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(54) **Detergent compositions.**

(57) Granular built detergent compositions containing specific mixtures of anionic surfactant, alkoxylated nonionic surfactant and water-soluble cationic surfactant. In highly preferred compositions, the anionic surfactant comprises a sulfate or stulfonate anionic surfactant or a mixture thereof with a fatty acid soap. Especially preferred compositions comprise a mixture of sulfonate and sulfate anionic surfactants. The compositions provide enhanced oil and grease removal from fabrics together with good clay soil detergency, whiteness maintenance and foam control characteristics under realistic multicycle wash conditions.

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DETERGENT COMPOSITIONS

This invention relates to detergent compositions. In particular, it relates to granular detergent compositions suitable for washing fabrics,clothes etc. in automatic washing machines with improved cleaning performance.

Cationic surfactants have been frequently incorporated into detergent compositions of various types. However, the inclusion of such cationic surfactants is generally for the purpose of providing some adjunct fabric care benefit, and not for the purpose of cleaning. For example, certain cationic surfactants have been included in detergent compositions for the purpose of yielding a germicidal or sanitization benefit to washed surfaces, as is disclosed in U.S. Patent 2,742,434, Kopp, issued April 17, 1956; U.S. Patent 3,539,520, Cantor et al, issued November 10, 1970; and U.S. Patent 3,965,026, Lancz, issued June 22, 1976. Other cationic surfactants such as ditallowdimethylammonium chloride, have been included in detergent compositions for the purpose of yielding a fabric-softening benefit, as disclosed in U.S. Patent 3,607,763, Salmon et al, issued September 21, 1971; and U.S. Patent 3,644,203, Lamberti et al, issued February 22, 1972. Such components are also disclosed as being included in detergent compositions for the purpose of controlling static, as well as softeing laundered fabrics, in U.S. Patent 3,951,879, Wixon, issued April 20, 1976; and U.S. Patent 3,959,157 Inamorato, issued May 25, 1976.

Compositions comprising mixtures of anionic, cationic and nonionic surfactants are also known in the art. Thus, compositions conferring enhanced anti-static character to textiles washed therewith are described in B.P. 873,214 and Belgian Patent 829,162 while compositions having enhanced germicidal and detergency performance are

disclosed in B.P. 641,297.

In Applicants European Patent Application No. 225 there is also disclosed a granular detergent composition comprising a mixture of anionic, nonionic and water-soluble cationic surfactants providing improved cleaning performance, especially on greasy and oily soils. For optimum grease detergency performance, however, these compositions require relatively high levels of the cationic and nonionic surfactant components in relation to the anionic surfactant level and this can result in a lack of "robustness", particularly in the areas of clay soil detergency and whiteness maintenance, when the compositions are used in multicycle wash-wear treatments in the presence of rinse-added cationic fabric softener. Moreover, high levels of cationic surfactant can also have a deleterious and intractible effect on the composition's foaming characteristics, thereby raising additional problems of automatic washing machine compatibility. If, on the other hand, the cationic surfactant component is reduced to a level at which foam regulation is no longer a problem, the beneficial grease detergency characteristics of prior art compositions are found to be greatly diminished, particularly when such compositions are used under realistic soil and fabric load/wash liquor ratio conditions.

The Applicants have now discovered, however, that excellent grease and oil removal performance can be secured simultaneously with good clay soil detergency and whiteness maintenance, under realistic multicycle wash-wear conditions, including carry-over of rinse-added softener, by selecting specified mixtures and ratios of anionic, nonionic and water-soluble cationic surfactant materials. The Applicants have further discovered that compositions having improved washing machine compatibility and grease/oil removal performance together with good multicycle clay soil detergency and whiteness maintenance, can be secured by selecting certain anionic, nonionic and water-soluble

cationic surfactant mixtures, wherein the anionic surfactant comprises either a combination of sulfonate and sulfate surfactants or a combination of a sulfate or sulfonate surfactant on the one hand and a fatty acid soap on the other hand.

The invention thus provides granular detergent compositions suitable for heavy duty laundering purposes having improved washing machine compatibility and improved cleaning performance especially on greasy and oily soils without detriment to detergency performance on clay soils and without detriment to the soil suspending or fabric whitening characteristics of the compositions, under realistic soil, fabric load and multi wash-rinse-wear cycle conditions.

According to the present invention, there is provided a granular detergent composition characterized by:-

(a) from about 2% to about 30% of a surfactant system consisting essentially of anionic surfactant, alkoxylated nonionic surfactant, and up to 2%, preferably from 0.2% to 1.5% of water-soluble C_8-C_{16} alkyl quaternary ammonium cationic surfactant, wherein the weight ratio of anionic surfactant:cationic surfactant is from 5.1:1 to 50:1 and the weight ratio of anionic surfactant:nonionic surfactant is from 5.9:1 to 1:3, and

(b) at least about 10% of detergency builder.

Detergent compositions of the present invention contain as an essential ingredient a multi-component active system comprising anionic surfactant, alkoxylated nonionic and water-soluble cationic surfactants. In highly preferred embodi-ments, the anionic surfactant, in turn, comprises a mixture of sulfate and sulfonate surfactants or a mixture of sulfate/sulfonate surfactant with a fatty acid soap. This active system is generally in the range from about 4% to about 20%, more preferably from about 6% to about 15% by weight of the compositions. The weight ratio of anionic: cationic surfactant in the present compositions varies in the range from 5.1:1 to 50:1, especially from about 6:1 to about 20:1, the weight ratio of nonionic:cationic surfactant from about 20:1 to about 1:1, especially from about 10.1 to about 1:1, and the weight

ratio of anionic:nonionic surfactant from 5.9:1 to about 1:3, especially from about 4:1 to about 1:1.

