



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b>  <b>C11D 3/386</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/05748</b>  <b>(43) International Publication Date:</b> 12 February 1998 (12.02.98)
<p><b>(21) International Application Number:</b> PCT/US96/12612</p> <p><b>(22) International Filing Date:</b> 1 August 1996 (01.08.96)</p> <p><b>(71) Applicant</b> (<i>for all designated States except US</i>): THE PROCTER &amp; GAMBLE COMPANY [US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p><b>(72) Inventors; and</b>  <b>(75) Inventors/Applicants</b> (<i>for US only</i>): BAECK, Andre, Cesar [BE/BE]; Putsesteenweg 273, B-2820 Bonheiden (BE). JONES, Lynda, Anne [GB/GB]; 21 Mayfield Road, Gosforth, Newcastle-upon-Tyne NE3 4ME (GB). OHTANI, Ryohi [JP/JP]; 7-19, Uedanaka-machi, Nishinomiya, Hyogo (JP). PRAMOD, Kakumanu [IN/US]; 7986 Kingfisher Lane, West Chester, OH 45069 (US). RAI, Saroj [US/US]; 8287 Fox Knoll Drive, West Chester, OH 45069 (US). SHOWELL, Michael, Stanford [US/US]; 810 Finney Trail, Cincinnati, OH 45224 (US).</p> <p><b>(74) Agents:</b> REED, T., David et al.; The Procter &amp; Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p>		<p><b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b>  <i>With international search report.</i></p>
<p><b>(54) Title:</b> DETERGENT COMPOSITIONS COMPRISING IMPROVED AMYLASE FOR DINGY FABRIC CLEAN-UP</p> <p><b>(57) Abstract</b></p> <p>The present invention relates to the use of a specific amylase enzyme in a laundry detergent composition for boosting fabric laundry performance, especially on dingy stains and soils.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

DETERGENT COMPOSITIONS COMPRISING IMPROVED AMYLASE  
FOR DINGY FABRIC CLEAN-UP

TECHNICAL FIELD

The present invention relates to the use of a specific amylase enzyme in laundry detergent compositions for boosting fabric laundry performance, especially on dingy stains and soils.

BACKGROUND OF THE INVENTION

For a number of years amylase enzymes have been used for a variety of different purposes, the most important of which are starch liquefaction, textile desizing, starch modification in the paper and pulp industry, and for brewing and baking. A further use of amylases which is becoming increasingly important, is the removal of starch containing soils and stains during the washing of fabrics, hard surfaces and dishes.

Indeed, amylase enzymes have long been recognised in dishwashing, hard surface cleaning and laundry compositions to provide the removal of starchy food residues or starchy films from dishware, flatware, glasses and hard surfaces or to provide cleaning performance on starchy soils as well as other soils typically encountered in laundry applications.

WO/94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO94/18314 Genencor, published August 18, 1994; WO96/05295, Genencor published February 22, 1996 and WO/95/10603, Novo Nordisk A/S, published April 20, 1995.

Other amylases known for use in cleaning compositions include both  $\alpha$ - and  $\beta$ -amylases.  $\alpha$ -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; 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).

Examples of commercial  $\alpha$ -amylases products are Termamyl® Ban® Duramyl® and Fungamyl®, all available from Novo Nordisk A/S Denmark and Maxamyl® available from Gist Brocades and Purafact Ox Am® from Genencor.

Recently new amylases have been identified and are described in WO/95/26397, Novo Nordisk A/S, published October 05, 1995, disclosing an  $\alpha$ -amylase having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10. Variants of these new amylases demonstrating at least one of the following properties relative to the parent enzymes : 1) improved thermal stability, 2) oxidation stability and 3) reduced calcium ion dependency properties. Examples of other desirable improvements or modifications of properties

(relative to the parent- $\alpha$ -amylase) which may be achieved with a variant according to the present invention are : increased stability and/or  $\alpha$ -amylolytic activity at neutral to relatively high pH values, increased  $\alpha$ -amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for  $\alpha$ -amylase variant to the pH of the medium, have been described in the co-pending application by Novo Nordisk PCT/DK96/00056, and are hereinafter referred as "specific amylase".

Therefore, while amylase is known to act on starchy stains, there remains a substantial technical challenge in formulating laundry components comprising specific amylase 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 specific amylase enzymes designed to be especially effective at dingy clean up.

It has been surprisingly found that specific amylase enzymes provide unexpected superior dingy clean up, whiteness maintenance and overall cleaning performance. Such performance is illustrated but not limited to excellent dingy soil removal present e.g. on pillow cases, T-shirts and sock bottoms.

It is therefore an object of the present invention to provide effective dingy stain removal and overall cleaning benefits through laundry compositions containing specific amylase.

### SUMMARY OF THE INVENTION

This invention relates to the use of a specific amylase in a laundry detergent composition to provide especially effective surface cleaning of textiles.

The present invention relates to the laundering of fabrics to maintain or increase whiteness and provide dingy clean up, by contacting fabrics in need of whiteness and/or dingy clean up with an aqueous solution formed from a detergent composition comprising a specific amylase at a concentration and for a sufficient period such that the dingy cleaning performance of said composition is increased.

### DETAILED DESCRIPTION OF THE INVENTION

Without limitation by theory, it is believed that dingy soils and stains are the result of combinations of various types of soils. For instance, 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. 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. It is further believed that compounds present in the sebum oxidise to contribute to the yellowing of the fabrics. Particulate soils comprise mostly airborne soil and floor/ground dust and include topsoil and products produced during the incomplete combustion of petroleum products. "Dingy clean up" means the ability of a detergent composition to remove such dingy soil built-up, over one or more washes, resulting in a measurable improvement in fabric appearance.

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 the washed fabrics is maintained at a high level during the complete life cycle of washing & wearing.

#### Specific Amylase Enzymes

An essential component of the detergent compositions of the present invention is a specific amylase enzyme. Such specific amylase enzymes include those described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056. These enzymes are incorporated into detergent compositions at a level from 0.0001% to 0.1% pure enzyme by weight of the total composition, preferably at a level of from 0.00018% to 0.060%, more preferably from 0.00024% to 0.048% pure enzyme by weight of total weight composition.

Specific amylase enzymes for use in the detergent compositions of the present invention therefore include :

(a)  $\alpha$ -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas®  $\alpha$ -amylase activity assay. Such Phadebas®  $\alpha$ -amylase activity assay is described at pages 9-10, WO95/26397.

(b)  $\alpha$ -amylases according (a) comprising the amino sequence shown in SEQ ID No. 1 or an  $\alpha$ -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No.1.

(c)  $\alpha$ -amylases according (a) comprising the amino sequence shown in SEQ ID No.2 or an  $\alpha$ -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No.2.

(d)  $\alpha$ -amylases according (a) comprising the following amino sequence in the N-terminal : His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp (SEQ ID No.3) or an  $\alpha$ -amylase being at least 80% homologous with the amino acid sequence shown (SEQ ID No.3) in the N-terminal.

