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(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
One Procter & Gamble Plaza
Cincinnati
Ohio 45202 (US)

(72) Inventor: **Buckley, Christopher David**
71 Windsor Terrace,
South Gosforth
Newcastle on Tyne NE3 1YL (GB)
Inventor: **Hindson, Allyson Jane**
4 Castleton Close,
Cramlington
Northumberland NE23 9YS (GB)

(74) Representative: **Canonici, Jean-Jacques et al**
Procter & Gamble European Technical Center N.V.
Temselaan 100
B-1853 Strombeek-Bever (BE)

(54) **Softening through the wash compositions.**

(57) A detergent composition comprising a crystalline layered silicate having the formula

$NaMSi_xO_{2x+1}\ yH_2O$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. and a flocculating polymer selected from polymers and copolymers derived from monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, ethylene imine or mixtures thereof characterized in that said detergent composition comprises less than 5% of clay by weight of the detergent composition.

Rank Xerox (UK) Business Services
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Field of Invention

The present invention relates to detergent compositions containing a silicate softening system. More in particular, the present invention relates to softening through the wash detergent compositions comprising layered silicates and flocculating polymers.

Background of the Invention

Detergent compositions providing fabric softening throughout the wash cycle have been described in art. In particular, clays are well known as fabric softening agents through the wash. The relative ability of the softening clays to meet various performance criteria is very much depending on the presence and concentration of adjunct detergent ingredients.
An example of such adjunct detergent ingredient is the presence of nonionic surfactants.
Said nonionic surfactants, when used at substantial concentrations inhibit the deposition of the clay onto the fabric. So far it was therefore necessary to limit the level of nonionic surfactants in clay containing softening through the wash compositions.

It has now been found that the combination of layered silicate and a flocculating polymer provide an efficient softening system which is fully compatible with nonionic surfactants. This finding allows to formulate detergent compositions which have both excellent softening and cleaning performance.

Another type of adjunct detergent ingredient that can be added to detergent compositions are dye transfer inhibiting polymers. Said polymers are added to detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto other fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Polymers have been used within detergent compositions to inhibit dye transfer. Examples of such polymers are vinylpyrrolidone polymers such as described EP-A-265 257 and EP 508 034. Unfortunately, said vinylpyrrolidone polymers tend to interact with the clays formulated therewith. Accordingly, the dye transfer inhibiting performance of the polymers and the softening performance of the clays are negatively affected.

It has now been found that polyvinylpyrrolidone polymers are very compatible with the silicate softening system in that the dye transfer inhibiting performance of the polymers is not negatively affected in the presence of the silicate softening system. In addition, it has been found that the softening performance of layered silicates formulated with dye transfer inhibiting polymers has been maintained.

This finding allows us to formulate detergent compositions which have both excellent dye transfer inhibiting properties and softening performance.

According to the present invention, an alternative softening system is obtained which provides softening through the wash performance without adversely affecting the overall detergency performance of the detergent formulated therewith.

Layered silicates have been described in WO 92/03525 as builders in detergent compositions.
Accordingly, the present invention allows to use the silicates in a dual function, e.g. builder and softener thereby facilitating the formulation of compact detergents.

Summary of the Invention

The present invention relates to detergent compositions comprising layered silicate and flocculating polymers.

Detailed description of the invention

The compositions of the present invention comprise as an essential element a crystalline layered sodium silicate having the general formula

$NaMSi_xO_{2x+1}\ yH_2O$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0 164 514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purposes of the present invention x, in the general formula above has a value of 2,3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the α, β, γ and δ-forms of $Na_2Si_20_5$. These materials are available from Hoechst AG FRG as respectively NaSKS-5, NaSKS7, NaSKS-11 and NaSKS-6. The most preferred material is $-Na_2Si_20_5$, NaSKS-6.

Flocculating agents

The softening system herein comprises a flocculating agent.

