions B and once with Composition C. The results were as follows:

	<u>A</u>	<u>B</u>	<u>C</u>
Δ-HWUF avg.	-10.5	-14.0	-26.5
Least Significant			
10 Difference (.05)	2.5	2.5	2.5

There was significantly less soil redeposition on the swatches with Compositions A and B than with Composition C. This result indicates that the alkyl sulfate detergent surfactant, which was not present in Composition C, is essential to prevent soil redeposition. Also, Composition B. had somewhat more soil redeposition than Composition A. This is due to the decreased level of alkyl sulfate detergent surfactant of Composition B.

EXAMPLE IV

20 Wash water solutions were prepared that represented the following compositions:

	<u>A</u>	<u>B</u>	<u>C</u>
Sodium α-olefin sulfonate	0	0	12.1
Sodium C ₁₆ alkyl paraffin sulfonate	0	12.1	0
25 C ₁₃ LAS	5.1	5.6	5.6
C ₄₅ AS	12.1	0	0
C ₁₂ alkyltrimethylammonium chloride	3.1	3.1	3.1
30 C ₉₁ AE _{2.5T}	3.1	3.1	3.1
Sodium carbonate	22.5	22.5	22.5
Sodium tripolyphosphate	36.5	36.5	36.5
Sodium nitrilotriacetate	5.7	5.7	5.7
Sodium sulfate	9.9	9.9	9.9
35 Sodium silicate (1.6 r)	1.8	1.8	1.8
Optical brightener	.27	.27	.27

Soil removal capabilities of each of the compositions were then compared by determining the Cleaning Index by the same procedure as described in Example I. The results were as follows:

5		<u>A</u>	<u>B</u>	<u>C</u>
	Cleaning Index	0	-1.06	-.66
	Least Significant Difference			
	(.05)	.31	.31	.31

Composition A provided significantly more soil removal than Compositions B and C. It is believed that this is because Compositions B and C did not contain an alkyl sulfate detergent surfactant. Therefore, the alkyl sulfate detergent surfactant is also essential for soil removal.

15 EXAMPLE V

Wash water solutions were prepared that represented the following compositions.

		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
	Sodium tallow primary				
20	alkyl sulfate	0	11.8	0	0
	C ₄₆ linear primary AS	0	0	0	12.8
	C ₁₃ LAS	5.0	5.0	5.5	5.5
	C ₄₅ AS	11.8	0	12.8	0
	C ₁₂ alkyltrimethylammonium				
25	chloride	3.1	3.1	3.3	3.3
	C ₉₁ AE _{2.5T}	3.1	3.1	3.3	3.3
	Sodium carbonate	22.6	22.6	24.9	24.9
	Sodium tripolyphosphate	36.7	36.7	28.4	28.4
	Sodium nitrilotriacetate	5.7	5.7	8.8	8.8
30	Sodium sulfate	10.0	10.0	10.8	10.8
	Sodium silicate (1.6 r)	1.8	1.8	2.0	2.0
	Optical brightener	.27	.27	.27	.27

Soil removal capability of Composition A was compared to that of Composition B by determining the Cleaning Index by the same procedure as described in Example

I. Such comparison was also made between Compositions C and D. The results were as follows:

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Cleaning Index	0	-.96	0	-1.2
Least Significant Difference (.05)	..55	.55	.7	.7

Composition A provided significantly more soil removal than Composition B and Composition C provided significantly more soil removal than Composition D. This result is due to that the length of the longest portion of the alkyl sulfate detergent surfactant of Compositions B and D is too long.

EXAMPLE VI

Wash water solutions were prepared that represented the following compositions:

	<u>A</u>	<u>B</u>	<u>C</u>
C ₁₃ LAS	0	2.4	5.0
C ₄₅ AS	16.7	14.3	11.7
C ₁₂ alkyltrimethylammonium chloride	3.0	3.0	3.0
C ₉₁ AE _{2.5T}	3.0	3.0	3.0
Sodium carbonate	22.9	22.9	22.9
Sodium tripolyphosphate	36.6	36.6	36.6
Sodium nitrilotriacetate	5.7	5.7	5.7
Sodium sulfate	9.9	9.9	9.9
Sodium silicate (1.6 r)	1.8	1.8	1.8
Optical brightener	.23	.23	.23

