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# (54) CLEANING COMPOSITIONS INCLUDING MANNANASE ENZYME AND AMINES

(57) Cleaning compositions that include a mannanase enzyme and an amine. Methods of making and using such cleaning compositions. Use of a mannanase enzyme and an amine.

### Description

#### REFERENCE TO A SEQUENCE LISTING

5 [0001] This application contains a Sequence Listing in computer readable form, which is incorporated herein by reference.

#### FIELD OF THE INVENTION

[0002] The present invention relates to cleaning compositions that include a mannanase enzyme and an amine. The present invention also relates to methods of making such cleaning compositions. The present invention also relates to the use of a mannanase enzyme and an amine.

#### BACKGROUND OF THE INVENTION

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**[0003]** The detergent formulator is constantly aiming to improve the performance of detergent compositions. One particular challenge is the removal of certain malodorous soils from surfaces such as textiles. Such soils may build up over time, including on collars and cuffs where incomplete cleaning may occur.

**[0004]** Certain mannanase enzymes have been found to be effective on such soils, but their efficiency can be improved, particularly when such soils are present in combination with other soils, such as greasy soils.

[0005] There is a need for improved cleaning compositions that include mannanase enzymes.

#### SUMMARY OF THE INVENTION

[0006] The present invention relates to cleaning compositions that include a mannanase enzyme comprising a polypeptide having mannan endo-1,4-beta-mannosidase activity (EC 3.2.1.78) that catalyzes the hydrolysis of 1,4-3-D-mannosidic linkages in mannans, galactomannans and/or glucomannans, and/or optionally having at least 60% sequence identity to SEQ ID NO: 1 or having at least 81% sequence identity to SEQ ID NO: 2 or having at least 75% sequence identity to SEQ ID NO: 3 or having at least 65% sequence identity to SEQ ID NO: 4 or having at least 75% sequence identity to SEQ ID NO: 5; and an amine selected from the group consisting of etheramines, cyclic amines, polyamines, oligoamines, and combinations thereof. Preferably the mannanase is a member of the glycoside hydrolase family 26.
[0007] The present invention relates to methods of cleaning a surface, such as a textile, that include mixing a cleaning composition as described herein with water to form an aqueous liquor and contacting a surface with the aqueous liquor in a laundering step.

**[0008]** The present invention also relates to the use of the mannanase enzyme to enhance the greasy-stain removal of an amine selected from the group consisting of etheramines, cyclic amines, polyamines, oligoamines, and combinations thereof.

**[0009]** The present invention also relates to the use of an amine selected from the group consisting of etheramines, cyclic amines, polyamines, oligoamines, and combinations thereof, to enhance the stain-removal and/or malodor-reducing benefits of the mannanase enzyme.

**[0010]** Preferably the mannanase is a variant having at least 60% sequence identity to SEQ ID NO: 1 or having at least 81% sequence identity to SEQ ID NO: 2 or having at least 75% sequence identity to SEQ ID NO: 3 or having at least 65% sequence identity to SEQ ID NO: 4 or having at least 75% sequence identity to SEQ ID NO: 5.

## 45 DETAILED DESCRIPTION OF THE INVENTION

**[0011]** The present invention relates to cleaning compositions comprising a mannanase enzyme and an amine, selected from the group consisting of etheramines, cyclic amines, polyamines, oligoamines, and combinations thereof, preferably comprising an etheramine. Without wishing to be bound by theory, it is believed that certain malodor-causing soils become trapped under greasy soils on certain surfaces, such as textiles. It is further believed that the compositions of the invention help to lift the greasy soils, facilitating the soil-removing (and malodor-reducing) benefits of the mannanases described herein.

[0012] The components of the compositions and processes of the present invention are described in more detail below. [0013] As used herein, the articles "a" and "an" when used in a claim, are understood to mean one or more of what is claimed or described. As used herein, the terms "include," "includes," and "including" are meant to be non-limiting. The compositions of the present invention can comprise, consist essentially of, or consist of, the components of the present invention.

[0014] The terms "substantially free of" or "substantially free from" may be used herein. This means that the indicated

material is at the very minimum not deliberately added to the composition to form part of it, or, preferably, is not present at analytically detectable levels. It is meant to include compositions whereby the indicated material is present only as an impurity in one of the other materials deliberately included. The indicated material may be present, if at all, at a level of less than 1%, or less than 0.1%, or less than 0.01%, or even 0%, by weight of the composition.

**[0015]** As used herein, the term "etheramine" includes the term "polyetheramine" and includes amines that have one or more ether groups.

**[0016]** Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

[0017] All temperatures herein are in degrees Celsius (°C) unless otherwise indicated. Unless otherwise specified, all measurements herein are conducted at 20°C and under the atmospheric pressure.

[0018] In all embodiments of the present invention, all percentages are by weight of the total composition, unless specifically stated otherwise. All ratios are weight ratios, unless specifically stated otherwise.

[0019] It should be understood that every maximum numerical limitation given throughout this specification includes every lower numerical limitation, as if such lower numerical limitations were expressly written herein. Every minimum numerical limitation given throughout this specification will include every higher numerical limitation, as if such higher numerical limitations were expressly written herein. Every numerical range given throughout this specification will include every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

**[0020]** As used herein, the term "alkoxy" is intended to include C1-C8 alkoxy and C1-C8 alkoxy derivatives of polyols having repeating units such as butylene oxide, glycidol oxide, ethylene oxide or propylene oxide.

[0021] As used herein, unless otherwise specified, the terms "alkyl" and "alkyl capped" are intended to include C1-C18 alkyl groups, or even C1-C6 alkyl groups.

[0022] As used herein, unless otherwise specified, the term "aryl" is intended to include C3-12 aryl groups.

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[0023] As used herein, unless otherwise specified, the term "arylalkyl" and "alkaryl" are equivalent and are each intended to include groups comprising an alkyl moiety bound to an aromatic moiety, typically having C1-C18 alkyl groups and, in one aspect, C1-C6 alkyl groups.

**[0024]** The terms "ethylene oxide," "propylene oxide" and "butylene oxide" may be shown herein by their typical designation of "EO," "PO" and "BO," respectively.

**[0025]** As used herein, the term "cleaning and/or treatment composition" includes, unless otherwise indicated, granular, powder, liquid, gel, paste, unit dose, bar form and/or flake type washing agents and/or fabric treatment compositions.

[0026] As used herein, "cellulosic substrates" are intended to include any substrate which comprises cellulose, either 100% by weight cellulose or at least 20% by weight, or at least 30 % by weight or at least 40 or at least 50 % by weight or even at least 60 % by weight cellulose. Cellulose may be found in wood, cotton, linen, jute, and hemp. Cellulosic substrates may be in the form of powders, fibers, pulp and articles formed from powders, fibers and pulp. Cellulosic fibers, include, without limitation, cotton, rayon (regenerated cellulose), acetate (cellulose acetate), triacetate (cellulose triacetate), and mixtures thereof. Typically cellulosic substrates comprise cotton. Articles formed from cellulosic fibers include textile articles such as fabrics. Articles formed from pulp include paper.

**[0027]** As used herein, the term "maximum extinction coefficient" is intended to describe the molar extinction coefficient at the wavelength of maximum absorption (also referred to herein as the maximum wavelength), in the range of 400 nanometers to 750 nanometers.

**[0028]** As used herein "average molecular weight" is reported as a weight average molecular weight, as determined by its molecular weight distribution; as a consequence of their manufacturing process, polymers disclosed herein may contain a distribution of repeating units in their polymeric moiety.

[0029] As used herein the term "variant" refers to a polypeptide that contains an amino acid sequence that differs from a wild type or reference sequence. A variant polypeptide can differ from the wild type or reference sequence due to a deletion, insertion, or substitution of a nucleotide(s) relative to said reference or wild type nucleotide sequence. The reference or wild type sequence can be a full-length native polypeptide sequence or any other fragment of a full-length polypeptide sequence. A polypeptide variant generally has at least about 70% amino acid sequence identity with the reference sequence, 80% amino acid sequence identity within the reference sequence, 80% amino acid sequence identity within the reference sequence, 86% amino acid sequence identity with the reference sequence, 87% amino acid sequence identity with the reference sequence, 88% amino acid sequence identity with the reference sequence, 90% amino acid sequence identity with the reference sequence, 91% amino acid sequence identity with the reference sequence, 91% amino acid sequence identity with the reference sequence, 93% amino acid sequence identity with the reference sequence, 95% amino acid sequence identity with the reference sequence, 95% amino acid sequence identity with the reference sequence, 95% amino acid sequence identity with the reference sequence, 97% amino acid sequence identity with the reference sequence, 97% amino acid sequence identity with the reference sequence, 97% amino acid sequence identity with the reference sequence, 97% amino acid sequence identity with the reference sequence, 97% amino acid sequence identity with the reference sequence, 97% amino acid sequence identity with the reference sequence, 97% amino acid sequence identity with the reference sequence, 97% amino acid sequence identity with the reference sequence, 98% amino acid sequence identity with the reference sequence, 97%

quence, 98.5% amino acid sequence identity with the reference sequence or 99% amino acid sequence identity with the reference sequence.