As mentioned above, the cationic surfactant component of the composition of the invention is characterised as being water-soluble. By water solubility, we refer in this context to the solubility of cationic surfactant in monomeric form, the limit of solubility being determined by the onset of micellisation and measured in terms of critical micelle concentration (C.M.C.). The cationic surfactant should thus have a C.M.C. for the pure material greater than about 200 p.p.m. and preferably greater than about 500 p.p.m., specified at 30°C and in distilled water. Literature values are taken where possible, especially surface tension or conductimetric values - see Critical Micelle Concentrations of Aqueous Surfactant Systems, P. Mukerjee and K.J. Mysels, NSRDS-NBS 36, (1971).

Another desirable feature is that the system itself must be water-dispersible or water-soluble in combination with the remainder of the detergent composition. This implies that, in an equilibrium aqueous mixture of the detergent composition (containing about 1000 p.p.m. of surfactant) the surfactant system exists in one or more liquid (as opposed to solid) surfactant/water phases. Expressed in another way, the surfactant system should have a Krafft point of no higher than about 25°C.

A further essential component of the present compositions is at least 10%, preferably from about 20% to about 70% by weight of a detergency builder, for example, a water-soluble inorganic or organic electrolyte. Suitable electrolytes have an equivalent weight of less than about 210, especially less than about 100 and include the common alkaline polyvalent calcium ion sequestering agents. Water-insoluble calcium ion exchange materials can also be used with advantage, however. Surprisingly, it is found that the grease removal performance of the present composi-

tions depends sensitively on the ionic strength and the level of free hardness ions in the detergent liquor and these parameters must be closely controlled for optimum performance. Thus, when the compositions are used in about 1% solution, the builder:surfactant weight ratio is preferably greater than about 1:3, more preferably greater than about 4:1 and especially greater than about 8:1.

Optimum grease and particulate detergency also depends sensitively on the choice of nonionic surfactant and especially desirable from the viewpoint of grease detergency are biodegradable nonionic surfactants having a lower consolute temperature in the range from about 25°C to about 65°C, more preferably from about 30°C to about 50°C Highly suitable nonionic surfactants of this type have the general formula $RO(CH_2CH_2O)_nH$ wherein R is primary or secondary branched or unbranched C_9-C_{15} alkyl or alkenyl and n (the average degree of ethoxylation) is from 2 to 10, especially from 3 to 9. More hydrophilic nonionic detergents can be employed for providing particulate detergency and anti-redeposition, however, for instance, nonionic detergents of the general formula given above wherein R is primary or secondary, branched or unbranched C_8-C_{24} alkyl or alkenyl and n is from 11 to 40. Combinations of the two classes of nonionic surfactants can also be used with advantage of course.

The compositions of the present invention are preferably formulated to have a pH of at least about 6 in the laundry solution at conventional usage concentrations (about 1% by weight) in order to optimize cleaning performance. More preferably, they are alkaline in nature when placed in the laundry solution and have a pH greater than about 7, especially greater than about 8.

The individual components of the composition of the invention will now be described in detail.

The cationic surfactant is a water-soluble quaternary ammonium compound having a critical micelle concentration of at least 200 ppm at 30°C. In structural terms, the preferred cationic surfactant comprises from 1 to about 4 quaternary ammonium groups of which only one has the general formula:-

$$R^1R_3^2N^+$$

wherein each R^1 is a hydrophobic alkyl, alkenyl or alkaryl group totalling from 8 to 16, preferably 10 to 14 carbon atoms optionally linked to the quaternary nitrogen via ether, alkoxy, ester or amide groups, and each R^2 is an alkyl group containing from one to four carbon atoms or a benzyl group with no more than one R^2 in a molecule being benzyl.

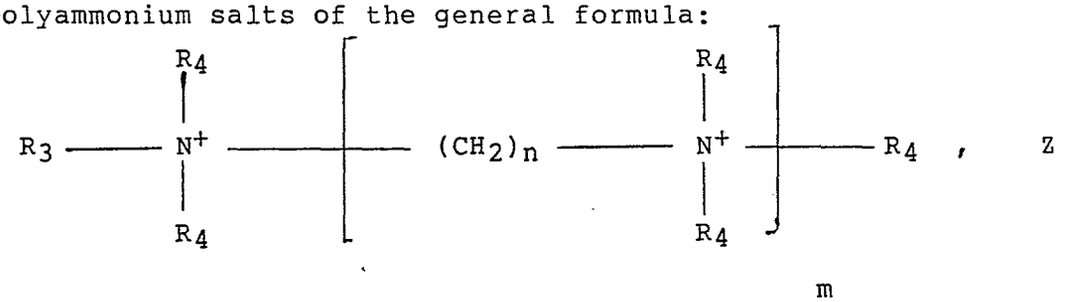
A highly preferred group of cationic surfactants of this type has the general formula:-

$$R^1R_3^2N^+Z$$

wherein R^1 is selected from C_8-C_{16}, preferably C_{10}-C_{14} alkyl, alkenyl and alkaryl groups; R^2 is selected from C_1-C_4 alkyl and benzyl groups; and Z is an anion in number to give electrical neutrality.

Preferred compositions of this mono-long chain type include those in which R^1 is a C_{10}-C_{14} alkyl group and R is methyl. Particularly preferred compositions of this class include C_{12} alkyl trimethylammonium halide, C_{14} alkyl trimethylammonium halide and coconut alkyl trimethylammonium halide.

Another group of useful cationic compounds are the polyammonium salts of the general formula:



m

wherein R_3 is selected from C_8 to C_{16} alkyl, alkenyl and alkaryl groups; each R_4 is C_1-C_4 alkyl; n is from 1 to 6; and m is from 1 to 3.