Soil removal capabilities of each of the compositions were then compared by determining the Cleaning Index by the same procedure as described in Example I. The results were as follows:

	<u>A</u>	<u>B</u>	<u>C</u>
Cleaning Index	-.76	-.61	0
Least Significant Difference (.05)	.35	.35	.35
Molar ratio of C ₁₂ alkyltrimethylammonium chloride:C ₁₃ LAS	0	1.7	.83

Composition C provided significantly more soil removal than Compositions A and B. It is believed that this is because Composition A and B did not contain a sufficient level of C₁₃ LAS in order to form a sufficient level of cationic surfactant-alkyl sulfonate detergent surfactant complex.

EXAMPLE VII

Wash water solutions were prepared that represented the following compositions:

	<u>A</u>	<u>B</u>
C ₁₃ LAS	7.3	7.5
C ₄₅ AE ₁ S	5.4	5.6
C ₄₅ AS	5.5	5.7
C ₁₂ alkyltrimethylammonium chloride	3.3	3.4
C ₉₁ AE _{2.5} T	3.3	0
Sodium carbonate	24.9	25.7
Sodium tripolyphosphate	28.4	29.4
Sodium nitrilotriacetate	8.7	9.1
Sodium sulfate	10.8	11.2
Sodium silicate	2.0	2.0
Optical brightener	.3	.3

Soil removal capabilities of each of the compositions were then compared by determining the Cleaning Index by the same procedure as described in Example I. The results were as follows:

	<u>A</u>	<u>B</u>
Cleaning Index	0	-.5
Least Significant Difference (.05)	.50	.50

Composition A, which contains an optional nonionic surfactant, provided only marginally significantly more soil removal than Composition B.

EXAMPLE VIII

Wash water solutions were prepared that represented the following compositions:

		<u>A</u>	<u>B</u>
	C ₁₃ LAS	5.4	5.5
	C ₄₅ AS	10.1	10.2
5	C ₁₂ alkyltrimethylammonium chloride	2.6	0
	C ₁₂ primary amine (pKa 10.8)	0	1.8
	C ₉₁ ^{AE} 2.5T	3.1	3.1
	Sodium carbonate	23.4	23.5
	Sodium tripolyphosphate	37.4	37.6
10	Sodium nitrilotriacetate	5.8	5.9
	Sodium sulfate	10.1	10.2
	Sodium silicate (1.6r)	1.9	1.9
	Optical brightener	.2	.2

Soil removal capabilities of each of the compositions were then compared by determining the Cleaning Index by the same procedure as described in Example I. The initial pH of the wash liquor was 10.1. The results were as follows:

		<u>A</u>	<u>B</u>
20	Cleaning Index	0	-.40
	Least Significant Difference (.05)	.97	.97

Composition B, which contains an amine surfactant, did not remove significantly less soil than Composition A, which contains an alkylammonium surfactant.

When dihexyldimethylammonium chloride is substituted for the C₁₂ alkyltrimethylammonium chloride, the cool water, e.g., 20°C, performance is improved.

EXAMPLE IX

The following is a composition within the invention that contains a water soluble salt of a fatty acid:

	Sodium laurate	5.7
	$\text{C}_{10}\text{H}_{21}\text{O}-(\text{CH}_2)_3\overset{\text{CH}_3}{\underset{ }{\text{N}}}[(\text{CH}_2)_2\text{OH}]_2$	2.7
	C ₄₅ AS	7.2
35	C ₁₃ LAS	3.9
	Sodium sulfate	29.0

Sodium carbonate	16.1
Sodium tripolyphosphate	32.2
Sodium silicate (1.6r)	3.0
Optical brightener	.2

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EXAMPLE X

The following is a granular detergent composition within the invention that has a density of about .73 grams/cubic centimeter:

10	C ₁₂ alkyl trimethylammonium chloride	3.0
	C ₁₃ LAS	4.9
	C ₄₅ AS	11.3
	C ₄₅ AE ₇	1.6
	Sodium carbonate	22.3
15	Sodium tripolyphosphate	27.5
	Sodium nitrilotriacetate	7.8
	Sodium sulfate	12.9
	Sodium silicate (1.6 r)	1.8
	Optical brightener	.22
20	Water	6.7