A polypeptide is considered to be X% homologous to the parent amylase if a comparison of the respective amino acid sequences, performed via algorithms, such as the one described by Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of X%

(e)  $\alpha$ -amylases according (a-d) wherein the  $\alpha$ -amylase is obtainable from an alkalophilic Bacillus species; and in particular, from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935.

In the context of the present invention, the term "obtainable from" is intended not only to indicate an amylase produced by a Bacillus strain but also an amylase encoded by a DNA sequence isolated from such a Bacillus strain and produced in an host organism transformed with said DNA sequence.

(f)  $\alpha$ -amylase showing positive immunological cross-reactivity with antibodies raised against an  $\alpha$ -amylase having an amino acid sequence corresponding respectively to SEQ ID No.1, ID No.2 or ID No.3.

(g) Variants of the following parent  $\alpha$ -amylases which (i) have one of the amino acid sequences shown in SEQ ID No.1, ID No.2 or ID No.4 respectively, or (ii) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an  $\alpha$ -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence



encoding an  $\alpha$ -amylase having one of said amino acid sequence; in which variants :

1. at least one amino acid residue of said parent  $\alpha$ -amylase has been deleted; and/or
2. at least one amino acid residue of said parent  $\alpha$ -amylase has been replaced by a different amino acid residue; and/or
3. at least one amino acid residue has been inserted relative to said parent  $\alpha$ -amylase;

said variant having an  $\alpha$ -amylase activity and exhibiting at least one of the following properties relative to said parent  $\alpha$ -amylase : increased thermostability, increased stability towards oxidation, reduced Ca ion dependency, increased stability and/or  $\alpha$ -amylolytic activity at neutral to relatively high pH values, increased  $\alpha$ -amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for  $\alpha$ -amylase variant to the pH of the medium.

Said variants are described in the co-pending patent application PCT/DK96/00056.

#### Detergent components

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

The compositions of the invention may be formulated as hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components.

The compositions of the invention can also be used as detergent additive products. Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

If needed the density of the granular laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 600 to 950 g/litre of composition measured at 20°C.

The "compact" form of the granular laundry detergent compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition.

In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition.

The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides.

A preferred filler salt is sodium sulphate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents.

Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

#### Surfactant system

The detergent compositions according to the present invention can additionally comprise a surfactant system wherein the surfactant can be selected from anionic and/or nonionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of detergent compositions in accordance with the present invention.

Preferred systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene

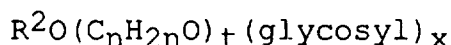
oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal<sup>TM</sup> CO-630, marketed by the GAF Corporation; and Triton<sup>TM</sup> X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxyates (e.g., alkyl phenol ethoxyates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include Tergitol<sup>TM</sup> 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear alcohol with 9 moles ethylene oxide), Tergitol<sup>TM</sup> 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol<sup>TM</sup> 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup> 23-3 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 3.0 moles of ethylene oxide), Neodol<sup>TM</sup> 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>TM</sup> 45-5 (the condensation

product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, Kyro<sup>TM</sup> EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O30 or O50 (the condensation product of C<sub>12</sub>-C<sub>14</sub> alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

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

The preferred alkylpolyglycosides have the formula



wherein R<sup>2</sup> is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10,

preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

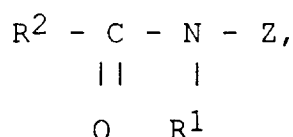
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic<sup>TM</sup> surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that

the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C<sub>8</sub>-C<sub>14</sub> alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C<sub>8</sub>-C<sub>18</sub> alcohol ethoxylates (preferably C<sub>10</sub> avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

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



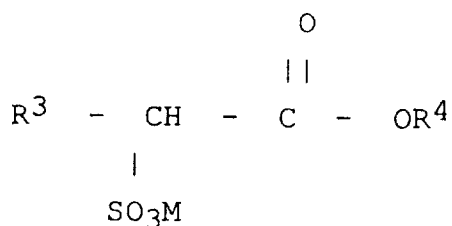
wherein R<sup>1</sup> is H, or R<sup>1</sup> is C<sub>1-4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5-31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R<sup>1</sup> is methyl, R<sup>2</sup> is a straight C<sub>11-15</sub> alkyl or C<sub>16-18</sub> alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

When included in such detergent compositions, the nonionic surfactant systems of the present invention act to

improve the greasy/oily stain removal properties of such detergent compositions across a broad range of cleaning conditions.

Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

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



wherein R<sup>3</sup> is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof, R<sup>4</sup> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl, and R<sup>4</sup> is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO<sub>3</sub>M wherein R preferably is a C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl having a



C<sub>10</sub>-C<sub>20</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C<sub>12</sub>-C<sub>16</sub> are preferred for lower wash temperatures (e.g. below about 50°C) and C<sub>16</sub>-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulfonates, C<sub>8</sub>-C<sub>24</sub> olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C<sub>8</sub>-C<sub>24</sub> alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C<sub>6</sub>-C<sub>12</sub> diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates,

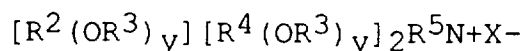
and alkyl polyethoxy carboxylates such as those of the formula  $RO(CH_2CH_2O)_k-CH_2COO-M^+$  wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula  $RO(A)_mSO_3M$  wherein R is an unsubstituted C<sub>10</sub>-C<sub>24</sub> alkyl or hydroxyalkyl group having a C<sub>10</sub>-C<sub>24</sub> alkyl component, preferably a C<sub>12</sub>-C<sub>20</sub> alkyl or hydroxyalkyl, more preferably C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(1.0)M), C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (2.25) sulfate (C<sub>12</sub>-C<sub>18</sub>E(2.25)M), C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (3.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(3.0)M),

and C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (4.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(4.0)M), wherein M is conveniently selected from sodium and potassium.

Cationic deterative surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbonyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



wherein R<sup>2</sup> is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R<sup>3</sup> is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH(CH<sub>2</sub>OH)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and mixtures thereof; each R<sup>4</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, benzyl ring structures formed by joining the two R<sup>4</sup> groups, -CH<sub>2</sub>CHOH-CHOHCH(R<sup>6</sup>)CHOHCH<sub>2</sub>OH wherein R<sup>6</sup> is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R<sup>5</sup> is the same as R<sup>4</sup> or is an alkyl chain wherein the total number of carbon atoms of R<sup>2</sup> plus R<sup>5</sup> is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

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



wherein R<sub>1</sub> is C<sub>8</sub>-C<sub>16</sub> alkyl, each of R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is independently C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxy alkyl, benzyl, and -(C<sub>2</sub>H<sub>4</sub>)<sub>x</sub>H where x has a value from 2 to 5, and X is an anion. Not more than one of R<sub>2</sub>, R<sub>3</sub> or R<sub>4</sub> should be benzyl.