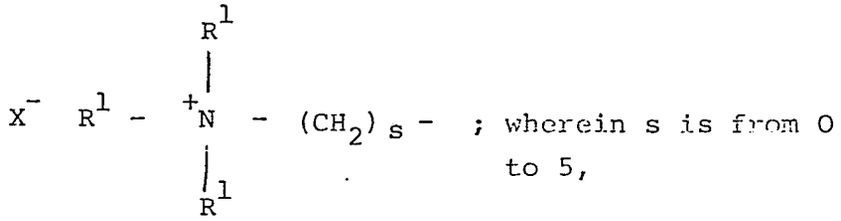
A specific example of a material in this group is:

(1) Coco-alkyl—N^+(CH_3)—$(CH_2)_3$—N^+(CH_3)$_3$, $(CH_3CO_2^-)_2$

A further preferred type of cationic component, which is described in U.S. Patent 4,260,529 and incorporated herein by reference has the formula:

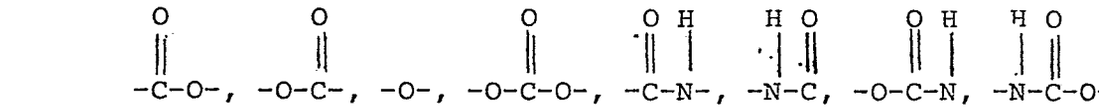
$$R^2 - (Z^1)_a - (R^3)_n - Z^2 - (CH_2)_m - \overset{R^1}{\underset{R^1}{N^+}} - R^1 \quad X^-$$

wherein R^1 is C_1 to C_4 alkyl; R^2 is C_8 to C_{16} straight or branched chain alkyl or alkenyl, alkyl benzene, or



; wherein s is from 0 to 5,

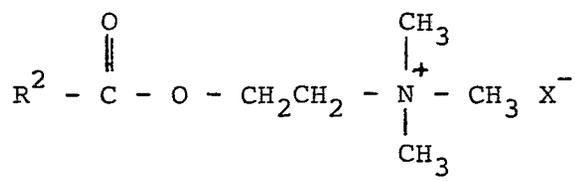
R^3 is C_1 to C_{16} alkyl or alkenyl; a is 0 or 1; n is 0 or 1; m is from 1 to 5; Z^1 and Z^2 are each selected from the group consisting of:



and wherein at least one of said groups is selected from the group consisting of ester, reverse ester, amide and reverse amide; and X is an anion which makes the compound water-soluble, preferably selected from the group consisting of halide, methyl sulfate, hydroxide, and nitrate preferably chloride, bromide or iodine.

In addition to the advantages of the other cationic surfactants disclosed herein, this particular cationic component is enviromentally desirable, since it is biode-, gradable, both in terms of its long alkyl chain and its nitrogen-containing segment.

Particularly preferred cationic surfactants of this type are the choline ester derivatives having the following formula:

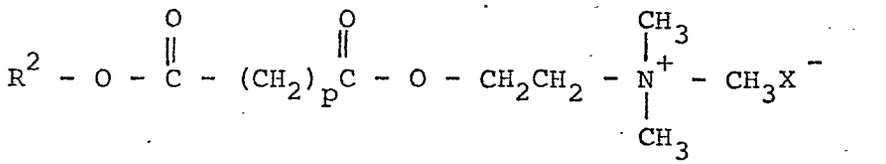


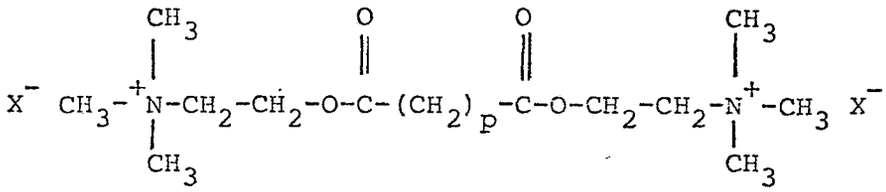
as well as those wherein the ester linkage in the above formula is replaced with a reverse ester, amide or reverse amide linkage.

Particularly preferred examples of this type of cationic surfactant include caproyl choline ester quaternary ammonium halides (R^2 = C_9 alkyl), palmitoyl choline

ester quaternary ammonium halides (R^2 = C_{15} alkyl), myristoyl choline ester quaternary ammonium halides (R^2 = C_{13} alkyl), lauroyl chloine ester ammonium halides (R^2 = C_{11} alkyl), and capryloyl choline ester quaternary ammonium halides (R^2 = C_7 alkyl).

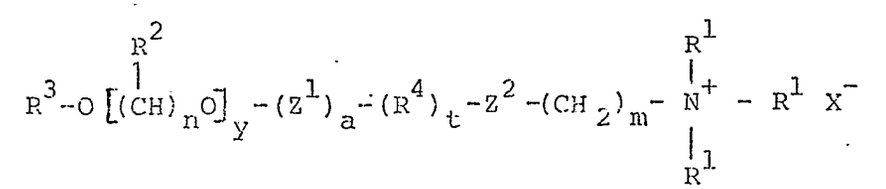
Additional preferred cationic components of the choline ester variety are given by the structural formulas below, wherein p may be from 0 to 16.



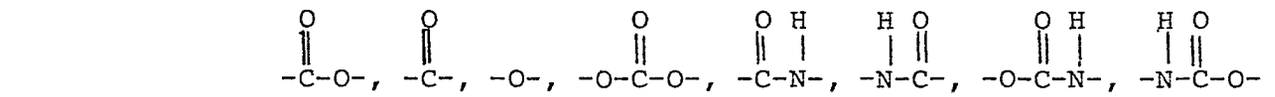


The preferred choline-derivative cationic substances, discussed above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, forming the desired cationic material. The choline-derived cationic materials may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then used to quaternize triethanolamine, forming the desired cationic component.