[0030] As used herein, the term "solid" includes granular, powder, bar and tablet product forms.

[0031] As used herein, the term "fluid" includes liquid, gel, paste, and gas product forms.

#### Cleaning Composition

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[0032] The present disclosure relates to cleaning and/or treatment compositions. The cleaning composition may be selected from the group of light duty liquid detergents compositions, heavy duty liquid detergent compositions, solid, for example particulate/powder or "dry" cleaning compositions, hard surface cleaning compositions, detergent gels commonly used for laundry, bleaching compositions, laundry additives, fabric enhancer compositions, shampoos, body washes, other personal care compositions, and mixtures thereof. The cleaning composition may be a hard surface cleaning composition (such as a dishwashing composition) or a laundry composition (such as a heavy duty liquid or solid detergent composition).

[0033] The cleaning compositions may be in any suitable form. The composition can be selected from a liquid, solid, or combination thereof. As used herein, "liquid" includes free-flowing liquids, as well as pastes, gels, foams and mousses. Non-limiting examples of liquids include light duty and heavy duty liquid detergent compositions, fabric enhancers, detergent gels commonly used for laundry, bleach and laundry additives. Gases, e.g., suspended bubbles, or solids, e.g. particles, may be included within the liquids. A "solid" as used herein includes, but is not limited to, powders, agglomerates, and mixtures thereof. Non-limiting examples of solids include: granules, microcapsules, beads, noodles, and pearlised balls. Solid compositions may provide a technical benefit including, but not limited to, through-the-wash benefits, pre-treatment benefits, and/or aesthetic effects.

[0034] The cleaning composition may be in the form of a unitized dose article, such as a tablet or in the form of a pouch. Such pouches typically include a water-soluble film, such as a polyvinyl alcohol water-soluble film, that at least partially encapsulates a composition. Suitable films are available from MonoSol, LLC (Indiana, USA). The composition can be encapsulated in a single or multi-compartment pouch. A multi-compartment pouch may have at least two, at least three, or at least four compartments. A multi-compartmented pouch may include compartments that are side-by-side and/or superposed. The composition contained in the pouch may be liquid, solid (such as powders), or combinations thereof. Preferably the composition of the invention is a liquid.

### Mannanases

[0035] The composition comprises a mannanase enzyme. The term "mannanase" herein means a polypeptide having mannan endo-1,4- beta-mannosidase activity (EC 3.2.1.78) from the glycoside hydrolase family 26 that catalyzes the hydrolysis of 1 ,4-3-D-mannosidic linkages in mannans, galactomannans and glucomannans. Alternative names of mannan endo-1,4-beta-mannosidase are 1,4-3-D-mannan mannanohydrolase; endo-1,4-3-mannanase; endo- $\beta$ -1,4-mannase;  $\beta$ -mannanase B; 3-1,4-mannan 4-mannanohydrolase; endo-3-mannanase; and  $\beta$ -D-mannanase. Preferred mannanases are members of the glycoside hydrolase family 26.

**[0036]** For purposes of the present disclosure, mannanase activity may be determined using the Reducing End Assay as described in the experimental section of WO 2015040159.

Suitable examples from class EC 3.2.1.78 are described in WO 2015040159, such as the mature polypeptide SEQ ID NO: 2 described therein.

[0037] Preferred mannanases are variants having at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 81 %, at least 82%, at least 83%, at least 84%, at least 85%, at least 86%, at least 87%, at least 88%, at least 89%, at least 90%, at least 91 %, at least 92%, at least 93%, at least 94%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99% or 100% sequence identity to the mature polypeptide SEQ ID NO: 1 from *Ascobolus stictoideus;* [0038] Preferred mannanases are variants having at least 81 %, at least 82%, at least 83%, at least 84%, at least 85%, at least 86%, at least 87%, at least 88%, at least 89%, at least 90%, at least 91 %, at least 92%, at least 93%, at least 94%, at least 95%, at least 95%, at least 95%, at least 97%, at least 98%, at least 99% or 100% sequence identity to the mature polypeptide SEQ ID NO: 2 from *Chaetomium virescens*.

**[0039]** Preferred mannanases are variants having at least 75%, at least 76%, at least 77%, at least 78%, at least 79%, at least 80%, at least 81%, at least 82%, at least 83%, at least 84%, at least 85%, at least 86%, at least 87%, at least 88%, at least 89%, at least 90%, at least 91 %, at least 92%, at least 93%, at least 94%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99% or 100% sequence identity to the mature polypeptide SEQ ID NO: 3 from *Preussia aemulans*.

**[0040]** Preferred mannanases are variants having at least at least 65%, at least 66%, at least 67%, at least 68%, at least 69%, at least 70%, at least 71%, at least 72%, at least 73%, at least 74%, at least 75%, at least 76%, at least 77%, at least 78%, at least 80%, at least 81%, at least 82%, at least 83%, at least 84%, at least 85%, at least 85%,

86%, at least 87%, at least 88%, at least 89%, at least 90%, at least 91 %, at least 92%, at least 93%, at least 94%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99% or 100% sequence identity to the mature polypeptide SEQ ID NO: 4 from *Yunnania penicillata*.

**[0041]** Preferred mannanases are variants having at least at least 75%, at least 76%, at least 77%, at least 78%, at least 79%, at least 80%, at least 81%, at least 82%, at least 83%, at least 84%, at least 85%, at least 86%, at least 87%, at least 88%, at least 89%, at least 90%, at least 91%, at least 92%, at least 93%, at least 94%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99% or 100% sequence identity to the mature polypeptide SEQ ID NO: 5 from *Myrothecium roridum*. Preferably the mannanase is an isolated mannanase.

**[0042]** Preferably the mannanase enzyme is present in the cleaning compositions in an amount from 0.001 to 1 wt% based on active protein in the composition, or from 0.005 to 0.5 wt% or from 0.01 to 0.25 wt%. Preferably the mannanase enzyme is present in the laundering aqueous liquor in an amount of from 0.01ppm to 1000ppm of the mannanase enzyme, or from 0.05 or from 0.1ppm to 750 or 500ppm. The mannanases or compositions comprising them may also give rise to biofilm-disrupting effects.

### Amines

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**[0043]** The cleaning compositions described herein may contain an amine selected from the group consisting of etheramines, cyclic amines, polyamines, oligoamines (e.g., triamines, diamines, pentamines, tetraamines), and combinations thereof, preferably in an amount from about 0.1% to about 10%, or from about 0.2% to about 5%, or from about 0.5% to about 4%, or from about 0.1% to about 2%, by weight of the composition, of the amine. The amine can be subjected to protonation depending on the pH of the cleaning medium in which it is used. **[0044]** Preferably the amine comprises an amine selected from the group consisting of oligoamines, etheramines, cyclic amines, and combinations thereof. In some aspects, the amine is not an alkanolamine. In some aspects, the amine is not a polyalkyleneimine.

**[0045]** Examples of suitable oligoamines include tetraethylenepentamine, triethylenetetraamine, diethylenetriamine, and mixtures thereof. Etheramines and cyclic amines are described in more detail below.

#### Etheramines

**[0046]** Preferably the amine comprises an etheramine. The cleaning compositions may contain from about 0.1% to about 10%, or from about 0.2% to about 5%, or from about 0.5% to about 4%, by weight of the composition, of an etheramine.

[0047] The etheramine preferably has a weight average molecular weight of less than about grams/mole 1000 grams/mole, or from about 100 to about 800 grams/mole, or from about 200 to about 450 grams/mole, or from about 290 to about 1000 grams/mole, or from about 290 to about 900 grams/mole, or from about 300 to about 700 grams/mole, or from about 300 to about 450 grams/mole. Preferably the weight average molecular weight is from about 150, or from about 200, or from about 350, or from about 500 grams/mole, to about 1000, or to about 900, or to about 800 grams/mole.

[0048] A preferred etheramine is represented by the structure of Formula (I):

$$Z_{1}\text{-}A_{1} \xrightarrow{\text{-}(OA_{2})} \underbrace{(OA_{3})_{(y_{1}\text{-}1)}}_{O} \underbrace{(OA_{3})_{(x_{1}\text{-}1)}}_{O} \underbrace{(A_{4}O)_{(x_{1}\text{-}1)}}_{(x_{1}\text{-}1)} \underbrace{(A_{5}O)_{(x_{1}\text{-}1)}}_{(x_{1}\text{-}1)} A_{6}\text{-}Z_{2}$$

Formula (I)

where each of  $R_1$ - $R_6$  is independently selected from H, alkyl, cycloalkyl, aryl, alkylaryl, or arylalkyl, where at least one of  $R_1$ - $R_6$  is different from H, typically at least one of  $R_1$ - $R_6$  is an alkyl group having 2 to 8 carbon atoms, each of  $A_1$ - $A_6$  is independently selected from linear or branched alkylenes having 2 to 18 carbon atoms, each of  $Z_1$ - $Z_2$  is independently selected from OH or NH $_2$ , where at least one of  $Z_1$ - $Z_2$  is NH $_2$ , typically each of  $Z_1$  and  $Z_2$  is NH $_2$ , where the sum of x+y is in the range of about 2 to about 200, or about 2 to about 20, or about 2 to about 3 to about 8, or about 2 to about 2 to about 200, or about 2 to about 3 to about 3, or about 2 to about 2 to about 4, where

 $x_1 \ge 1$  and  $y_1 \ge 1$ .