The compositions herein comprise, from 0.05% to 20% by weight of the silicate, of flocculating agent, if its molecular weight is 150.000-800.000 and from 0.005% to 2%, by weight of the silicate, if its molecular weight is from 800.000 to 5 million. Most of these materials are fairly long chain polymers and copolymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, ethylene imine. Gums, like guar gum, are suitable as well.

Preferred are polymers of ethylene oxide, acryl amide, or acrylic acid. For proper interaction with the silicate, the polymers should be fairly long chain, i.e., have a weight average molecular weight of at least 100,000. For sufficient water-solubility the weight average molecular weight of the polymers should not exceed 10 million. Most preferred are polymers having a weight average molecular weight of from 150.000 to 1 million.

It should be understood that clay is present in the detergent compositions according to the present invention by less than 5% by weight of the detergent composition. More preferably, the clay is present in the detergent composition by less than than 1%, most preferably the detergent composition is substantially free of clay.

DETERGENT ADJUNCTS

A wide range of surfactants can be used in the detergent compositions. A typical listing of nonionici, anionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961.

NONIONICS :

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal™ CO- 630, marketed by the GAF Corporation; and Triton™ X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol™ 15-S-9 (the condensation product of C_{11}-C_{15} linear alcohol with 9 moles ethylene oxide), Tergitol™ 24-L-6 NMW (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol™ 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-6.5 (the condensation product of C_{12}-C_{13} linear alcohol with 6.5 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-4 (the condensation product of C_{14}-C_{15} linear alcohol with 4 moles of ethylene oxide) marketed by Shell Chemical Company, and Kyro™ EOB (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglucosides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglucosides and tallow alkyl tetra-, penta-, and hexaglucosides.

The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)_t(\text{glycosyl})_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position).
The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

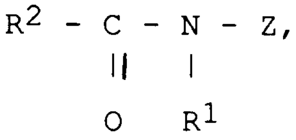
Although not preferred, the condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant of the nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C_8-C_{14} alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C_8-C_{18} alcohol ethoxylates (preferably C_{10} avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydoxy fatty acid amide surfactants.

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



$$R^2-\underset{\underset{O}{\|}}{C}-\underset{\underset{R^1}{|}}{N}-Z,$$

wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

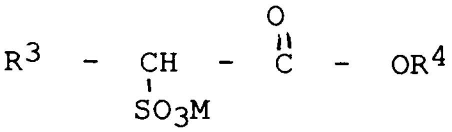
When included in such laundry detergent compositions, the nonionic surfactant systems of the present invention act to improve the greasy/oily stain removal properties of such laundry detergent compositions across a broad range of laundry conditions.

ANIONIC SURFACTANTS

Suitable anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12}-$C_{18}E(1.0)M$), C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12}-$C_{18}E(2.25)M$), C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12}-$C_{18}E(3.0)M$), and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12}-$C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



$$R^3-\underset{\underset{SO_3M}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OR^4$$

wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10}-C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10}-C_{16} alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants hereof are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethylammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C_{12}-C_{16} are preferred for lower wash temperatures (e.g. below about 50 ° C) and C_{16-18} alkyl chains are preferred for higher wash temperatures (e.g. above about 50 ° C).

Other anionic surfactants useful for detersive purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulfonates, C_8-C_{22} primary of secondary alkanesulfonates, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C_{12}-C_{18} monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C_6-C_{12} diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k$-CH_2COO-$M+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

The laundry detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as nonionic surfactants other than those already described herein. Preferred cationic surfactant systems include nonionic and ampholytic surfactants. Cationic detersive surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula :

$$[R^2(OR^3)_y][R^4(OR^3)_y]_2R^5N+X-$$

wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH$-$CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; 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 about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :

$$R_1R_2R_3R_4N^+X^- \qquad (i)$$

wherein R_1 is C_8-C_{16} alkyl, each of R_2, R_3 and R_4 is independently C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and - $(C_2H_{4 0})_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2, R_3 or R_4 should be benzyl.

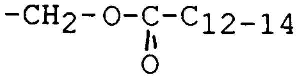
The preferred alkyl chain length for R_1 is C_{12}-C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis.

Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;

coconut methyl dihydroxyethyl ammonium chloride or bromide;
decyl triethyl ammonium chloride;
decyl dimethyl hydroxyethyl ammonium chloride or bromide;
C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
coconut dimethyl hydroxyethyl ammonium chloride or bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl (ethenoxy)$_4$ ammonium chloride or bromide;
choline esters (compounds of formula (i) wherein R_1 is



$$-CH_2-O-\underset{\underset{O}{\|}}{C}-C_{12-14}$$

alkyl and $R_2R_3R_4$ are methyl).
di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 25%, preferably from about 3% to about 15% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the laundry detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

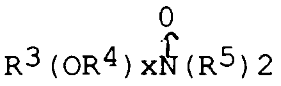
When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in laundry detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



$$R^3(OR^4)_x\overset{\overset{O}{\uparrow}}{N}(R^5)_2$$

wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures therof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The present invention further provides laundry detergent compositions comprising at least 1% by weight, preferably from about 3% to about 65%, more preferably from about 10% to about 25% by weight of total surfactants.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B or HS.

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phtalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates. Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (sks/6), and a water-soluble carboxylate chelating agent such as citric acid.

A suitable chelant for inclusion in the detergent compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include Na_2EDDS and Na_4EDDS. Examples of such preferred magnesium salts of EDDS include MgEDDS and Mg_2EDDS. The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

Preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Other builder materials that can form part of the builder system for use in granular compositions the purposes of the invention include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amiono polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW

2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Detergent ingredients that can be included in the detergent compositions of the present invention include bleaching agents.

These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present bleaching compounds will typically be present at levels of from about 1% to about 10%, of the detergent composition. In general, bleaching compounds are optional components in non-liquid formulations, e.g. granular detergents. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition.

The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art.

In a method aspect, this invention further provides a method for cleaning fabrics, fibers, textiles, at temperatures below about 50 ° C, especially below about 40 ° C, with a detergent composition containing polyamine N-oxide containing polymers, optional auxiliary detersive surfactants, optional detersive adjunct ingredients, and a bleaching agent.

The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

Preferably, the bleaches suitable for the present invention include peroxygen bleaches. Examples of suitable water-soluble solid peroxygen bleaches include hydrogen peroxide releasing agents such as hydrogen peroxide, perborates, e.g. perborate monohydrate, perborate tetrahydrate, persulfates, percarbonates, peroxydisulfates, perphosphates and peroxyhydrates. Preferred bleaches are percarbonates and perborates.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylethylenediamine (TAED), nonanoyloxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5,-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters (ATC) such as disclosed in Copending European Patent Application No. 91870207.7.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Other peroxygen bleaches suitable for the present invention include organic peroxyacids such as percarboxylic acids.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

Other detergent ingredients that can be included are detersive enzymes which can be included in the detergent formulations for a wide variety of purposes including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of refugee dye transfer.

The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.05 mg to about 3 mg, of active enzyme per gram of the composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B.subtilis and B.licheniforms. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames Alcalase, Savinase and Esperase by Novo Industries A/S (Denmark) and Maxatase by International Bio-Synthetics, Inc. (The Netherlands) and FN-base by Genencor, Optimase and opticlean by MKC.

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A is described in European Patent Application 130,756. Protease B is described in European Patent Application Serial No. 87303761.8. Amylases include, for example, -amylases obtained from a special strain of B.licheniformis, described in more detail in British Patent Specification No. 1,296,839 (Novo). Amylolytic proteins include, for example, Rapidase, Maxamyl (International Bio-Synthetics, Inc.) and Termamyl, (Novo Industries).

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from Humicola insolens. Suitable cellulases are also disclosed in GB-A-2.075.028 ; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800, and cellulases produced by a fungus of Bacillus N or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusc (Dolabella Auricula Solander).

Other suitable cellulases are cellulases originated from Humicola Insulens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Such cellulase are described in Copending European patent application No. 93200811.3, filed March 19, 1993.

Especially suitable cellulase are the cellulase having color care benefits. Examples of such cellulases are cellulase described in European patent application No. 91202879.2, filed November 6, 1991 Carezyme (Novo).

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunoligical cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P".

Especially suitable Lipase are lipase such as M1 Lipase (Ibis) and Lipolase (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes of pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase.

Peroxidase-containing detergent compositions are disclosed, for example, in PCT Internation Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.

In liquid formulations, an enzyme stabilization system is preferably utilized. Enzyme stabilization techniques for aqueous detergent compositions are well known in the art. For example, one technique for enzyme stabilization in aqueous solutions involves the use of free calcium ions from sources such as calcium acetate, calcium formate and calcium propionate. Calcium ions can be used in combination with short chain carboxylic acid salts, preferably formates. See, for example, U.S. patent 4,318,818. It has also been proposed to use polyols like glycerol and sorbitol. Alkoxy-alcohols, dialkylglycoethers, mixtures of polyvalent alcohols with polyfunctional aliphatic amines (e.g., such as diethanolamine, triethanolamine, di-isopropanolamime, etc.), and boric acid or alkali metal borate. Enzyme stabilization techniques are additionally disclosed and exemplified in U.S. patent 4,261,868, U.S. Patent 3,600,319, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5. Non-boric acid and borate stabilizers are preferred. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319 and 3,519,570.

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent aplication N 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

Especially preferred detergent ingredients are combinations with technologies which also provide a type of color care benefit. Examples to these technologies are polyvinylpyrrolidone polymers such as described in EP 0 508 034. The detergent compositions herein contain a polyvinylpyrrolidone ("PVP" having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 20,000. Suitable polyvinylpyrrolidones are commercially available from GAF Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (average molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

Polyvinylpyrrolidones known to persons skilled in the detergent field; see for example EP-A-262,897 and EP-A-256,696. Th amount of polyvinylpyrrolidone used in the present detergent compositions should be from about 0.01% to about 5% by weight of the detergent, preferably from about 0.05% to about 3% by weight, and more preferably from about 0.1% to about 2% by weight. The amount of polyvinylpyrrolidone delivered in the wash solution is from about 0.5 ppm to about 300 ppm, preferably from about 1 ppm to about 60 ppm, more preferably from about 1 ppm to about 30 ppm, and most preferably from about 1 ppm to about 20 ppm.

Preferred polymers for inhibiting dye transfer are polyamine-N-oxide containing polymers such as described in Copending European patent application No. 92202168.8 and No. 93201198.4.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However, the amount of amine oxide groups present in the polyamine oxide containing polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

The polyamine N-oxide containing polymers of the present invention are typically present from 0.001 to 10%, more preferably from 0.0-1 to 2%, most preferred from 0.05 to 1% by weight of the detergent composition.

Other preferred polymers are N-vinylimidazole N-vinylpyrrolidone copolymers such as described in Copending European patent application No. 93870155.4.

The N-vinylimidazole N-vinylpyrrolidone polymers have an average molecular weight range from 5000-1,000,000, preferably from 20 000-200,000.

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

Other examples of detergent ingredients that provide a type of color care benefit are cellulase, peroxidase and metallo catalysts. Such metallo catalysts are described in copending European Patent application No. 92870181.2.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures.

Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alcanols. Suitable 2-alkyl-alcanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N° 92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^R.

Other preferred suds controlling agents are described in EP 495 345. These suds controlling agents comprise a silicone antifoam compound, a carrier material and an organic coating material further containing glycerol at a weight ratio with the silicone antifoam compound of 1:2 to 3:1.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Other components used in detergent compositions may be employed, such as soil-suspending agents soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and non-encapsulated and encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616.

Other suitable water soluble encapsulating materials comprise dextrins derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrins are,preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consisits of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydrideacrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium $4,4^1$-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-$2:2^1$ disulphonate, disodium 4, - 4^1-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-$2:2^1$ - disulphonate, disodium $4,4^1$ - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-$2:2^1$ - disulphonate, monosodium $4^1,4^{11}$ -bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2-sulphonate, disodium $4,4^1$ -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-$2,2^1$ - disulphonate, disodium $4,4^1$ -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-$2,2^1$ disulphonate, disodium $4,4^1$bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6- ylamino)stilbene-$2,2^1$disulphonate and sodium 2(stilbyl-4^{11}-(naphtho-$1^1,2^1$:4,5)-1,2,3 - triazole-2^{11}-sulphonate.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.
These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula

$$(CH_3(PEG)_{43})_{0.75}(POH)_{0.25}[T\text{-}PO)_{2.8}(T\text{-}PEG)_{0.4}]T(PO\text{-}H)_{0.25}((PEG)_{43}CH_3)_{0.75}$$

where PEG is $-(OC_2H_4)O-$,PO is (OC_3H_6O) and T is $(pcOC_6H_4CO)$.

Also very useful are modified polyesters as random copolymers of dimethyl terephtalate, dimethyl sulfoisophtalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephtalic acid, about 16% by weight of propane - 1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoid acid and about 15% by weight of sulfoisophtalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

The detergent compositions according to the invention can be in liquid, paste, gels, bars or granular forms. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt. The liquid compositions according to the present invention can also be in "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically, the water content of the concentrated liquid detergent is less than 30%, more preferably less than 20%, most preferably less than 10% by weight of the detergent compositions.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 75 °C, especially 20 to 60, but the polymers are effective at up to 95 °C and higher temperatures. The pH of the treatment solution is preferably from 7 to 11, especially from 7.5 to 10.5.

The process and compositions of the invention can also be used as detergent additive products.

Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

The detergent compositions according to the present invention include compositions which are to be used for cleaning substrates, such as fabrics, fibers, hard surfaces, skin etc., for example hard surface cleaning compositions (with or without abrasives), laundry detergent compositions, automatic and non automatic dishwashing compositions.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention, said scope being determined according to claims which follow.

EXAMPLE I (A/B/C/D)

The efficiency of the layered silicate/flocculating polymer combination as a softening system was assessed by measuring the softening performance.

The softening performance was measured by a launderometer test. The test procedure was as follows : 3.5 kg of clean fabric laundry loads were washed in an automatic drum washing machine Miel 423 at 60 °C. The hardness of the water was 2mM Calcium and the composition concentration was 0.7% in the wash liquor.

A bundle of soiled fabrics containing fabrics which were stained with particulate soil was washed with a detergent composition with/without the silicate softening system.

Comparative softening assessment was done by expert judges using a scale of 0 to 4 panel-score-units (PSU). In this scale 0 is given for no difference and 4 is given for maximum difference.

A granular detergent composition according to the present invention is prepared, having the following compositions :

Table I

% by weight of the total detergent composition	
Linear alkyl benzene sulphonate	13.70
Tallow alkyl sulphate	5.9
C_{45} alcohol 7 times ethoxylated	4.00
Trisodium citrate	5.00
Zeolite	26.00
Maleic acid actylic acid copolymer	4.9
Diethylenetriaminepentamethylene Phosphonic acid	0.6
Protease	1.5
carboxymethylcellulose	1.5
suds supressor (silicone)	0.3

Example I demonstrates the softening performance of the layered silicate in combination with the flocculating polymer versus compositions containing layered silicate without flocculating polymers. The flocculating polymer that was used is polyethylene oxide having an average molecular weight of 300,000. The layered silicate that was used is layered silicate (SKS-6).

Experimental conditions :

pH = 10.5
Wash Temperature : 40 ° C

A : A detergent composition according to Table I which contains no layered silicate and no flocculating polymer.
B : A detergent composition according to Table I which contains 9% of layered silicate and no flocculating polymer.
C : A detergent composition according to Table I containing 0.3% of flocculating polymer and no layered silicate.
D : A detergent composition according to Table I containing 0.3% flocculating polymer and 9% layered silicate.

Results :

PSU values for the softening performance (reference IA).
Bleeding fabric composition: 100% cotton) and PSU values

	IB	IC	ID
PSU	0	0	1.5

The above results demonstrate that the combination of the flocculating polymers and silicate provides statistically significant softening performance.

EXAMPLE II (A/B) :

The efficiency of the silicate softening system was assessed by measuring the softening and cleaning performance.

The softening and cleaning performance was measured by a launderometer test. The test procedure was as follows : 3.5 kg of clean fabric laundry loads were washed in an automatic drum washing machine Miel 423 at 60 ° C. The hardness of the water was 2mM Calcium and the composition concentration was 0.7% in the wash liquor.

A bundle of soiled fabrics containing fabrics which were stained with particulate soil was washed with a detergent composition with/without the silicate softening system. Comparative softening and cleaning assessment was done by expert judges using a scale of 0 to 4 panel-score-units (PSU).

In this scale 0 is given for no difference and 4 is given for maximum difference.

A : A detergent composition according to Table I which contains no layered silicate and no flocculating polymer.

B : A detergent composition according to Table I which contains 9% of layered silicate and 0.3% of a flocculating polymer.

Experimental conditions :

pH = 10.5
Wash Temperature : 40 ° C

RESULTS

	A	B
SOFTENING (psu)	0	+1.5
CLEANING (psu)	0	+0

As can be seen from the above, the cleaning performance is not negatively affected by the presence of the silicate softening system.

EXAMPLE I (A/B/C/D/E)

A compact granular detergent composition according to the present invention is prepared, having the following formulation:

% by weight of the total detergent composition					
	A	B	C	D	E
Linear alkyl benzene sulphonate	11.40	-	-	-	5
Polyhydroxy fatty acid amide	-	10	-	5	5
Alkyl alkoxylated sulfate	-	-	9	9	9
Tallow alkyl sulphate	1.80	1.80	1.80	4	4
C_{45} alkyl sulphate	3.00	3.00	3.00	-	-
C_{45} alcohol 7 times ethoxylated	4.00	4.00	4.00	-	-
Tallow alcohol 11 times ethoxylated	1.80	1.80	1.80	5	5
Dispersant	0.07	0.07	0.07	0.07	0.07
Silicone fluid	0.80	0.80	0.80	0.80	0.80
Trisodium citrate	14.00	14.00	14.00	14.00	14.00
Citric acid	3.00	3.00	3.00	3.00	3.00
Zeolite	32.50	32.50	32.50	32.50	32.50
Maleic acid acrylic acid co-polymer	5.00	5.00	5.00	5.00	5.00
Carezyme	0.1	0.1	0.1	0.1	0.1
Alkalase/BAN	0.60	0.60	0.60	0.60	0.60
Lipolase	0.36	0.36	0.36	0.36	0.36
Savinase	0.6	0.6	0.6	0.6	0.6
Sodium silicate	2.00	2.00	2.00	2.00	2.00
Sodium sulphate	3.50	3.50	3.50	3.50	3.50
Polyvinyl pyrrolidone	0-1	0-1	0-1	0-1	0-1
Perborate	-	-	-	15	-
TAED		-		5	5
Percarbonate	-	-	-		20
Layered Silicate	9	9	9	9	9
polyethylene oxide	0.3	0.3	0.3	0.3	0.3
foam control agent(*)	0.1	0.1	0.1	0.1	0.1
Perfume	0.4	0.4	0.4	0.4	0.4
Perfume encapsulated	0.4	0.4	0.4	0.4	0.4
Minors	up to 100				

(*) Suds suppressor : agglomerate comprising 11% by weight of the component of polydimethylsiloxane, 14% Tallow alcohol ethoxylated, 5% of C12-C22 hydrogenated fatty acids and 70% starch.

The above compositions (Example I (A/B/C/D/E)) were very good at displaying excellent softening, cleaning and detergency performance with outstanding color-care performance on colored fabrics and mixed loads of colored and white fabrics.

EXAMPLE II (A/B/C/D)

A liquid detergent composition according to the present invention is prepared, having the following compositions :

% by weight of the total detergent composition				
	A	**B**	**C**	**D**
Linear alkylbenzene sulfonate	10	-	-	-
Polyhydroxy fatty acid amide	-	5	-	3
Alkyl alkoxylated sulfate	-	-	9	4
Alkyl sulphate	4	8	4	15
Fatty alcohol (C_{12}-C_{15}) ethoxylate	12	12	12	5
Fatty acid	10	10	10	10
Oleic acid	4	4	4	-
Citric acid	1	1	1	1
Diethylenetriaminepentamethylene Phosphonic acid	1.5	1.5	1.5	1.5
NaOH	3.4	3.4	3.4	3.4
Propanediol	1.5	1.5	1.5	1.5
Ethanol	10	10	10	10
Ethoxylated tetraethylene pentamine	0.7	0.7	0.7	0.7
Thermamyl R 300 KNU/g	0.1	0.1	0.1	0.1
Carezyme R 5000 CEVU/g	0.02	0.02	0.02	0.02
Protease 40 mg/g	1.8	1.8	1.8	1.8
Lipolase R 100 KLU/g	0.1	0.1	0.1	0.1
Endoglucanase A 5000 CEVU/g	0.5	0.5	0.5	0.5
Suds supressor (ISOFOL^{r})	2.5	2.5	2.5	2.5
H_2O_2	7.5	7.5	-	-
Polyvinyl pyrrolidone	0.1-1	0.1-1	0.1-1	0.1-1
layered silicate	9	9	9	9
polyethylene oxide	0.3	0.3	0.3	0.3
Minors	up to 100			

EXAMPLE III (A/B/C/D/E)

A compact granular detergent composition according to the present invention is prepared, having the following formulation:

% by weight of the total detergent composition					
	A	B	C	D	E
Linear alkyl benzene sulphonat	11.40	-	-	-	-
Polyhydroxy fatty acid amide	-	10	-	-	-
Alkyl alkoxylated sulfate	-	-	9	9	9
Tallow alkyl sulphate	1.80	1.80	1.80	1.80	1.80
C_{45} alkyl sulphate	3.00	3.00	3.00	3.00	3.00
C_{45} alcohol 7 times ethoxylate	4.00	4.00	4.00	4.00	4.00
Tailors alcohol 11 times ethoxylated	1.80	1.80	1.80	1.80	1.80
Dispersant	0.07	0.07	0.07	0.07	0.07
Silicone fluid	0.80	0.80	0.80	0.80	0.80
Trisodium citrate	14.00	14.00	14.00	14.00	14.00
Citric acid	3.00	3.00	3.00	3.00	3.00
Zeolite	32.50	32.50	32.50	32.50	32.50
Diethylenetriamine pentanethylene phosphonic acid	0.6	0.6	0.6	0.6	0.6
Maleic acid acrylic acid copolymer	5.00	5.00	5.00	5.00	5.00
Carezyme	0.1	0.1	0.1	0.1	0.1
Savinase	0.60	0.60	0.60	0.60	0.60
Lipolase	0.36	0.36	0.36	0.36	0.36
Sodium silicate	2.00	2.00	2.00	2.00	2.00
Sodium sulphate	3.50	3.50	3.50	3.50	3.50
Percarbonate	-	-	-	20	-
Perborate	15	15	15	-	-
TAED	5	-	5	5	-
N-vinylimidazole N-vinylpyrrolidone copolymer	0.1-1	0.1-1	0.1-1	0.1-1	0.1-1
Metallo catalyst	0.1-1	0.1-1	0.1-1	0.1-1	0.1-1
Poly(4-vinylpyridine)-N-oxide	0.1-1	0.1-1	0.1-1	0.1-1	0.1-1
layered silicate	9	9	9	9	9
polyethylene oxide	0.3	0.3	0.3	0.3	0.3
peroxidase	-	0.1	0.1	-	-
Minors	up to 100				

EXAMPLE IV (A/B/C/D)

A liquid detergent composition according to the present invention is prepared, having the following compositions :

% by weight off the total detergent composition				
	A	**B**	**C**	**D**
Linear alkylbenzene sulfonate	10	-	-	-
Polyhydroxy fatty acid amide	-	5	-	3
Alkyl alkoxylated sulfate	-	-	9	4
Alkyl sulphate	4	8	4	15
Fatty alcohol (C_{12}-C_{15}) ethoxylate	12	12	12	5
Fatty acid	10	10	10	10
Oleic acid	4	4	4	-
Citric acid	1	1	1	1
Diethylenetriaminepentamethylene Phosphonic acid	1.5	1.5	1.5	1.5
NaOH	3.4	3.4	3.4	3.4
Propanediol	1.5	1.5	1.5	1.5
Ethanol	10	10	10	10
Ethoxylated tetraethylene pentamine	0.7	0.7	0.7	0.7
Thermamyl R 300 KNU/g	0.1	0.1	0.1	0.1
Carezyme R 5000 CEVU/g	0.02	0.02	0.02	0.02
Protease 40 mg/g	1.8	1.8	1.8	1.8
Lipolase R 100 KLU/g	0.1	0.1	0.1	0.1
Endoglucanase A 5000 CEVU/g	0.5	0.5	0.5	0.5
Suds supressor (ISOFOL^r)	2.5	2.5	2.5	2.5
H_2O_2	7.5	7.5	-	-
N-vinylimidazole N-vinylpyrrolidone copolymer	0.1-1	0.1-1	0.1-1	0.1-1
Metallo catalyst	0.1-1	0.1-1	0.1-1	0.1-1
Poly(4-vinylpyridine)-N-oxide	0.1-1	0.1-1	0.1-1	0.1-1
layered silicate	9	9	9	9
polyethylene oxide	0.3	0.3	0.3	0.3
peroxidase	0.1	0.1	-	-
Minors	up to 100			

The above compositions (Example II (A/B/C/D), III (A/B/C/D/E) and IV (A/B/C/D) were very good at displaying excellent cleaning and detergency performance with outstanding color-care performance on colored fabrics and mixed loads of colored and white fabrics.

Claims

1. A detergent composition comprising a crystalline layered silicate having the formula

   $NaMSi_xO_{2x+1}\ yH_2O$

   wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. and a flocculating polymer selected from polymers and copolymers derived from monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, ethylene imine or mixtures thereof characterized in that said detergent composition comprises less than 5% of clay by weight of the detergent composition.

2. A detergent composition according to claim 1 wherein x has a value of 2.

3. A detergent composition according to claims 1 -2 wherein M is sodium.

4. A detergent composition according to claims 1-3 wherein the silicate is α, β, γ or δ -Na2Si2O5

5. A detergent composition according to claims 1-4 wherein the flocculating polymer is a polymer of ethylene oxide, acryl amide, or acrylic acid.

6. A detergent composition according to claims 1-5 further characterized in that clay is present in an amount less than 1% by weight of the detergent composition, more preferably is substantially free of clay.

7. A detergent composition according to claims 1-6 further comprising surfactants, builders and enzymes.

8. A detergent composition according to claims 1-7 which is a in the form of a liquid, granular, paste, bar or gel.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 9041

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.6)
A	WO-A-92 07928 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) * page 1, paragraph 4 - page 2; examples * ---	1-8	C11D3/12 C11D3/37
A	WO-A-92 18594 (THE PROCTER & GAMBLE COMPANY) * claims; example 2 * ---	1-8	
A	EP-A-0 267 371 (HOECHST AG.) * the whole document * ---	1-8	
A	WO-A-92 07932 (THE PROCTER & GAMBLE COMPANY) * claims 1,3; example 7 * ---	1-8	
A	WO-A-92 16608 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) * claims; examples * ---	1-8	
A	EP-A-0 160 873 (HOECHST AG.) * the whole document * ---	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP-A-0 012 346 (BAYER AG.) * the whole document * -----	1	C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 April 1994	Blas, V

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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