Another type of novel particularly preferred cationic material, described in U.S. Patent 4,228,042 and incorporated herein by reference, are those having the formula:



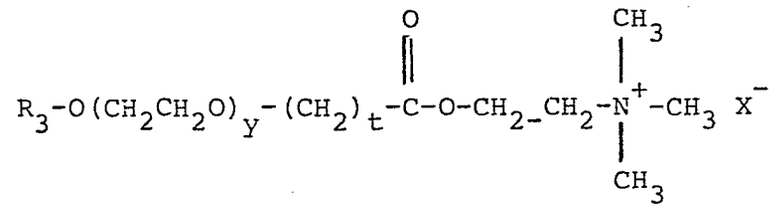
In the above formula, each R^1 is a C_1 to C_4 alkyl group, preferably a methyl group. Each R^2 is either hydrogen or C_1 to C_3 alkyl, preferably hydrogen. R^3 is a C_8 to C_{16} straight or branched chain alkyl, alkenyl, or alkyl benzyl group, preferably a C_8 to C_{16} alkyl group, most preferably a C_{12} alkyl group. R^4 is a C_1 to C_{10} alkylene or alkenylene group. n is from 2 to 4, preferably 2; y is from 1 to 20, preferably from about 1 to 10, most preferably about 7; a may be 0 or 1; t may be 0 or 1; and m is from 1 to 5, preferably 2. Z^1 and Z^2 are each selected from the group consisting of

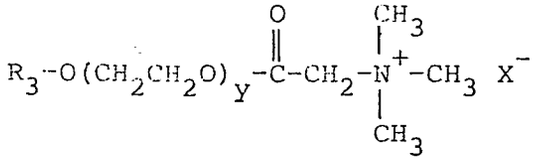


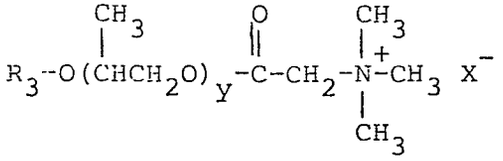
and wherein at least one of said groups is selected from the group consisting of ester, reverse ester, amide and reverse amide. X is an anion which will make the compound water-soluble and is selected from the group consisting of halides, methylsulfate, hydroxide and nitrate, particularly chloride, bromide and iodide.

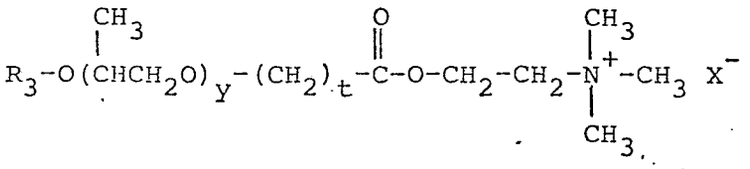
These surfactants, when used in the compositions of the present invention, yield excellent particulate soil, body soil, and grease and oil soil removal. In addition, the detergent compositions control static and soften the fabrics laundered therewith, and inhibit the transfer of dyes in the washing solution. Further, these novel cationic surfactants are environmentally desirable, since both their long chain alkyl segments and their nitrogen segments are biodegradable.

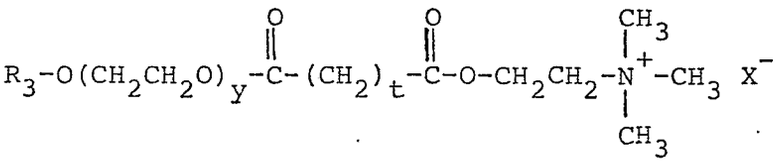
Preferred embodiments of this type of cationic component are the choline esters (R^1 is a methyl group and Z^2 is an ester or reverse ester group), particular formulas of which are given below by which t is 0 or 1 and y is from 1 to 20.

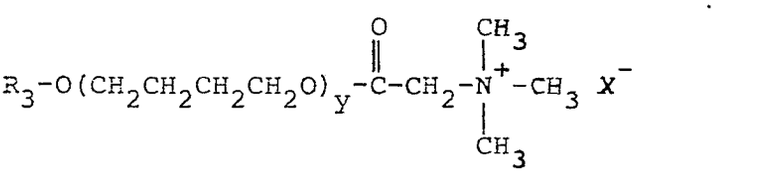


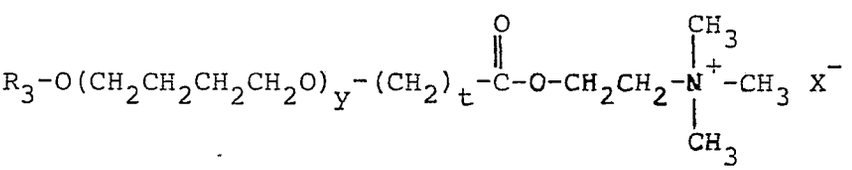












The preferred choline derivatives, described above, may be prepared by the reaction of a long chain alkyl polyalkoxy (preferably polyethoxy) carboxylate, having an alkyl chain of desired length, with oxalyl chloride, to form the corresponding acid chloride. The acid chloride is then reacted with dimethylaminoethanol to form the appropriate amine ester, which is then quaternized with a methyl halide to form the desired choline ester compound. Another way of preparing these compounds is by the direct esterification of the appropriate long chain ethoxylated carboxylic acid together with 2-haloethanol or dimethyl aminoethanol, in the presence of heat and an acid catalyst. The reaction product formed is then quaternized with methylhalide.