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

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

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

coconut trimethyl ammonium chloride or bromide;  
 coconut methyl dihydroxyethyl ammonium chloride or bromide;  
 decyl triethyl ammonium chloride;  
 decyl dimethyl hydroxyethyl ammonium chloride or bromide;  
 $C_{12-15}$  dimethyl hydroxyethyl ammonium chloride or bromide;  
 coconut dimethyl hydroxyethyl ammonium chloride or bromide;  
 myristyl trimethyl ammonium methyl sulphate;  
 lauryl dimethyl benzyl ammonium chloride or bromide;  
 lauryl dimethyl (ethenoxy)<sub>4</sub> ammonium chloride or bromide;  
 choline esters (compounds of formula (i) wherein  $R_1$  is  $CH_2-CH_2-O-C-C_{12-14}$  alkyl and  $R_2R_3R_4$  are methyl).

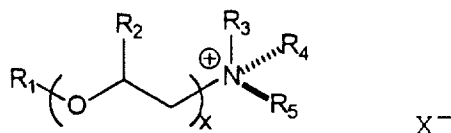


di-alkyl imidazolines [compounds of formula (i)].

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

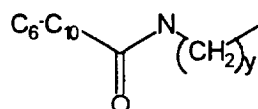
Quaternary ammonium surfactants suitable for the present invention have the formula (I):

19



Formula I

whereby R1 is a short chainlength alkyl (C6-C10) or alkylamidoalkyl of the formula (II) :



Formula II

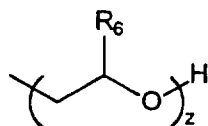
y is 2-4, preferably 3.

whereby R2 is H or a C1-C3 alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R3, R4 and R5 are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxyated alkyl of the formula III,

whereby X<sup>-</sup> is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

R6 is C<sub>1</sub>-C<sub>4</sub> and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby

R<sub>1</sub> is C<sub>8</sub>, C<sub>10</sub> or mixtures thereof, x=0,

R<sub>3</sub>, R<sub>4</sub> = CH<sub>3</sub> and R<sub>5</sub> = CH<sub>2</sub>CH<sub>2</sub>OH.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

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

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

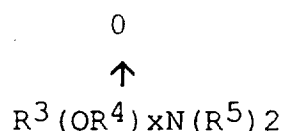
Zwitterionic surfactants are also suitable for use in detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary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

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the

group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

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



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

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

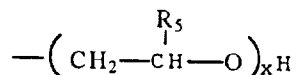
When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The detergent composition of the present invention may preferably further comprise a cosurfactant selected from the group of primary or tertiary amines.

Suitable primary amines for use herein include amines according to the formula  $R_1NH_2$  wherein  $R_1$  is a  $C_6$ - $C_{12}$ , preferably  $C_6$ - $C_{10}$  alkyl chain or  $R_4X(CH_2)_n$ ,  $X$  is  $-O-$ ,  $-C(O)NH-$  or  $-NH-$ ,  $R_4$  is a  $C_6$ - $C_{12}$  alkyl chain  $n$  is between 1 to 5, preferably 3.  $R_1$  alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 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, 1-decylamine and laurylamine. Other preferred primary amines include  $C_8$ - $C_{10}$  oxypropylamine, octyloxypropylamine, 2-ethylhexyloxypropylamine, lauryl amido propylamine and amido propylamine.

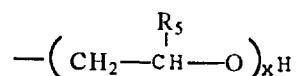
Suitable tertiary amines for use herein include tertiary amines having the formula  $R_1R_2R_3N$  wherein  $R_1$  and  $R_2$  are  $C_1$ - $C_8$  alkylchains or



$R_3$  is either a  $C_6$ - $C_{12}$ , preferably  $C_6$ - $C_{10}$  alkyl chain, or  $R_3$  is  $R_4X(CH_2)_n$ , whereby  $X$  is  $-O-$ ,  $-C(O)NH-$  or  $-NH-$ ,  $R_4$  is a  $C_4$ - $C_{12}$ ,  $n$  is between 1 to 5, preferably 2-3.  $R_5$  is H or  $C_1$ - $C_2$  alkyl and  $x$  is between 1 to 6.

$R_3$  and  $R_4$  may be linear or branched;  $R_3$  alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

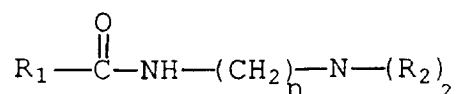
Preferred tertiary amines are  $R_1R_2R_3N$  where  $R_1$  is a  $C_6$ - $C_{12}$  alkyl chain,  $R_2$  and  $R_3$  are  $C_1$ - $C_3$  alkyl or



where  $R_5$  is H or  $CH_3$  and  $x = 1-2$ .



Also preferred are the amidoamines of the formula:



wherein  $R_1$  is  $C_6$ - $C_{12}$  alkyl;  $n$  is 2-4,  
preferably  $n$  is 3;  $R_2$  and  $R_3$  is  $C_1$ - $C_4$

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco 1-3diaminopropane, coconut-alkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine. The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

#### *Other detergent enzymes*

The detergent compositions can in addition to specific amylase enzymes further comprise one or more enzymes which provide cleaning performance and/or fabric care benefits. Preferred enzymes are proteases.

Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, other amylases, xylanases, lipases, esterases, cutinases, pectinases, reductases, oxidases, phenoloxidases, lipxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases chondroitinase, laccase or mixtures thereof.

A preferred combination is a cleaning composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

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

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

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 bromo-peroxidase.

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.

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.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Nordisk A/S (Denmark), those sold under the tradename Maxatase, Maxacal, Maxapem and Properase by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Also proteases described in our co-pending application USSN 08/136,797 can be included in the detergent composition of the invention. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Especially suitable lipases are lipases such as M1 Lipase<sup>R</sup> and Lipomax<sup>R</sup> (Gist-Brocades) and Lipolase<sup>R</sup> and Lipolase Ultra<sup>R</sup> (Novo) which have found to be very effective when used in combination with the compositions of the present invention.

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. Suitable cutinases are described in WO 94/14963 and WO 94/14964. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Other amylases ( $\alpha$  and/or  $\beta$ ) can be included for removal of carbohydrate-based stains. Suitable amylases are Termamyl<sup>R</sup>, (Novo Nordisk), Fungamyl<sup>R</sup> and BAN<sup>R</sup> (Novo Nordisk).

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in the copending European patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

#### *Color care benefits*

Technologies which provide a type of color care benefit can also be included. Examples of these technologies are metallo catalysts for color maintenance. Such metallo catalysts are described in the European patent EP 0 596 184 and in the copending European Patent Application No. 94870206.3.

*Bleaching agent*

Bleach systems that can be included in the detergent compositions of the present invention include bleaching agents such as PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%. In general, bleaching compounds are optional components in non-liquid formulations, e.g. granular detergents.

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

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

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

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium

dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

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

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

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

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These

materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

#### *Builder system*

The compositions according to the present invention may further comprise a builder system.

Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyposphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

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

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ( $\text{Na}_2\text{Si}_2\text{O}_5$ ).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368,

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

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

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-



carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

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

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.

