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(54) **DINGY FABRIC CLEAN-UP WITH AMYLASE ENZYME IN DETERGENT COMPOSITIONS**

REINIGEN VON SCHMUTZIGEN GEWEBEN MIT AMYLASE ENTHALTENDEN
WASCHMITTELZUSAMMENSETZUNGEN

NETTOYAGE DE TISSUS SOUILLES ET TERNES PAR AMYLASE DANS DES COMPOSITIONS
DETERGENTES

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(56) References cited:
WO-A-94/02597 **WO-A-94/18314**
WO-A-95/10603 **WO-A-96/25478**
US-A- 4 686 063 **US-A- 4 770 815**

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DescriptionTECHNICAL FIELD

5 **[0001]** The present invention relates to granule, liquid, or bar detergent compositions comprising certain levels of specially selective amylase enzymes which boost fabric laundry performance especially on dingy stains and soil. The detergent compositions preferably further comprise other enzymes and surfactants.

BACKGROUND OF THE INVENTION

10 **[0002]** It has been found that amylase enzymes in detergent compositions provide surprisingly effective cleaning. These amylase enzymes show new and unexpected dingy cleaning benefits and whiteness maintenance.

[0003] Amylase enzymes have long been recognized in dishwashing compositions to provide the removal of starchy food residues or starchy films from dishware, flatware, and glasses. A typical amylolytic enzyme for use in dishwash is TERMAMYL^R available from Novo Nordisk S/A. Therefore, while amylase is known to act on starch stains, there remains a substantial technical challenge in formulating laundry components comprising amylase and surfactants in such a manner as to meet the consumer's need for superior cleaning performance on starchy soils as well as other soils typically encountered in laundry applications. Moreover, such detergent compositions must provide an excellent value and a safe, environmentally acceptable product which leaves laundered fabrics, especially those particularly prone to dingy soiling, in dingy-free and undamaged condition. A need therefore exists for the development of detergent compositions comprising amylase enzymes designed to be especially effective at dingy clean up.

20 **[0004]** It is an object of the instant invention to provide improved laundry compositions containing amylolytic enzymes which provide effective dingy stain removal and overall cleaning benefits. It is a further object to provide a means for maintaining whiteness of fabrics using laundry compositions containing amylase enzyme and surfactant. In another aspect of the invention, it is an object herein to provide fully-formulated laundry compositions wherein the amylases are combined with additional selected ingredients so as to deliver superior cleaning results. These and other objects are secured herein, as will be seen from the following disclosures.

BACKGROUND ART

30 **[0005]** WO/94/02597, Novo Nordisk A/S, published Feb. 3, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO 94/18314 A, Genecor, published August 18, 1994, and WO 95/10603, Novo Nordisk A/S, published April 20, 1995, and WO 96/25478, published August 22, 1996.

35 **[0006]** Suitable amylases for use in the compositions of this invention include both α and β amylases. α -amylases are known in the art and include those disclosed in U.S. Pat. no. 5,003,257; U.S. Pat. No. 4,686,063; EP 252,666; WO 91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent Specification No. 1,296,839 (Novo).

SUMMARY OF THE INVENTION

40 **[0007]** It has now surprisingly been discovered that amylase enzymes, particularly those recently developed by conventional genetic engineering techniques, provide unexpected, superior dingy clean up, whiteness maintenance, and overall cleaning performance. Such performance is illustrated by, but not limited to, excellent soil removal on pillow cases, T-shirts and sock bottoms.

45 **[0008]** This invention relates to liquid, granule, or bar detergent compositions which provide especially effective surface cleaning of textiles. This invention also relates to methods for cleaning fabrics using such detergent compositions.

[0009] A laundry detergent composition is provided which is especially effective for cleaning and whitening dingy fabrics laundered therewith. Such a composition comprises:

50 A. a detergent surfactant which is selected from the group consisting of anionic, nonionic, cationic, ampholytic and zwitterionic surfactants and combinations thereof, and which is presented to the extent of from about 1% to about 40% by weight of the composition thereof; and

B. one or more amylase enzymes which are present in an amount that ranges from about 0.001 mg to about 2 mg of active amylase enzyme per gram of composition and that is effective to increase the whiteness of dingy fabrics laundered with laundry solutions formed from said detergent compositions in comparison with similar compositions which contain no amylase. Such compositions contain less than 0.01% by weight of a nonionic polysaccharide ether having a molecular weight of more than 10,000.

[0010] The present invention also relates to methods for laundering fabrics to maintain or increase whiteness and provide dingy cleanup, said method comprising contacting fabrics in need of whiteness and dingy clean-up with an aqueous solution formed from a detergent composition as described above comprising surfactant and amylase enzyme at a concentration such that the whitening performance of said composition is increased in comparison with similar compositions which contain no amylase.

[0011] The present invention also relates to a method for laundering fabrics to reduce the odors associated with soils and stains, said method comprising contacting stained and soiled fabrics in need of odor control with an aqueous solution formed from a detergent composition comprising surfactant and amylase enzyme, said detergent composition is present at a concentration such that the reduction in odor associated with said soils and stains is increased as compared to the reduction in odor associated with soiled fabrics washed with similar compositions which contain no amylase.

[0012] Finally, the present invention relates to methods for laundering fabrics to maintain or increase whiteness and provide dingy cleanup, said method comprising contacting fabrics in need of whiteness and dingy clean-up with an aqueous solution formed from a detergent composition comprising surfactant and amylase enzyme in multiple wash cycles or for a sufficient period of time such that the fabrics appear whitened and less dingy.

[0013] All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The detergent compositions herein are preferably nonphosphate laundry detergents which contain amylase enzyme and surfactants for good cleaning of soiled laundry. For purposes of this invention, the term "liquid" refers to detergent compositions in any suitable liquid form, e.g., structured liquids, isotropic liquids and gels.

[0015] The laundry detergent compositions herein provide effective and efficient surface cleaning of textiles, particularly on dingy stains over a wide range of laundry washing temperatures. Examples of dingy stains are those typically found on pillow cases, T-shirts, and sock bottoms. Laundry wash solutions are preferably at temperatures between 5°C and 95°C, preferably between 10°C and 60°C, for this cleaning benefit.

[0016] Without limitation by theory, it is believed that dingy soils and stains are the result of combinations of fatty soils and particulate soils. Fatty soils comprise lipids, proteins, and pigments that are deposited on fabrics from contact with human or animal skin. The majority of lipids are secreted from the sebaceous gland as sebum. Proteins and pigments from skin fragments are liberated by the breakdown of skin cells. Particulate soils comprise mostly airborne soil and floor/ground dust. It is believed that sebum is the major soil present on laundry, and its removal is important because unremoved fat acts as a matrix to hold particulate soils. Further it is believed that compounds present in the sebum oxidize to contribute to yellowing of fabrics. Particulate soils include topsoil and products produced during the incomplete combustion of petroleum products. "Dingy clean-up", as used herein, means the ability of a detergent composition to remove such dingy soil build-up, over one or more washes, resulting in a measurable improvement in fabric appearance.

[0017] Whiteness maintenance is the monitoring of the whiteness of wash & wear fabrics over a number of washing cycles. A good performing detergent has a good whiteness maintenance profile, i.e. it ensures that the whiteness of washed fabrics is maintained at a high level during the complete life cycle of wearing & washing.

[0018] "Whitening performance", as used herein, means the relative ability of laundry detergent compositions comprising certain selected amylase to produce dingy clean-up and/or whiteness maintenance results.

[0019] The performance on dingy clean-up can be measured in terms of the Hunter Whiteness Values (W), which is calculated according to the following equation:

$$W = (7L^2 - 40Lb) / 700$$

wherein L, a, b are determined from a tristimulus meter reading and represent a three axis opponent color scale system based on the theory that color is perceived by black-white (L), red-green (a), and yellow-blue (b) sensations. The higher the value for W, the better the whiteness performance and dingy clean-up. See R. S. Hunter and R. W. Harold, The Measurement of Appearance, Second Ed., John Wiley & Sons, New York, 1987 and ASTM Standards on Color and Appearance Measurement, Third Ed., ASTM, Philadelphia, PA, 1991.

[0020] Amylase Enzymes - The detergent compositions of the present invention comprise from 0.001 mg to 2 mg, preferably from 0.01 to 1 mg, of active amylase enzyme per gram of composition. Stated otherwise, the compositions herein will typically comprise from 0.0001% to 0.2%, preferably 0.001%-0.1%, by weight of active enzyme. In yet another aspect of the invention herein the detergent composition comprises from 0.15% to 0.2% of active enzyme.

[0021] Suitable amylases for use in the compositions of this invention include both α and β amylases. α -amylases are known in the art and include those disclosed in U.S. Pat. no. 5,003,257; EP 252,666; WO 91/00353; WO 96/05295;

FR 2,676,456; EP 285,123; EP 525,610; and EP 368,341. Preferred amylases include Termamyl[®] (Novo Nordisk) and BAN[®] (Novo Nordisk). Termamyl[®] is described in British Patent Specification No. 1,296,839 (Novo).

[0022] Highly preferred amylases of this invention include those amylases having improved stability in detergents, especially improved oxidative stability. In general, the stability-enhanced amylases can be obtained from Novo Nordisk A/S, or from Genencor International.

[0023] Preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* alpha-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Methionine (Met) was identified as the most likely residue to be modified and substituted with any of the naturally occurring L-amino acids.

[0024] As noted, "oxidative stability-enhanced" amylases are preferred for use herein. Such amylases are non-limitingly illustrated by the following:

(a) An amylase according to the hereinbefore incorporated WO/94/02597, Novo Nordisk A/S, published Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine (preferably threonine), of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TERMAMYL[®], or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B. subtilis*, or *B. stearothermophilus*;

(b) Stability-enhanced amylases, including Purafact Ox Am[®], as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson and in WO 94/18314A, published August 18, 1994. Therein it was noted that improved oxidative stability amylases have been made by Genencor from *B.licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366, and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant; See also WO 96/05295 from Genencor International which discloses amylases having M197T, M15T and W138Y variants;

(c) Particularly preferred herein are amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S. These amylases, disclosed as WO 9510603, published April 1995, are known by the tradename Duramyl[®] and are those referred to by the supplier as QL37+M197T.

[0025] Any other oxidatively stable amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases.

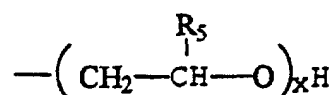
[0026] Detergent Surfactant - The compositions of this invention also include from 1 to 40 weight % of water-soluble detergent surfactant selected from the group consisting of anionics, nonionics, cationic, zwitterionics, ampholytics, and mixtures thereof. From 2 to 25 weight % of detergent surfactant is preferred and from 5 to 15 weight % is most preferred. Example of preferred surfactants include amine surfactants, salts of C₁₁₋₁₃ linear alkyl benzene sulfonate, C₁₂₋₁₆ alkyl sulfate and/or methyl ester sulfonates. In one embodiment, the preferred surfactant is an amine.

[0027] Detergent surfactants useful herein are listed in U.S. Patents 3,664,961, Norris, issued May 23, 1972, and 3,919,678, Laughlin et al, issued December 30, 1975, both incorporated herein by reference. The following are representative examples of detergent surfactants useful in the present compositions.

[0028] One class of preferred surfactants for use herein includes primary amines according to the formula R₁R₂R₃N wherein R₁ and R₂ are both H, R₃ is a C₄-C₁₈, preferably C₆-C₁₂ alkyl chain, R₃ alkyl chains may be straight or branched and may be interrupted with up to 12 ethylene oxide moieties, most preferably interrupted with up to 5 ethylene oxide moieties. Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, laurylamine, palmitylamine, stearylamine, oleylamine, coconutalkylamine, tallowalkyl-amine.

[0029] Other suitable primary amines include amines according to the formula R₁R₂R₃N wherein R₁ and R₂ are both H; R₃ is R₄X(CH₂)_n, X is -O-, -C(O)NH- or -NH-, R₄ is a C₄-C₁₈, preferably C₆-C₁₂ alkyl chain and R₄ may be branched or straight, n is between 1 to 5. Preferred amines according to the formula herein above 3-isopropoxypropylamine, 3-(2-methoxyethoxy)-propylamine and 2-(2-aminoethoxy)-ethanol, C₈-C₁₀ octyl oxy propylamine, 2-ethylhexyloxypropylamine, lauryl amido propylamine and coco amido propylamine.

[0030] Suitable tertiary amines for use herein include tertiary amines having the formula R₁R₂R₃N wherein neither R₁ nor R₂ is H; R₁ and R₂ are C₁-C₈ alkylchains or

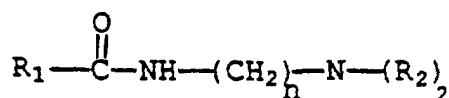


whereby x is between 1 to 6; R₃ is either a C₄-C₁₈, preferably C₆-C₁₂ alkyl chain, or R₃ is R₄X(CH₂)_n, whereby X is -O-, -C(O)NH- or -NH-, R₄ is a C₄-C₁₈, n is between 1 to 5, and R₅ is H or C₁-C₂ alkyl. R₃, R₄ are preferably C₆-C₁₂ alkyl chains and may be straight or branched; R₃ alkyl chains may be interrupted with up to 12 ethylene oxide moieties, most preferably interrupted with up to 5 ethylene oxide moieties.

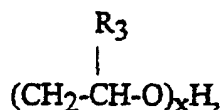
[0031] Suitable tertiary amines for use herein include coconutalkyldimethylamine, dimethyloleylamine, hexa-decyltris (ethyleneoxy)dimethylamine, tallowalkylbis(2-hydroxyethyl)amine, stearylbis(2-hydroxyethyl)amine and oleylbis (2-hydroxyethyl)amine.

[0032] Of all of the foregoing amines the preferred materials are the trialkyl amines marketed under the tradename ADOGEN, the long chain alkyldimethyl amines marketed under the tradename ARMEEN and the ethoxylated amines marketed under the tradename ETHOMEEN. The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable for odor characteristics are n-dodecyl-dimethylamine (ARMEEN DM12D) and bishydroxyethyl-coconutalkylamine (ETHOMEEN C/12, BEROL 307) and oleylamine 7 times ethoxylated (BEROL 28), lauryl amido propylamine and coco amido propylamine.

[0033] Other suitable amines include tertiary amines having the formula



wherein R₁ is C₄-C₁₀, preferably C₈-C₁₀ alkyl; n is 2-4, preferably n is 3; R₂ is C₁-C₄ or



whereby x is 1-5, R₃ is H or C₁-C₂ alkyl.

[0034] Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

[0035] Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from 8 to 24 carbon atoms, and preferably from 12 to 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

[0036] Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 10 to 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from 9 to 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from 11 to 13, abbreviated as C₁₁₋₁₃LAS.

[0037] Other anionic surfactants herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from 8 to 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl group contains from 10 to 20 carbon atoms.

[0038] Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids

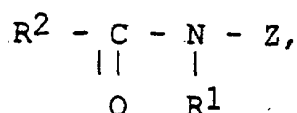
containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

[0039] Water-soluble nonionic surfactants are also useful in the compositions of the invention. Such nonionic materials 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.

[0040] Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 15 carbon atoms, in either a straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alkyl phenol.

[0041] Preferred nonionics are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 9 to 15 carbon atoms with from 4 to 8 moles of ethylene oxide per mole of alcohol.

[0042] Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.

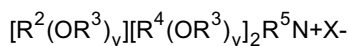


wherein R¹ is H, or R¹ is C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R¹ is methyl, R² is a straight C₁₁₋₁₅ alkyl or C₁₆₋₁₈ alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

[0043] Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

[0044] Zwitterionic surfactants include derivatives of aliphatic, quaternary, ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from 8 to 18 carbon atoms.

[0045] 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 :



wherein R² is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof, each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R⁴ groups, -CH₂CHOH-CHOH-COR⁶-CHOH-CH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than 18; each y is from 0 to about 10 and the sum of the y values is from 0 to 15; and X is any compatible anion.

[0046] Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein R_1 is C_8 - C_{16} alkyl, each of R_2 , R_3 and R_4 is independently C_1 - C_4 alkyl, C_1 - C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2 , R_3 or R_4 should be benzyl.

[0047] The preferred alkyl chain length for R_1 is C_{12} - C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2 , R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

[0048] Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are:

coconut trimethyl ammonium chloride or bromide;
coconut methyl dihydroxyethyl ammonium chloride or bromide;
decyl triethyl ammonium chloride;
decyl dimethyl hydroxyethyl ammonium chloride or bromide;
 C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
coconut dimethyl hydroxyethyl ammonium chloride or bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl (ethenoxy) $_4$ ammonium chloride or bromide;
choline esters (compounds of formula (i) wherein R_1 is $CH_2-CH_2-O-C(O)-C_{12-14}$ alkyl and $R_2R_3R_4$ are methyl);
di-alkyl imidazolines [compounds of formula (i)].

[0049] Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

[0050] When included therein, the laundry detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from 1% to 10% by weight of such cationic surfactants.

[0051] Adjunct Ingredients - The compositions herein can optionally include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition (e.g., perfumes, colorants, dyes,). The following are illustrative examples of such adjunct materials.

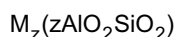
[0052] Optional Detergency Builder - From 1 to 80, preferably 20 to 70, weight % of detergency builder can optionally be, and preferably is, included herein. Inorganic as well as organic builders can be used. Preferred builders include those selected from fatty acids, citrates, carbonates, silicates, sulfates, phosphates, aluminosilicates, and combinations thereof.

[0053] Inorganic detergency builders include, but are not limited to, the alkali metal, ammonium and alkanolanunonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions (hereinafter, collectively "borate builders"), can also be used. Preferably, non-borate builders are used in the compositions of the invention intended for use at wash conditions less than 50°C, especially less than 40°C.

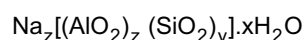
[0054] Examples of silicate builders are the alkali metal silicates, particularly those having a $SiO_2:Na_2O$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck, incorporated herein by reference. However, other silicates may also be useful.

[0055] 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 published on November 15, 1973, the disclosure of which is incorporated herein by reference.

[0056] Aluminosilicate builders are useful in the present invention. Aluminosilicate builders include those having the empirical formula:



wherein M is sodium, potassium, ammonium or substituted ammonium, z is from 0.5 to 2; and y is 1; this material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate. 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 about 0.5, and x is an integer from 15 to 264. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), and Zeolite X.

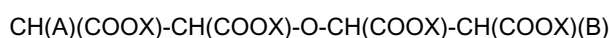
[0057] Specific examples of polyphosphates are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta phosphate in which the degree of polymerization ranges from 6 to 21, and salts of phytic acid.

[0058] Organic detergent builders preferred for the purposes of the present invention include polycarboxylate compounds which have a plurality of carboxylate groups, preferably at least 3 carboxylates.

[0059] 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, or alkanolammonium salts are preferred.

[0060] One important category of polycarboxylate builders encompasses the ether polycarboxylates. Examples of useful ether polycarboxylates include oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al., U.S. Patent 3,635,830, issued January 18, 1972, both of which are incorporated herein by reference.

[0061] 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)-CH₂(COOX); and X is H or a salt-forming cation. Suitable examples of these builders are disclosed in U.S. Patent 4,663,071, issued to Bush et al., on May 5, 1987.

[0062] 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, all of which are incorporated herein by reference.

[0063] Other useful detergency builders include the ether hydroxypolycarboxylates and the copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid.

[0064] Still other useful detergency builders include tartrate mono succinate or tartrate disuccinate.

[0065] Organic polycarboxylate builders also include the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids. Examples include the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, and nitrilotriacetic acid.

[0066] Also included are polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, and carboxymethyloxysuccinic acid, and soluble salts thereof.

[0067] Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders which can also be used in the compositions herein.

[0068] Other carboxylate builders include the carboxylated carbohydrates disclosed in U.S. Patent 3,723,322, Diehl, issued March 28, 1973, incorporated herein by reference.

[0069] 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, Bush, issued January 28, 1986, incorporated herein by reference. Useful succinic acid builders include the C₅-C₂₀ alkyl succinic acids and salts thereof. The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

[0070] Examples of useful builders also include sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentane-tetracarboxylate, water-soluble polyacrylates, and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

[0071] Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226, Crutchfield et al., issued March 13, 1979, incorporated herein by reference.

[0072] Polycarboxylate builders are also disclosed in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference. 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 methylenemalononic acid.

[0073] Other organic builders known in the art can also be used. For example, fatty acids, also known as monocarboxylic acids, and soluble salts thereof, having long chain hydrocarbyls can be utilized. These would include materials generally referred to as "soaps." Chain lengths of C₁₀-C₂₀ are typically utilized. The hydrocarbyls can be saturated or unsaturated.

[0074] Preferably the detergency builder herein is selected from the group consisting of the salts, preferably the sodium salt, of carbonate, silicate, sulfate, phosphate, aluminosilicate, and citric acid and mixtures thereof.

[0075] Second Enzyme - Optional, and preferred, ingredients include second enzymes. Said second enzymes include enzymes selected from proteases, lipases, cellulases, hemicellulases, peroxidases, gluco-amylases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases or mixtures thereof. Highly preferred are protease, lipase, peroxidase, cellulase, and mixtures thereof. By "second enzyme" is meant one or more enzymes in addition to amylase which are also added to the composition.

[0076] The amount of second enzyme used in the composition varies according to the type of enzyme and the use intended. In general, from 0.0001 to 1.0, more preferably 0.001 to 0.5, weight % of the composition on an active basis of these second enzymes are preferably used.

[0077] Purified or nonpurified forms of these enzymes may be used. Enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants.

[0078] Lipase Enzymes - Lipase enzymes which optionally may be considered for inclusion in the detergent compositions of the present invention include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Lipases include M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R (Novo).

[0079] The lipases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

[0080] A preferred component of the detergent composition according to the invention is the D96L lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa*. Preferably the *Humicola lanuginosa* strain DSM 4106 is used. This enzyme is preferably incorporated into the composition in accordance with the invention at a level of from 50 LU to 8500 LU per liter wash solution. More preferably the variant D96L is present at a level of from 100 LU to 7500 LU per liter of wash solution, and most preferably at a level of from 150 LU to 5000 LU per liter of wash solution.

[0081] By D96L lipolytic enzyme variant is meant the lipase variant as described in patent application WO 92/05249 viz. wherein the native lipase ex *Humicola lanuginosa* aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L.

[0082] To determine the activity of the enzyme D96L the standard LU assay was used (Analytical method, internal Novo Nordisk number AF 95/6-GB 1991.02.07). A substrate for D96L was prepared by emulsifying glycerine tributyrat (Merck) using gum-arabic as emulsifier. Lipase activity was assayed at pH 7 using pH stat, method. One unit of lipase activity (LU/mg) is defined as the amount needed to liberate one micromole fatty acid per minute.

[0083] The D96L variant of the native *Humicola lanuginosa* lipase has the additional advantage of delivering a significant benefit in whiteness maintenance when compared to the wildtype lipase.

[0084] Protease Enzymes - Protease enzymes are optionally present at levels sufficient to provide from 0.001 to 0.1 Anson units (AU) of activity per gram of composition. The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. More preferred is serine proteolytic enzyme of bacterial origin. Purified or nonpurified forms of enzyme may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants. Particularly preferred by way of proteolytic enzyme is bacterial serine proteolytic enzyme obtained from *Bacillus*, *Bacillus subtilis* and/or *Bacillus licheniformis*. Suitable commercial proteolytic enzymes which may be considered for inclusion in the present invention compositions include Alcalase®, Biosam®, Esperase®, Durazym®, Savinase®, Maxatase®, Maxacal®, and Maxapem® 15 (protein engineered Maxacal); Purafect® and subtilisin BPN and BPN'.

[0085] Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. More preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991, which is incorporated herein by reference. Genetically modified variants, particularly of Protease C, are also included herein.

[0086] Preferred proteolytic enzymes are selected from the group consisting of Savinase®, Esperase®, Maxacal®, Purafect®, BPN', Protease A and Protease B, and mixtures thereof. Bacterial serine protease enzymes obtained from *Bacillus subtilis* and/or *Bacillus licheniformis* are preferred.

[0087] An especially preferred protease herein referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for the amino acid residue at a position in said carbonyl hydrolase equivalent to position +76,

preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the concurrently filed patent application of A. Baeck et al. entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/322,676, filed October 13, 1994, which is incorporated herein by reference in its entirety.

[0088] The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

[0089] Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

[0090] Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo).

[0091] Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromoperoxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.

[0092] Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

[0093] Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor). The cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

[0094] Enzyme Stabilizers - The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Alternatively, stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from 1 to 30, preferably from 2 to 20, more preferably from 5 to 15, and most preferably from 8 to 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from 0.05 to 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

[0095] It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from 0.05% to 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

[0096] The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from 0.25% to 10%, preferably from 0.5% to 5%, more preferably from 0.75% to 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromophenylboronic acid) can also be used in place of boric acid.

[0097] Other Ingredients - Other ingredients suitable for use in the present compositions, such as water, perfume, carriers, hydrotropes, processing aids, brightener, conditioners such as fumed silica, polyethylene glycol, dyes and colorants, and peroxyacids, can be included. Preferred ingredients are from 0.5 to 5 wt.% of the composition of poly-

ethylene glycol (preferably with molecular weight between 5,000 and 10,000, most preferably 8,000), from 0.01 to 0.7 wt.% of fluorescent whitening and/or brightening agents, and from 0.01 to 1.0 wt.% of perfume. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl₂, MgSO₄, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

[0098] Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

[0099] To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

[0100] Liquid detergent compositions can 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 surfactant, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

[0101] Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

[0102] A preferred silicone suds controlling agent is disclosed in Bartollbta et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12^R.

[0103] Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

[0104] Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^R.

[0105] The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

[0106] Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

[0107] Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616.

[0108] Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

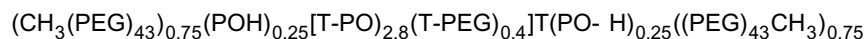
[0109] Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously men-

tioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

[0110] Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4'-bis(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-sodium 4,4'-bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphos-tyryl)biphenyl.

[0111] Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance; fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

[0112] Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4 116 885 and 4 711 730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_n\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pOC}_6\text{H}_4\text{CO})$.

[0113] Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate; ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

[0114] The selected polyesters herein contain 46% by weight of dimethyl terephthalic acid, 16% by weight of propane -1.2 diol, 10% by weight ethylene glycol 13% by weight of dimethyl sulfobenzoic acid and 15% by weight of sulfoisophthalic acid, and have a molecular weight of 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

[0115] Fabric softening agents can also be incorporated into laundry detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

[0116] Levels of smectite clay are normally in the range from 5% to 15%, more preferably from 8% to 12% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

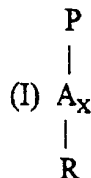
[0117] The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

[0118] The detergent compositions according to the present invention may comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other

articles in the wash.

[0119] Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof.

[0120] The polyamine N-oxide polymers suitable for use contain units having the following structure formula:



wherein P is a polymerisable unit, whereto 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(O), CO₂, C(O), -O-, -S-, -N-; x is O or 1; R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

[0121] 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.

[0122] 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.

[0123] 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.

[0124] Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

[0125] 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.

[0126] Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

[0127] 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.

[0128] Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

[0129] 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, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

[0130] 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 preferred PKa < 6.

[0131] 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.

[0132] Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

[0133] The N-vinylimidazole N-vinylpyrrolidone polymers which may be used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 20,000-200,000.

[0134] 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.

[0135] 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".

[0136] 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.

[0137] 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.

[0138] 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.

[0139] The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 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). 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).

[0140] 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 2,500 to 400,000, preferably from 5,000 to 200,000 more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

[0141] The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

[0142] The detergent compositions herein 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 11. 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.

[0143] The liquid detergent composition is added to the wash, usually at levels of 60 to 240 ml 1/4 to 1 cup.).

[0144] This invention further provides a method for cleaning fabrics in the wash by contacting the fabrics with a wash solution which contains an effective amount of the detergent compositions hereinbefore described. Agitation is preferably provided in the washing machine for good cleaning. Washing is preferably followed by drying the wet fabric in a conventional clothes dryer. An effective amount of the liquid detergent composition in the washing machine is preferably from 500 to 7000 ppm, more preferably from 1000 to 3000 ppm.

[0145] The following examples illustrate the compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

[0146] In the detergent compositions, the abbreviated component identifications have the following meanings:

Amine	Selected from coconutalkyldimethylamine, dimethyloleylamine, hexa-
Surfactants	decyltris (ethyleneoxy)dimethylamine, tallowalkylbis(2-hydroxyethyl)amine, stearyl
LAS	bis(2-hydroxyethyl)amine and oleoylbis(2-hydroxyethyl)amine, and mixtures thereof
TAS	Sodium linear C ₁₂ alkyl benzene sulphonate
AS	Sodium tallow alkyl sulphate
SAS	Sodium C ₈ - C ₁₈ alkyl sulfate
APG	C ₁₂ -C ₁₄ secondary (2,3) alkyl sulfate in the form of the sodium salt.
AEC	Alkyl polyglycoside surfactant of formula C ₁₂ - (glycosyl) _x , where x is 1.5
SS	Alkyl ethoxycarboxylate surfactant of formula C ₁₂ ethoxy (2) carboxylate.
25EY	Secondary soap surfactant of formula 2-butyl octanoic acid
43EY	A C ₁₂ -C ₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
XYEVS	A C ₁₄ - C ₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
Nonionic	C _{1X} - C _{1Y} sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole
	C ₁₃ -C ₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafax LF404 by BASF GmbH

(continued)

	CFAA	C ₁₂ -C ₁₄ alkyl N-methyl glucamide
5	TFAA	C ₁₆ -C ₁₈ alkyl N-methyl glucamide.
	Silicate	Amorphous Sodium Silicate (SiO ₂ :N ₂ O ratio = 2.0)
	NaSKS-6	Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
	Carbonate	Anhydrous sodium carbonate
	Phosphate	Sodium tripolyphosphate
10	MA/AA	Copolymer of 1:4 maleic/acrylic acid, average molecular weight 80,000
	Polyacrylate	Polyacrylate homopolymer with an average molecular weight of 8,000 sold under the tradename PA30 by BASF GmbH
	Zeolite A	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ · 27H ₂ O having a primary particle size in the range from 1 to 10 micrometers
15	Citrate	Tri-sodium citrate dihydrate
	Citric	Citric Acid
	Perborate	Anhydrous sodium perborate monohydrate bleach, empirical formula NaBO ₂ · H ₂ O ₂
	PB4	Anhydrous sodium perborate tetrahydrate
20	Percarbonate	Anhydrous sodium percarbonate bleach of empirical formula 2Na ₂ CO ₃ · 3H ₂ O ₂
	TAED	Tetraacetyl ethylene diamine
	Paraffin	Paraffin oil sold under the tradename Winog 70 by Wintershall.
	Xylanase	Xylanolytic enzyme sold under the tradenames Pulpzyme HB or SP431 by Novo Nordisk A/S or Lyxasan (Gist-Brocades) or Optipulp or Xylanase (Solvay).
25	Protease	Proteolytic enzyme sold under the tradename Savinase® by Novo Nordisk A/S.
	Protease D	Proteolytic enzyme which is a <i>Bacillus lentus</i> subtilisin variant N76D/S103A/V104I, according to the numbering of <i>Bacillus amyloliquefaciens</i> subtilisin.
	Amylase	Amylolytic enzyme sold under the tradename Termamyl® by Novo Nordisk A/S
30	Lipase	Lipolytic enzyme sold under the tradename Lipolase® by Novo Nordisk A/S
	D96L Lipase	Variant of the native lipase derived from <i>Humicola lanuginosa</i>
	Peroxidase	Peroxidase enzyme
	Cellulase	Cellulosic enzyme sold under the tradename Carezyme® or Celluzyme® by Novo Nordisk A/S.
	CMC	Sodium carboxymethyl cellulose
35	HEDP	1,1-hydroxyethane diphosphonic acid
	DETPMP	Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060®
	PVP	Polyvinyl pyrrolidone polymer
40	EDDS	Ethylenediamine -N, N'- disuccinic acid, [S,S] isomer in the form of the sodium salt.
	Suds Suppressor	25% paraffin wax Mpt50°C, 17% hydrophobic silica, 58% paraffin oil or 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form
	SCS	Sodium cumene sulphonate
	Sulphate	Anhydrous sodium sulphate.
45	HMWPEO	High molecular weight polyethylene oxide
	PGMS	Polyglycerol monostearate having a tradename of Radiesurf 248
	TAE 25	Tallow alcohol ethoxylate (25)

In the following examples all levels of enzyme quoted are expressed as % active enzyme by weight of the composition:

EXAMPLE I

[0147] The wash performance of amylase enzyme is evaluated in non-phosphate liquid detergent prepared according to the following composition:

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Material	Wt. %
C ₁₂ -C ₁₄ alkyl N-methyl glucamide	3.0
NaC25 AE2.5S	17.0
Neodol 23-9	1.0
Citric Acid builder	2.0
Fatty Acid builder	3.0
Ethane	3.0
Propanediol	5.0
NaOH	3.0
Sodium formate	0.05
Borax	2.5
Methylethyleneamine	1.0
Protease	0.2
Amylase*	0.2
Silicone Antifoam	0.1
PEI 189 E15-18	
(Ethoxylated tetraethylene pentamine)	1.0
Water and miscellaneous	to 100%

[0148] The following amylases are substituted for the amylase enzyme at the levels listed below: Termamyl®, Genecor's Purafact Ox Am®, and Duramyl®.

[0149] To a top-loading automatic washing machines is added 2.3 kg (5 lbs.) of naturally soiled fabrics and 64 liters of 35°C [95°F] city water having a hardness of 103 ppm [6 gr/gal]. To each machine is added 120 ml [1/2 cup] of liquid detergent with the amylase enzyme.

[0150] The washing machines are then allowed to complete their normal washing and rinsing cycles, and the test fabrics are dryer dried. This procedure is repeated four times.

[0151] After completion of the four cycles, the fabrics are arranged under suitable lighting for comparison of soil and stain removal. The fabrics show improved whiteness.

EXAMPLE II

[0152] Heavy duty liquid fabric cleaning compositions suitable for use in the pretreatment of stained fabrics, and for use in a machine laundering method, in accord with the invention are prepared as follows:

	I	II	III	IV	V
Amine	10.0	15.0	5.0	10.0	5.0
24AS	20.0	20.0	20.0	20.0	20.0
SS	5.0	5.0	5.0	5.0	5.0
Citrate	1.0	1.0	1.0	1.0	1.0
12E ₃	13.0	13.0	13.0	13.0	13.0
Monethanolamine	2.5	2.5	2.5	2.5	2.5
Protease	0.005	0.01	0.1	0.0	0.005
Amylase	0.005	0.05	0.2	0.0004	0.01
Cellulase	0.0	0.04	0.004	0.001	0.0
Water/propylene glycol/ethanol (100:1:1)					

[0153] Amylase enzymes include: Termamyl®, Genecor's Purafact Ox Am®, and Duramyl®.

EXAMPLE III

[0154] Heavy duty liquid fabric cleaning compositions in accord with the invention are prepared as follows:

	I	II	III	IV
LAS acid form	-	-	25.0	-
C ₁₂₋₁₄ alkenyl succinic acid	3.0	8.0	10.0	-
Citric acid	10.0	15.0	2.0	2.0
25AS acid form	8.0	8.0	-	15.0
25AE2S acid form	-	3.0	-	4.0
25AE7	-	8.0	-	6.0
25AE3	8.0	-	-	-
CFAA	-	-	-	6.0
DETPMP	0.2	-	1.0	1.0
Fatty acid	-	-	-	10.0
Oleic acid	1.8	-	1.0	-
Ethanol	4.0	4.0	6.0	2.0
Propanediol	2.0	2.0	6.0	10.0
Xylanase	0.05	0.0	0.05	0.0
Amylase	0.005	0.01	0.2	0.0001
Coco-alkyl dimethyl hydroxy ethyl ammonium chloride	-	-	3.0	-
Smectite clay	-	-	5.0	-
PVP	1.0	2.0	-	-
Perborate	-	1.0	-	-
Phenol sulphonate	-	0.2	-	-
Peroxidase	-	0.01	-	-
NaOH	pH 7.5	pH 7.5	pH 7.5	pH 7.5
Water/minors	to 100%	to 100%	to 100%	to 100%

[0155] Amylase enzymes include: Termamyl® , Genecor's Purafact Ox Am®, and Duramyl® .

EXAMPLE IV

[0156] Heavy duty liquid fabric cleaning compositions in accord with the invention are prepared as follows:

	I	II	III
CFAA	5.0	4.5	3.9
25AS acid form	15.0	13.0	7.5
25AE2S acid form	9.0	8.0	11.0
Amine surfactants C8-10 amine	2.0	2.0	2.5
Fatty acid builder	5.0	4.0	3.5
Citric acid	4.0	3.5	3.0
Carzeye cellulase	0.27	0.0	0.05

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(continued)

	I	II	III
Lipolase lipase	0.15	0.0	0.075
Protease D	0.05	0.05	-
Protease	-	-	0.1
Xylanase	0.05	0.05	0.05
Amylase	0.015	0.05	0.1
DETPMP chelant	1.0	1.0	0.75
Soil release polymer	0.2	0.25	0.15
Dispersing agent	0.25	0.7	1.2
Waters/minors	Up to 100%		

[0157] Amylase enzymes include: Termamyl®, Genecor's Purafact Ox Am®, and Duramyl®.

EXAMPLE V

[0158] Granular fabric cleaning compositions in accord with the invention are prepared as follows:

	A	B
LAS	22.0	22.0
Phosphate	23.0	23.0
Carbonate	23.0	23.0
Silicate	14.0	14.0
Zeolite A	8.2	8.2
DETPMP	0.4	0.4
Sodium Sulfate	5.5	5.5
Protease	0.01	0.02
Cellulase	0.001	-
Amylase*	0.01	0.1
Water/minors	to 100%	to 100%

*Amylase enzymes include: Termamyl®, Genecor's Purafact Ox Am®, and Duramyl®.

[0159] Aqueous crutcher mixes of heat and alkali stable components of the detergent compositions are prepared and spray-dried and the other ingredients are dry-mixed so that they contain the ingredients tabulated at the levels shown.

EXAMPLE VI

[0160] Granular fabric cleaning compositions in accord with the invention are prepared as follows:

	A	B
LAS	12.0	12.0
Zeolite A	26.0	26.0
SS	4.0	4.0
SAS	5.0	5.0

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(continued)

	A	B
Citrate	5.0	5.0
Sodium Sulfate	17.0	17.0
Perborate	16.0	16.0
TAED	5.0	-
Protease	0.06	0.03
Amylase*	0.01	0.2
Water/minors	up to 100%	up to 100%

*Amylase enzymes include: Termamyl®, Genecor's Purafact Ox Am®, and Duramyl®.

[0161] Aqueous crutcher mixes of heat and alkali stable components of the detergent compositions are prepared and spray-dried and the other ingredients are dry-mixed so that they contain the ingredients tabulated at the levels shown.

EXAMPLE VII

[0162] Granular fabric cleaning compositions in accord with the invention which are especially useful in the laundering of coloured fabrics are prepared as follows:

LAS	11.4	10.7
TAS	1.8	2.4
TFAA	-	3.0
45AS	3.0	5.0
45E7	4.0	-
25E3S	-	3.0
68E11	1.8	1.8
Citrate	14.0	15.0
Citric acid	3.0	2.5
Zeolite A	32.5	32.1
Na-SKS-6	-	9.0
MA/AA	5.0	5.0
DETPMP	1.0	0.2
Xylanase	0.01	-
Protease	0.02	0.02
D96L	0.0005	0.01
Amylase*	0.03	0.2
Silicate	2.0	2.5
Sulphate	3.5	5.2
PVP	0.3	0.5
Poly (4-vinyl-pyridine)-N-oxide/copolymer of vinyl-imidazole and vinyl-pyrrolidone	-	0.2
Perborate	0.5	1.0

*Amylase enzymes include: Termamyl®, Genecor's Purafact Ox Am®, and Duramyl®.

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(continued)

Peroxidase	0.01	0.01
Phenol sulfonate	0.1	0.2
water/minors	up to 100%	up to 100%

[0163] Aqueous crutcher mixes of heat and alkali stable components of the detergent compositions are prepared and spray-dried and the other ingredients are dry-mixed so that they contain the ingredients tabulated at the levels shown.

EXAMPLE VIII

[0164] A laundry bar suitable for hand-washing soiled fabrics is prepared comprising the following ingredients.

Component	Weight %
Linear alkyl benzene sulfonate	30
Phosphate (as sodium tripoly-phosphate)	7
Sodium carbonate	20
Sodium pyrophosphate	7
Coconut monoethanolamide	2
Zeolite A (0.1-10 microns)	5
Carboxymethylcellulose	0.2
Polyacrylate (MW 1400)	0.2
N-acyl caprolactam	5
Sodium perborate tetrahydrate	10
Brightener, perfume	0.2
Amylase Enzyme	0.05
CaSO ₄	1
MgSO ₄	1
Water	4
Filler*	Balance to 100%
Amylase enzymes include: Termamyl®, Genecor's Purafact Ox Am®, and Duramyl®.	

*Can be selected from convenient materials such as CaCO₃, talc, clay, silicates, and the like.

[0165] A detergent laundry bar is extruded in conventional soap or detergent bar making equipment as commonly used in the art.

EXAMPLE IX

[0166] A compact granular fabric cleaning composition is prepared as follows:

	I	II	III
Component	Wt %	Wt %	Wt %
LAS	-	8.0	-
TAS	-	2.0	-

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(continued)

	I	II	III
<u>Component</u>	<u>Wt %</u>	<u>Wt %</u>	<u>Wt %</u>
45AS	8.0	-	10.0
25E3S	2.0	0.5	3.0
25E5	-	5.0	5.0
25E3	5.0	-	-
TFAA	2.5	-	2.5
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	-	1.0	-
Zeolite A	17.0	15.0	25.0
NaSKS-6	12.0	10.0	12.0
Citric acid	3.0	2.0	3.0
Sodium citrate	-	-	10.0
Carbonate	7.0	8.0	7.0
MA/AA	5.0	1.0	5.0
CMC	0.4	0.4	0.4
Poly (4-vinylpyridine)-N-oxide/	0.2	-	0.2
Protease	0.05	0.03	0.05
Lipase*	0.002	0.004	0.002
Cellulase	0.001	-	0.001
Amylase	0.01	0.006	0.006
TAED	6.0	3.0	-
Percarbonate	22.0	20.0	-
NACA-OBS	-	3.0	-
EDDS	0.3	0.2	0.3
Granular suds suppressor	3.5	3.0	3.5
water/minors (sulfate)	Up to 100%		

*Lipase is selected from Lipolase™ or Lipolase Ultra™ (known as DL96L), both supplied by Novo Nordisk.

EXAMPLE X

[0167] A high density, compact granular detergent composition is prepared as follows:

	I	II	III
<u>Component</u>	<u>Wt. %</u>	<u>Wt. %</u>	<u>Wt. %</u>
AS	7.4	5	16
AES	0.8	-	-
LAS	12	21	10
AE	3	3	3
Polyhydroxy fatty acid amide	1	-	-
Cationic quaternary ammonium compounds	1	1	1

(continued)

	<u>I</u>	<u>II</u>	<u>III</u>
<u>Component</u>	<u>Wt. %</u>	<u>Wt. %</u>	<u>Wt. %</u>
Amylase Enzyme	0.001	0.05	0.1
Biosam® Protease	0.001	0.005	-
Zeolites	17	7	27
Na SKS-6	6	3.3	-
Citric Acid	1	-	-
Polycarboxylate	3	7	2
Chelant	0.4	-	0.6
Carbonate	18	10	28
Silicate	4	11	0.5
Perborate	11	4	29
Nonanoyl oxybenzene sulfonate	2.5	3	-
TAED	4.8	-	5
Soil release polymer	0.3	0.3	0.3
PEG	0.8	-	1.5
Suds Control	0.3	0.2	0.3
Sulfate	To Balance	To Balance	To Balance
Amylase enzymes include: Termamyl®, Genecor's Purafact Ox Am®, and Duramyl®.			

Claims

1. A laundry detergent composition which is especially effective for cleaning and whitening dingy fabrics laundered therewith, which composition comprises :

A. detergent surfactant which is selected from group consisting of anionic, nonionic, cationic, ampholytic and zwitterionic surfactants and combinations thereof, and which is present to the extent of from 1% to 40% by weight of the composition herein; and

B. one or more amylase enzymes which are present in an amount that ranges from 0.001 mg to 2 mg of active amylase enzyme per gram of composition and that is effective to increase the whiteness of dingy fabrics laundered with laundry solutions formed from said detergent composition in comparison with similar compositions which contain no amylase;

wherein said composition contains less than 0.01% by weight of a nonionic polysaccharide ether having a molecular weight of more than 10,000.

2. A detergent composition according to Claim 1 wherein

A. the detergent surfactant comprises from 2% to 25% by weight of the composition and is a nonionic or anionic surfactant; and

B. the active amylase enzyme comprises from 0.01 mg to 1 mg of active amylase enzyme per gram of composition.

3. A detergent composition according to Claim 2 wherein the amylase enzyme is enhanced from substitution using any naturally occurring L-amino acid located in the 197 position of *B.Licheniformis* or the homologous position

variation of a similar parent amylase.

4. A detergent composition according to Claim 3 wherein

- 5 A the amylase enzyme is enhanced from substitution using threonine of the methionine residue located in position 197 of *B.Licheniformis* or the homologous position variation of a similar parent amylase;
 B. the surfactant is selected from the amines, salts of C₁₁₋₁₃ linear alkyl benzene sulfonate, C₁₂₋₁₆ alkyl sulfate, methyl ester sulfonate and combinations of these surfactants; and
 C. the composition further comprises from 20% to 70% by weight of the composition of a detergent builder.

5. A detergent composition according to Claim 4 wherein the composition further comprises from 20% to 70% by weight of the composition of a detergency builder selected from fatty acids, citrates, carbonates, silicates, sulfates, phosphates, aluminosilicates, and combinations thereof.

6. A detergent composition according to Claim 5 further comprising proteolytic enzyme.

7. A method for laundering fabrics to increase whiteness and provide dingy cleanup thereof, said method comprising contacting fabrics in need of whiteness and dingy clean-up with an aqueous solution formed from a detergent composition of Claim 1 at a concentration such that the whitening performance of said composition is increased in comparison with similar compositions which contain no amylase.

8. A method for laundering fabrics to increase whiteness and provide dingy cleanup thereof, said method comprising contacting fabrics in need of whiteness and dingy clean-up with an aqueous solution formed from a detergent composition according to Claim 1 in multiple wash cycles such that the fabrics appear whitened and less dingy.

9. A method for laundering fabrics to reduce the odors associated with soils and stains, said method comprising contacting stained and soiled fabrics in need of odor control with an aqueous solution formed from a detergent composition comprising surfactant and amylase enzyme according to Claim 1.

10. A detergent composition according to Claim 1 in granular form.

11. A detergent composition according to Claim 1 in liquid form.

Patentansprüche

1. Wäschewaschmittelzusammensetzung, welche insbesondere zum Reinigen und Aufhellen von damit gewaschenen, schmutzigen Textilien wirksam ist, welche Zusammensetzung umfaßt:

40 A. Waschtensid, das aus der anionische, nichtionische, kationische, ampholytische und zwitterionische Tenside und Kombinationen hiervon umfassenden Gruppe gewählt ist und das in einem Anteil von 1 bis 40 Gew.-% der Zusammensetzung vorliegt; und

45 B. ein oder mehrere Amylaseenzyme, die in einer Menge im Bereich von 0,001 mg bis 2 mg aktives Amylaseenzym pro Gramm der Zusammensetzung vorliegen und welche wirksam sind, den Weißgrad von mit Wäschelösungen, die aus der Waschmittelzusammensetzung gebildet sind, gewaschenen, schmutzigen Textilien, im Vergleich zu ähnlichen Zusammensetzungen, welche keine Amylase enthalten, zu erhöhen;

50 wobei die Zusammensetzung weniger als 0,01 Gew.-% eines nichtionischen Polysaccharidethers mit einem Molekulargewicht von mehr als 10.000 enthält.

2. Waschmittelzusammensetzung nach Anspruch 1, wobei

55 A. das Waschtensid 2 bis 25 Gew.-% der Zusammensetzung umfaßt und ein nichtionisches oder anionisches Tensid ist; und

B. das aktive Amylaseenzym 0,01 mg bis 1 mg aktives Amylaseenzym pro Gramm der Zusammensetzung umfaßt.

3. Waschmittelzusammensetzung nach Anspruch 2, wobei das Amylaseenzym durch Substitution verstärkt ist unter Verwendung irgend einer natürlich vorkommenden L-Aminosäure, welche in der 197-Position von *B.Licheniformis* oder der homologen Positionsvariation einer ähnlichen Stamm-Amylase lokalisiert ist.

4. Waschmittelzusammensetzung nach Anspruch 3, wobei

A. das Amylaseenzym durch Substitution verstärkt ist unter Verwendung von Threonin des Methioninrestes, lokalisiert in der 197-Position von *B.Licheniformis* oder der homologen Positionsvariation einer ähnlichen Stamm-Amylase;

B. das Tensid gewählt ist aus den Aminen, Salzen von linearem C₁₁₋₁₃-Alkylbenzolsulfonat, C₁₂₋₁₆-Alkylsulfat, Methylestersulfonat und Kombinationen dieser Tenside; und

C. die Zusammensetzung weiterhin 20 bis 70 Gew.-% der Zusammensetzung eines Waschmittelbuilders umfaßt.

5. Waschmittelzusammensetzung nach Anspruch 4, wobei die Zusammensetzung weiterhin 20 bis 70 Gew.-% der Zusammensetzung eines Waschmittelbuilders umfaßt, gewählt aus Fettsäuren, Citraten, Carbonaten, Silicaten, Sulfaten, Phosphaten, Aluminosilicaten und Kombinationen hiervon.

6. Waschmittelzusammensetzung nach Anspruch 5, umfassend weiterhin proteolytisches Enzym.

7. Verfahren zum Waschen von Textilien, um den Weißgrad zu erhöhen und eine Entfernung deren Verschmutzung vorzusehen, wobei das Verfahren das Kontaktieren von Textilien, welche einen Weißgrad und eine Schmutzentfernung benötigen, mit einer aus einer Waschmittelzusammensetzung nach Anspruch 1 gebildeten, wäßrigen Lösung bei einer solchen Konzentration umfaßt, daß die Aufhellungsleistung der Zusammensetzung erhöht ist, im Vergleich mit ähnlichen Zusammensetzungen, welche keine Amylase enthalten.

8. Verfahren zum Waschen von Textilien, um den Weißgrad zu erhöhen und eine Entfernung deren Verschmutzung vorzusehen, wobei das Verfahren das Kontaktieren von Textilien, welche einen Weißgrad und eine Schmutzentfernung benötigen, mit einer aus einer Waschmittelzusammensetzung nach Anspruch 1 gebildeten, wäßrigen Lösung in mehrfachen Waschzyklen umfaßt, so daß die Textilien aufgehellt und weniger schmutzig erscheinen.

9. Verfahren zum Waschen von Textilien, um mit Verschmutzungen und Flecken verbundene Gerüche zu verringern, wobei das Verfahren das Kontaktieren befleckter und verschmutzter Textilien, welche eine Geruchsregulierung benötigen, mit einer wäßrigen Lösung umfaßt, die aus einer Waschmittelzusammensetzung, umfassend Tensid und Amylaseenzym gemäß Anspruch 1, gebildet ist.

10. Waschmittelzusammensetzung nach Anspruch 1 in Granulatform.

11. Waschmittelzusammensetzung nach Anspruch 1 in flüssiger Form.

Revendications

1. Composition détergente pour le linge, qui est particulièrement efficace pour nettoyer et blanchir des textiles ternes lavés avec elle, ladite composition comprenant :

A. un tensioactif détergent qui est choisi dans l'ensemble comprenant les tensioactifs anioniques, non ioniques, cationiques, ampholytes et zwitterioniques et leurs combinaisons, et qui est présent à raison de 1 à 40 % en poids par rapport à la composition ; et

B. une ou plusieurs enzymes amylases, qui sont présentes en une quantité comprise entre 0,001 mg et 2 mg d'enzyme amylase active par gramme de composition, et qui est efficace pour augmenter la blancheur de textiles ternes lavés avec des solutions de blanchissage formées à partir de ladite composition détergente, par comparaison avec des compositions analogues ne contenant pas d'amylase ;

où ladite composition contient moins de 0,01 % en poids d'un éther de polysaccharide non ionique ayant une masse moléculaire supérieure à 10 000.

2. Composition détergente selon la revendication 1, dans laquelle

- A. le tensioactif détergent représente de 2 % à 25 % en poids de la composition et est un tensioactif non ionique ou anionique ; et
B. l'enzyme amylase active représente de 0,01 mg à 1 mg d'enzyme amylase active par gramme de composition.

3. Composition détergente selon la revendication 2, dans laquelle l'enzyme amylase est améliorée grâce à une substitution qui utilise un acide L-aminé naturel quelconque situé sur la position 197 de *B. licheniformis* ou la variante de position homologue d'une amylase précurseur analogue.

4. Composition détergente selon la revendication 3, dans laquelle

A. l'enzyme amylase est améliorée grâce à une substitution utilisant une thréonine sur le résidu de méthionine situé sur la position 197 de *B. licheniformis* ou la variante de position homologue d'une amylase précurseur analogue ;

B. le tensioactif est choisi parmi les amines, les sels (alkyle linéaire en C₁₁₋₁₃)benzènesulfonates, (alkyle en C₁₂₋₁₆)sulfates, méthylester-sulfonates et les combinaisons de ces tensioactifs ; et

C. la composition comprend en outre de 20 % à 70 % en poids, par rapport à la composition, d'un adjuvant de détergence.

5. Composition détergente selon la revendication 4, dans laquelle la composition comprend en outre de 20 % à 70 % en poids, par rapport à la composition, d'un adjuvant de détergence choisi parmi les acides gras, les citrates, les carbonates, les silicates, les sulfates, les phosphates, les aluminosilicates et leurs combinaisons.

6. Composition détergente selon la revendication 5, qui comprend en outre une enzyme protéolytique.

7. Procédé de blanchissage de textile pour augmenter la blancheur et supprimer leur caractère terne, ledit procédé comprenant la mise en contact des textiles que l'on veut blanchir et dont on veut supprimer le caractère terne avec une solution aqueuse formée à partir d'une composition détergente selon la revendication 1 à une concentration telle que les performances de blanchiment de ladite composition soient améliorées par comparaison avec celle des compositions analogues ne contenant pas d'amylase.

8. Procédé de blanchissage de textile pour augmenter la blancheur et en supprimer le caractère terne, ledit procédé comprenant la mise en contact des textiles que l'on veut blanchir et dont on veut supprimer le caractère terne avec une solution aqueuse formée à partir d'une composition détergente selon la revendication 1 dans le cadre de plusieurs cycles de lavage, de façon que les textiles présentent un aspect blanchi et moins terne.

9. Procédé de blanchissage de textile pour réduire les odeurs associées aux salissures et aux taches, ledit procédé comprenant la mise en contact des textiles salis et tachés ayant besoin d'une suppression de leur odeur avec une solution aqueuse formée à partir d'une composition détergente comprenant un tensioactif et une enzyme amylase selon la revendication 1.

10. Composition détergente selon la revendication 1 sous forme granulaire.

11. Composition détergente selon la revendication 1 sous forme liquide.