The anionic surfactant component of the present compositions preferably comprises either a mixture of sulfonate and sulfate surfactant in a weight ratio of from about 5:1 to about 1:5, more preferably from 5:1 to about 1:1, especially from about 4:1 to about 1.5:1, or a mixture of sulfonate/sulfate surfactants with a fatty acid soap. Such mixtures preferably have a weight ratio of sulfate or sulfonate surfactant to soap of at least about 1:1, especially from about 1:1 to about 20:1.

Regarding the fatty acid soap (i.e., a water-soluble salt of a higher fatty acid), this can be selected from the ordinary alkali metal (sodium, potassium), ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24, preferably from about 10 to about 22 and especially from about 16 to about 22 carbon atoms in the alkyl chain. Suitable fatty acids can be obtained from natural sources such as, for instance, from oil, soybean oil, caster oil, tallow, whale and fish oils, grease, lard and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Napthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from tallow and hydrogenated fish oil.

The sulfate or sulfonate anionic surfactants for use herein can be defined generally as water-soluble salts, particularly alkali metal, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 22, especially from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.)

Suitable synthetic anionic surfactants are water-soluble salts of alkyl benzene sulfonates, alkyl sulfates, alkyl polyethoxy ether sulfates, paraffin sulfonates, alpha-olefin sulfonates, alpha-sulfo-carboxylates and their esters, alkyl glyceryl ether sulfonates, fatty acid monoglyceride sulfates and sulfonates, alkyl phenol polyethoxy ether sulfates, 2-acyloxy-alkane-1-sulfonate, and beta-alkyloxy alkane sulfonate.

Examples of the detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8-C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; and sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in U.S.P. 2,220,099 and 2,477,383 and those prepared by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis)or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS.

A preferred alkyl ether sulfate surfactant component of the present invention is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of about 12 to 16 carbon atoms, preferably from about 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from about 1 to 4 mols of ethylene oxide.

Other anionic detergent compounds herein include the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble salts of esters of α-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; water-soluble salts of paraffin sulfonates containing from about 8 to 24, especially 14 to 18 carbon atoms, and β-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Anionic sulfate/sulfonate surfactant mixtures preferred herein include 5:1 to 1:5 mixtures of an alkyl benzene sulfonate having from 9 to 15 carbon atoms in the alkyl radical and mixtures thereof, the cation being an alkali metal preferably sodium; and either an alkyl sulfate having from 10 to 20 carbon atoms in the alkyl radical or an ethoxy sulfate having from 10 to 20 carbon atoms in the alkyl

radical and from 1 to 30 ethoxy groups and mixtures thereof, having an alkali metal cation, preferably sodium.

The nonionic detergent materials can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic detergents include:

1. The polyethylene oxide condensates of alkyl phenol, eg. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 1 to 40 moles, preferably from 2 to 10 moles of ethylene oxide per mole of alkyl phenol. The alkyl substitutent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene or nonene. Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 5 moles of ethylene oxide per mole of phenol; nonylphenol condensed with 9 moles of ethylene oxide per mole of nonylphenol and di-iso-octylphenol condensed with 5 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 1 to about 40 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 15 carbon atoms and is ethoxylated with between 2 and 10, desirably between 3 and 9 moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent detergency performance on fatty and greasy soils, and in the presence of hardness sensitive

anionic surfactants such as alkyl benzene sulphonates. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived) from natural fats of prepared by the Ziegler process from ethylene, eg. myristyl, cetyl, stearyl alcohols), or partly branched such as the Dobanols and Neodols which have about 25% 2-methyl branching (Dobanol and Neodol being Trade Names of Shell) or Synperonics, which are understood to have about 50% 2-methyl branching (Synperionic is a trade name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45-4, Dobanol 45-7, Dobanol 45-11, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from about 9 to 16 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.

3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of about 1500 to 1800. Such synthetic nonionic detergents are available on the market under the trade name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

A highly preferred mixture of surfactants comprises a C_{8-22} alkyl benzene sulfonate and a C_{9-15} alkanol ethoxylated with from 3 to 9 moles of ethylene oxide per mole of alkanol. A specific preferred mixture comprises C_{12} alkyl benzene sulfonate and C_{14-15} alcohol-(7)-ethoxylate. A C_{18-22} fatty acid soap can also be included.

The detergent composition of the invention also contains at least about 10% of a detergency builder, especially a water-soluble inorganic or organic electrolyte. Suitable 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 include water-insoluble calcium ion exchange materials, however. Non-limiting examples of suitable water-soluble, inorganic detergent builders include: alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates, silicates, sulfates and chlorides. Specific examples of such salts include sodium and potassium tetraborates, perborates, bicarbonates, carbonates, tripolyphosphates, orthophosphates, pyrophosphates, hexametaphosphates and sulfates.

Examples of suitable organic alkaline detergency builders include: (1) water-soluble amino carboxylates and aminopolyacetates, for example, sodium and potassium glycinates, ethylenediamine tetraacetates, nitrilotriacetates, and N-(2-hydroxyethyl)nitrilo diacetates 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.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent No. 755.038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

Another type of detergency builder material useful in the present compositions and processes 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 Belgium Patent 814,874, issued November 12, 1974, incorporated herein by reference. This patent discloses and claims detergent compositions containing sodium aluminosilicates having the formula

$$Na_z(AlO_2)_z(SiO_2)_yXH_2O \quad ,$$

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 about 15 to about 264, said aluminosilicates having a calcium ion exchange capacity of at least 200 milligrams equivalent/gram and a calcium ion exchange rate of at least about 2 grains/gallon/minute/gram. A preferred material is

$$Na_{12}(SiO_2\ AlO_2)_{12}27H_2O$$

The compositions of the present invention can be supplemented by all manner of detergent components, either by including such components in the aqueous slurry to be dried or by admixing such components with the compositions of the invention following the drying step. Soil suspending agents at about 0.1% to 10% by weight such as water-soluble salts of carboxymethyl-cellulose, carboxyhydroxymethyl cellulose, and polyethylene glycols having a molecular weight of about 400 to 10,000 are common components of the present invention. Dyes, pigment optical brighteners, and perfumes can be added in varying amounts as desired.

Other materials such as fluorescers, enzymes in minor amounts, anti-caking agents such as sodium sulfo-succinate, and sodium benzoate can also be added. Enzymes suitable for use herein include those discussed in U.S. Patents 3,519,570 and 3,533,139 to McCarty and McCarty et al issued July 7, 1970 and Janury 5, 1971 respectively.

Anionic fluorescent brightening agents are well-known materials, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2'-disulphonate, disodium 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' -disulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl) -stilbene-2,2'disulphonate, disodium 4,4'bis-(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene -2,2'disulphonate and sodium 2(stilbyl-4''-(naphtho-1',2' :4,5)-1,2,3-triazole-2''-sulphonate.

An alkali metal, or alkaline earth metal, silicate can also be present. The alkali metal silicate preferably is used in an amount from 0.5% to 10% preferably from 3% to 8%. Suitable silicate solids have a molar ratio of SiO_2/ alkali metal$_2$0 in the range from about 0.5 to about 4.0, but

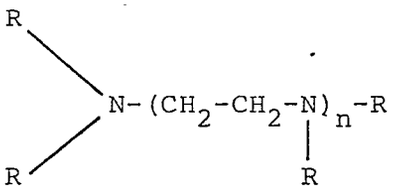
much more preferably from 1.0 to 1.8, especially about 1.6. The alkali metal silicates suitable herein can be commercial preparations of the combination of silicon dioxide and alkali metal oxide, fused together in varying proportions.

The present compositions also contain additional suds regulating components in an amount of from about 0.05% to about 3%. Preferred are microcrystalline waxes having a melting point in the range from 35°C-115°C and saponification value of less than 100. The microcrystalline waxes are substantially water-insoluble, but are water-dispersible in the presence of organic surfactants. Preferred microcrystalline waxes having a melting point from about 65°C to 100°C, a molecular weight in the range from 400-1000; and a penetration value of at least 6, measured at 77°C by ASTM-D1321. Suitable examples of the above waxes include microcrystalline and oxidized microcrystalline petrolatum waxes; Fischer-Tropsch and oxidized Fischer-Tropsch waxes; ozokerite; ceresin; montan wax; beeswax, candelilla; and carnauba wax.

The granular detergent compositions herein can also advantageously contain a peroxy bleaching component in an amount from about 3% to about 40% by weight, preferably from about 8% to about 33% by weight. Examples of suitable peroxy bleach components for use herein include perborates, persulfates, persilicates, perphosphates, percarbonates, and more generally all inorganic and organic peroxy bleaching agents which are known to be adapted for use in the subject compositions. The composition can also advantageously include a bleach activator which is normally an organic compound containing and N-acyl, or an O-acyl (preferably acetyl) group. Preferred materials are N,N,N',N'-tetraacetyl ethylene diamine and N,N,N',N'-tetraacetylglycouril. The bleach activator is preferably added at a level from 0.5% to 5% by weight of composition.

A further preferred ingredient of the instant compositions is from about 0.01 to about 4%, especially from about 0.1 to about 1.0% by weight of a polyphosphonic acid or salt thereof which is found to provide bleachable stain detergency benefits.

Especially preferred polyphosphonates have the formula:-



wherein each R is $CH_2PO_3H_2$ or a water-soluble salt thereof and n is from 0 to 2. Examples of compounds within this class are aminotri-(methylenephosphonic acid), ethylene diamine tetra (methylenephosphonic acid) and diethylene triamine penta (methylene phosphonic acid). Of these, ethylene diamine tetra (methylene phosphonic acid) is particularly preferred.

A further optional component is from about 0.1% to about 3%, especially from about 0.25% to about 1.5% of a polymeric material having a molecular weight of from 2000 to 2,000,000 and which is a copolymer of maleic acid or anhydride and a polymerisable monomer selected from C_1-C_{12} alkyl vinyl ethers, acrylic and methacrylic acid and C_1-C_{20} esters thereof, alkenes having from 2 to 12 carbon atoms, N-vinyl pyrrolidone and styrene. Highly preferred examples of such carboxylates are 1:1 styrene/maleic acid copolymer, di-isobutylene/maleic acid copolymers and methyl vinyl ether/maleic acid copolymers. Other suitable polycarboxylates are poly-α-hydroxy acrylates and lactones thereof as described in Belgian Patent 817,678 and B.P. 1,425,307.

When used in commercial laundry or household washing machines, the compositions of the invention are used as aqueous solutions containing from about 100 to about 3000 p.p.m., especially from about 500 to about 1500 p.p.m. of surfactant.

In a process aspect of the invention, there is provided a method of making the detergent compositions of the invention comprising the steps of spray-drying a crutcher mix containing the anionic, cationic and builder components and subsequently absorbing the nonionic surfactant in liquid or molten form into the spray-dried granules.

