Composition de détergent granulaire d’une amylase, un agent polymère inhibant le transfert des couleurs et moins de 2 % en poids d’un dispersant pouvant consister en un homopolymère d’acide acrylique, ou un copolymère d’acide maléique et d’acide acrylique, ou un de leurs sels, d’un poids moléculaire moyen supérieur à 1000, ou un polyéthylèneglycol d’un poids moléculaire inférieur à 4000.

A granular detergent composition containing an amylase, a polymeric dye transfer inhibition agent, and less than 2 % by weight of a dispersing agent being a homopolymer of acrylic acid or copolymer of maleic and acrylic acid or salt thereof, with an average molecular weight above 1,000, or a polyethylene glycol with a molecular weight below 4,000.
Title: AMYLASE-CONTAINING GRANULAR DETERGENT COMPOSITIONS

Abstract

A granular detergent composition containing an amylase, a polymeric dye transfer inhibition agent, and less than 2% by weight of a dispersing agent being a homopolymer of acrylic acid or copolymer of maleic and acrylic acid or salt thereof, with an average molecular weight above 1,000, or a polyethylene glycol with a molecular weight below 4,000.
AMYLASE-CONTAINING GRANULAR
DETERGENT COMPOSITIONS

Technical Field

The present invention relates to granular detergent compositions, exhibiting excellent soil removal properties especially on particulate stains.

Background of the invention

Polymeric dispersing agents have been commonly used in detergent compositions to assist in removal of particulate soil from textiles. Typically used species are homopolymers of acrylic acid, and copolymers of acrylic acids having an average molecular weight above 1,000, available from BASF under the trade mark Sokalan, as well as polyethylene glycols with a molecular weight above 4,000. Among these, copolymers of acrylic and maleic acids having an average MW in the range of 2,000 to 100,000 are the most typically used.

On the other hand, other types of ingredients which are quite useful to the detergent formulator, are dye transfer inhibiting polymers. Said polymers are added to detergent compositions in order to inhibit the transfer from dyes of colored fabrics onto other fabrics washed therewith. These polymers have the ability to complex the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

The presence of such dye transfer inhibition agents in granular detergent compositions, however can lead to certain negatives in particulate soil removal/suspension, especially if dispersing agents of the above type are not used.
The present invention now permits the use of dye-transfer inhibition agents in granular compositions, without the need to use dispersing agents such as described above.

The compositions of the invention exhibit excellent particular soil removal properties, as well as an optimal biodegradability profile.

It has surprisingly been found that the above results can be met through the use of an amylase enzyme in conjunction with dye transfer inhibition agents, while keeping the level of conventional dispersing agents, such as described above, to minimal or nil.

Summary of the Invention

The present invention provides a granular detergent composition comprising, by weight, from 0.05% to 1.5% amylase, from 0.01% to 2% polymeric dye transfer inhibition agent, from 0% to 2% of a dispersing agent comprising a homopolymer of acrylic acid or copolymer of maleic acid and acrylic acid or salt thereof, with an average molecular weight above 1,000, or a polyethylene glycol with a molecular weight above 4,000, surfactant and builder.

Detailed description of the Invention

Amylase

The composition herein comprise as an essential ingredient an amylase enzyme.

Suitable amylases include, for example, -amylases obtained from a special strain of B. licheniforms,
described in more detail in GB-1,296,839 (Novo). Preferred commercially available amylases include for example, Rapidase, sold by International Bio-Synthetics Inc. and Termamyl, sold by Novo Nordisk A/S.

Other suitable amylases are fungal species such as Fungamyl® commercially available from Novo Nordisk A/S.

The amylase should be used at levels of from 0.05 to 1.5% by weight of the detergent composition. When a bacterial amylase such as Termamyl® is used, the level of amylase should be such as to provide an activity typically in the range of 1 to 500 KNU/100 g of detergent composition (Kilo Novo Units). Examples are so-called TermamylR 60T and TermamylR 120T (ex. Novo Nordisk).