A suitable chelant for inclusion in the detergent compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include  $\text{Na}_2\text{EDDS}$  and  $\text{Na}_4\text{EDDS}$ . Examples of such preferred magnesium salts of EDDS include  $\text{MgEDDS}$  and  $\text{Mg}_2\text{EDDS}$ . The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

Preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

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

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

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

#### *Suds suppressor*

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

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially

available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

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

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

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.

#### Others

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.

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

Other suitable water soluble encapsulating materials comprise 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.

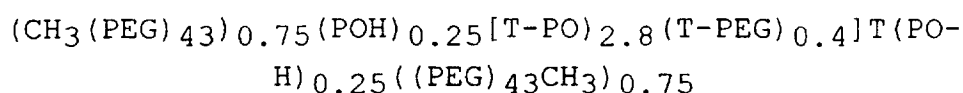
Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic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

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-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-tri-azin-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-so-dium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylami-no)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred

brighteners are the specific brighteners of copending European Patent application No. 95201943.8.

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

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



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

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.

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

Is is well known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the specific amylase enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

#### *Softening agents*

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.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% 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.

#### *Dye transfer inhibition*

The detergent composition of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

#### *Polymeric dye transfer inhibiting agents*

The detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally

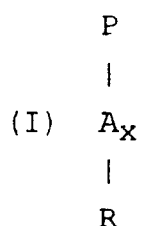
incorporated into detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

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.

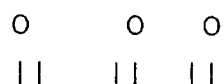
Addition of such polymers also enhances the performance of the enzymes according the invention.

#### a) Polyamine N-oxide polymers

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.

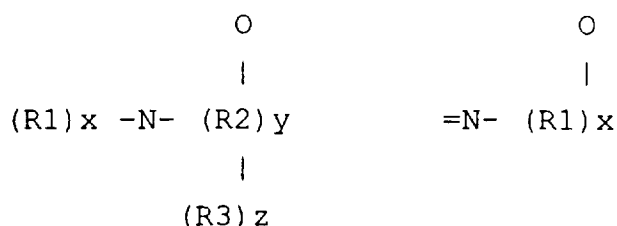


A is NC, CO, C, -O-, -S-, -N- ; x is 0 or 1;

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.



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



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

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

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

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

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

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

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

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

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

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a  $PK_a < 10$ , preferably  $PK_a < 7$ , more preferred  $PK_a < 6$ .

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

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

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

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

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

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

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

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to

N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinylloxazolidone :

The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye

transfer inhibiting agent. Said polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

f) Cross-linked polymers :

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups on the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling.

Such cross-linked polymers are described in the co-pending patent application 94870213.9

Method of washing

The cleaning compositions according to the invention can be liquid, paste, gels, bars, tablets, powder or granular forms. Granular compositions can also be in "compact " form, the liquid compositions can also be in a "concentrated" form.

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with

rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting fabrics with a laundering solution in the usual manner and exemplified hereunder.

The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5 °C to 95 °C, especially between 10°C and 60°C. However, specific amylase enzymes within the specified enzymatic concentration, have demonstrated superior starch cleaning even for wash cycles occurring at very low temperatures (between 10°C and 25°C). The pH of the treatment solution is preferably from 7 to 11.

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

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

LAS : Sodium linear C<sub>12</sub> alkyl benzene  
sulphonate

TAS : Sodium tallow alkyl sulphate

CXYAS : Sodium C<sub>1X</sub> - C<sub>1Y</sub> alkyl sulfate

- 25EY : A C<sub>12</sub>-C<sub>15</sub> predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
- CXYEZ : A C<sub>1X</sub> - C<sub>1Y</sub> predominantly linear primary alcohol condensed with an average of Z moles of ethylene oxide
- XYEzs : C<sub>1X</sub> - C<sub>1Y</sub> sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole
- QAS : R<sub>2</sub>.N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>OH) with R<sub>2</sub> = C<sub>12</sub>-C<sub>14</sub>
- Soap : Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut oils.
- Nonionic : C<sub>13</sub>-C<sub>15</sub> 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 Plurafac LF404 by BASF GmbH.
- CFAA : C<sub>12</sub>-C<sub>14</sub> alkyl N-methyl glucamide
- TFAA : C<sub>16</sub>-C<sub>18</sub> alkyl N-methyl glucamide.
- TPKFA : C<sub>12</sub>-C<sub>14</sub> topped whole cut fatty acids.
- DEQA : Di-(tallow-oxy-ethyl) dimethyl ammonium chloride.
- DTDMAMS : Ditalow dimethyl ammonium methylsulfate.

- SDASA : 1:2 ratio of stearyldimethyl amine:triple-pressed stearic acid.
- Neodol 45-13 : C14-C15 linear primary alcohol ethoxylate, sold by Shell Chemical CO.
- Silicate : Amorphous Sodium Silicate ( $\text{SiO}_2:\text{Na}_2\text{O}$  ratio = 2.0)
- NaSKS-6 : Crystalline layered silicate of formula  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ .
- Carbonate : Anhydrous sodium carbonate with a particle size between 200  $\mu\text{m}$  and 900 $\mu\text{m}$ .
- Bicarbonate : Anhydrous sodium bicarbonate with a particle size between 400  $\mu\text{m}$  and 1200 $\mu\text{m}$ .
- STPP : Anhydrous sodium tripolyphosphate
- MA/AA : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 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  $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$  having a primary particle size in the range from 0.1 to 10 micrometers
- Citrate : Tri-sodium citrate dihydrate of activity 86,4% with a particle size distribution between 425  $\mu\text{m}$  and 850  $\mu\text{m}$ .



Citric	: Anhydrous citric acid
PB1	: Anhydrous sodium perborate monohydrate bleach, empirical formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
PB4	: Anhydrous sodium perborate tetrahydrate
Percarbonate	: Anhydrous sodium percarbonate bleach of empirical formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
TAED	: Tetraacetyl ethylene diamine.
NOBS	: Nonanoyloxybenzene sulfonate in the form of the sodium salt.
Photoactivated Bleach	: Sulfonated zinc phtlocyanine encapsulated in dextrin soluble polymer.
Protease	: Proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents W091/06637 and/or W095/10591 and/or EP 251 446.
Amylase	: Specific amylase according to the present invention.
Lipase	: Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S
Cellulase	: Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.

- CMC : Sodium carboxymethyl cellulose.
- HEDP : 1,1-hydroxyethane diphosphonic acid.
- DETPMP : Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060.
- PVNO : Poly(4-vinylpyridine)-N-Oxide.
- PVPVI : Poly (4-vinylpyridine)-N-oxide/copolymer of vinyl-imidazole and vinyl-pyrrolidone.
- Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
- Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.
- Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
- Granular Suds Suppressor : 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form
- SRP 1 : Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone.
- SRP 2 : Diethoxylated poly (1,2 propylene terephthalate) short block polymer.

Sulphate : Anhydrous sodium sulphate.

HMWPEO : High molecular weight polyethylene oxide

PEG : Polyethylene glycol.

Encapsulated perfume particles : Insoluble fragrance delivery technology utilising zeolite 13x, perfume and a dextrose/glycerin agglomerating binder.

Example 1

The following laundry detergent compositions were prepared in accord with the invention:

	I	II	III	IV	V	VI
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
QAS	-	0.8	0.8	-	0.8	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5	1.5	1.5	1.5	1.5
DETPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Protease	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026
Amylase	0.0009	0.0003	0.0009	0.05	0.002	0.01
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
Photoactivated bleach (ppm)	15	15	15	15	15	15
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions of bulk density 750 g/litre were prepared in accord with the invention:

	I	II	III
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
QAS	0.8	2.0	2.0
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Sodium sulfate	39.8	-	14.3
PB4	5.0	12.7	-
TAED	0.5	3.1	-
DETPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Protease	0.0026	0.0085	0.045
Lipase	0.003	0.003	0.003
Cellulase	0.0006	0.0006	0.0006
Amylase	0.0008	0.005	0.0002
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04

Encapsulated	0.3	0.3	0.3
perfume particles			
Silicone antifoam	0.5	2.4	2.4
Minors/misc to			
100%			

Example 3

The following detergent formulations, according to the present invention were prepared, where I is a phosphorus-containing detergent composition, II is a zeolite-containing detergent composition and III is a compact detergent composition:

	I	II	III
Blown Powder			
STPP	24.0	-	24.0
Zeolite A	-	24.0	-
C45AS	9.0	6.0	13.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DETPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10.0
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Photoactivated	0.02	0.02	0.02
bleach			
Protease	0.01	0.01	0.01
Lipase	0.009	0.009	0.009
Amylase	0.002	0.0004	0.01

Dry mixed sodium sulfate	3.0	3.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670



Example 4

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, according to the present invention were prepared:

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	-
Sodium sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DETPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Protease	0.026	0.016	0.047
Lipase	0.009	0.009	0.009
Amylase	0.005	0.0003	0.01

56

Cellulase	0.004	0.004	0.004
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	9.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	700	700	700

Example 5

The following detergent formulations, according to the present invention were prepared:

	I	II	III	IV
LAS	20.0	14.0	24.0	22.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
STPP	30.0	18.0	30.0	22.0
Silicate	9.0	5.0	10.0	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DETPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.008	0.01	0.025	0.026
Amylase	0.007	0.004	0.0003	0.002
Lipase	0.004	0.002	0.004	0.002
Cellulase	0.00035	0.0001	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NOBS	2.0	1.0	-	-
Balance	100	100	100	100
(Moisture and Miscellaneous)				

Example 6

The following detergent formulations, according to the present invention were prepared:

	I	II	III	IV
Blown Powder				
Zeolite A	30.0	22.0	6.0	6.7
Na SkS-6	-	-	-	3.3
Polycarboxylate	-	-	-	7.1
Sodium sulfate	19.0	5.0	7.0	-
MA/AA	3.0	3.0	6.0	-
LAS	14.0	12.0	22.0	21.5
C45AS	8.0	7.0	7.0	5.5
Cationic	-	-	-	1.0
Silicate	-	1.0	5.0	11.4
Soap	-	-	2.0	-
Brightener 1	0.2	0.2	0.2	-
Carbonate	8.0	16.0	20.0	10.0
DETPMP	-	0.4	0.4	-
Spray On				
C45E7	1.0	1.0	1.0	3.2
Dry additives				
PVPVI/PVNO	0.5	0.5	0.5	-
Protease	0.052	0.01	0.01	0.01
Lipase	0.009	0.009	0.009	0.009
Amylase	0.0008	0.0015	0.02	0.0004
Cellulase	0.0002	0.0002	0.0002	0.0002
NOBS	-	6.1	4.5	3.2
PB1	1.0	5.0	6.0	3.9
Sodium sulfate	-	6.0	-	to
				balance
Balance (Moisture and Miscellaneous)	100	100	100	

Example 7

The following high density and bleach-containing detergent formulations, according to the present invention were prepared:

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodium sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DETPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Protease	0.01	0.01	0.01
Lipase	0.009	0.009	0.009
Amylase	0.005	0.003	0.02

60

Cellulase	0.002	0.002	0.002
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 8

The following high density detergent formulations, according to the present invention were prepared:

	I	II
Agglomerate		
C45AS	11.0	14.0
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DETPMP	0.4	0.4
Spray On		
C25E5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	5.0	7.0
Percarbonate	20.0	20.0
SRP 1	0.3	0.3
Protease	0.015	0.015
Lipase	0.009	0.009
Cellulase	0.002	0.002
Amylase	0.005	0.005
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850

Example 9

The following granular detergent formulations, according to the present invention were prepared:

	I	II	III	IV	V
LAS	21.0	25.0	18.0	18.0	-
Coco C12-14 AS	-	-	-	-	21.9
AE3S	-	-	1.5	1.5	2.3
Decyl dimethyl hydroxyethyl NH <sub>4</sub> +Cl	-	0.4	0.7	0.7	0.8
Nonionic	1.2	-	0.9	0.5	-
Coco C12-14 Fatty Alcohol	-	-	-	-	1.0
STPP	44.0	25.0	22.5	22.5	22.5
Zeolite A	7.0	10.0	-	-	8.0
MA/AA	-	-	0.9	0.9	-
SRP1	0.3	0.15	0.2	0.1	0.2
CMC	0.3	2.0	0.75	0.4	1.0
Carbonate	17.5	29.3	5.0	13.0	15.0
Silicate	2.0	-	7.6	7.9	-
Protease	0.007	0.007	0.007	0.007	0.007
Amylase	0.008	0.004	0.003	0.004	0.04
Lipase	0.003	0.003	0.003	-	-
Cellulase	-	0.001	0.001	0.001	0.001
NOBS	-	-	-	1.2	1.0
PB1	-	-	-	2.4	1.2
Diethylene triamine penta acetic acid	-	-	-	0.7	1.0
Diethylene triamine penta methyl phosphonic acid	-	-	0.6	-	-
Mg Sulfate	-	-	0.8	-	-
Photoactivated bleach	45	50	15	45	42
	ppm	ppm	ppm	ppm	ppm
Brightener 1	0.05	-	0.04	0.04	0.04
Brightener 2	0.1	0.3	0.05	0.13	0.13
Water and Minors	up to 100%				



Example 10

The following liquid detergent formulations, according to the present invention were prepared:

	I	II	III	IV	V	VI	VII	VIII
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
QAS	-	-	-	-	3.0	1.0	-	-
TPKFA	2.0	-	13.0	2.0	-	15.0	7.0	7.0
Rapeseed	-	-	-	5.0	-	-	4.0	4.0
fatty acids								
Citric	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl/ tetradecenyl	12.0	10.0	-	-	15.0	-	-	-
succinic acid								
Oleic acid	4.0	2.0	1.0	-	1.0	-	-	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.-
Propanediol								
Mono Ethanol	-	-	-	5.0	-	-	9.0	9.0
Amine								
Tri Ethanol	-	-	8	-	-	-	-	-
Amine								
NaOH (pH)	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2
Ethoxylated	0.5	-	0.5	0.2	-	-	0.4	0.3
tetra- ethylene pentamine								
DETPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-
SRP 2	0.3	-	0.3	0.1	-	-	0.2	0.1
PVNO	-	-	-	-	-	-	-	0.10
Protease	.016	.016	.013	.008	.048	.016	0.01	.019

Lipase	-	.002	-	.001	-	-	.003	.003
Amylase	.002	.002	.0005	.04	.0008	.0008	.005	.005
Cellulase	-	-	-	.001	-	-	.002	.001
Boric acid	0.1	0.2	-	2.0	1.0	1.5	2.5	2.5
Na formate	-	-	1.0	-	-	-	-	-
Ca chloride	-	0.01	-	0.01	-	-	-	-
		5						
Bentonite	-	-	-	-	4.0	4.0	-	-
clay								
Suspending	-	-	-	-	0.6	0.3	-	-
clay SD3								
Balance	100	100	100	100	100	100	100	100
Moisture and								
Miscellaneous								

Example 11

Granular fabric cleaning compositions which provide "softening through the wash" capability were prepared in accord with the present invention :

	I	II
45AS	-	10.0
LAS	7.6	-
68AS	1.3	-
45E7	4.0	-
25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
PB1	15.0	-
Percarbonate	-	15.0
TAED	5.0	5.0
Smectite clay	10.0	10.0
HMWPEO	-	0.1
Protease	0.02	0.01
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.001	-
Silicate	3.0	5.0
Carbonate	10.0	10.0
Granular suds suppressor	1.0	4.0
CMC	0.2	0.1
Water/minors	Up to 100%	

Example 12

The following rinse added fabric softener composition was prepared in accord with the present invention :

Softener active	20.0
Amylase	0.001
Cellulase	0.001
HCL	0.03
Antifoam agent	0.01
Blue dye	25ppm
CaCl <sub>2</sub>	0.20
Perfume	0.90
Water / minors	Up to 100%

Example 13

The following fabric softener composition was prepared in accord with the present invention :

	I	II	III
DEQA	2.60	19.00	-
DTDMAMS	-	-	-
SDASA	-	-	70.0
			0
Stearic acid of IV=0	0.30	-	-
Neodol 45-13	-	-	13.0
			0
Hydrochloride acid	0.02	0.02	-
Ethanol	-	-	1.00
PEG	-	0.60	-
Amylase	0.001	0.0005	0.01
Perfume	1.00	1.00	0.75
Digeranyl Succinate	-	-	0.38
Silicone antifoam	0.01	0.01	-
Electrolyte	-	600ppm	-
Dye	100ppm	50ppm	0.01
Water and minors	100%	100%	

Example 14

Syndet bar fabric cleaning compositions were prepared in accord with the present invention :

	I	II	III	IV
C26 AS	20.00	20.00	20.00	20.00
CFAA	5.0	5.0	5.0	5.0
LAS (C11-13)	10.0	10.0	10.0	10.0
Sodium carbonate	25.0	25.0	25.0	25.0
Sodium pyrophosphate	7.0	7.0	7.0	7.0
STPP	7.0	7.0	7.0	7.0
Zeolite A	5.0	5.0	5.0	5.0
CMC	0.2	0.2	0.2	0.2
Polyacrylate (MW 1400)	0.2	0.2	0.2	0.2
Coconut monethanolamide	5.0	5.0	5.0	5.0
Amylase	0.01	0.02	0.01	0.01
Protease	0.3	-	0.5	0.05
Brightener, perfume	0.2	0.2	0.2	0.2
CaSO <sub>4</sub>	1.0	1.0	1.0	1.0
MgSO <sub>4</sub>	1.0	1.0	1.0	1.0
Water	4.0	4.0	4.0	4.0

Filler\* : balance to 100%

\*Can be selected from convenient materials such as CaCO<sub>3</sub>, talc, clay (Kaolinite, Smectite), silicates, and the like.

## SEQUENCE DESCRIPTION : SEQ ID No. 1

His His Asn Gly Thr Asn Gly Thr Met Met Gln Tyr Phe Glu Trp Tyr  
 1                      5                      10                      15  
 Leu Pro Asn Asp Gly Asn His Trp Asn Arg Leu Arg Asp Asp Ala Ala  
                     20                      25                      30  
 Asn Leu Lys Ser Lys Gly Ile Thr Ala Val Trp Ile Pro Pro Ala Trp  
                     35                      40                      45  
 Lys Gly Thr Ser Gln Asn Asp Val Gly Tyr Gly Ala Tyr Asp Leu Tyr  
                     50                      55                      60  
 Asp Leu Gly Glu Phe Asn Gln Lys Gly Thr Val Arg Thr Lys Tyr Gly  
 65                      70                      75                      80  
 Thr Arg Asn Gln Leu Gln Ala Ala Val Thr Ser Leu Lys Asn Asn Gly  
                     85                      90                      95  
 Ile Gln Val Tyr Gly Asp Val Val Met Asn His Lys Gly Gly Ala Asp  
                     100                      105                      110  
 Gly Thr Glu Ile Val Asn Ala Val Glu Val Asn Arg Ser Asn Arg Asn  
                     115                      120                      125  
 Gln Glu Thr Ser Gly Glu Tyr Ala Ile Glu Ala Trp Thr Lys Phe Asp  
                     130                      135                      140  
 Phe Pro Gly Arg Gly Asn Asn His Ser Ser Phe Lys Trp Arg Trp Tyr  
 145                      150                      155                      160  
 His Phe Asp Gly Thr Asp Trp Asp Gln Ser Arg Gln Leu Gln Asn Lys  
                     165                      170                      175  
 Ile Tyr Lys Phe Arg Gly Thr Gly Lys Ala Trp Asp Trp Glu Val Asp  
                     180                      185                      190  
 Thr Glu Asn Gly Asn Tyr Asp Tyr Leu Met Tyr Ala Asp Val Asp Met  
                     195                      200                      205  
 Asp His Pro Glu Val Ile His Glu Leu Arg Asn Trp Gly Val Trp Tyr  
                     210                      215                      220  
 Thr Asn Thr Leu Asn Leu Asp Gly Phe Arg Ile Asp Ala Val Lys His  
 225                      230                      235                      240  
 Ile Lys Tyr Ser Phe Thr Arg Asp Trp Leu Thr His Val Arg Asn Thr  
                     245                      250                      255  
 Thr Gly Lys Pro Met Phe Ala Val Ala Glu Phe Trp Lys Asn Asp Leu  
                     260                      265                      270

Gly Ala Ile Glu Asn Tyr Leu Asn Lys Thr Ser Trp Asn His Ser Val  
275 280 285  
Phe Asp Val Pro Leu His Tyr Asn Leu Tyr Asn Ala Ser Asn Ser Gly  
290 295 300  
Gly Tyr Tyr Asp Met Arg Asn Ile Leu Asn Gly Ser Val Val Gln Lys  
305 310 315 320  
His Pro Thr His Ala Val Thr Phe Val Asp Asn His Asp Ser Gln Pro  
325 330 335  
Gly Glu Ala Leu Glu Ser Phe Val Gln Gln Trp Phe Lys Pro Leu Ala  
340 345 350  
Tyr Ala Leu Val leu Thr Arg Glu Gln Gly Tyr Pro Ser Val Phe Tyr  
355 360 365  
Gly Asp Tyr Tyr Gly Ile Pro Thr His Gly Val Pro Ala Met Lys Ser  
370 375 380  
Lys Ile Asp Pro leu Leu Gln Ala Arg Gln Thr Phe Ala Tyr Gly Thr  
385 390 395 400  
Gln His Asp Tyr Phe Asp His His Asp Ile Ile Gly Trp Thr Arg Glu  
405 410 415  
Gly Asn Ser Ser His Pro Asn Ser Gly Leu Ala Thr Ile Met Ser Asp  
420 425 430  
Gly Pro Gly Gly Asn Lys Trp Met Tyr Val Gly Lys Asn Lys Ala Gly  
435 440 445  
Gln Val Trp Arg Asp Ile Thr Gly Asn Arg Thr Gly Thr Val Thr Ile  
450 455 460  
Asn Ala Asp Gly Trp Gly Asn Phe Ser Val Asn Gly Gly Ser Val Ser  
465 470 475 480  
Val Trp Val Lys Gln  
485



## SEQUENCE DESCRIPTION : SEQ ID No. 2

His His Asn Gly Thr Asn Gly Thr Met Met Gln Tyr Phe Glu Trp His  
 1 5 10 15  
 Leu Pro Asn Asp Gly Asn His Trp Asn Arg Leu Arg Asp Asp Ala Ser  
 20 25 30  
 Asn Leu Arg Asn Arg Gly Ile Thr Ala Ile Trp Ile Pro Pro Ala Trp  
 35 40 45  
 Lys Gly Thr Ser Gln Asn Asp Val Gly Tyr Gly Ala Tyr Asp Leu Tyr  
 50 55 60  
 Asp Leu Gly Glu Phe Asn Gln Lys Gly Thr Val Arg Thr Lys Tyr Gly  
 65 70 75  
 Thr Arg Ser Gln Leu Glu Ser Ala Ile His Ala Leu Lys Asn Asn Gly  
 80 85 90 95  
 Val Gln Val Tyr Gly Asp Val Val Met Asn His Lys Gly Gly Ala Asp  
 100 105 110  
 Ala Thr Glu Asn Val Leu Ala Val Glu Val Asn Pro Asn Asn Arg Asn  
 115 120 125  
 Gln Glu Ile Ser Gly Asp Tyr Thr Ile Glu Ala Trp Thr Lys Phe Asp  
 130 135 140  
 Phe Pro Gly Arg Gly Asn Thr Tyr Ser Asp Phe Lys Trp Arg Trp Tyr  
 145 150 155  
 His Phe Asp Gly Val Asp Trp Asp Gln Ser Arg Gln Phe Gln Asn Arg  
 160 165 170 175  
 Ile Tyr Lys Phe Arg Gly Asp Gly Lys Ala Trl Asp Trp Glu Val Asp  
 180 185 190  
 Ser Glu Asn Gly Asn Tyr Asp Tyr Leu Met Tyr Ala Asp Val Asp Met  
 195 200 205  
 Asp His Pro Glu Val Val Asn Glu Leu Arg Arg Trp Gly Glu Trp Tyr  
 210 215 220  
 Thr Asn Thr Leu Asn Leu Asp Gly Phe Arg Ile Asp Ala Val Lys His  
 225 230 235  
 Ile Lys Tyr Ser Phe Thr Arg Asp Trp Leu Thr His Val Arg Asn Ala  
 240 245 250 255  
 Thr Gly Lys Glu Met Phe Ala Val Ala Glu Phe Trp Lys Asn Asp Leu  
 260 265 270

Gly Ala Leu Glu Asn Tyr Leu Asn Lys Thr Asn Trp Asn His Ser Val  
275 280 285  
Phe Asp Val Pro Leu His Tyr Asn Leu Tyr Asn Ala Ser Asn Ser Gly  
290 295 300  
Gly Asn Tyr Asp Met Ala Lys Leu Leu Asn Gly Thr Val Val Gln Lys  
305 310 315  
His Pro Met His Ala Val Thr Phe Val Asp Asn His Asp Ser Gln Pro  
320 325 330 335  
Gly Glu Ser Leu Glu Ser Phe Val Gln Glu Trp Phe Lys Pro Leu Ala  
340 345 350  
Tyr Ala Leu Ile Leu Thr Arg Glu Gln Gly Tyr Pro Ser Val Phe Tyr  
355 360 365  
Gly Asp Tyr Tyr Gly Ile Pro Thr His Ser Val Pro Ala Met Lys Ala  
370 375 380  
Lys Ile Asp Pro Ile Leu Glu Ala Arg Gln Asn Phe Ala Tyr Gly Thr  
385 390 395  
Gln His Asp Tyr Phe Asp His His Asn Ile Ile Gly Trp Thr Arg Glu  
400 405 410 415  
Gly Asn Thr Thr His Pro Asn Ser Gly Leu Ala Thr Ile Met Ser Asp  
420 425 430  
Gly Pro Gly Gly Glu Lys Trp Met Tyr Val Gly Gln Asn Lys Ala Gly  
435 440 445  
Gln Val Trp His Asp Ile Thr Gly Asn Lys Pro Gly Thr Val Thr Ile  
450 455 460  
Asn Ala Asp Gly Trp Ala Asn Phe Ser Val Asn Gly Gly Ser Val Ser  
465 470 475  
Ile Trp Val Lys Arg  
480

**SEQUENCE DESCRIPTION : SEQ ID No. 3**

His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-  
Asn-Asp

## SEQUENCE DESCRIPTION : SEQ ID No. 4

AAPFNGTMMQ	YFEWYLPDDG	TLWTKVANE	NNLSSLGITA	LWLPPAYKGT
SRSDVGYGVY	DLYDLGEFNO	KGAVRTKYGT	KAQYLQAIQA	
	AAHAGMQVYA			
DVVFDHKGGA	DGTEWVDAVE	VNPSDRNQEI	SGTYQIQAWT	KFDFPGRGNT
YSSFQWRWYH	FDGVDWDESR	KLSRIYKFRG	IGKAWDWEVD	
TENGNIDYLM				
YADLDMDHPE	VVTELKSWGK	WYVNTTNIDG	FRLDAVKHIK	FSFFPDWLSD
VRSQTGKPLF	TVGEYWSYDI	NKLHNYIMKT	NGTMSLFDAP	LHNKFYTASK
SGGTDFMRTL	MTNTLMKDQP	TLAVTFVDNH	DTEPGQALQS	
	WVDPWFKPLA			
YAFILTRQEG	YPCVFYGDYY	GIPQYNIPSL	KSKIDPLLIA	RRDYAYGTQH
DYLDHSDIIG	WTREGVTEKP	GSGLAALITD	GPGGSKWMYV	
GKQHAGKVFY				
DLTGNRSDTV	TINSDGWGEF	KVNGGSVSVW	VPRKTTVSTI	AWSITTRPWT
DEFVRWTEPR	LVAWP			

CLAIMS

1. Use of a specific amylase in a laundry detergent composition, selected from :

(a)  $\alpha$ -amylase characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas®  $\alpha$ -amylase activity assay and/or;

(b)  $\alpha$ -amylase according (a) comprising the amino sequence shown in SEQ ID No. 1 or an  $\alpha$ -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No.1 and/or;

(c)  $\alpha$ -amylase according (a) comprising the amino sequence shown in SEQ ID No.2 or an  $\alpha$ -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No.2 and/or;

(d)  $\alpha$ -amylase according (a) comprising the following amino sequence in the N-terminal : His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp (SEQ ID No.3) or an  $\alpha$ -amylase being at least 80% homologous with the amino acid sequence shown (SEQ ID No.3) in the N-terminal and/or;

(e)  $\alpha$ -amylase according (a-d) wherein the  $\alpha$ -amylase is obtainable from an alkalophilic Bacillus species and/or

(f)  $\alpha$ -amylase according to (e) wherein the amylase is obtainable from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935 and/or;

(g)  $\alpha$ -amylase showing positive immunological cross-reactivity with antibodies raised against an  $\alpha$ -amylase having an amino acid sequence corresponding respectively to SEQ ID No.1, ID No.2 or ID No.3 and/or;

(h) Variant of a parent  $\alpha$ -amylase, which parent  $\alpha$ -amylase (i) has one of the amino acid sequences shown in SEQ ID No.1, ID No.2 or ID No.4 respectively, or (ii) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity

with an antibody raised against an  $\alpha$ -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an  $\alpha$ -amylase having one of said amino acid sequence; in which variants :

- (i) at least one amino acid residue of said parent  $\alpha$ -amylase has been deleted; and/or
- (ii) at least one amino acid residue of said parent  $\alpha$ -amylase has been replaced by a different amino acid residue; and/or
- (iii) at least one amino acid residue has been inserted relative to said parent  $\alpha$ -amylase;

said variant having an  $\alpha$ -amylase activity and exhibiting at least one of the following properties relative to said parent  $\alpha$ -amylase : increased thermostability, increased stability towards oxidation, reduced Ca ion dependency, increased stability and/or  $\alpha$ -amylolytic activity at neutral to relatively high pH values, increased  $\alpha$ -amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for  $\alpha$ -amylase variant to the pH of the medium;

to provide effective cleaning and whitening of dingy fabrics.

2. Use of a specific amylase according claim 1 wherein said  $\alpha$ -amylase in a laundry detergent composition is comprised at a level from 0.0001% to 0.1%, preferably at a level from 0.00018% to 0.060%, more preferably at a level of from 0.00024% to 0.048% pure enzyme by weight of total composition.

3. Use of a specific amylase in a laundry detergent composition according to any of the preceding claims wherein said laundry detergent composition further comprises a protease.

4. Use of a specific amylase in a laundry detergent composition according to any of the preceding claims wherein said laundry detergent composition further comprises one or more components selected from anionic, nonionic, cationic, amphoteric and zwitterionic surfactants, suds suppressors, soil suspension and anti-redeposition agents, smectite clays and the like.

5. Use of a specific amylase in a laundry detergent composition according to any of the preceding claims wherein said laundry detergent composition is a granular detergent composition containing no more than 15% by weight of inorganic filler salt.

6. Use of a specific amylase in a laundry detergent composition according to claims 1-4 wherein said laundry detergent composition is a heavy duty liquid composition.

7. Use of a specific amylase in a laundry detergent composition according to any of the preceding claims wherein said laundry detergent composition further comprises other enzymes providing cleaning performance and/or fabric care benefits.

8. Use of a specific amylase in a laundry detergent composition according claim 1 wherein said laundry detergent composition is in the form of a detergent additive.

# INTERNATIONAL SEARCH REPORT

Inter      nal Application No  
PCT/US 96/12612

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6    C11D3/386

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6    C11D

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

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 97 04067 A (PROCTER & GAMBLE ;PRAMOD KAKUMANU (US); HORNER THOMAS WILHELM (BE)) 6 February 1997 see page 5, paragraph 2; claims; examples ---	1-8
E	EP 0 756 000 A (PROCTER & GAMBLE) 29 January 1997 see page 2, line 55 - page 3, line 22; claims; examples ---	1-8
A	WO 95 10603 A (NOVONORDISK AS ;BISGAARD FRANTZEN HENRIK (DK); BORCHERT TORBEN VED) 20 April 1995 see page 63, line 1 - line 11; claims 1,40-45,49; figures 4,5; examples 8,10 --- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

25 March 1997

Date of mailing of the international search report

18.04.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Loiselet-Taisne, S



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 96/12612

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 18314 A (GENENCOR INT) 18 August 1994 cited in the application see claims 1,27-30 ---	1
A,P	WO 96 23873 A (NOVONORDISK AS ;BISGAARD FRANTZEN HENRIK (DK); SVENDSEN ALLAN (DK)) 8 August 1996 cited in the application see page 5, line 19 - page 6, line 22 see page 7, line 5 - line 10; claims ---	
A	WO 95 26397 A (NOVONORDISK AS ;OUTTRUP HELLE (DK); BISGAARD FRANTZEN HENRIK (DK);) 5 October 1995 cited in the application see claims -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCI/US 96/12612

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9704067 A	06-02-97	EP 0755999 A	29-01-97
		EP 0756000 A	29-01-97
		EP 0756001 A	29-01-97
		WO 9704066 A	06-02-97
		WO 9704053 A	06-02-97
		WO 9704054 A	06-02-97
-----			
EP 0756000 A	29-01-97	EP 0755999 A	29-01-97
		EP 0756001 A	29-01-97
		WO 9704066 A	06-02-97
		WO 9704067 A	06-02-97
		WO 9704053 A	06-02-97
		WO 9704054 A	06-02-97
-----			
WO 9510603 A	20-04-95	AU 7807494 A	04-05-95
		CA 2173329 A	20-04-95
		CN 1134725 A	30-10-96
		EP 0722490 A	24-07-96
		FI 961524 A	30-05-96
-----			
WO 9418314 A	18-08-94	AU 6239294 A	29-08-94
		BR 9405720 A	28-11-95
		CN 1118172 A	06-03-96
		CZ 9502057 A	13-12-95
		EP 0689589 A	03-01-96
		FI 953797 A	10-08-95
		HU 72920 A	28-06-96
		JP 8506491 T	16-07-96
		NO 953147 A	28-09-95
		PL 310326 A	11-12-95
-----			
WO 9623873 A	08-08-96	AU 4483396 A	21-08-96
-----			
WO 9526397 A	05-10-95	AU 2067795 A	17-10-95
		CA 2186592 A	05-10-95
		EP 0753057 A	15-01-97
		FI 963861 A	27-09-96
		ZA 9502565 A	21-12-95
-----			