The compositions of the invention can also be provided in the form of two or more component products, which are either mixed before use or added separately to a laundry solution to provide a concentration of the four-component surfactant system of from about 100 to about 3000 p.p.m., especially from about 500 to about 1500 p.p.m. Each component product includes one or more of the active ingredients of the surfactant system and a mixture of the products in prescribed amounts should have the requisite granular form. In a preferred embodiment, one product is formulated as a conventional anionic or nonionic detergent composition suitable for use in the main wash cycle of an automatic laundry or washing machine, and the other is formulated as a cationic containing additive or booster product for use simultaneously with the conventional detergent during the main wash. In addition to the cationic, the additive product will contain nonionic and/or anionic surfactant such that the total composition formed by mixing the component products in specified amounts has the requisite surfactant components and levels thereof.

The compositions of the invention can also be formulated as special prewash compositions designed for use before the main wash stage of the conventional laundering cycle. Such prewash compositions will normally consist of a single product component containing the defined active system.

In the Examples which follow, the abbreviations used have the following designations:

LAS	: Linear C_{12} alkyl benzene sulfonate
TAS	: Tallow alkyl sulfate
TAE_n	: Tallow alcohol ethoxylated with n moles of ethylene oxide per mole alcohol.
MTMAC	: Myristyl trimethyl ammonium chloride.
CTMAC	: Coconut alkyl trimethyl ammonium chloride.
Dobanol 45-E-7	: A C_{14}-C_{15} oxo-alcohol with 7 moles of ethylene oxide, marketed by Shell.
Dobanol 45-E-3	: A C_{14}-C_{15} oxo-alcohol with 3 moles of ethylene oxide, marketed by Shell.
Silicate	: Sodium silicate having an SiO_2: Na_2O ratio of 1.6.
Wax	: Microcrystalline wax - Witcodur 272 M.pt 87°C.
Gantrez AN119	: Trade name for maleic anhydride/ vinyl methyl ether copolymer, believed to have an average molecular weight of about 240,000, marketed by GAF. This was pre-hydrolysed with NaOH before addition.
Brightener	: Disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene-2:2'- disulphonate.
TAED	: Tetraacetyl ethylene diamine.
Dequest 2060	: Trade name for diethylene triamine penta (methylene phosphonic acid) marketed by Monsanto.
Dequest 2040	: Trade name for ethylene diamine tetra(methylene phosphonic acid) marketed by Monsanto.

EXAMPLES 1-5

The following compositions are prepared by spray-drying an aqueous slurry of the ingredients except for the Dobanol-derived nonionic surfactants which is sprayed onto the spray-dried granules, and the sodium perborate, TAED and enzyme which are dry mixed into the composition.

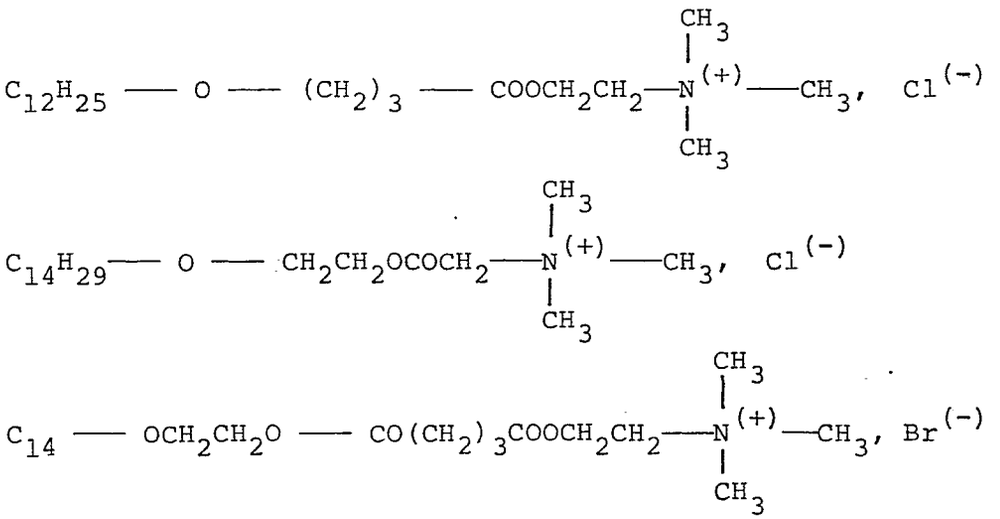
	EXAMPLES				
	1	2	3	4	5
	%	%	%	%	%
LAS	4	9.5	7	12	5
MTMAC	1	1.5	-	2	-
CTMAC	-	-	1	-	1
Dobanol 45-E-7	9	4	5	8	5
Dobanol 45-E-4	-	2	-	4	-
TAE_{11}	-	-	-	-	1
TAE_{25}	1	-	-	-	-
Hyfac (Trade Mark)	-	-	-	-	3
Tallow Soap	3	-	-	-	-
Pentasodium tripolyphosphate	5	10	29	25	22
Disodium pyrophosphate	-	10	3	-	3
Zeolite A (particle size 5μ)	25	5	-	-	-
Gantrez AN119	-	1	0.2	1	0.4
Dequest 2040	0.1	-	0.1	-	0.5
Dequest 2060	0.3	0.5	-	-	-
Silicate	10	4	6	10	8
Protease enzyme	-	-	0.3	0.7	-
Sodium perborate	25	30	24	20	26
TAED	1.5	-	2	-	-
Wax	3	2	2	3	1
Brightener	0.6	0.7	0.5	0.3	0.1
Sodium sulphate, moisture and miscellaneous	——— to 100 ———				

N.B. The level of Zeolite A is given on an anhydrous basis; the material contains 21% water of crystallisation.

These products provide enhanced oil and grease stain-removal performance and improved foam control characteristics without detriment to particulate clay soil detergency, whiteness maintenance and fluorescer brightening characteristics on both natural and man-made fabrics at both high and low wash temperatures.