EXAMPLE XI

The following is an enzyme-containing detergent composition within the invention:

	Enzymes (Alcalase)	.8
25	C ₁₃ LAS	5.2
	C ₄₅ AS	13.5
	C ₁₂ alkyltrimethylammonium chloride	3.5
	C ₉₁ AE _{2.5T}	1.7
	Sodium carbonate	13.1
30	Sodium tripolyphosphate	42.0
	Sodium nitrilotriacetate	6.6
	Sodium sulfate	11.4
	Sodium silicate (1.6 r)	2.1
	Optical brightener	.26

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This composition provides the desired superior performance on conventional soils in addition to being extremely effective on enzyme-sensitive stains.

EXAMPLE XII

5 The following is a composition within the invention that contains a water soluble salt of a fatty acid:

	Sodium laurate	5.7
	C ₁₂ alkyltrimethylammonium chloride	2.7
	C ₂₃ ^{AE} _{6.5}	1.5
10	C ₄₅ AS	7.2
	C ₁₃ LAS	3.9
	Sodium sulfate	27.5
	Sodium carbonate	16.1
	Sodium tripolyphosphate	32.2
15	Sodium silicate (1.6r)	3.0
	Optical brightener	.2

EXAMPLE XIII

		<u>A</u>	<u>B</u>
	C ₁₃ LAS	7.5	7.5
20	C ₄₅ AS	7.5	7.5
	C ₁₂ alkyltrimethylammonium chloride	2	2
	C ₂₃ AE _{6.5}	2	2
	Na ₂ CO ₃	20	15
	Sodium nitrilotriacetate	0	15
25	Sodium hydrated Zeolite A (1-3μ)	25	20
	Na ₂ SO ₄	25	20
	Sodium silicate (1.6 r)	2.5	2.5
	Minors, water, etc.	Balance	Balance

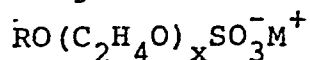
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CLAIMS

1. A detergent composition comprising, by weight:

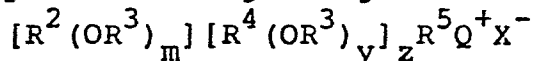
- (a) from 2% to 50% of a water-soluble alkyl sulfate detergent surfactant having the formula:



wherein R is an alkyl chain having from 8 to 18 carbon atoms saturated or unsaturated, wherein the longest linear alkyl portion of the chain extending from the head group is no more than 15 carbon atoms on the average; M is any compatible cation and x is from 0 to 4;

- (b) from 1/4% to 12% of a cationic surfactant selected from:

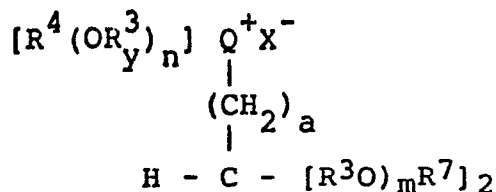
- (i) compounds having the general formula:



wherein Q is N, P or S; z is 1 if Q is S and 2 if Q is N or P; R^2 is selected from alkyl and alkyl benzyl groups having from 6 to 16 carbon atoms excluding the benzyl group; each R^3 is selected from $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2-\text{CH}(\text{CH}_3)-$, $-\text{CH}_2\text{CH}(\text{CH}_2\text{OH})-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, and mixtures thereof; each R^4 is selected from H when y is not 0, C_{1-4} alkyl, C_{1-4} hydroxyalkyl, benzyl groups, ring structures formed by joining the two R^4 groups, and $-\text{CH}_2\text{CHOHCHOHCHOR}^6\text{CHOHCH}_2\text{OR}^6$ wherein each R^6 is H or any hexose wherein at least one R^6 is H; R^5 is selected from $[\text{R}^2(\text{OR}^3)_m]$, $[\text{R}^4(\text{OR}^3)_y]$ and ring structures formed by joining any of the carbon atoms of R^2 and R^5 wherein the total number of carbon atoms of R^2 plus R^5 is not more than 18, a benzene ring being treated as equivalent to 2 carbon atoms and wherein, if R^4 is less than 4 carbon atoms then R^2 contains from 8 to 16 carbon atoms excluding the benzyl group; each y is from 0 to 3, m is from 0 to 3 and X is any compatible anion; and

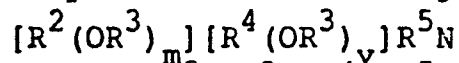
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(ii) compounds having the general formula:



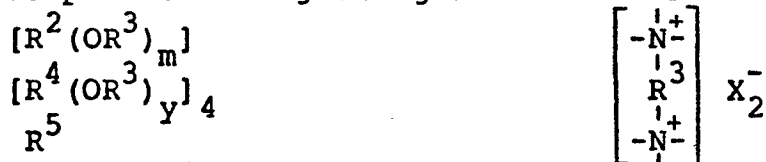
wherein Q, R³, R⁴, y, m and X are as defined above; n is 2 if Q is S and 3 if Q is N or P; each R⁷ is selected from an alkyl or alkyl benzyl group containing at least 1 carbon atom excluding the benzyl group and said R⁷ groups can be joined to form 5 or 6 membered ring structures, and wherein the sum of the carbon atoms of [(R³O)_mR⁷]₂ is from 9 carbon atoms to 16 carbon atoms when m is 0 and from 10 carbon atoms to 18 carbon atoms when m is from 1 to 3, a benzene ring being treated as equivalent to 2 carbon atoms; and a is from 0 to 3;

(iii) aliphatic amines having the general formula:



wherein R², R³, R⁴, R⁵, m and y are as defined above and the pKa is at least 1/2 unit above the initial pH of the wash liquor;

(iv) compounds having the general formula:



wherein R², R³, R⁴, R⁵, m, y and X are as defined above;

v) compounds having the general formula:



wherein R², R³, R⁴, R⁵, m and y are as defined above and the pKa is at least 1/2 unit above the initial pH of the wash liquor;

and mixtures thereof;

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- (c) from 1/2% to 50% of a sulfonate detergent surfactant selected from the water soluble salts of C₉₋₁₅ alkyl benzene sulfonates, C₈₋₂₄ paraffin sulfonates, C₈₋₂₄ alkyl glyceryl ether sulfonates and esters of alpha-sulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group, and C₁₋₆ alkyl or aryl sulfonates containing an ether, ester or amide linkage to a C₇₋₁₅ alkyl chain;
- (d) from 0% to 50% of a nonionic detergent surfactant; and
- (e) from 0% to 70% of a detergency builder;
- wherein the molar ratio of (b):(c) is less than 1.5.

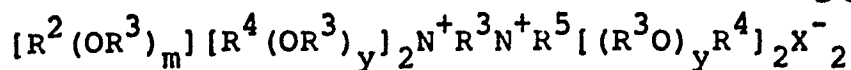
2. The detergent composition of Claim 1 wherein the cationic surfactant (b) is selected from:

- (i) compounds having the general formula:

$$[R^2(OR^3)_m][R^4(OR^3)_y]_zR^5Q^+X^-$$
 wherein Q is N, P or S; z is 1 if Q is S and 2 if Q is N or P; R² is an alkyl or alkyl benzyl group having from 8 to 16 carbon atoms in the alkyl chain; each R³ is selected from -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from H when y is not 0, C₁₋₄ alkyl, C₁₋₄ hydroxyalkyl, benzyl groups, ring structures formed by joining the two R⁴ groups, and -CH₂CHOHCHOHCHCOR⁶CHOHCH₂OH wherein R⁶ is H or any hexose; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than 18; each y is from 0 to 3, m is from 0 to 3 and X is any compatible anion; and
- (ii) aliphatic amines having the formula:

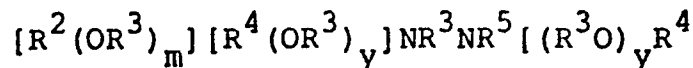
$$[R^2(OR^3)_m][R^4(OR^3)_y]R^5N$$
 wherein R², R³, R⁴, R⁵, m and y are the same as defined above and the pKa is at least 1/2 unit above the initial pH of the wash water;
- (iii) compounds having the general formula:

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wherein R^2 , R^3 , R^4 , R^5 , m , y and X are as defined above;

(iv) compounds having the general formula:

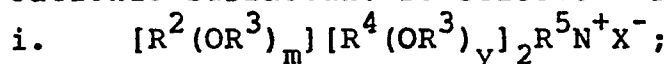


wherein R^2 , R^3 , R^4 , R^5 , m and y are as defined above and the pK_a is at least 1/2 unit above the initial pH of the wash water; and mixtures thereof.

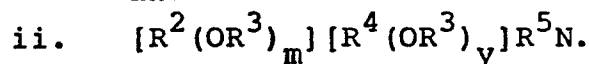
3. A composition according to either one of Claims 1 and 2 wherein the alkylsulfate detergent surfactant is from 3% to 30%, preferably from 5% to 20%, the cationic surfactant is from 1/2% to 8%, preferably from 1/2% to 6% and the sulfonate detergent surfactant is from 2% to 30%, preferably from 3% to 20%.

4. A composition according to any one of Claims 1-3 wherein the alkylsulfate detergent surfactant is selected from alkali metal, ammonium, and substituted ammonium salts of C_{12-15} primary and C_{12-18} secondary alkyl sulfates.

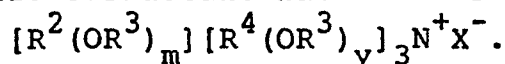
5. A composition according to any one of Claims 1-4 wherein the cationic surfactant is selected from:



and



6. A composition according to any one of Claims 1-4 wherein the cationic surfactant has the formula:



7. A composition according to any one of Claims 1-6 wherein the cationic surfactant is selected from chloride, bromide, methylsulfate salts of C_{8-12} alkyl trimethyl ammonium

surfactants, C₈₋₁₂ alkylhydroxyethyldimethyl ammonium
surfactants, C₈₋₁₂ alkylmethyldihydroxyethyl ammonium
surfactants, C₁₀₋₁₄ alkoxydihydroxyethylmethyl ammonium
surfactants and C₁₀₋₁₄ alkoxyhydroxyethyldimethyl ammonium
surfactants.

8. A composition according to any one of Claims 1-7 wherein the sulfonate detergent surfactant is a secondary alkyl benzene sulfonate having from 9 to 15, preferably from 11 to 13 carbon atoms in the alkyl chain.

9. A composition according to any one of Claims 1-8 wherein the molar ratio of (b):(c) is less than 1.

10. A composition according to any one of Claims 1-9 wherein the sum of the equimolar levels of cationic surfactant and sulfonate detergent surfactant is at least 2%, preferably at least 5% of the total level of anionic surfactant.

11. A composition according to any one of Claims 1-10 wherein the detergency builder is from 10% to 60%, preferably from 20% to 50% by weight of the composition.

12. A composition according to Claim 11 wherein the detergency builder is selected from tripolyphosphates, hexametaphosphates and higher polymerization species, citrates, nitrilotriacetates and water-soluble polyacetals and mixtures thereof.

13. A composition according to any one of Claims 1-12 wherein the nonionic surfactant is from .5% to 10%, preferably from 1% to 5% by weight of the composition.

14. A composition according to Claim 13 wherein the nonionic surfactant is selected from fatty acid amide, amine oxide and ethoxylated alcohol detergent surfactants.

15. A composition according to any one of Claims 1-14 wherein enzymes are present at a level of from .2% to 3% by weight of the composition. 0087914

16. A composition according to any one of Claims 1-15 wherein water soluble salts of fatty acids are present at levels up to 10%.

17. A composition according to Claim 16 wherein the water soluble salts of fatty acids have from 8 to 18 carbon atoms, preferably from 12 to 14 carbon atoms.

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D,A	EP-A-0 026 529 (PROCTER & GAMBLE LTD.) * Page 21; claim 1 *		C 11 D 1/65 C 11 D 1/12 C 11 D 1/38 C 11 D 1/40
D,A	US-A-4 235 759 (K. OHBU et al.) * Claim 1 *		
A	DE-A-2 350 008 (PROCTER & GAMBLE EUROPEAN TECHNICAL CENTER) * Claim 1 *		
A	EP-A-0 026 528 (PROCTER & GAMBLE LTD.) * Abstract; pages 27, 28; examples 4-11 *		
A	DE-A-2 648 304 (PROCTER & GAMBLE EUROPEAN TECHNICAL CENTER) * Claim 1 *		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
Place of search BERLIN			Examiner SCHULTZE D
Date of completion of the search 03-05-1983			
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			