[0049] In the etheramine of Formula (I), each of  $A_1$ - $A_6$  is preferably independently selected from ethylene, propylene, or butylene, typically each of  $A_1$ - $A_6$  is propylene, preferably each of  $A_1$  and  $A_6$  is independently selected from linear alkanediyl groups having 2 to 18 carbon atoms, or 2-10 carbon atoms, or 2-5 carbon atoms; each of  $A_2$ ,  $A_3$ ,  $A_4$ , and  $A_5$  is independently selected from linear or branched alkanediyl groups having 2 to 18 carbon atoms, preferably 2-10 carbon atoms, most preferably 2-5 carbon atoms. In the etheramine of Formula (I), preferably each of  $R_1$ ,  $R_2$ ,  $R_5$ , and  $R_6$  may be H and each of  $R_3$  and  $R_4$  may be independently selected from C1-C16 alkyl or aryl, typically each of  $R_1$ ,  $R_2$ ,  $R_5$ , and  $R_6$  is H and each of  $R_3$  and  $R_4$  is independently selected from a butyl group, an ethyl group, a methyl group, a propyl group, or a phenyl group. In the etheramine of Formula (I),  $R_3$  is preferably an ethyl group, each of  $R_1$ ,  $R_2$ ,  $R_5$ , and  $R_6$  is H, and  $R_4$  is a butyl group. In the etheramine of Formula (I), perferably each of  $R_1$  and  $R_2$  is H and each of  $R_3$ ,  $R_4$ ,  $R_5$ , and  $R_6$  is independently selected from an ethyl group, a methyl group, a butyl group, a phenyl group, or H.

[0050] Preferably the amine comprises an etheramine represented by the structure of Formula (II):

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$$\begin{array}{c} (A_{7}O) \xrightarrow{(x-1)+(y-1)+1} (A_{8}O) \xrightarrow{(x_{1}-1)+(y_{1}-1)+1} A_{9} \cdot Z_{4} \\ R_{7} \xrightarrow{R_{8}} (R_{12}) \xrightarrow{R_{10}} R_{11} \end{array}$$

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Formula (II)

each of  $R_7$ - $R_{12}$  is independently selected from H, alkyl, cycloalkyl, aryl, alkylaryl, or arylalkyl, where at least one of  $R_7$ - $R_{12}$  is different from H, typically at least one of  $R_7$ - $R_{12}$  is an alkyl group having 2 to 8 carbon atoms, each of  $A_7$ - $A_9$  is independently selected from linear or branched alkylenes having 2 to 18 carbon atoms, each of  $Z_3$ - $Z_4$  is independently selected from OH or NH $_2$ , where at least one of  $Z_3$ - $Z_4$  is NH $_2$ , typically each of  $Z_3$  and  $Z_4$  is NH $_2$ , where the sum of x+y is in the range of about 2 to about 200, or about 2 to about 20, or about 2 to about 3, or about 2 to about 4, where x $\ge$ 1 and y $\ge$ 1, and the sum of  $x_1$  +  $y_1$  is in the range of about 2 to about 20, or about 2 to about 3, or about 3 to about 8, or about 2 to about 4, where  $x_1$  and  $x_2$  1 and  $x_3$  1 and  $x_4$  2 1 and  $x_4$  2 1 and  $x_4$  2 1 and  $x_4$  3 about 3 to about 3 to about 4, where

**[0051]** In the etheramine of Formula (II), each of  $A_7$ - $A_9$  may be independently selected from ethylene, propylene, or butylene, typically each of  $A_7$ - $A_9$  is propylene.  $A_9$  may be selected from linear alkanediyl groups having 2 to 18 carbon atoms, or 2-10 carbon atoms, or 2-5 carbon atoms; each of  $A_7$  and  $A_8$  may be independently selected from linear or branched alkanediyl groups having 2 to 18 carbon atoms, or 2-10 carbon atoms, or 2-5 carbon atoms. In the etheramine of Formula (II), each of  $R_7$ ,  $R_8$ ,  $R_{11}$ , and  $R_{12}$  may be H and each of  $R_9$  and  $R_{10}$  may be independently selected from C1-C16 alkyl or aryl; each of  $R_7$ ,  $R_8$ ,  $R_{11}$ , and  $R_{12}$  may be H and each of  $R_9$  and  $R_{10}$  may bes independently selected from a butyl group, an ethyl group, a methyl group, a propyl group, or a phenyl group. In the etheramine of Formula (II),  $R_9$  may be an ethyl group, each of  $R_7$ ,  $R_8$ ,  $R_{11}$ , and  $R_{12}$  may be H, and  $R_{10}$  may be a butyl group. In the etheramine of Formula (II), each of  $R_7$  and  $R_8$  may be H and each of  $R_9$ ,  $R_{10}$ ,  $R_{11}$ , and  $R_{12}$  may be independently selected from an ethyl group, a propyl group, a propyl group, a phenyl group, or H.

[0052] Suitable etheramines are represented by Formula A, Formula B, and Formula C:

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where n+m is from about 0 to about 8, or from about 0 to about 6, or from about 1 to about 6.

[0053] The etheramine preferably comprises a mixture of a compound of Formula (I) and a compound of Formula (II). [0054] The etheramine of Formula (I) or Formula (II) may have a weight average molecular weight of 100 grams/mole to 1000 grams/mole, or from about 100 to about 800 grams/mole, or from about 200 to about 450 grams/mole.

[0055] The etheramine preferably comprises an etheramine mixture comprising at least 90%, by weight of the etheramine mixture, of the etheramine of Formula (I), the etheramine of Formula(II), the etheramine of Formula(III) or a mixture thereof. The etheramine may comprise a etheramine mixture comprising at least 95%, by weight of the etheramine mixture, of the etheramine of Formula (I), the etheramine of Formula(II) and the etheramine of Formula(III). [0056] The etheramine of Formula (I) and/or the etheramine of Formula (II) are obtainable by known methods, such as those disclosed in US2014/0296127A1. The etheramines of Formula (I) and/or Formula (II) may be obtained by:

a) reacting a 1,3-diol of formula (1) with a  $C_2$ - $C_{18}$  alkylene oxide to form an alkoxylated 1,3-diol, wherein the molar ratio of 1,3-diol to  $C_2$ - $C_{18}$  alkylene oxide is in the range of about 1:2 to about 1:10,

where  $R_1$ - $R_6$  are independently selected from H, alkyl, cycloalkyl, aryl, alkylaryl, or arylalkyl, where at least one of  $R_1$ - $R_6$  is different from H; and

b) aminating the alkoxylated 1,3-diol with ammonia.

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[0057] Suitable 1,3-diols include 2,2-dimethyl-1,3-propane diol, 2-butyl-2-ethyl-1,3-propane diol, 2-pentyl-2-propyl-1,3-propane diol, 2-(2-methyl)butyl-2-propyl-1,3-propane diol, 2,2,4-trimethyl-1,3-propane diol, 2,2-diethyl-1,3-propane diol, 2-methyl-2-propyl-1,3-propane diol, 2-ethyl-1,3-propane diol, 2-pentyl-2-methyl-1,3-propane diol, 2-ethyl-1,3-propane diol, 2-ethyl-2-methyl-1,3-propane diol, 2-isopropyl-2-methyl-1,3-propane diol, or a mixture thereof. In some aspects, the 1,3-diol is selected from 2-butyl-2-ethyl-2-ethyl-1,3-propane diol, 2-ethyl-2-ethyl-2-ethyl-1,3-propane diol, 2-ethyl-2-e

1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2-methyl-2-phenyl-1,3-propanediol, or a mixture thereof. Typically used 1,3-diols are 2-butyl-2-ethyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2-methyl-2-phenyl-1,3-propanediol.

[0058] The degree of amination for the etheramine of Formula (I) and/or Formula (II) may be from about 50% to about 100%, or from about 60% to about 100%, or from about 70% to about 100%.

[0059] The degree of amination may be calculated from the total amine value (AZ) divided by sum of the total acetylables value (AC) and tertiary amine value (tert. AZ) multiplied by 100: (Total AZ/ (AC+tert. AZ))x100). The total amine value (AZ) is determined according to DIN 16945. The total acetylables value (AC) is determined according to DIN 53240. The secondary and tertiary amines are determined according to ASTM D2074-07. The hydroxyl value is calculated from (total acetylables value + tertiary amine value)- total amine value.

[0060] The cleaning compositions of the present invention preferably comprises an etheramine represented by Formula (III),

$$\begin{array}{c} A_{1} \longrightarrow A_{4} \longrightarrow Z_{1} \\ A_{1} \longrightarrow A_{2} \longrightarrow A_{3} \longrightarrow A_{5} \longrightarrow Z_{2} \\ A_{3} \longrightarrow A_{3} \longrightarrow A_{6} \longrightarrow Z_{3} \end{array}$$

Formula (III)

where

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R is selected from H or a C1-C6 alkyl group,

each ofk<sub>1</sub>, k<sub>2</sub>, and k<sub>3</sub> is independently selected from 0, 1, 2, 3, 4, 5, or 6,

each of  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$ ,  $A_5$ , and  $A_6$  is independently selected from a linear or branched alkylene group having from about 2 to about 18 carbon atoms or mixtures thereof,

 $x\ge1$ ,  $y\ge1$ , and  $z\ge1$ , and the sum of x+y+z is in the range of from about 3 to about 100, and each of  $Z_1$ ,  $Z_2$ , and  $Z_3$  is independently selected from NH<sub>2</sub> or OH, where at least two of  $Z_1$ ,  $Z_2$ , and  $Z_3$  are NH<sub>2</sub>.

[0061] R may be H or a C1-C6 alkyl group selected from methyl, ethyl, or propyl. R may be H or a C1-C6 alkyl group selected from ethyl.

**[0062]** Each of $k_1$ ,  $k_2$ , and  $k_3$  may be independently selected from 0, 1, or 2. Each of $k_1$ ,  $k_2$ , and  $k_3$  may be independently selected from 0 or 1. At least two of $k_1$ ,  $k_2$ , and  $k_3$  may be 1, or even each of  $k_1$ ,  $k_2$ , and  $k_3$  may be 1.

45 [0063] Each of  $Z_1$ ,  $Z_2$ , and  $Z_3$  may be  $NH_2$ .

**[0064]** All A groups (i.e.,  $A_1$ - $A_6$ ) may be the same, at least two A groups may be the same, at least two A groups may be different, or all A groups may be different from each other. Each of  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$ ,  $A_5$ , and  $A_6$  may be independently selected from a linear or branched alkylene group having from about 2 to about 10 carbon atoms, or from about 2 to about 6 carbon atoms, or from about 2 to about 4 carbon atoms, or mixtures thereof. At least one, or at least three, of  $A_1$ - $A_6$  may be a linear or branched butylene group. Each of  $A_4$ ,  $A_5$ , and  $A_6$  may be a linear or branched butylene group. Each of  $A_1$ - $A_6$  may be a linear or branched butylene group.

[0065] The variables x, y, and/or z may be independently selected and should be equal to 3 or greater, meaning that that the etheramine may have more than one  $[A_1 - O]$  group, more than one  $[A_2 - O]$  group, and/or more than one  $[A_3 - O]$  group.  $A_1$  may be selected from ethylene, propylene, butylene, or mixtures thereof.  $A_2$  may be selected from ethylene, propylene, butylene, or mixtures thereof.  $A_3$  may be selected from ethylene, propylene, butylene, or mixtures thereof. When  $A_1$ ,  $A_2$ , and/or  $A_3$  are mixtures of ethylene, propylene, and/or butylenes, the resulting alkoxylate may have a blockwise structure or a random structure.

[0066]  $[A_1 - O]_{x-1}$  can be selected from ethylene oxide, propylene oxide, butylene oxide, or mixtures thereof.  $[A_2 - O]_{y-1}$ 

can be selected from ethylene oxide, propylene oxide, butylene oxide, or mixtures thereof.  $[A_3 - O]_{z-1}$  can be selected from ethylene oxide, propylene oxide, butylene oxide, or mixtures thereof.

[0067] The sum of x+y+z may be in the range of from about 3 to about 100, or from about 3 to about 30, or from about 3 to about 10, or from about 5 to about 10.

**[0068]** When the etheramine is a etheramine of Formula (III) where R is a C2 alkyl group (i.e., ethyl) and optionally each of $k_1$ ,  $k_2$ , and  $k_3$  is 1, the molecular weight of the etheramine may be from about 500 to about 1000, or to about 900, or to about 800 grams/mole. When the etheramine is an etheramine of Formula (III) where R is a C2 alkyl group (i.e., ethyl) and optionally each of $k_1$ ,  $k_2$ , and  $k_3$  is 1, it may be that at least one A group (i.e., at least one of A1, A2, A3, A4, A5, or A6) is not a propylene group. When the etheramine is an etheramine of Formula (III) where R is a C2 alkyl group (i.e., ethyl) and optionally each of $k_1$ ,  $k_2$ , and  $k_3$  is 1, it may be that at least one A group (i.e., at least one of A1, A2, A3, A4, A5, or A6) is an ethylene group or a butylene group, or even that at least one A group (i.e., at least one of A1, A2, A3, A4, A5, or A6) is a butylene group.

**[0069]** The composition preferably comprises an etheramine selected from the group consisting of Formula D, Formula E, Formula F, and mixtures thereof:

$$H_2N$$
 $O$ 
 $n$ 
 $NH_2$ 
Formula D,

Formula E

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where average n is from about 0.5 to about 5, or about 1 to about 3, or about 1 to about 2.5;

**[0070]** The etheramines of Formula (III) are obtainable by known methods, such as those disclosed in US2015/0057212A1. The etheramines of Formula (III) may be obtained by a process comprising the following steps:

a) reacting a low-molecular-weight, organic triol, such as glycerine and/or 1,1,1-trimethylolpropane, with  $C_2$ - $C_{18}$  alkylene oxide, to form an alkoxylated triol, where the molar ratio of the low-molecular-weight organic triol to the alkylene oxide is in the range of about 1:3 to about 1:10, and b) aminating the alkoxylated triol with ammonia.

Formula F.

[0071] The low-molecular-weight triol can be selected from glycerine, 1,1,1-trimethylolpropane, or mixtures thereof. [0072] The etheramine of Formula (III) may have a weight average molecular weight of from about 500 to about 1000, or to about 900, or to about 800 grams/mole.

[0073] The degree of amination for the etheramine of Formula (III) may be may be from about 67% to about 100%, or from about 85% to about 100%. The degree of amination is calculated as described about in regard to the etheramines of Formula (I) and (II).

[0074] The cleaning compositions described herein may contain an etheramine as represented by the structure of Formula (IV):

$$H_2N$$
 $R$ 
 $O$ 
 $NH_2$ 
 $R$ 

# Formula (IV)

where each R group is independently selected from the group consisting of H, a methyl group, and an ethyl group, where at least one R group is a methyl group, x is in the range of about 2 to about 300. x indicates the average number of repeated units or basic building blocks that constitute the polymer, x may be a whole number or a fraction. x may be in the range of about 2 and about 20, or about 2 to about 10.

**[0075]** The primary amino groups of the etheramine of formula (IV) may be protonated, that is, ammonium groups. The etheramine according to the invention may comprise at least one repeated unit based on propylene oxide (R = a methyl group in formula (IV)) in the polymer backbone. The etheramine may have between about 2 and about 10 propylene oxide-based (PO) units. In the mentioned ranges (for the PO units), the hydrophobicity of the etheramine may provide for an improved cleaning on grease and particulate stains.

**[0076]** Preferred suitable etheramines according to the invention are marketed by Huntsman Corp. Texas under the trade names, Jeffamine® D-230, Jeffamine® D-400, Jeffamine® ED-600, and by BASF under the trade names Baxxodur EC301, EC302.

[0077] The etheramine may be represented by the structure of Formula (E):

$$H_2N$$

$$O$$

$$X$$

$$NH_2$$
Formula (E)

## where x is about 2.5.

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**[0078]** The etheramine of formula (IV) may have a weight average molecular weight of about 200 to about 1000 grams/mole, or about 230 to about 700 grams/mole, or about 450 grams/mole.

[0079] The etheramine of Formula (IV) is obtainable by:

a) reacting a propane-1,2-diol of formula (2) with a  $C_2$ - $C_{18}$  alkylene oxide to form an alkoxylated propane-1,2-diol, wherein the molar ratio of propane-1,2-diol to  $C_2$ - $C_{18}$  alkylene oxide is in the range of about 1:2 to about 1:10,

# b) aminating the alkoxylated propane-1,2-diol with ammonia.

[0080] The degree of amination for the etheramine of Formula (IV) may be from about 50% to about 100%, typically

from about 60% to about 100%, and more typically from about 70% to about 100%. The degree of amination is calculated as described about in regard to the etheramines of Formula (I) and (II).

[0081] The etheramines useful in the present invention are effective for removal of stains, particularly grease, from soiled material. Detergent compositions containing the etheramines of the invention also do not exhibit the cleaning negatives seen with conventional amine-containing detergent compositions on hydrophilic bleachable stains, such as coffee, tea, wine, or particulates. Additionally, unlike conventional amine-containing detergent compositions, the etheramines of the invention do not contribute to whiteness negatives on white fabrics. Furthermore, it is believed that the etheramines of the present invention are effective at facilitating mannanase enzyme efficacy.

[0082] The etheramines useful in the invention may be used in the form of a water-based, water-containing, or water-free solution, emulsion, gel or paste of the etheramine together with an acid such as, for example, citric acid, lactic acid, sulfuric acid, methanesulfonic acid, hydrogen chloride, e.g., aqeous hydrogen chloride, phosphoric acid, or mixtures thereof. Alternatively, the acid may be represented by a surfactant, such as, alkyl benzene sulfonic acid, alkylsulfonic acid, monoalkyl esters of sulphuric acid, mono alkylethoxy esters of sulphuric acid, fatty acids, alkyl ethoxy carboxylic acids, and the like, or mixtures thereof. When applicable or measurable, the preferred pH of the solution or emulsion ranges from pH 3 to pH 11, or from pH 6 to pH 9.5, even more preferred from pH 7 to pH 8.5.

### Cyclic Amines

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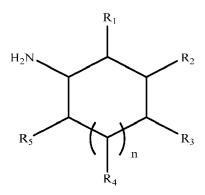
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**[0083]** It may be preferred for the amine to comprise a cyclic amine. The cleaning compositions may include from about 0.1% to about 10%, or from about 0.2% to about 5%, or from about 0.5% to about 3%, by weight the composition, of a cyclic amine.

[0084] The cyclic amine may be represented by the structure of Formula (V):



Formula (V)

**[0085]** The substituents "Rs" may be independently selected from  $NH_2$ , H and linear, branched alkyl or alkenyl from 1 to 10 carbon atoms. For the purpose of this invention, "Rs" includes R1-R5. At least one of the "Rs" needs to be  $NH_2$ . The remaining "Rs" may be independently selected from  $NH_2$ , H and linear or branched alkyl or alkenyl having from 1 to 10 carbon atoms. n may be from 0 to 3; n may be 1.

**[0086]** The amine of the invention may be a cyclic amine with at least two primary amine functionalities. The primary amines can be in any position in the cycle but it has been found that in terms of grease cleaning, better performance may be obtained when the primary amines are in positions 1,3. It has also been found advantageous in terms of grease cleaning amines in which one of the substituents is -CH3 and the rest are H.

[0087] The term "cyclic amine" as used herein encompasses a single cyclic amine and a mixture thereof.

[0088] The cyclic amine can be subjected to protonation depending on the pH of the cleaning medium in which it is used.

# Adjuncts

[0089] The cleaning compositions described herein preferably include other adjunct components, for example selected from surfactants, fabric shading dyes, fabric care benefit agent; additional enzyme; deposition aid; rheology modifier; builder; chelant; bleach; bleaching agent; bleach precursor; bleach booster; bleach activator, bleach catalyst; perfume and/or perfume microcapsules; perfume loaded zeolite; starch encapsulated accord; polyglycerol esters; whitening agent; pearlescent agent; enzyme stabilizing systems; scavenging agents including fixing agents for anionic dyes, complexing agents for anionic surfactants, and mixtures thereof; optical brighteners or fluorescers; polymer including but not limited to soil release polymer and/or soil suspension polymer; dispersants; antifoam agents; non-aqueous

solvent; fatty acid; suds suppressors, e.g., silicone suds suppressors; cationic starches; scum dispersants; substantive dyes; colorants; opacifier; antioxidant; hydrotropes such as toluenesulfonates, cumenesulfonates and naphthalenesulfonates; color speckles; colored beads, spheres or extrudates; clay softening agents; anti-bacterial agents. Additionally or alternatively, the compositions may comprise surfactants, and/or solvent systems. Quaternary ammonium compounds may be present, particularly in fabric enhancer compositions, such as fabric softeners, and comprise quaternary ammonium cations that are positively charged polyatomic ions of the structure  $NR_4^+$ , where R is an alkyl group or an aryl group.

### Additional Enzymes

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[0090] Preferably the composition of the invention comprises additional enzymes, for example selected from lipases, amylases, proteases, nucleases, pectate lyases, cellulases, cutinases, and mixtures thereof. The cleaning compositions preferably comprise one or more additional enzymes from the group selected from nucleases. The cleaning compositions preferably comprises one or more additional enzymes selected from the group amylases, lipases, proteases, pectate lyases, cellulases, cutinases, and mixtures thereof. Preferably, the cleaning compositions comprises one or more additional enzymes selected from lipases and mixtures thereof. Preferably the cleaning compositions comprise one or more additional enzymes selected from lipases. The compositions may also comprise hemicellulases, peroxidases, xylanases, pectinases, keratinases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase and mixtures thereof. When present in the composition, the aforementioned additional enzymes may be present at levels from about 0.00001% to about 2%, from about 0.0001% to about 1% or even from about 0.001% to about 0.5% enzyme protein by weight of the composition. Preferably the or each additional enzyme is present in the laundering aqueous liquor in an amount of from 0.01ppm to 1000 ppm of the active enzyme protein, or from 0.05 or from 0.1ppm to 750 or 500ppm.

#### **Nucleases**

**[0091]** Preferably the composition additionally comprises a nuclease enzyme. The nuclease enzyme is an enzyme capable of cleaving the phosphodiester bonds between the nucleotide subunits of nucleic acids. Suitable nuclease enzymes may be deoxyribonuclease or ribonuclease enzyme or a functional fragment thereof. By functional fragment or part is meant the portion of the nuclease enzyme that catalyzes the cleavage of phosphodiester linkages in the DNA backbone and so is a region of said nuclease protein that retains catalytic activity. Thus it includes truncated, but functional versions, of the enzyme and/or variants and/or derivatives and/or homologues whose functionality is maintained.

[0092] Preferably the nuclease enzyme is a deoxyribonuclease, preferably selected from any of the classes E.C. 3.1.21.x, where x=1, 2, 3, 4, 5, 6, 7, 8 or 9, E.C. 3.1.22.y where y=1, 2, 4 or 5, E.C. 3.1.30.z where z= 1 or 2, E.C. 3.1.31.1 and mixtures thereof. Nuclease enzymes from class E.C. 3.1.21.x and especially where x=1 are particularly preferred. Nucleases in class E.C. 3.1.22.y cleave at the 5' hydroxyl to liberate 3' phosphomonoesters. Enzymes in class E.C. 3.1.30.z may be preferred as they act on both DNA and RNA and liberate 5'-phosphomonoesters. Suitable examples from class E.C. 3.1.31.2 are described in US2012/0135498A, such as SEQ ID NO:3 therein. Such enzymes are commercially available as DENARASE® enzyme from c-LECTA. Nuclease enzymes from class E.C. 3.1.31.1 produce 3'phosphomonoesters.

**[0093]** Preferably, the nuclease enzyme comprises a microbial enzyme. The nuclease enzyme may be fungal or bacterial in origin. Bacterial nucleases may be most preferred. Fungal nucleases may be most preferred.

[0094] The microbial nuclease is obtainable from *Bacillus*, such as a *Bacillus licheniformis* or *Bacillus subtilis* bacterial nucleases. A preferred nuclease is obtainable from *Bacillus licheniformis*, preferably from strain El-34-6. A preferred deoxyribonuclease is a variant of *Bacillus licheniformis*, from strain El-34-6 nuclease defined in SEQ ID NO:6 herein, or variant thereof, for example having at least 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto. Other suitable nucleases are defined in SEQ ID NO: 7 herein, or variant thereof, for example having at least 70% or 75% or 80% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto. Other suitable nucleases are defined in SEQ ID NO: 8 herein, or variant thereof, for example having at least 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto.

**[0095]** A fungal nuclease is obtainable from *Aspergillus*, for example *Aspergillus oryzae*. A preferred nuclease is obtainable from *Aspergillus oryzae* defined in SEQ ID NO: 9 herein, or variant thereof, for example having at least 60% or 70% or75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto.

[0096] Another suitable fungal nuclease is obtainable from *Trichoderma*, for example *Trichoderma harzianum*. A preferred nuclease is obtainable from *Trichoderma harzianum* defined in SEQ ID NO: 10 herein, or variant thereof, for example having at least 60% or 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto. [0097] Other fungal nucleases include those encoded by the DNA sequences of *Aspergillus oryzae* RIB40, *Aspergillus* 

oryzae 3.042, Aspergillus flavus NRRL3357, Aspergillus parasiticus SU-1, Aspergillus nomius NRRL13137, Trichoderma reesei QM6a, Trichoderma virens Gv29-8, Oidiodendron maius Zn, Metarhizium guizhouense ARSEF 977, Metarhizium majus ARSEF 297, Metarhizium robertsii ARSEF 23, Metarhizium acridum CQMa 102, Metarhizium brunneum ARSEF 3297, Metarhizium anisopliae, Colletotrichum fioriniae PJ7, Colletotrichum sublineola, Trichoderma atroviride IMI 206040, Tolypocladium ophioglossoides CBS 100239, Beauveria bassiana ARSEF 2860, Colletotrichum higginsianum, Hirsutella minnesotensis 3608, Scedosporium apiospermum, Phaeomoniella chlamydospora, Fusarium verticillioides 7600, Fusarium oxysporum f. sp. cubense race 4, Colletotrichum graminicola M1.001, Fusarium oxysporum FOSC 3a, Fusarium avenaceum, Fusarium langsethiae, Grosmannia clavigera kw1407, Claviceps purpurea 20.1, Verticillium longisporum, Fusarium oxysporum f. sp. cubense race 1, Magnaporthe oryzae 70-15, Beauveria bassiana D1-5, Fusarium pseudograminearum CS3096, Neonectria ditissima, Magnaporthiopsis poae ATCC 64411, Cordyceps militaris CM01, Marssonina brunnea f. sp. 'multigermtubi' MB\_m1, Diaporthe ampelina, Metarhizium album ARSEF 1941, Colletotrichum gloeosporioides Nara gc5, Madurella mycetomatis, Metarhizium brunneum ARSEF 3297, Verticillium alfalfae VaMs.102, Gaeumannomyces graminis var. tritici R3-111a-1, Nectria haematococca mpVI 77-13-4, Verticillium longisporum, Verticillium dahliae VdLs.17, Torrubiella hemipterigena, Verticillium longisporum, Verticillium dahliae VdLs.17, Botrytis cinerea B05.10, Chaetomium globosum CBS 148.51, Metarhizium anisopliae, Stemphylium lycopersici, Sclerotinia borealis F-4157, Metarhizium robertsii ARSEF 23, Myceliophthora thermophila ATCC 42464, Phaeosphaeria nodorum SN15, Phialophora attae, Ustilaginoidea virens, Diplodia seriata, Ophiostoma piceae UAMH 11346, Pseudogymnoascus pannorum VKM F-4515 (FW-2607), Bipolaris oryzae ATCC 44560, Metarhizium guizhouense ARSEF 977, Chaetomium thermophilum var. thermophilum DSM 1495, Pestalotiopsis fici W106-1, Bipolaris zeicola 26-R-13, Setosphaeria turcica Et28A, Arthroderma otae CBS 113480 and Pyrenophora tritici-repentis Pt-1C-BFP.

[0098] Preferably the nuclease is an isolated nuclease.

**[0099]** Preferably the nuclease enzyme is present in the laundering aqueous liquor in an amount of from 0.01ppm to 1000 ppm of the nuclease enzyme, or from 0.05 or from 0.1ppm to 750 or 500ppm.

# <sup>25</sup> Acetylglucosaminidases.

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**[0100]** Preferably the composition comprises an acetylglucosaminidase enzyme, preferably a  $\beta$ -N-acetylglucosaminidase enzyme from E.C. 3.2.1.52, preferably an enzyme having at least 70%, or at least 75% or at least 80% or at least 85% or at least 90% or at least 95% or at least 95% or at least 95% or at least 95% or at least 97% or at least 99% or at least 910 or at least 910 or at least 95% or at least 95%

### Galactanase Enzyme

**[0101]** The compositions preferably additionally comprise an endo-beta-1,6-galactanase enzyme an extracellular polymer-degrading enzyme. The term "endo-beta-1,6-galactanase" or "a polypeptide having endo-beta-1,6-galactanase activity" means a endo-beta-1,6-galactanase activity (EC 3.2.1.164) that catalyzes the hydrolytic cleavage of 1,6-3-D-galactooligosaccharides with a degree of polymerization (DP) higher than 3, and their acidic derivatives with 4-O-meth-ylglucosyluronate or glucosyluronate groups at the non-reducing terminals.

**[0102]** For purposes of the present disclosure, endo-beta-1,6-galactanase activity is determined according to the procedure described in WO 2015185689 in Assay I. Suitable examples from class EC 3.2.1.164 are described in WO 2015185689, such as the mature polypeptide SEQ ID NO: 2 described therein. Preferably the galactanase enzyme is selected from Glycoside Hydrolase (GH) Family 30.

**[0103]** Preferably, the endo-beta-1,6-galactanase comprises a microbial enzyme. The endo-beta-1,6-galactanase may be fungal or bacterial in origin. Bacterial endo-beta-1,6-galactanase may be most preferred. Fungal endo-beta-1,6-galactanase may be most preferred.

**[0104]** A bacterial endo-beta-1,6-galactanase is obtainable from *Streptomyces*, for example *Streptomyces davawensis*. A preferred endo-beta-1,6-galactanase is obtainable from *Streptomyces davawensis* JCM 4913 defined in SEQ ID NO: 12 herein, or a variant thereof, for example having at least 40% or 50% or 60% or 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identity thereto.

[0105] Other bacterial endo-beta-1,6-galactanase include those encoded by the DNA sequences of *Streptomyces avermitilis* MA-4680 with the amino acid sequence SEQ ID NO: 13 herein, or a variant thereof, for example having at least 40% or 50% or 60% or 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identity thereto. [0106] A fungal endo-beta-1,6-galactanase is obtainable from *Trichoderma*, for example *Trichoderma harzianum*. A preferred endo-beta-1,6-galactanase is obtainable from *Trichoderma harzianum* defined in SEQ ID NO: 14 herein, or a variant thereof, for example having at least 40% or 50% or 60% or 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto.

**[0107]** Other fungal endo-beta-1,6-galactanases include those encoded by the DNA sequences of *Ceratocystis fimbriata* f. sp. Platani, *Muscodor strobelii* WG-2009a, *Oculimacula yallundae, Trichoderma viride* GD36A, *Thermomyces* 

stellatus, Myceliophthora thermophilia.

**[0108]** Preferably the galactanase has an amino acid sequence having at least 60%, or at least 80%, or at least 90% or at least 95% identity with the amino acid sequence shown in SEQ ID NO:12, SEQ ID NO:13 or SEQ ID NO:14. Preferably the galactanase is an isolated galactanase.

**[0109]** Preferably the galactanase enzyme is present in a laundering aqueous liquor in an amount of from 0.01ppm to 1000 ppm of the galactanase enzyme, or from 0.05 or from 0.1ppm to 750 or 500ppm.

**[0110]** The compositions of the invention comprising both mannanase and galactanase may be particularly effective against sticky soils and for improved cleaning. It is believed the two enzymes function together in a complementary way.

## Further Glycosyl Hydrolases

**[0111]** The composition may comprise a glycoside hydrolase selected from GH family 39 and GH family 114 and mixtures thereof, for example as described in co-pending applications having applicants reference numbers CM4645FM and CM4646 FM, respectively.

#### Proteases.

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**[0112]** Preferably the composition comprises one or more proteases. Suitable proteases include metalloproteases and serine proteases, including neutral or alkaline microbial serine proteases, such as subtilisins (EC 3.4.21.62). Suitable proteases include those of animal, vegetable or microbial origin. In one aspect, such suitable protease may be of microbial origin. The suitable proteases include chemically or genetically modified mutants of the aforementioned suitable proteases. In one aspect, the suitable protease may be a serine protease, such as an alkaline microbial protease or/and a trypsin-type protease. Examples of suitable neutral or alkaline proteases include:

- (a) subtilisins (EC 3.4.21.62), preferably those derived from *Bacillus sp.*, such as *B. lentus*, *B. alkalophilus*, *B. subtilis*, *B. amyloliquefaciens*, *B. pumilus* and *B. gibsonii* and *B. akibaii* described in WO2004067737, WO2015091989, WO2015091990, WO2015024739, WO2015143360, US 6,312,936 B1, US 5,679,630, US 4,760,025, US7,262,042 and WO09/021867, DE102006022216A1, DE102006022224A1, WO2015089447, WO2015089441, WO2016066756, WO2016066757, WO2016069557, WO2016069563, WO2016069569...
- (b) trypsin-type or chymotrypsin-type proteases, such as trypsin (e.g., of porcine or bovine origin), including the *Fusarium* protease described in WO 89/06270 and the chymotrypsin proteases derived from *Cellumonas* described in WO 05/052161 and WO 05/052146.
- (c) metalloproteases, preferably those derived from *Bacillus amyloliquefaciens* described in WO 07/044993A2; from *Bacillus, Brevibacillus, Thermoactinomyces, Geobacillus, Paenibacillus, Lysinibacillus* or *Streptomyces spp.* Described in WO2014194032, WO2014194054 and WO2014194117; from *Kribella alluminosa* described in WO2015193488; and from *Streptomyces* and *Lysobacter* described in WO2016075078.
- (d) protease having at least 90% identity to the subtilase from Bacillus sp. TY145, NCIMB 40339, described in WO92/17577 (Novozymes A/S), including the variants of this Bacillus sp TY145 subtilase described in WO2015024739, and WO2016066757.

[0113] Preferred proteases include those derived from Bacillus gibsonii or Bacillus Lentus.

[0114] Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzyme®, Kannase®, Liquanase®, Liquanase Ultra®, Savinase Ultra®, Ovozyme®, Neutrase®, Everlase® and Esperase® by Novozymes A/S (Denmark), those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Properase®, Purafect®, Purafect Prime®, Purafect Ox®, FN3®, FN4®, Excellase® and Purafect OXP® by Genencor International, those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes, those available from Henkel/ Kemira, namely BLAP (sequence shown in Figure 29 of US 5,352,604 with the following mutations S99D + S101 R + S103A + V104I + G159S, hereinafter referred to as BLAP), BLAP R (BLAP with S3T + V4I + V199M + V205I + L217D), BLAP X (BLAP with S3T + V4I + V205I) and BLAP F49 (BLAP with S3T + V4I + A194P + V199M + V205I + L217D) - all from Henkel/Kemira; and KAP (*Bacillus alkalophilus* subtilisin with mutations A230V + S256G + S259N) from Kao, or as disclosed in WO2009/149144, WO2009/149145, WO2010/56653, WO2010/566640, WO2011/072117, US2011/0237487, WO2011/140316, WO2012/151480, EP2510092, EP2566960 OR EP2705145.

# Amylases

**[0115]** Preferably the composition may comprise an amylase. Suitable alpha-amylases include those of bacterial or fungal origin. Chemically or genetically modified mutants (variants) are included. A preferred alkaline alpha-amylase is derived from a strain of Bacillus, such as Bacillus licheniformis, Bacillus amyloliquefaciens, Bacillus stearothermophilus,

Bacillus subtilis, or other Bacillus sp., such as Bacillus sp. NCIB 12289, NCIB 12512, NCIB 12513, DSM 9375 (USP 7,153,818) DSM 12368, DSMZ no. 12649, KSM AP1378 (WO 97/00324), KSM K36 or KSM K38 (EP 1,022,334). Preferred amylases include:

- (a) the variants described in WO 94/02597, WO 94/18314, WO96/23874 and WO 97/43424, especially the variants with substitutions in one or more of the following positions versus the enzyme listed as SEQ ID No. 2 in WO 96/23874: 15, 23, 105, 106, 124, 128, 133, 154, 156, 181, 188, 190, 197, 202, 208, 209, 243, 264, 304, 305, 391, 408, and 444. (b) the variants described in USP 5,856,164 and WO99/23211, WO 96/23873, WO00/60060 and WO 06/002643, especially the variants with one or more substitutions in the following positions versus the AA560 enzyme listed as SEQ ID No. 12 in WO 06/002643: 26, 30, 33, 82, 37, 106, 118, 128, 133, 149, 150, 160, 178, 182, 186, 193, 203, 214, 231, 256, 257, 258, 269, 270, 272, 283, 295, 296, 298, 299, 303, 304, 305, 311, 314, 315, 318, 319, 339, 345, 361, 378, 383, 419, 421, 437, 441, 444, 445, 446, 447, 450, 461, 471, 482, 484, preferably that also contain the deletions of D183\* and G184\*.
- (c) variants exhibiting at least 90% identity with SEQ ID No. 4 in WO06/002643, the wild-type enzyme from Bacillus SP722, especially variants with deletions in the 183 and 184 positions and variants described in WO 00/60060, which is incorporated herein by reference.
  - (d) variants exhibiting at least 95% identity with the wild-type enzyme from Bacillus sp.707 (SEQ ID NO:7 in US 6,093, 562), especially those comprising one or more of the following mutations M202, M208, S255, R172, and/or M261. Preferably said amylase comprises one or more of M202L, M202V, M202S, M202T, M202I, M202Q, M202W, S255N and/or R172Q. Particularly preferred are those comprising the M202L or M202T mutations.
  - (e) variants described in WO 09/149130, preferably those exhibiting at least 90% identity with SEQ ID NO: 1 or SEQ ID NO:2 in WO 09/149130, the wild-type enzyme from Geobacillus Stearophermophilus or a truncated version thereof:
  - (f) variants as described in EP2540825 and EP2357220, EP2534233; (g) variants as described in WO2009100102 and WO2010115028.

[0116] Suitable commercially available alpha-amylases include DURAMYL®, LIQUEZYME®, TERMAMYL®, TERMAMYL ULTRA®, NATALASE®, SUPRAMYL®, STAINZYME®, STAINZYME PLUS®, FUNGAMYL® and BAN® (Novozymes A/S, Bagsvaerd, Denmark), KEMZYM® AT 9000 Biozym Biotech Trading GmbH Wehlistrasse 27b A-1200 Wien Austria, RAPIDASE®, PURASTAR®, ENZYSIZE®, OPTISIZE HT PLUS®, POWERASE® and PURASTAR OXAM® (Genencor International Inc., Palo Alto, California) and KAM® (Kao, 14-10 Nihonbashi Kayabacho, 1-chome, Chuoku Tokyo 103-8210, Japan). In one aspect, suitable amylases include NATALASE®, STAINZYME® and STAINZYME PLUS® and mixtures thereof.

# 35 Lipases

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[0117] Preferably the composition comprises one or more lipases, including "first cycle lipases" such as those described in U.S. Patent 6,939,702 B1 and US PA 2009/0217464. Preferred lipases are first-wash lipases. In one embodiment of the invention the composition comprises a first wash lipase. First wash lipases includes a lipase which is a polypeptide having an amino acid sequence which: (a) has at least 90% identity with the wild-type lipase derived from Humicola lanuginosa strain DSM 4109; (b) compared to said wild-type lipase, comprises a substitution of an electrically neutral or negatively charged amino acid at the surface of the three-dimensional structure within 15A of E1 or Q249 with a positively charged amino acid; and (c) comprises a peptide addition at the C-terminal; and/or (d) comprises a peptide addition at the N-terminal and/or (e) meets the following limitations: i) comprises a negative amino acid in position E210 of said wild-type lipase; ii) comprises a negatively charged amino acid in the region corresponding to positions 90-101 of said wild-type lipase; and iii) comprises a neutral or negative amino acid at a position corresponding to N94 or said wild-type lipase and/or has a negative or neutral net electric charge in the region corresponding to positions 90-101 of said wild-type lipase. Preferred are variants of the wild-type lipase from Thermomyces lanuginosus comprising one or more of the T231R and N233R mutations. The wild-type sequence is the 269 amino acids (amino acids 23 - 291) of the Swissprot accession number Swiss-Prot 059952 (derived from Thermomyces lanuginosus (Humicola lanuginosa)). Preferred lipases include those sold under the tradenames Lipex® and Lipolex® and Lipolean®. Other suitable lipases include those described in European Patent Application No. 12001034.3 or EP2623586.

# Endoglucanases

**[0118]** Other preferred enzymes include microbial-derived endoglucanases exhibiting endo-beta-1,4-glucanase activity (E.C. 3.2.1.4), including a bacterial polypeptide endogenous to a member of the genus Bacillus which has a sequence of at least 90%, 94%, 97% and even 99% identity to the amino acid sequence SEQ ID NO:2 in US7,141,403B2)

and mixtures thereof. Suitable endoglucanases are sold under the tradenames Celluclean® and Whitezyme® (Novozymes A/S, Bagsvaerd, Denmark).

#### Pectate Lyases

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**[0119]** Other preferred enzymes include pectate lyases sold under the tradenames Pectawash®, Pectaway®, Xpect® and mannanases sold under the tradenames Mannaway® (all from Novozymes A/S, Bagsvaerd, Denmark), and Purabrite® (Genencor International Inc., Palo Alto, California).

# Cleaning Cellulase

**[0120]** The cleaning composition described herein may additionally comprise a cleaning cellulase. The cellulase may be an endoglucanase. The cellulase may have endo beta 1,4- glucanase activity and a structure which does not comprise a class A Carbohydrate Binding Module (CBM). A class A CBM is defined according to A. B. Boraston et al. Biochemical Journal 2004, Volume 382 (part 3) pages 769-781. In particular, the cellulase does not comprise a class A CBM from families 1, 2a, 3, 5 and 10.

[0121] The cellulase may be a glycosyl hydrolase having enzymatic activity towards amorphous cellulose substrates, wherein the glycosyl hydrolase is selected from GH families 5, 7, 12, 16, 44 or 74. Preferably, the cellulase is a glycosyl hydrolase selected from GH family 5. A preferred cellulase is Celluclean, supplied by Novozymes. This preferred cellulase is described in more detail in WO2002/099091. The glycosyl hydrolase (GH) family definition is described in more detail in Biochem J. 1991, v280, 309-316. Another preferred cellulase is a glycosyl hydrolase having enzymatic activity towards both xyloglucan and amorphous cellulose substrates, wherein the glycosyl hydrolase is selected from GH families 5, 12, 44 or 74. Preferably, the glycosyl hydrolase selected from GH family 44.

**[0122]** For purposes of the present invention, the degree of identity between two amino acid sequences is determined using the Needleman-Wunsch algorithm (Needleman and Wunsch, 1970, J. Mol. Biol. 48: 443-453) as implemented in the Needle program of the EMBOSS package (EMBOSS: The European Molecular Biology Open Software Suite, Rice et al, 2000, Trends in Genetics 16: 276-277), preferably version 3.0.0 or later. The optional parameters used are gap open penalty of 10, gap extension penalty of 0.5, and the EBLOSUM62 (EMBOSS version of BLOSUM62) substitution matrix. The output of Needle labeled "longest identity" (obtained using the -nobrief option) is used as the percent identity and is calculated as follows: (Identical Residues x 100)/(Length of Alignment - Total Number of Gaps in Alignment).

[0123] Suitable cleaning cellulase glycosyl hydrolases are selected from the group consisting of: GH family 44 glycosyl hydrolases from *Paenibacillus polyxyma* (wild-type) such as XYG1006 described in WO 01/062903 or are variants thereof; GH family 12 glycosyl hydrolases from *Bacillus licheniformis* (wild-type) such as Seq. No. ID: 1 described in WO 99/02663 or are variants thereof; GH family 5 glycosyl hydrolases from *Bacillus agaradhaerens* (wild type) or variants thereof; GH family 5 glycosyl hydrolases from *Bacillus* (wild type) such as XYG1034 and XYG 1022described in WO 01/064853 or variants thereof; GH family 74 glycosyl hydrolases from *Jonesia sp.* (wild type) such as XYG1020 described in WO 2002/077242 or variants thereof; and GH family 74 glycosyl hydrolases from *Trichoderma Reesei* (wild type), such as the enzyme described in more detail in Sequence ID no. 2 of WO03/089598, or variants thereof.

**[0124]** Preferred glycosyl hydrolases are selected from the group consisting of: GH family 44 glycosyl hydrolases from *Paenibacillus polyxyma* (wild-type) such as XYG1006 or are variants thereof.

**[0125]** Typically, the cellulase modifies the fabric surface during the laundering process so as to improve the removal of soils adhered to the fabric after the laundering process during wearing and usage of the fabric, in subsequent wash cycles. Preferably, the cellulase modifies the fabric surface during the laundering process so as to improve the removal of soils adhered to the fabric after the laundering process during wearing and usage of the fabric, in the subsequent two, or even three wash cycles.

**[0126]** Typically, the cellulase is used at a concentration of 0.005ppm to 1.0ppm in the aqueous liquor during the first laundering process. Preferably, the cellulase is used at a concentration of 0.02ppm to 0.5ppm in the aqueous liquor during the first laundering process.

## Surfactant system

**[0127]** The cleaning composition preferably comprises a surfactant system. The cleaning composition preferably comprises from about 1% to about 80%, or from 1% to about 60%, preferably from about 5% to about 50% more preferably from about 8% to about 40%, by weight of the cleaning composition, of a surfactant system.

[0128] Surfactants suitable for use in the surfactant system may be derived from natural and/or renewable sources.

[0129] The surfactant system may comprise an anionic surfactant, more preferably an anionic surfactant selected from the group consisting of, alkyl benzene sulfonate, alkyl sulfate, alkyl alkoxy sulfate, especially alkyl ethoxy sulfate, paraffin sulfonate and mixtures thereof, alkyl benzene sulfonates are particularly preferred. The surfactant system may

further comprise a surfactant selected from the group consisting of nonionic surfactant, cationic surfactant, amphoteric surfactant, zwitterionic surfactant, and mixtures thereof. The surfactant system preferably comprises a nonionic surfactant, for example an ethoxylated nonionic surfactant. The surfactant system may comprise an amphoteric surfactant, for example an amine oxide surfactant, such as an alkyl dimethyl amine oxide. The surfactant system may comprise a zwitterionic surfactant, such as a betaine.

**[0130]** The most preferred surfactant system for the detergent composition of the present invention comprises from 1% to 40%, preferably 6% to 35%, more preferably 8% to 30% weight of the total composition of an anionic surfactant, preferably comprising an alkyl benzene sulphonate. The preferred surfactant system may optionally in addition comprise an alkyl alkoxy sulfate surfactant, more preferably an alkyl ethoxy sulfate, optionally combined with 0.5% to 15%, preferably from 1% to 12%, more preferably from 2% to 10% by weight of the composition of amphoteric and/or zwitterionic surfactant, more preferably an amphoteric and even more preferably an amine oxide surfactant, especially an alkyl dimethyl amine oxide.

**[0131]** Preferably the composition further comprises a nonionic surfactant, especially an alcohol alkoxylate in particular an alcohol ethoxylate nonionic surfactant. Most preferably the surfactant system comprises an anionic and a nonionic surfactant, preferably the weight ratio of the anionic to nonionic surfactant is from 25:1 to 1:2.

### Anionic surfactant

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**[0132]** Anionic surfactants may be in salt form or acid form, typically in the form of a water-soluble sodium, potassium, ammonium, magnesium or mono-, di- or tri- C2-C3 alkanolammonium salt, with the sodium cation being the usual one chosen.

## Sulfonate Surfactant

[0133] Suitable anionic sulfonate surfactants for use herein include water-soluble salts of C8-C18 alkyl or hydroxyalkyl sulfonates; C11-C18 alkyl benzene sulfonates (LAS), modified alkylbenzene sulfonate (MLAS) as discussed in WO 99/05243, WO 99/05242, WO 99/05244, WO 99/05082, WO 99/05084, WO 99/05241, WO 99/07656, WO 00/23549, and WO 00/23548; methyl ester sulfonate (MES); and alpha-olefin sulfonate (AOS). Those also include the paraffin sulfonates may be monosulfonates and/or disulfonates, obtained by sulfonating paraffins of 10 to 20 carbon atoms. The sulfonate surfactant may also include the alkyl glyceryl sulfonate surfactants.

### Sulfated anionic surfactant

**[0134]** Preferably the sulfated anionic surfactant is alkoxylated, more preferably, an alkoxylated branched sulfated anionic surfactant having an alkoxylation degree of from about 0.2 to about 4, even more preferably from about 0.3 to about 3, even more preferably from about 0.4 to about 1.5 and especially from about 0.4 to about 1. Preferably, the alkoxy group is ethoxy. When the sulfated anionic surfactant is a mixture of sulfated anionic surfactants, the alkoxylation degree is the weight average alkoxylation degree of all the components of the mixture (weight average alkoxylation degree). In the weight average alkoxylation degree calculation the weight of sulfated anionic surfactant components not having alkoxylated groups should also be included.

Weight average alkoxylation degree = (x1 \* alkoxylation degree of surfactant 1 + x2 \* alkoxylation degree of surfactant 2 + ....) / <math>(x1 + x2 + ....)

wherein x1, x2, ... are the weights in grams of each sulfated anionic surfactant of the mixture and alkoxylation degree is the number of alkoxy groups in each sulfated anionic surfactant.

**[0135]** Preferably, the branching group is an alkyl. Typically, the alkyl is selected from methyl, ethyl, propyl, butyl, pentyl, cyclic alkyl groups and mixtures thereof. Single or multiple alkyl branches could be present on the main hydrocarbyl chain of the starting alcohol(s) used to produce the sulfated anionic surfactant used in the detergent of the invention. Most preferably the branched sulfated anionic surfactant is selected from alkyl sulfates, alkyl ethoxy sulfates, and mixtures thereof

**[0136]** The branched sulfated anionic surfactant can be a single anionic surfactant or a mixture of anionic surfactants. In the case of a single surfactant the percentage of branching refers to the weight percentage of the hydrocarbyl chains that are branched in the original alcohol from which the surfactant is derived.

**[0137]** In the case of a surfactant mixture the percentage of branching is the weight average and it is defined according to the following formula:

Weight average of branching (%)= [(x1 \* wt% branched alcohol 1 in alcohol 1 + x2 \* wt% branched alcohol 2 in alcohol 2 + ....) / <math>(x1 + x2 + ....)] \* 100

wherein x1, x2, ... are the weight in grams of each alcohol in the total alcohol mixture of the alcohols which were used as starting material for the anionic surfactant for the detergent of the invention. In the weight average branching degree calculation the weight of anionic surfactant components not having branched groups should also be included.

**[0138]** Suitable sulfate surfactants for use herein include water-soluble salts of C8-C18 alkyl or hydroxyalkyl, sulfate and/or ether sulfate. Suitable counterions include alkali metal cation or ammonium or substituted ammonium, but preferably sodium.

**[0139]** The sulfate surfactants may be selected from C8-C18 primary, branched chain and random alkyl sulfates (AS); C8-C18 secondary (2,3) alkyl sulfates; C8-C18 alkyl alkoxy sulfates (AExS) wherein preferably x is from 1-30 in which the alkoxy group could be selected from ethoxy, propoxy, butoxy or even higher alkoxy groups and mixtures thereof.

**[0140]** Alkyl sulfates and alkyl alkoxy sulfates are commercially available with a variety of chain lengths, ethoxylation and branching degrees. Commercially available sulfates include, those based on Neodol alcohols ex the Shell company, Lial - Isalchem and Safol ex the Sasol company, natural alcohols ex The Procter & Gamble Chemicals company.

**[0141]** Preferred alkyl sulfates are those in which the anionic surfactant is an alkyl ethoxy sulfate with a degree of ethoxylation of from about 0.2 to about 3, more preferably from about 0.3 to about 2, even more preferably from about 0.4 to about 1.5, and especially from about 0.4 to about 1. They are also preferred anionic surfactant having a level of branching of from about 5% to about 40%, even more preferably from about 10% to 35% and especially from about 20% to 30%.

### Nonionic surfactant

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**[0142]** Preferably the surfactant system comprises a nonionic surfactant, in an amount of from 0.1% to 40%, preferably 0.2% to 20%, most preferably 0.5% to 10% by weight of the composition. Suitable nonionic surfactants include the condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 10 to 18 carbon atoms, preferably from 10 to 15 carbon atoms with from 2 to 18 moles, preferably 2 to 15, more preferably 5-12 of ethylene oxide per mole of alcohol. Highly preferred nonionic surfactants are the condensation products of guerbet alcohols with from 2 to 18 moles, preferably 2 to 15, more preferably 5-12 of ethylene oxide per mole of alcohol.

**[0143]** Other suitable non-ionic surfactants for use herein include fatty alcohol polyglycol ethers, alkylpolyglucosides and fatty acid glucamides.

## Amphoteric surfactant

[0144] The surfactant system may include amphoteric surfactant, such as amine oxide. