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<p>(21) International Application Number: PCT/US92/05269 (22) International Filing Date: 24 June 1992 (24.06.92) (30) Priority data: 91201773.8 8 July 1991 (08.07.91) EP (34) Countries for which the regional or international application was filed: BE et al. (71) Applicant (for all designated States except US): THE PROCTER &amp; GAMBLE COMPANY [US/US]; One Procter &amp; Gamble Company, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only) : CONVENTS, Andre, Christian [BE/BE]; Drielandenstraat 14, B-1831 Diegem (BE). BUSCH, Alfred [DE/BE]; Handelsstraat 210, B-1840 Londerzeel (BE). PRETTY, Alastair, John [GB/GB]; 4 Whinbank Darras Hall, Newcastle Upon Tyne NE20 9HX (GB).</p>	<p>(74) Agent: HUGHETT, Eileen, L.; The Procter &amp; Gamble Company, Ivorydale Technical Center, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US). (81) Designated States: CA, CS, FI, HU, JP, KR, NO, PL, RU, US, OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). <b>Published</b> <i>With international search report.</i></p>	
<p>(54) Title: DETERGENT COMPOSITIONS CONTAINING POLYHYDROXY FATTY ACID AMIDE SURFACTANTS AND A CLAY SOFTENING SYSTEM</p>		
<div style="text-align: center; margin-top: 100px;"> <math display="block">  \begin{array}{ccccccc}  &amp; &amp; \text{O} &amp; &amp; \text{R}^1 &amp; &amp; \\  &amp; &amp;    &amp; &amp;   &amp; &amp; \\  \text{R}^2 &amp; - &amp; \text{C} &amp; - &amp; \text{N} &amp; - &amp; \text{Z}  \end{array}  \quad (\text{I})  </math> </div>		
<p>(57) Abstract</p> <p>Detergent compositions are disclosed, comprising a polyhydroxy fatty acid amide surfactant of formula (I), wherein R<sup>1</sup> is H, C<sub>1</sub>-C<sub>4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5</sub>-C<sub>31</sub> hydrocarbyl and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls connected directly to said chain, or alkoxyated derivatives thereof and a clay-softening system.</p>		

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DETERGENT COMPOSITIONS CONTAINING POLYHYDROXY  
FATTY ACID AMIDE SURFACTANTS AND A CLAY  
SOFTENING SYSTEM

Field of Invention

The present invention relates to softening through the wash compositions containing a clay softening system.

Background of the Invention

Clays, in particular smectite clays are known fabric-softening agents, and their use in fabric-softening through the wash has been disclosed in the art. Representative of this art is GB-B-1 400 898. Yet, it is equally well recognized that deposition of these clays is far from complete; in fact, under typical European laundry conditions, less than half of the available clay is deposited onto the fabrics, the remainder being rinsed away with the laundry liquor during the subsequent rinsing steps.

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One reason for the incomplete deposition has found to be the negative interaction between clay and conventional nonionic surfactants when used at substantial levels (i.e. in excess of 4%) .

So far it was therefore necessary to limit the level of nonionic surfactants in clay-containing softening through the wash compositions in order to achieve good softening performance of the clay, or to add a clay-flocculating agent, such as disclosed in EP-A-299 575.

It has now been found that certain polyhydroxy fatty acid amides which act as nonionic surfactant, are better compatible with fabric softening clays .

This finding allows to formulate softening through the wash compositions which exhibit better cleaning performance due to the higher levels of nonionic surfactant now affordable, and in better softening performance, due to the increased deposition of clay, without the absolute need for clay-flocculating agents.

#### Background Art on polyhydroxy fatty acid amides

A variety of polyhydroxy fatty acid amides have been described in the art. U.S. Patent 2,965,576 and G.B. Patent 809,060 relate to detergent compositions containing anionic surfactants and certain amide surfactants, which can include N-methyl glucamide, added as a low temperature suds enhancing agent.

U.S. Patent 2,703,798 relates to aqueous detergent compositions containing the condensation reaction product of N-alkyl glucamine and an aliphatic ester of a fatty acid. The product of this reaction is said to be useable in aqueous detergent compositions without further purification.

PCT International Application WO 83/04412 relates to amphiphilic compounds containing polyhydroxyl aliphatic

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groups said to be useful for a variety of purposes including use as surfactants in cosmetics, drugs, shampoos, lotions, and eye ointments.

U.S. Patent 2,982,737 relates to detergent bars containing urea, sodium lauryl sulfate anionic surfactant, and an N-alkylglucamide nonionic surfactant which is selected from N-methyl, N-sorbityl lauramide and N-methyl, N-sorbityl myristamide.

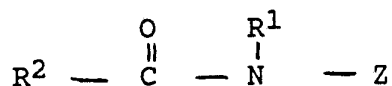
Other glucamide surfactants are disclosed, for example in DT 2,226,872, which relates to washing compositions comprising one or more surfactants and builder salts selected from polymeric phosphates, sequestering agents, and washing alkalis.

G.B. Patent 745,036 relates to heterocyclic amides and carboxylic esters thereof that are said to be useful as chemical intermediates, emulsifiers, wetting and dispersing agents, detergents, textile softeners, etc.

#### Summary of the Invention

The present invention provides a detergent compositions comprising :

- (a) at least about 1% by weight of a polyhydroxy fatty acid amide surfactant of the formula :



wherein  $R^1$  is H,  $C_1$ - $C_4$  hydrocarbyl, 2 hydroxyethyl, 2-hydroxypropyl, or a mixture thereof,  $R^2$  is  $C_5$ - $C_{31}$  hydrocarbyl and

Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls connected directly to said chain, or alkoxylated derivatives thereof;

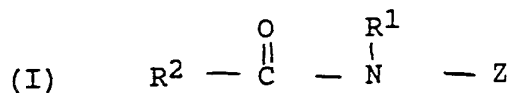
(b) a clay-softening system.

### Detailed Description of the Invention

#### Polyhydroxy Fatty Acid Amide Surfactant

The compositions hereof will comprise at least about 1%, typically from about 3% to about 50%, preferably from about 3% to about 30%, of the polyhydroxy fatty acid amide surfactant described below.

The polyhydroxy fatty acid amide surfactant component of the present invention comprises compounds of the structural formula :



wherein :  $R^1$  is H,  $C_1$ - $C_4$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably  $C_1$ - $C_4$  alkyl, more preferably  $C_1$  or  $C_2$  alkyl, most preferably  $C_1$  alkyl (i.e., methyl); and  $R^2$  is a  $C_5$ - $C_{31}$  hydrocarbyl, preferably straight chain  $C_7$ - $C_{19}$  alkyl or alkenyl, more preferably straight chain  $C_9$ - $C_{17}$  alkyl or alkenyl, most preferably straight chain  $C_{11}$ - $C_{17}$  alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a reducing sugar in reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. It should be understood that these corn syrups may yield a mix of sugar components for Z. Z preferably will be selected from the

group consisting of  $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2-\text{OH}$ ,  $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-(\text{CHOH})_2-(\text{CHOR}')-(\text{CHOH})-\text{CH}_2\text{OH}$ , and alkoxyated derivatives thereof, where  $n$  is an integer from 3 to 5, inclusive, and  $R'$  is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein  $n$  is 4, particularly  $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$ .

In formula (I),  $R^1$  can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

$R^2-\text{CO}-\text{N}<$  can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, U.S. Patent 2,965,576, U.S. Patent 2,703,798 and U.S. Patent 1,985,424.

In a preferred process for producing N-alkyl or N-hydroxyalkyl, N-deoxyglycityl fatty acid amides wherein the glycityl component is derived from glucose and the N-alkyl or N-hydroxyalkyl functionality is N-methyl, N-ethyl, N-propyl, N-butyl, N-hydroxyethyl, or N-hydroxypropyl, the product is made by reacting N-alkyl- or N-hydroxyalkyl glucamine with a fatty ester selected from fatty methyl esters, fatty ethyl esters, and fatty triglycerides in the

presence of a catalyst selected from the group consisting of trilithium phosphate, trisodium phosphate, tripotassium phosphate, tetrasodium pyrophosphate, pentapotassium tripolyphosphate, lithium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, disodium tartrate, dipotassium tartrate, sodium potassium tartrate, trisodium citrate, tripotassium citrate, sodium basic silicates, potassium basic silicates, sodium basic aluminosilicates, and potassium basic aluminosilicates, and mixtures thereof. The amount of catalyst is preferably from about 0.5 mole % to about 50 mole %, more preferably from about 2.0 mole % to about 10 mole %, on an N-alkyl or N-hydroxyalkyl-glucamine molar basis. The reaction is preferably carried out at from about 138°C to about 170°C for typically from about 20 to about 90 minutes. When triglycerides are utilized as the fatty ester, the reaction is also preferably carried out using from about 1 to about 10 weight % of a phase transfer agent, calculated on a weight percent basis of total reaction mixture, selected from saturated fatty alcohol polyethoxylates, alkylpolyglycosides, linear glycamide surfactant, and mixtures thereof.

Preferably, this process is carried out as follows :

- (a) preheating the fatty ester to about 138°C to about 170°C;
- (b) adding the N-alkyl or N-hydroxyalkyl glucamine to the heated fatty acid ester and mixing to the extent needed to form a two-phase liquid/liquid mixture;
- (c) mixing the catalyst into the reaction mixture; and
- (d) stirring for the specified reaction time.

Also preferably, from about 2% to about 20% of preformed linear N-alkyl/N-hydroxyalkyl, N-linear glucosyl fatty acid amide product is added to the reaction mixture, by weight of the reactants, as the phase transfer agent if the fatty



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ester is a triglyceride. This seeds the reaction, thereby increasing reaction rate.

The polyhydroxy "fatty acid" amide materials used herein also offer the advantages to the detergent formulator that they can be prepared wholly or primarily from natural, renewable, non-petrochemical feedstocks and are degradable. They also exhibit low toxicity to aquatic life.

It should be recognized that along with the polyhydroxy fatty acid amides of Formula (I), the processes used to produce them will also typically produce quantities of nonvolatile by-product such as esteramides and cyclic polyhydroxy fatty acid amide. The level of these by-products will vary depending upon the particular reactants and process conditions. Preferably, the polyhydroxy fatty acid amide incorporated into the detergent compositions hereof will be provided in a form such that the polyhydroxy fatty acid amide-containing composition to be added to the detergent contains less than about 10%, preferably less than about 4%, of cyclic polyhydroxy fatty acid amide. The preferred processes described above are advantageous in that they can yield rather low levels of by-products, including such cyclic amide by-product.

#### The clay softening system

The clay softening system comprises a fabric softening clay and, although this is not strictly necessary, it may additionally comprise a clay flocculating agent and/or a humectant.

The fabric softening clay  
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The clay softening system hereof will comprise a fabric softening clay present in an amount of at least 0.5%, preferable from 4% to 30% by weight of the detergent composition. The preferred clays are of the smectite type.

Smectite type clays are widely used as fabric softening ingredients in detergent compositions. Most of these clays have a cation exchange capacity of at least 50 meq./100g.

Smectite clays can be described as three-layer expandable materials, consisting of aluminosilicates or magnesium silicates.

There are two distinct classes of smectite-type clays; in the first, aluminium oxide is present in the silicate crystal lattice, in the second class of smectites, magnesium oxide is present in the silicate crystal lattice.

The general formulas of these smectites are  $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2$  and  $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_2$ , for the aluminium and magnesium oxide type clay, respectively. The range of the water of hydration can vary with the processing to which the clay has been subjected. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , as well as  $\text{H}^+$  can be co-present in the water of hydration to provide electrical neutrality.

It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in equilibrium exchange reactions with cations present in aqueous solutions. In such equilibrium reactions, one equivalent weight of solution cation

replaces an equivalent of sodium, for example, and it is customary to measure clay cation exchange capacity in terms of milliequivalents per 100g. of clay (meq/100g.).

The cation exchange capacity of clays can be measured in several ways, including electro dialysis, by exchange with ammonium ion followed by titration, or by a methylene blue procedure, all as set forth in Grimshaw, *The Chemistry and Physics of Clays*, Interscience Publishers, Inc. pp. 264-265 (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. for kaolinites to about 150 meq/100 g., and greater, for certain clays of the montmorillonite variety. Illite clays have an ionexchange capacity somewhere in the lower portion of the range, ca. 26 meq/100 g. for an average illite clay.

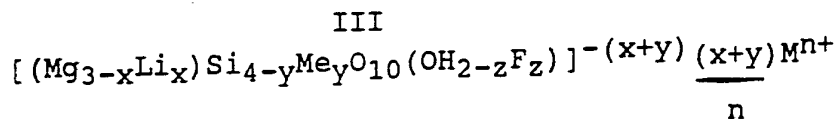
It has been determined that illite and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the instant compositions. Indeed such illite and kaolinite clays constitute a major component of clay soils. However, smectites, such as nontronite having a ionexchange capacity of approximately 50 meq/100 g.; saponite, which has an ionexchange capacity greater than 70 meq/100g., have been found to be useful fabric softeners.

The smectite clays commonly used for this purpose herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under commercial names such as "fooler clay" (clay found in a relatively thin vein above the main bentonite or montmorillonite veins in the Black Hills) and various tradenames such as Thixogel #1 (also, "Thixo-Jell") and Gelwhite GP from Georgia Kaolin Co. Elizabeth, New Jersey; Volclay BC and Volclay #325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH 450, from

International Minerals and Chemicals; and Veegum Pro and Veegum F, from R.T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained under the foregoing commercial and tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

Preferred for use herein are the montmorillonite clays having an ion exchange capacity of 50 to 100 meq/100 g which corresponds to ca 0.2 to 0.6 layer charge.

Quite suitable are hectorites of natural origin, in the form of particles having the general formula



wherein  $\text{Me}^{\text{III}}$  is Al, Fe, or B; or  $y=0$ ;  $\text{M}^{n+}$  is a monovalent ( $n=1$ ) or divalent ( $n=2$ ) metal ion, for example selected from Na, K, Mg, Ca, Sr.

In the above formula, the value of  $(x+y)$  is the layer charge of the hectorite clay.

Such hectorite clays are preferably selected on the basis of their layer charge properties, i.e. at least 50% is in the range of from 0.23 to 0.31.

More suitable are hectorite clays of natural origin having a layer charge distribution such that at least 65% is in the range of from 0.23 to 0.31.

The hectorite clays suitable in the present composition should preferably be sodium clays, for better softening activity.

Sodium clays are either naturally occurring, or are naturally-occurring calcium-clays which have been treated so as to convert them to sodium-clays. If calcium-clays are used in the present compositions, a salt of sodium can be

added to the compositions in order to convert the calcium clay to a sodium clay. Preferably, such a salt is sodium carbonate, typically added at levels of up to 5% of the total amount of clay.

Examples of hectorite clays suitable for the present compositions include Bentone EW and Macaloid, from NL Chemicals, N.J., U.S.A., and hectorites from Industrial Mineral Ventures.

#### Clay-flocculating agents

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The compositions herein may comprise, from 0.05% to 20% by weight of the clay, of flocculating agent, if its molecular weight is 150.000-800.000 and from 0.005% to 2 %, by weight of the clay, 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 clay particles, 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 5 million.

The organic humectant optionally employed in the clay agglomerates herein, may be any of the various water soluble materials utilized for such a purpose. The organic humectant is preferably selected from the group consisting of a) aliphatic hydrocarbon polyols having from 2 to 9 carbon atoms; b) ether alcohols derived from the polyols of a); c) ester alcohols derived from the polyols of a); d) mono- and oligosaccharides; and mixtures thereof.

Highly preferred humectants include glycerol, ethylene glycol, propylene glycol and the dimers and trimers of glycerol, of ethylene glycol and of propylene glycol.

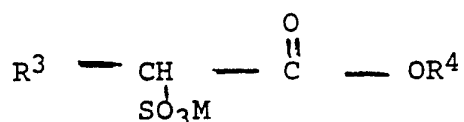
The clay softening system can comprise from 0.5% to 30%, preferably from 2% to 15%, of the humectant by weight of the clay.

#### Deterasive Surfactant System

In addition to the polyhydroxy fatty acid amide herein, the present compositions may contain one or more additional surfactants which can be anionic, cationic or nonionic. Typically the surfactant system will include one or more anionic and/or nonionic surfactants in addition to the polyhydroxy fatty acid amide. It is especially preferred to include an anionic surfactant for effective overall cleaning under a wide variety of wash conditions. In particular, the benefits of this invention are especially realized when the compositions hereof include hardness sensitive surfactants such as alkyl sulfates, alkyl ester sulfonates (e.g., methyl ester sulfonates), alkyl alkoxyated sulfonates (e.g., alkyl ethoxyated sulfonates), and alkyl benzene sulfonates (e.g., linear alkyl benzene sulfonate). The further inclusion of a conventional nonionic surfactant, such as an alkyl

ethoxylate or an alkyl polyglycoside, as described below, is desirable. However, the levels of such conventional nonionic surfactants in clay-containing detergent compositions have to be limited, in view of a negative interaction with the clay. (Accordingly, conventional nonionic surfactants should not be present at levels in excess of 4% by weight of the detergent composition.) Typically, the amount of additional deterative surfactant present is from 1% to 50% by weight, of the detergent composition, preferably from 3% to 40%, more preferably from 5% to 30%.

Suitable anionic surfactants include alkyl ester sulfonate surfactants of the structural formula :



wherein R<sup>3</sup> is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof, R<sup>4</sup> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salts would include metal salts such as sodium, potassium, and lithium salts, and substituted or unsubstituted ammonium salts, such as methyl-, dimethyl-, trimethyl-, and quaternary ammonium cations, e.g. tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine, and triethanolamine. Preferably, R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl, and R<sup>4</sup> is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R<sup>3</sup> is C<sub>14</sub>-C<sub>16</sub> alkyl.

Alkyl sulfate surfactants of the formula ROSO<sub>3</sub>M wherein R is a C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C<sub>10</sub>-C<sub>20</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, and M is H or a

cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like. Typically, alkyl chains of C<sub>12</sub>-C<sub>16</sub> are preferred for lower wash temperatures (e.g., below 50°C) and C<sub>16</sub>-C<sub>18</sub> alkyl chains are preferred for higher wash temperatures (e.g., above 50°C).

Alkyl alkoxyated sulfate surfactants of the formula RO(A)<sub>m</sub>SO<sub>3</sub>M wherein R is an unsubstituted C<sub>10</sub>-C<sub>24</sub> alkyl or hydroxyalkyl group having a C<sub>10</sub>-C<sub>24</sub> alkyl component, preferably a C<sub>12</sub>-C<sub>20</sub> alkyl or hydroxyalkyl, more preferably C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between 0.5 and 6, more preferably between 0.5 and 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 ethoxyated sulfates as well as alkyl propoxyated 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 and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate, C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (2.25) sulfate, C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (3.0) sulfate, and C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium.

These salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>9</sub>-C<sub>20</sub> linear



alkylbenzenesulphonates, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulphonates, and C<sub>8</sub>-C<sub>24</sub> olefinsulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, 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 N-acyl isethionates, acyl taurates, fatty acid amides of methyl tauride, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate, diesters of sulfosuccinate (especially saturated and unsaturated C<sub>6</sub>-C<sub>14</sub> diesters), N-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<sub>2</sub>CH<sub>2</sub>O)<sub>k</sub>CH<sub>2</sub>COO-M<sup>+</sup> wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation and fatty acids esterified with isethionic acid and neutralized with sodium hydroxide. 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 Shwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678.

Suitable conventional nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678. Exemplary, non-limiting classes of useful nonionic surfactants are :

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. Commercially available nonionic surfactants of this type include Igepal<sup>TM</sup>CO-630, marketed by the GAF Corporation; and Triton<sup>TM</sup>X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company.

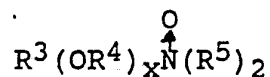
These surfactants are commonly referred to as alkyl phenol alkoxyates, e.g., alkyl phenol ethoxyates.

The condensation products of C<sub>12</sub>-22 aliphatic alcohols with from 1 to 25 moles of ethylene oxide. Examples of commercially available nonionic surfactants of this type include Tergitol<sup>TM</sup>15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear secondary alcohol with 9 moles ethylene oxide), Tergitol<sup>TM</sup>24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol<sup>TM</sup>45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup>23-6.5 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 6.5 moles of ethylene oxide), Neodol<sup>TM</sup>45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>TM</sup>45-4 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro<sup>TM</sup>EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. These surfactants are commonly referred to as alkyl ethoxyates.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. Examples of compounds of this type include certain of the commercially-available Pluronic<sup>TM</sup> surfactants, marketed by BASF.

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

Amine oxides, having the formula

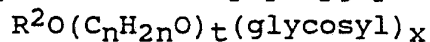


wherein  $R^3$  is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from 8 to 22 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms or mixtures thereof;  $x$  is from 0 to 3; and each  $R^5$  is an alkyl or hydroxyalkyl group containing from 1 to 3 carbon atoms or a polyethylene oxide group containing from 1 to 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.

Preferred are  $C_{10}$ - $C_{18}$  alkyl dimethyl amine oxides and  $C_8$ - $C_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides.

Alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986.

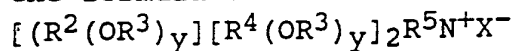
The preferred alkylpolyglycosides have the formula



wherein  $R^2$  is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms;  $n$  is 2 or 3, preferably 2;  $t$  is from 0 to 10, preferably 0; and  $x$  is from 1.3 to 10, preferably from 1.3 to 3, most preferably from 1.3 to 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 predominantly the 2-position.

Cationic deterative surfactants can also be included in detergent compositions of the present invention. Cationic

surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula :



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 10 and the sum of the  $y$  values is from 0 to about 15; and  $X$  is any compatible anion.

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044.

#### Other Surfactants

Ampholytic surfactants can be incorporated into the detergent compositions hereof. 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 chain or branched. 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 for examples of ampholytic surfactants.

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. 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 for examples of zwitterionic surfactants.

Ampholytic and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

#### Form of the composition and conditions of utilization

The compositions of the present invention can be either in particulate form, or in form of an aqueous dispersion of the clay particles, depending on the required conditions of utilization. In either form, the composition of the invention can be added during the main wash stage or during a rinse cycle of the washing process.

The particulate form encompasses both "regular" and high density "compact" executions.

#### Detergent Builders

Detergent compositions of the present invention can comprise inorganic or organic detergent builders to assist in mineral hardness control.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. Liquid formulations typically comprise at least 1%, more typically from 5% to 50%, preferably 5% to 30%, by weight of detergent builder.

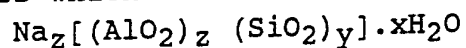
Granular formulations typically comprise at least 1%, more typically from 10% to 80%, preferably from 15% to 50% by weight of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of phosphonates, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates.

Examples of silicate builders are the alkali metal silicates, particularly those having a  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839. However, other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesquicarbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001.

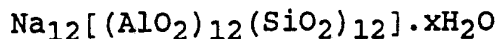
Aluminosilicate builders are especially useful in the present invention. Preferred aluminosilicates are zeolite builders which have the formula



wherein  $z$  and  $y$  are integers of at least 6, the molar ratio of  $z$  to  $y$  is in the range from 1.0 to 0.5, and  $x$  is an integer from 15 to 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be

crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula :



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Examples of phosphonate builder salts are the water-soluble salts of ethane 1-hydroxy-1, 1-diphosphonate particularly the sodium and potassium salts, the water-soluble salts of methylene diphosphonic acid e.g. the trisodium and tripotassium salts and the water-soluble salts of substituted methylene diphosphonic acids, such as the trisodium and tripotassium ethylidene, isopropylidene benzylmethylidene and halo methylidene phosphonates. Phosphonate builder salts of the aforementioned types are disclosed in U.S. Patent Nos. 3,159,581 and 3,213,030, U.S. Patent No. 3,422,021, and U.S. Patent Nos. 3,400,148 and 3,422,137.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates.

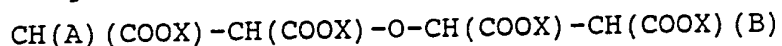
Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium salts, especially sodium salts, or ammonium and

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substituted ammonium (e.g., alkanolammonium) salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates. A number of ether polycarboxylates have been disclosed for use as detergent builders. Examples of useful ether polycarboxylates include oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, U.S. Patent 3,635,830.

A specific type of ether polycarboxylates useful as builders in the present invention also include those having the general formula :

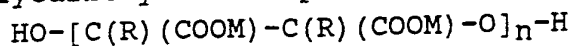


wherein A is H or OH; B is H or -O-CH(COOX)-CH<sub>2</sub>(COOX);

and X is H or a salt-forming cation. For example, if in the above general formula A and B are both H, then the compound is oxydisuccinic acid and its water-soluble salts. If A is OH and B is H, then the compound is tartrate monosuccinic acid (TMS) and its water-soluble salts. If A is H and B is -O-CH(COOX)-CH<sub>2</sub>(COOX), then the compound is tartrate disuccinic acid (TDS) and its water-soluble salts. Mixtures of these builders are especially preferred for use herein. Particularly preferred are mixtures of TMS and TDS in a weight ratio of TMS to TDS of from 97:3 to 20:80. These builders are disclosed in U.S. Patent 4,663,071.

Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates represented by the structure :





wherein M is hydrogen or a cation wherein the resultant salt is water-soluble, preferably an alkali metal, ammonium or substituted ammonium cation, n is from 2 to 15 (preferably n is from 2 to 10, more preferably n averages from 2 to 4) and each R is the same or different and selected from hydrogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> substituted alkyl (preferably R is hydrogen).

Still other ether polycarboxylates include copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxybenzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid.

Organic polycarboxylate builders also include the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids. Examples of polyacetic builder salts include the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid and nitrilotriacetic acid.

Also included are polycarboxylates, such as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, benzene pentacarboxylic acid, and carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof, is a polycarboxylate builder of particular importance for heavy duty liquid detergent formulations, but can also be used in granular compositions. Suitable salts include the metal salts such as sodium, lithium, and potassium salts, as well as ammonium and substituted ammonium salts.

Other carboxylate builders include the carboxylated carbohydrates disclosed in U.S. Patent 3,723,322, Diehl.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Alkyl succinic acids typically are of the general formula R-CH(COOH)CH<sub>2</sub>(COOH) i.e., derivatives of succinic acid, wherein R is hydrocarbon, e.g., C<sub>10</sub>-C<sub>20</sub> alkyl or alkenyl, preferably C<sub>12</sub>-C<sub>16</sub> or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents, all as described in the above-mentioned patents.

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

Specific examples of succinate builders include : laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263.

Examples of useful builders also include sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, water-soluble polyacrylates (these polyacrylates having molecular weight to above 2,000 can also be effectively utilized as dispersants), and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226. These polyacetal carboxylates can be prepared by bringing together, under polymerization conditions, an ester of glyoxylic acid and a polymerization initiator. The

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resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

Polycarboxylate builders are also disclosed in U.S. Patent 3,308,067. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalonic acid.

Other organic builders known in the art can also be used. For example, noncarboxylic acids, and soluble salts thereof, having long chain hydrocarbyls can be utilized. These would include materials generally referred to as "soaps". Chain lengths of C<sub>10</sub>-C<sub>20</sub> are typically utilized. The hydrocarbyls can be saturated or unsaturated.

#### Enzymes

Enzymes can be included in the detergent formulations for a 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. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE<sup>TM</sup> and SAVINASE<sup>TM</sup> by Novo Industries A/S (Denmark) and MAXATASE<sup>TM</sup> by International Bio-Synthetics, Inc. (The Netherlands).

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Amylolytic proteins include, for example, RAPIDASE™, International Bio-Synthetics, Inc. and TERMAMYL™, Novo Industries.

The cellulases usable in the present invention include both bacterial or fungal cellulase.

Suitable lipase enzymes for detergent usage include those sold under the tradename Lipolase<sup>R</sup> by Novo Industries.

Commercial deterative enzymes are typically used at levels of 0.001% to 2%, and higher, in the present compositions.

#### Bleaching Compounds - Bleaching Agents and Bleaching Activators

The detergent compositions hereof may contain bleaching agents or bleaching compositions containing bleaching agent and one or more bleaching activators.

One category of bleaching agents that can be used encompasses both a peroxyacid per se and systems which are able to yield peroxyacids in situ.

Peroxyacids "per se" are meant here to include the alkaline and alkaline-earth metal salts thereof. Peroxyacids and diperoxyacids are commonly used; examples are diperoxydodecanoic acid (DPDA) or peroxyphthalic acid.

Systems capable of delivering peracids in situ consist in a peroxygen bleaching agent and an activator thereof.

The peroxygen bleaching agents are those capable of yielding hydrogen peroxide in an aqueous solution; those compounds are well-known in the art, and include hydrogen

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peroxide, alkali-metal peroxides, organic peroxide bleaching agents such as urea peroxide, inorganic persalt bleaching agents such as the alkali metal perborates, percarbonates, perphosphates, persilicates, and the like.

Preferred are sodium perborate, commercially available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate.

The liberated hydrogen peroxide reacts with the bleach activator to form the peroxyacid bleach. Classes of bleach activators include esters, imides, imidazoles, oximes, and carbonates. In both classes, preferred materials include methyl o-acetoxy benzoates; sodium-p-acetoxy benzene sulfonates such as sodium 4-nonanoxyloxybenzene sulfonate; sodium-4-octanoxyloxybenzene sulfonate, and sodium-4-decanoxyloxybenzenesulfonate; biophenol A diacetate; tetra acetyl ethylene diamine; tetra acetyl hexamethylene diamine; tetra acetyl methylene diamine.

Other highly preferred peroxygen bleach activators which are disclosed in U.S. Patents 4,483,778 and 4,539,130, are alpha-substituted alkyl or alkenyl esters, such as sodium-4(2-chlorooctanoxyloxy)benzene sulfonate, sodium 4-(3,5,5-trimethyl hexanoxyloxy)benzene sulfonate. Suitable peroxyacids are also peroxygen bleach activators such as described in published European Patent Application No. 0 166 571, i.e., compounds of the general type  $RXAOOH$  and  $RXAL$ , wherein R is a hydroxycarbonyl group, X is a hetero-atom, A is a carbonyl bridging group and L is a leaving group, especially oxybenzenesulfonate.

#### Detersive adjuncts

The compositions herein can contain other ingredients which aid in their cleaning performance; this includes

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polymeric soil release agents, chelating agents, clay soil removal/anti-redeposition agents.

#### Polymeric dispersing agents

Polymeric dispersing agents, such as acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from 2,000 to 100,000, preferably from 5,000 to 75,000, most preferably from 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from 30:1 to 1:1, more preferably from 10:1 to 2:1. Water-soluble salts of such acrylic acid-maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal/anti-redeposition agent. Typical molecular weight ranges for these purposes range from 500 to 100,000, preferably from 1,000 to 50,000, more preferably from 1,500 to 10,000.

Optical brighteners and suds suppressors can be included in the compositions hereof.

Liquid detergent compositions can further contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing

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surfactants, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., propylene glycol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used.

The detergent compositions hereof will preferably be formulated such that during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Liquid product formulations preferably have a pH between 7.5 and 9.5, more preferably between 7.5 and 9.0. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

#### EXPERIMENTAL

This exemplifies a process for making a N-methyl, 1-deoxyglucityl lauramide surfactant for use herein. Although a skilled chemist can vary apparatus configuration, one suitable apparatus for use herein comprises a three-liter four-necked flask fitted with a motor-driven paddle stirrer and a thermometer of length sufficient to contact the reaction medium. The other two necks of the flask are fitted with a nitrogen sweep and a wide-bore side-arm (caution : a wide-bore side-arm is important in case of very rapid methanol evolution) to which is connected an efficient collecting condenser and vacuum outlet. The latter is connected to a nitrogen bleed and vacuum gauge, then to an aspirator and a trap. A 500 watt heating mantle with a variable transformer temperature controller ("Variac") used to heat the reaction is so placed on a lab-jack that it may be readily raised or lowered to further control temperature of the reaction.

N-methylglucamine (195 g., 1.0 mole, Aldrich, M4700-0) and methyl laurate (Procter & Gamble CE 1270, 220.9 g.,

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1.0 mole) are placed in a flask. The solid/liquid mixture is heated with stirring under a nitrogen sweep to form a melt (approximately 25 minutes). When the melt temperature reaches 145°C, catalyst (anhydrous powdered sodium carbonate, 10.5 g., 0.1 mole, J.T. Baker) is added. The nitrogen sweep is shut off and the aspirator and nitrogen bleed are adjusted to give 5 inches (5/31 atm.) Hg. vacuum (16343 Pa). From this point on, the reaction temperature is held at 150°C by adjusting the Variac and/or by raising or lowering the mantle.

Within 7 minutes, first methanol bubbles are sighted at the meniscus of the reaction mixture. A vigorous reaction soon follows. Methanol is distilled over until its rate subsides. The vacuum is adjusted to give about 10 inches Hg. (10/31 atm.) vacuum. The vacuum is increased approximately as follows (in inches Hg. at minutes): 10 at 3 (32686 at 9806 Pa), 20 at 7 (65372 at 22880 Pa), 25 at 10 (81715 at 32686 Pa). 11 minutes from the onset of methanol evolution, heating and stirring are discontinued coincident with some foaming. The product is cooled and solidifies.

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

Test procedure : 3.5 kg of clean fabric laundry loads were washed in an automatic drum washing machine Miele 423 at 60°C. The hardness of the water was 2,5 mM Calcium and the composition concentration was 0.7% in the wash liquor. For softness evaluation swatches of terry towel were line dried prior to assessment of softness. Comparative softness assessment was done by expert judges



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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. Softness was assessed after one and after four wash cycles. The following compositions are made :

<u>Ingredients</u>	<u>Percentage by weight</u>	
	<u>Reference I</u>	<u>Example I</u>
<b>Surfactant</b>		
Linear alkylbenzene sulfonate	8	8
Tallow alkyl sulphate	2	2
Alkyl trimethylammonium chloride	1.5	1.5
Fatty alcohol (C <sub>12</sub> -C <sub>15</sub> ) ethoxylate	5	-
N-methyl N-1-deoxyglucityl C <sub>12</sub> alkylamide	-	5
<b>Builder/chelants</b>		
Zeolite A	23	23
Copolymer of maleic and acrylic acid, sodium salt	5	5
<b>Bleach</b>		
Sodium perborate	12	12
N,N,N,T-Tetraacetyl ethylene diamine	4	4
<b>Perfume</b>		
	0.5	0.5
<b>Enzymes</b>		
Savinase	1.6	1.6
<b>Softness system</b>		
Smectite/montmorillonite clays	10.5	10.5
Glycerol	0.5	0.5
Polyethylene oxide	0	0
<b>Buffer</b>		
Carbonate	10.6	10.5
Silicate (2.0)	5	5
Admix and spray-on (suds suppression, miscellaneous,...)		balance to 100

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The softness performance of Example I (with 5% C<sub>12</sub> alkylamide base) was compared to Reference I (with 5% ethoxylated nonionic surfactant).

One wash cycle      Four wash cycles

Example I vs. Reference I      0.4 s                      0.8 s

A statistical significant improvement of the softness performance is observed with the product containing alkylamide-base (example I).

Example II

Also, compositions are prepared with clay-flocculating agent. The softness performance of the product with 5% alkylamide (example II) is compared versus the same product with 5% ethoxylated nonionic surfactant (reference II). The test conditions are identical to those described in example I.

Softness performance was assessed after one and after four washing cycles :

Again, a statistical significant better softness performance is observed with product containing alkylamide vs. the product containing ethoxylated nonionic surfactant.

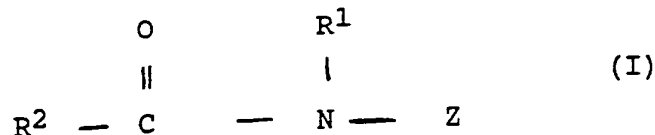
**Formulation examples**

Ingredients	Composition (% by weight)				Compact product		Liquid product
	I	II	III	IV	I	II	I
C <sub>11-12</sub> alkyl benzene sulfonate	7	5	4	-	8	-	10
Tallow alcohol sulfate (Na)	-	2	-	-	2	2	-
C <sub>14-15</sub> alkyl sulfate (Na)	-	-	3	4	-	6	1
A-Olefin (C <sub>12-18</sub> ) sulfonate (Na)	-	-	-	0.5	-	-	-
Tallow alcohol ethoxylate (EO <sub>11</sub> )	0.5	-	-	-	-	-	-
Fatty alcohol (C <sub>12-15</sub> ) ethoxylate (EO <sub>7</sub> )	-	-	-	0.5	-	-	-
Hydrogenated tallow fatty acid	-	0.5	-	-	-	-	-
C <sub>12-14</sub> Dimethyl (hydroethyl) ammonium chloride	-	-	1.5	1.5	1.5	1.5	-
N-Methyl N-1--deoxyglycyl C <sub>16-18</sub> alkyl amide	5	-	6	5	-	-	-
N-Methyl N-1-deoxyglycyl C <sub>12-14</sub> alkyl amide	-	5	-	-	5	5	7
Sodium tripolyphosphate	24	-	-	25	-	-	-
Zeolite A	-	20	20	-	23	19	-
Sodium citrate	-	5	5	-	-	6	-
Oleic fatty acid	-	-	-	-	-	-	1
Citric acid	-	-	-	-	-	-	2
C <sub>14-16</sub> alkyl succinate	-	-	-	-	-	-	10
1,2-Propanediol	-	-	-	-	-	-	3
Ethanol	-	-	-	-	-	-	7
Na Metaborate Octahydrate	-	-	-	-	-	-	1
Polyethylene oxide 5 MM molecular weight	0.05	-	-	0.05	-	-	-
Polyethylene oxide 0.3 MM molecular weight	-	0.3	-	-	0.3	0.3	-
Sodium Sulfate	12	10	15	5	-	-	-
Sodium Carbonate	5	7	-	15	11	11	-
Sodium Silicate	4	4	4	4	4	3	-
Sodium perborate (1 aq.)	15	15	18	15	11	12	-
N,N,N'-Tetraacetylene diamine	3	3	-	3	4	3	-
CMC	0.3	0.3	0.3	0.3	0.4	0.3	-
Polyacrylate (MW 1000-20 000)	-	1.5	-	-	-	-	-
Polyacrylate (MW4000-5000)	-	-	3	-	-	-	-
Maleic-acrylic copolymer	2	-	-	3	5	4	-
Enzymes	1	1	1	1.6	1.6	1	1.5
Montmorillonite clay	10	10	-	10	12	12	10
Hectorite clay	-	-	10	-	-	-	-
Admix and spray-on (perfumes, enzymes, savinase, buffer, sud suppression, miscellaneous, moisture and minors)	-	-	-	-	-	-	-
				balance to 100			

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## WHAT IS CLAIMED IS:

1. A detergent composition comprising a polyhydroxy fatty acid amide surfactant of the formula:



wherein R<sup>1</sup> is H, C<sub>1</sub>-C<sub>4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5</sub>-C<sub>31</sub> hydrocarbyl and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls connected directly to said chain, or alkoxyated derivatives thereof

and a clay-softening system.

2. A detergent composition according to claim 1 comprising at least 1% by weight of said polyhydroxy fatty acid amide.

3. A detergent composition according to claim 1 wherein said polyhydroxy fatty acid amide surfactant has the formula (I) wherein R is methyl, R is C-C alkyl or alkenyl, and Z is a glycityl derived from a reducing sugar, or an alkoxyated derivative thereof.

4. A detergent composition according to claim 1 wherein said clay softening system comprises a clay, in an amount of at least 0.5% by weight of the detergent composition.

5. A clay softening system according to claim 4 wherein said clay is a smectite-type clay.

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6. A detergent composition according to claim 1 wherein said clay softening system comprises a clay flocculating agent.

7. A detergent composition according to claim 1 wherein said clay softening system comprises a humectant.

8. A detergent composition according to claim 1 further comprising one or more auxiliary surfactants selected from the group consisting of anionic, cationic and nonionic deterative surfactants and mixtures hereof.

9. A detergent composition according to claim 8 wherein said nonionics are present at levels of less than 4% by weight of the detergent composition.

**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US92/05269

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :C11D 3/12, 3/32, 3/37, 3/43

US CL :252/548, 154, 155, 174.23, 174.24, 175, 8.8

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/548, 154, 155, 174.23, 174.24, 175, 8.8

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

ORBIT/WPAT - Searched patent family for US Patent No. 5,062,972, GB Patent No. 1,400,898, EP Patent No. 299,575, WO Patent No. 8304412 and DE Patent No. 2226872.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 2,662,073 (Mehltreter et al.) 08 December 1953 See claim 1.	1-9
A	US, A, 2,703,798 (Schwartz) 08 March 1955 See claims 1-10.	1-9
A	GB, A, 809,060 (Thomas Hedley & Co.) 18 February 1959 See claims 1-9.	1-9
Y	US, A, 2,965,576 (Wilson) 20 December 1960 See col. 1, line 53 - col. 2, line 60 and claims 1-11.	1-5, 8 and 9
A	US, A, 2,982,737 (Boettner et al.) 02 May 1961 See claims 1-7.	1-9
Y	US, A, 3,637,495 (Eckert et al.) 25 January 1972 (See Abstract).	1-4 and 6-9
<u>Y</u> Y	US, A, 3,852,211 (Ohren) 03 December 1974 See Abstract; col. 10, lines 53-61; and claims 1-17.	<u>1-5 and 8-9</u> 6

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

09 SEPTEMBER 1992

Date of mailing of the international search report

04 NOV 1992

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/05269

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB, A, 1,400,898 (Storm et al.) 23 July 1975 See claims 1-13.	1-9
<u>Y</u> Y	US, A, 9,915,882 (Nirschl et al.) 28 October 1975 See Abstract; col. 13, lines 35-49; and claims 1-10.	<u>1-5 and 8-9</u> 6
A	WO, A, 0,4412 (National Research Development Corp) 22 December 1983 See claims 1-30.	1-9
Y	EP, a, 0,299,575 (Raemdonck et al) 18 January 1989 See Abstract; pg. 2, lines 35-47; pg. 3, lines 8-35; and claims 1-14.	6
Y	EP, A, 0,387,426 (Busch et al.) 19 September 1990 See Abstract; pg. 3, lines 1-54; pg. 5, lines 36-53; pg. 6, lines 24-34; pg. 6, line 45 - pg. 7, line 12; and claims 1-15.	1-4 and 6-9