Products with enhanced performance are also obtained when the sodium alkyl benzene sulphonate is replaced by C_{10}-C_{22} olefine sulphonates, C_{10}-C_{20} paraffin sulphonates, and C_{10}-C_{20} alkyl ether sulphates.

The lauryl or myristyl trimethyl ammonium chloride in the above examples can be replaced by lauryl or myristyl-trimethyl ammonium bromide, decyl trimethyl ammonium chloride, dioctyl dimethyl ammonium bromide, coconut alkyl benzyl dimethyl ammonium chloride, C_{12} alkylbenzyl dimethyl ethyl ammonium chloride, C_{12} alkylbenzyl trimethyl ammonium chloride or one of the following compounds



EXAMPLES 6-10

The following compositions are prepared using the process of Examples 1 to 5.

	EXAMPLES				
	6 %	7 %	8 %	9 %	10 %
LAS	6	10	4	5	7
TAS	2	3	3	1	3
MTMAC	-	0.8	-	-	0.5
CTMAC	1	-	1	1	-
Dobanol 45-E-7	-	1	-	8	-
TAE_{11}	1	-	-	-	1
Hyfac (Trade Mark)	-	2	-	-	1
Tallow Soap	-	-	2	-	-
Pentasodium tripolyphosphate	24	18	15	25	33
Disodium pyrophosphate	-	-	-	3	-
Sodium orthophosphate	-	6	-	-	-
Zeolite A (particle size 5)	-	-	10	-	-
Gantrez AN119	1	1	0.2	1	0.4
Dequest 2040	0.2	-	0.1	-	0.1
Dequest 2060	-	0.4	-	-	0.1
Silicate	10	6	7	8	10
Protease enzyme	1	-	0.5	0.5	-
Sodium perborate	20	30	24	25	22
TAED	1.5	-	2	-	-
Wax	3	-	2	3	1
Parrafin wax	-	1	-	-	-
Brightener	0.6	0.7	0.5	0.3	0.1
Sodium sulphate, moisture and miscellaneous	——— to 100 ———				

N.B. The level of Zeolite A is given on an anhydrous basis; the material contains 21% water of crystallisation.

Under multi-wash-rinse-wear conditions, these products provide enhanced oil and grease stain-removal performance without detriment to particulate clay soil detergency, whiteness maintenance and fluorescer brightening characteristics on both natural and man-made fabrics at both high and low wash temperatures.

CLAIMS

1. A granular detergent composition characterized by:-

(a) from 2% to 30% of a surfactant system comprising:
(i) anionic surfactant,
(ii) alkoxylated nonionic surfactant, and
(iii) up to 2% of water-soluble mono C_8-C_{16} alkyl, alkenyl or alkaryl quaternary ammonium cationic surfactant,
wherein the weight ratio of anionic surfactant:cationic surfactant is from 5.1:1 to 50:1 and the weight ratio of anionic surfactant:nonionic surfactant is from 5.9:1 to 1:3, and

(b) at least 10% of detergency builder.

2. A composition according to Claim 1 characterized in that the anionic surfactant comprises a sulfate or sulfonate surfactant or a mixture thereof with fatty acid soap in a weight ratio of at least 1:1.

3. A composition according to Claim 1 or 2 characterized in that the anionic surfactant comprises a mixture of sulfonate and sulfate surfactants in a weight ratio of from 1:1 to 5:1, preferably from 1.5:1 to 4:1.

4. A composition according to Claims 2 or 3 characterized in that the sulfate or sulfonate anionic surfactant has a C_{10}-C_{20} alkyl or alkaryl group and the soap is a water-soluble salt of a C_{16}-C_{22} fatty acid, the weight ratio of sulfate or sulfonate surfactant to soap lying in the range from 5:4 to 10:1.

5. A composition according to any of Claims 1 to 4 characterized in that the cationic surfactant comprises from 1 to 4 quaternary ammonium groups of which no more than one has the general formula

$$R^1R_3^2N^+$$

wherein R^1 is a hydrophobic alkyl, alkenyl or alkaryl group totalling from 8 to 16 carbon atoms optionally linked to the quaternary nitrogen via ether, alkoxy, ester or amide groups, and each R^2 is an alkyl group containing from 1 to 4 carbon atoms or a benzyl group with no more than one R^2 in a molecule being benzyl.

6. A composition according to Claim 5 characterized in that the cationic surfactant has the general formula:-

$$R^1R_3^2N^+Z$$

wherein R^1 is selected from C_8-C_{16} alkyl, alkenyl and alkaryl groups; R^2 is selected from C_{1-4} alkyl and benzyl groups; and Z is an anion in number to give electrical neutrality.

7. A composition according to any of Claims 1 to 5 characterized in that the cationic surfactant is a water-soluble mono C_{10}-C_{14} alkyl, alkenyl or alkaryl quaternary ammonium surfactant.

8. A composition according to any of Claims 1 to 7 characterized in that the nonionic surfactant has the general formula $RO(CH_2CH_2O)_nH$ wherein R is branched or unbranched C_9-C_{15} alkyl and n, the average degree of ethoxylation, is from 3 to 9.

9. A composition according to any of Claims 1 to 8 characterized in that the weight ratio of anionic surfactant to cationic surfactant is from 6:1 to 20:1, the weight ratio of anionic surfactant to nonionic surfactant is from 4:1 to 1:1 and the surfactant system comprises from 4% to 20% of the detergent composition.

10. A compositions according to any of Claims 1 to 9 characterized in that it additionally comprises from 3% to 40% of peroxy bleach and from 0.5% to 5% of an organic peroxyacid bleach precursor.