When a fungal amylase such as Fungamyl® is used, the level should be such as to provide an activity in the range of from 1 to 5,000 FAU/100g of detergent composition (Fungal Apha Amylase Unit).

**The dye transfer inhibition agent**

The detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.02% to 1% by weight of a polymeric dye transfer inhibiting agent. Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylpyrrolidone polymers, polyvinylpyrrolidone polymers, polyvinylpyrrolidone polymers, polyvinylpyrrolidone polymers, and cross-linked variants of these polymers, and mixtures thereof.

a) **Polyamine N-oxide polymers**
The polyamine N-oxide polymers suitable for use contain units having the following structure: \[ P \]
\[ \text{(I)} A_x \]
\[ R \]

wherein \( P \) is a polymerisable unit, wherein the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

\( A \) is NC, CO, C, -O-, -S-, -N-; \( x \) is 0 or 1;

\( R \) are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures:

\[ \text{(R1)x} -\text{N-} \text{(R2)y} -\text{N-} \text{(R1)x} \]

wherein \( R_1, R_2, \) and \( R_3 \) are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, \( x \) or/and \( y \) or/and \( z \) is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.
The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof. Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides where the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.
Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylene, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

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 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. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferably PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000000; preferably from 1000 to 50000, more preferably from 2000 to 30000, most preferably from 3000 to 20000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight
range from 5,000-1,000,000, 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.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol. 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have 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.

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4.

c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP" having an average molecular weight of from about 2,500 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 15,000.
Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity 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.

d) Polyvinylloxazolidone:

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP" having an average molecular weight of from 

The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 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 15,000.

e) Polyvinylimidazole:

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP" having an average molecular weight of from 

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average about 2,500 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 15,000.

The polymeric dispersing agent

It is a particular feature of the present invention that conventional polymeric dispersing agents are not essential to achieve good particulate soil removal. Accordingly, such conventional polymers as homopolymers of acrylic acid and copolymers of acrylic and maleic acids and salts thereof, with an average molecular weight above 1,000, as well as polyethylene glycols with an average molecular weight above 4,000, can be dispensed of, or their levels minimized in the compositions of the present invention.

Preferred among those are copolymers of acrylic and maleic acid, normally in the form of their water-soluble salts. The average molecular weight of such copolymers in the acid form ranges from about 2,000 to 100,000, more preferably from about 5,000 to about 80,000, most preferably from about 7,000 to 70,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 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.

The level of the polymeric dispersants above should be kept below 2% by weight of the total detergent composition, and is preferably close to zero.

Alternative dispersing agents can be used optionally, as described hereinafter.
The granular detergent compositions herein are preferably laundry detergent compositions and contain a surfactant and a detergent builder as essential ingredients. Suitable surfactants and builders are described in detail hereinafter:

Alkyl Sulfate Surfactant

Alkyl sulfate surfactants hereof are water soluble salts or acids of the formula RO\(\text{SO}_3\text{M}\) wherein \(R\) preferably is a \(\text{C}_{10}-\text{C}_{24}\) hydrocarbyl, preferably an alkyl or hydroxyalkyl having a \(\text{C}_{10}-\text{C}_{20}\) alkyl component, more preferably a \(\text{C}_{12}-\text{C}_{18}\) alkyl or hydroxyalkyl, and \(M\) is \(\text{H}\) 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 piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of \(\text{C}_{12}-\text{C}_{16}\) are preferred for lower wash temperatures (e.g., below about 50°C) and \(\text{C}_{16}-\text{C}_{18}\) alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

Alkyl Alkoxylated Sulfate Surfactant

Alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula RO(A)\(_m\)SO\(_3\)M wherein \(R\) is an unsubstituted \(\text{C}_{10}-\text{C}_{24}\) alkyl or hydroxyalkyl group having a \(\text{C}_{10}-\text{C}_{24}\) alkyl component, preferably a \(\text{C}_{12}-\text{C}_{20}\) alkyl or hydroxyalkyl, more preferably \(\text{C}_{12}-\text{C}_{18}\) 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 and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines 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), 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.

Other Anionic Surfactants

Other anionic surfactants useful for detergent 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 alkylbenzenesulphonates, C_{8}-C_{22} primary or secondary alkanesulphonates, C_{8}-C_{24} 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, C_{8}-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C_{14-16} methyl ester sulfonates; 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 sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_{6}-C_{14} diesters), acyl sarcosinates, sulfates of alkyl polysaccharides such as the sulfates of alkyl polyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxyl carboxylates such as those of the formula RO(CH₂CH₂O)ₖCH₂COO⁻M⁺ wherein R is a C₈-C₂₂ 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 given 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.

Preferred surfactants for use in the compositions herein are the alkyl sulfates, alkyl alkoxylated sulfates, and mixtures thereof.

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.

Nonionic Surfactants

The present laundry detergent compositions preferably also comprise a nonionic surfactant.
While any nonionic surfactant may be normally employed in the present invention, two families of nonionics have been found to be particularly useful. These are nonionic surfactants based on alkoxylated (especially ethoxylated) alcohols, and those nonionic surfactants based on amidation products of fatty acid esters and N-alkyl polyhydroxy amine. The amidation products of the esters and the amines are generally referred to herein as polyhydroxy fatty acid amides. Particularly useful in the present invention are mixtures comprising two or more nonionic surfactants wherein at least one nonionic surfactant is selected from each of the groups of alkoxylated alcohols and the polyhydroxy fatty acid amides.

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

Particularly preferred for use in the present invention are nonionic surfactants such as the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 16 carbon atoms, in either a straight chain or branched chain configuration, with from about 4 to 25 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble condensation products of aliphatic alcohols containing from 8 to 22
carbon atoms, in either straight chain or branched configuration, with an average of up to 25 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 2 to 10 moles of ethylene oxide per mole of alcohol; and condensation products of propylene glycol with ethylene oxide. Most preferred are condensation products of alcohols having an alkyl group containing from about 12 to 15 carbon atoms with an average of about 3 to 7 moles of ethylene oxide per mole of alcohol, preferably 3 to 5.

The nonionic surfactant system herein can also include a polyhydroxy fatty acid amide component.

Polyhydroxy fatty acid amides may be produced by reacting a fatty acid ester and an N-alkyl polyhydroxy amine. The preferred amine for use in the present invention is N-(R1)-CH2(CH2OH)4-CH2-OH and the preferred ester is a C12-C20 fatty acid methyl ester. Most preferred is the reaction product of N-methyl glucamine with C12-C20 fatty acid methyl ester.

Methods of manufacturing polyhydroxy fatty acid amides have been described in WO 92 6073, published on 16th April, 1992. This application describes the preparation of polyhydroxy fatty acid amides in the presence of solvents. In a highly preferred embodiment of the invention N-methyl glucamine is reacted with a C12-C20 methyl ester. It also says that the formulator of granular detergent compositions may find it convenient to run the amidation reaction in the presence of solvents which comprise alkoxylated, especially ethoxylated (EO 3-8) C12-C14 alcohols (page 15, lines 22-27). This directly yields nonionic surfactant systems which are preferred in the present invention, such as
those comprising N-methyl glucamide and C12-C14 alcohols with an average of 3 ethoxylate groups per molecule.

Nonionic surfactant systems, and granular detergents made from such systems have been described in WO 92 6160, published on 16th April, 1992. This application describes (example 15) a granular detergent composition prepared by fine dispersion mixing in an Eirich RV02 mixer which comprises N-methyl glucamide (10%), nonionic surfactant (10%).

Both of these patent applications describe nonionic surfactant systems together with suitable manufacturing processes for their synthesis, which have been found to be suitable for use in the present invention.

The polyhydroxy fatty acid amide may be present in compositions of the present invention at a level of from 0% to 50% by weight of the detergent component or composition, preferably from 5% to 40% by weight, even more preferably from 10% to 30% by weight.

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.

The preferred alkylpolyglycosides have the formula

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

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 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 predominantly the 2-position.

**Other 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, including the semi-polar nonionic amine oxides described below.

Cationic detergent 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 alkyltrimethylammonium halogenides, and those surfactants having the formula:
\[ R^2(OR^3)y \{ R^4(OR^3)y \}_2 R^5 N^+ X^- \]
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, \(-CH_2COH-CHOHCOH_6CHOHCH_2OH\) 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.

Other cationic surfactants useful herein are also described in US 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 form 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 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 form 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, derivates of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quarternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at columns 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 form 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 form about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of form 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.
Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula:

\[ R^3(OR^4)\text{N}(R^5)\text{N}^+ \]

**Builder**

The laundry detergent compositions herein contain a builder, preferably non-phosphate detergent builders, although phosphate-containing species are not excluded in the content of the present invention. These can include, but are not restricted to alkali metal carbonates, bicarbonates, silicates, aluminosilicates, carboxylates and mixtures of any of the foregoing. The builder system is present in an amount of from 25% to 80% by weight of the composition, more preferably from 30% to 60% by weight.

Suitable silicates are those having an \( \text{SiO}_2 : \text{Na}_2\text{O} \) ratio in the range from 1.6 to 3.4, the so-called amorphous silicates of \( \text{SiO}_2 : \text{Na}_2\text{O} \) ratios from 2.0 to 2.8 being preferred.

Within the silicate class, highly preferred materials are crystalline layered sodium silicates of general formula

\[ \text{NaMSi}_x\text{O}_{2x} + 1 \cdot y\text{H}_2\text{O} \]

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-0164514 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 a preferred example of this formula comprise the form of Na$_2$Si$_2$O$_5$. These materials are available from Hoechst AG FRG as respectively NaSKS-5, NaSKS-7, NaSKS-11 and NaSKS-6. The most preferred material is Na$_2$Si$_2$O$_5$, NaSKS-6. Crystalline layered silicates are incorporated either as dry mixed solids, or as solid components of agglomerates with other components.

Whilst a range of aluminosilicate ion exchange materials can be used, preferred sodium aluminosilicate zeolites have the unit cell formula

\[ \text{Na}_z[(\text{AlO}_2)_z\cdot(\text{SiO}_2)_y]\cdot x\text{H}_2\text{O} \]

wherein *z* and *y* are at least about 6, the molar ratio of *z* to *y* is from about 1.0 to about 0.4 and *z* is from about 10 to about 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula

\[ \text{M}_z(z\text{AlO}_2\cdot y\text{SiO}_2) \]

wherein *M* is sodium, potassium, ammonium or substituted ammonium, *z* is from about 0.5 to about 2 and *y* is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO$_3$ hardness per gram of anhydrous aluminosilicate. Hydrated sodium Zeolite A with a particle size of from about 0.01 to 10 microns is preferred.

The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from about 10%
to about 28% of water by weight if crystalline, and potentially even higher amounts of water if amorphous. Highly preferred crystalline aluminosilicate ion exchange materials contain from about 18% to about 22% water in their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns. Amorphous materials are often smaller, e.g., down to less than about 0.01 micron. Preferred ion exchange materials have a particle size diameter of from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter by weight of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope.

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention 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 discussed in U.S. Pat. No. 3,985,669, Krummel et al., issued Oct. 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite X, P and MAP, the latter species being described in EPA 384 070. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is a Zeolite A having the formula

$$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot x\text{H}_2\text{O}$$
wherein x is from about 20 to about 30, especially about 27 and has a particle size generally less than about 5 microns.

Suitable carboxylate builders 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, diglycolic 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 Canadian Patent No. 973,771, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propanetricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829,1, and the 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 US Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphorus
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 carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic 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.

pH and density

The granular detergent compositions herein typically have a pH above 8.5, preferably in the range of from 9 to 11.

The present laundry granular compositions are preferably in a compact form, having a bulk density of at least 650 g/l, preferably at least 750g/l, but can also be in a conventional form, with densities in a range of from 200 g/l to 700 g/l.

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating
agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include: ethylenediaminetetraacetates, N-hydroxyethyleneaminitriacetates, nitrilotriacetates, ethylenediamine tetraprotonates, triethylenetetramine-hexacetates, diethylenetriaminepentaaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorous are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The granular detergent compositions and automatic dishwashing compositions herein have a pH above 8.5, preferably in the range of from 9 to 11.

The present laundry granular compositions are preferably in a compact form, having a bulk density of at least 650 g/l, preferably at least 750g/l, but can also be in a conventional form, with densities in a range of from 200 g/l to 700 g/l.

In another embodiment of the invention, are provided Automatic Dishwashing Compositions:

Automatic dishwashing compositions typically contain, in addition to the amylase of the invention, a builder, such as described above, a source of alkalinity, such as silicate or carbonate, and a bleaching agent, preferably percarbonate, those ingredients amounting to up to 70% of the formulation. Optional ingredients include polymers and other enzymes.

In still another embodiment of the invention, are provided Laundry Additive Compositions: such compositions preferably contain in addition to the
amylase of the invention, a bleaching agent at levels of from 15 to 80% by weight.

Other Ingredients

Other ingredients which are known for use in detergent compositions may also be used as optional ingredients in the various embodiments of the present invention, such as bleaching agents, bleach activators, polymers, biodegradable dispersing agents, other enzymes, suds suppressing agents, fabric softening agents, in particular fabric softening clay, as well as dyes, fillers, optical brighteners, pH adjusting agents, non builder alkalinity sources, enzyme stability agents, hydrotropes, solvents, perfumes.

Alternative dispersing agents

Such agents may be used in the present composition, as levels ranging from 1 to 6%. Among such dispersants can be mentioned polyvinylalcohols with a molecular weight up to 70,000, polyethylene glycols with a molecular weight below 4,000, preferable 1 to 3,000, or terpolymers of maleic/acrylic acid and vinyl alcohol having a molecular weight ranging from 3,000 to 70,000, with the percentage of vinyl alcohol being from 5 to 60%.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight of about 10,000. Polysuccinimide and acrylic-acrolein and mixtures thereof may also be used in this respect.

Other enzymes
Enzymatic materials other than the specific amylases herein can be incorporated into the detergent compositions herein. Suitable are proteases, lipases, cellulases, peroxidases, other amylases and mixtures thereof.

A suitable lipase enzyme is manufactured and sold by Novo Industries A/S (Denmark) under the trade mark Lipolase and mentioned along with other suitable lipases in EP-A-0258068 (Novo Nordisk).

Bleaching agents

In the embodiment of the present invention, the granular laundry detergent compositions herein contain a bleaching agent; however bleach-free granular detergent compositions are also desirable, particular for the treatment of certain fabrics requiring special care; therefore, such bleach-free detergent compositions are also encompassed by the present invention.

The bleaching agent, if used, is either an inorganic persalt such as perborate, persulfate, percarbonate or a preformed organic peracid or perimidic acid, such as N,N-phthaloylaminoperoxy caproic acid, 2-carboxyphthaloylaminoperoxy caproic acid, N,N-phthaloylaminoperoxy valeric acid, Nonyl amide of peroxy adipic acid, 1,12-diperoxydodecanedioic acid, Peroxybenzoic acid and ring substituted peroxybenzoic acid, Monoperoxyphthalic acid (magnesium salt, hexahydrate), Diperoxybrassylic acid.

The preferred bleaching agent is percarbonate.

The bleach-containing laundry detergent herein typically contain from 1% to 40%, preferably from 3% to 30% by weight, most preferably from 5% to 25% by weight of alkali metal percarbonate bleach, in the form of
particles having a mean size from 250 to 900 micrometers, preferably 500 to 700 micrometers.

The alkali metal percarbonate bleach is usually in the form of the sodium salt. Sodium percarbonate is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$. To enhance storage stability the percarbonate bleach can be coated with e.g. a further mixed salt of an alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1:2000 to 1:4, more preferably from 1:99 to 1:9, and most preferably from 1:49 to 1:19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $\text{Na}_3\text{SO}_4 \cdot n\cdot \text{Na}_2\text{CO}_3$, wherein $n$ is from 0.1 to 3, preferably $n$ is from 0.3 to 1.0 and most preferably $n$ is from 0.2 to 0.5.

Other suitable coating materials are sodium silicate, of $\text{SiO}_2: \text{Na}_2\text{O}$ ratio from 1.6:1 to 2.8:1, and magnesium silicate.

Commercially available carbonate/sulphate coated percarbonate bleach may include a low level of a heavy metal sequestrant such as EDTA, 1-hydroxyethylidene 1,1-diphosphonic acid (HEDP) or an aminophosphonate, that is incorporated during the manufacturing process.

Preferred heavy metal sequestrants for incorporation as described herein above include the organic phosphonates and amino alkylene poly(alkylene phosphonates) such as the alkali metal ethane 1-hydroxy diphosphonates, the nitrilo trimethylene phosphonates, the ethylene diamine tetra methylene phosphonates and the diethylene triamine penta methylene phosphonates.
Bleach activators

The bleach containing detergent compositions, according to the above-described embodiment, preferably contain from 1% to 20% by weight of the composition, preferably from 2% to 15% by weight, most preferably from 3% to 10% by weight of a peroxyacid bleach activator, in addition to the bleaching agent described above.

Peroxycacid bleach activators (bleach precursors) as additional bleaching components in accordance with the invention can be selected from a wide range of class and are preferably those containing one or more N- or O-acyl groups.

Suitable classes include anhydrides, esters, amides, and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789. The most preferred classes are esters such as are disclosed in GB-A-836,988, 864,798, 1,147,871 and 2,143,231 and amides such as are disclosed in GB-A-855,735 and 1,246,338.

Particularly preferred bleach activator compounds as additional bleaching components in accordance with the invention are the N-,N,N',N' tetra acetylated compounds of the formula
where \( x \) can be 0 or an integer between 1 and 6.

Examples include tetra acetyl methylene diamine (TAMD) in which \( x=1 \), tetra acetyl ethylene diamine (TAED) in which \( x=2 \) and Tetraacetyl hexylene diamine (TAHHD) in which \( x=6 \). These and analogous compounds are described in GB-A-907 356. The most preferred peroxyacid bleach activator as an additional bleaching component is TAED.

Another preferred class of peroxyacid bleach compounds are the amide substituted compounds of the following general formulae:

\[
\begin{align*}
R^1 & \quad \text{C} \quad \text{N} \quad R^2 \\
\text{R}^5 & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
R^1 & \quad \text{N} \quad \text{C} \quad R^2 \\
\text{R}^5 & \quad \text{C} \\
\end{align*}
\]

wherein \( R^1 \) is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, \( R^2 \) is an alkylene, arylene, and alkarylene group containing from about 1 to about 14 carbon atoms, and \( R^5 \) is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. \( R^1 \) preferably contains from about 6 to 12 carbon atoms. \( R^2 \) preferably contains from about 4 to 8 carbon atoms. \( R^1 \) may be straight chain or branched alkyl, substituted aryl or alkaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for \( R^2 \). The substitution can
including for example, tallow fat. Analogous structural variations are permissible for \( R^2 \). The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. \( R^5 \) is preferably \( \text{H} \) or methyl. \( R^1 \) and \( R^5 \) should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Another class of bleach activators to use in combination with percarbonate comprises \( C_8 \), \( C_9 \), and/or \( C_{10} \) (6-octanamidocaproyl) oxybenzenesulfonate, 2-phenyl-(4H)3,1 benzoxazin-4-one, benzoylelactam preferably benzoylecaprolactam and nonanoyl lactam preferably nonanoyl caprolactam.

**Polymers**

Also useful are certain organic polymers other than the dye transfer exhibiting or dispersants described herein above. Among such polymers may be mentioned sodium carboxy-lower alkyl celluloses and sodium hydroxy-lower alkyl celluloses, such as sodium carboxymethyl cellulose, sodium methyl cellulose and sodium hydroxypropyl cellulose. Molecular weights for such polymers vary widely but most are within the range of 2,000 to 100,000.

Other useful polymers include species known as soil release polymers, such as described in EPA 185 427 and EPA 311 342.
**EXAMPLE 1**

The following formulae were prepared:

<table>
<thead>
<tr>
<th></th>
<th>COMPOSITION</th>
<th>Example 1</th>
<th>Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% BY WEIGHT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear Alkyl Benzene Sulfonate</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Tallow Alkyl Sulfate</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C&lt;sub&gt;25&lt;/sub&gt; alkyl ethoxysulfate</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>C&lt;sub&gt;45&lt;/sub&gt; alcool 7 times ethoxylated</td>
<td>4.0</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Tallow alcohol ethoxylate 11 times ethoxylated</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Zeolite</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Trisodium citrate</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Carbonate</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Silicate</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Carboxymethylcellulose</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Soil release polymer</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Protease (Savinase)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Cellulase (1000 cepu)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Lipase (Lipolase) (100 KLU)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Perborate Tetrahydrate</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>TAED*</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>PVNO**</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Amylase</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(Termamyl 60KNPU</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Terpolymer***
Minors up to 100

* Tetraacetylene diamine
** Polyvinyl N-oxide
*** maleic anhydride/acrylic acid/vinylalcoholterpolymer. (10-30% vinylalcohol).

The compositions of Example 1 and Example 2 showed significantly better clay soil removal properties than the composition A.

Results are as follows (expressed in Panel Score Units):

<table>
<thead>
<tr>
<th>Clay stain removal based on clays from different geographical origins = (clays 1 to 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition A</td>
</tr>
<tr>
<td>Clay 1</td>
</tr>
<tr>
<td>Clay 2</td>
</tr>
<tr>
<td>Clay 3</td>
</tr>
<tr>
<td>Clay 4</td>
</tr>
</tbody>
</table>

* Significant difference at 95% confidence

Comparative 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.

Conditions: 40°C, Sotax, City water 12°H.
Stir rate 150 rpm, 30 minutes, cold
Rinse: clay stains painted onto flat cotton.
Additional detergent compositions according to the invention were prepared:

<table>
<thead>
<tr>
<th>Granular Laundry Detergents</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 4 5 6 7 8 9 10</td>
</tr>
<tr>
<td>Linear Alkyl Sulphionate</td>
<td>7 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td>Tallow Alkyl Sulphate</td>
<td>3 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td>Alkyl Sulphate</td>
<td>0 9 6 9 12 12 9 6</td>
</tr>
<tr>
<td>Alkyl Ethoxylate Sulphate</td>
<td>0.2 2 1 2 2 3 3 3</td>
</tr>
<tr>
<td>Alkyl tri-methyl Ammonium Chloride</td>
<td>0 0 2 0 0 0 0 0</td>
</tr>
<tr>
<td>Alkyl Ethoxylate</td>
<td>4 5 10 6 4 7 8 12</td>
</tr>
<tr>
<td>Alkyl-N-Methyl Glucosamide</td>
<td>0 2 3 3 1 3.5 3.5 3.5</td>
</tr>
<tr>
<td>Perborate</td>
<td>22 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td>Percarbonat</td>
<td>0 22 19 22 24 0 0 0</td>
</tr>
<tr>
<td>N,N,N,N-Tetra acetyl ethylene diamine</td>
<td>5 6 5 5 5 0 0 0</td>
</tr>
<tr>
<td>Diethylene tri-amine penta(methylene phosphonic acid)</td>
<td>0.4 0.5 0 0 0 0 0 0</td>
</tr>
<tr>
<td>S,S-Ethylene-di-succinic acid</td>
<td>0 0 0.5 0.5 0.5 0 0 0</td>
</tr>
<tr>
<td>Fungamyl 1600 FAU</td>
<td>0 0.125 0.2 0.2 0 0 0.3 0.3</td>
</tr>
<tr>
<td>Lipolase 165 KLU</td>
<td>0.3 0.2 0.2 0.2 0.2 0.2 0.2</td>
</tr>
<tr>
<td>Cellulase 1000 cevu</td>
<td>0.1 0.2 0.3 0.3 0.3 0.2 0.2</td>
</tr>
<tr>
<td>Granular Laundry Detergents</td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---</td>
</tr>
<tr>
<td>Examples</td>
<td>3</td>
</tr>
<tr>
<td>Protease (Savinase) 13KNPU</td>
<td>0.4</td>
</tr>
<tr>
<td>Termamyl 60 KNU</td>
<td>0.6</td>
</tr>
<tr>
<td>Alcalase 3 AU</td>
<td>0</td>
</tr>
<tr>
<td>Alumino Silicate (zeolite A)</td>
<td>21</td>
</tr>
<tr>
<td>Layered Silicate</td>
<td>0</td>
</tr>
<tr>
<td>Sodium Citrate</td>
<td>6</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>16</td>
</tr>
<tr>
<td>Sodium Silicate</td>
<td>3</td>
</tr>
<tr>
<td>Sulphate</td>
<td>4</td>
</tr>
<tr>
<td>Maleic &amp; Acrylic Acid Sodium Salt Copolymer MW ...</td>
<td>0</td>
</tr>
<tr>
<td>Carboxymethyl cellulose Sodium Salt</td>
<td>3</td>
</tr>
<tr>
<td>Soil Release Polymer</td>
<td>0.3</td>
</tr>
<tr>
<td>Polyvinylpyridine</td>
<td>0</td>
</tr>
<tr>
<td>Polyvinyl-N-Oxide (PVNO)</td>
<td>0.3</td>
</tr>
<tr>
<td>PVPVI</td>
<td>0</td>
</tr>
<tr>
<td>Polyethylene Glycol</td>
<td>0</td>
</tr>
<tr>
<td>MW 1000-3000</td>
<td>0</td>
</tr>
<tr>
<td>Terpolymer</td>
<td>0</td>
</tr>
<tr>
<td>Polyspartate</td>
<td>0</td>
</tr>
<tr>
<td>Minors</td>
<td>up to 110</td>
</tr>
</tbody>
</table>
What is claimed is:

1. A granular detergent composition comprising, by weight, from 0.05% to 1.5% amylase, from 0.01% to 2% polymeric dye transfer inhibition agent, from 0% to 2% of a dispersing agent comprising a homopolymer of acrylic acid or copolymer of maleic acid and acrylic acid or salt thereof, with an average molecular weight above 1,000, or a polyethylene glycol with a molecular weight above 4,000, surfactant and builder.

2. A detergent composition according to claim 1 wherein the dye transfer inhibition agent is selected from the group consisting of polyamine N-oxide polymers, copolymers of N-vinyl-pyrrolidone and N-vinylimidazole, polyvinyl pyrrolidone, polyvinylloxazolidone, polyvinylimidazole (and cross linked variants of these polymers) and mixtures thereof.

3. A detergent composition according to claim 1 wherein the amylase is a fungal or bacterial amylase.

4. A detergent composition according to claim 1 which additionally contains a polymer selected from the group consisting of terpolymers of maleic acid, acrylic acid, and vinyl alcohol, polyaspartates, polyvinylalcohols, polyethylene glycols with an average molecular weight below 4,000, poly-succinimide, acrylic-acrolein and mixtures thereof.

5. A detergent composition according to claim 4 wherein said polyethylene glycols have a molecular weight in the range of 1,000 to 3,000.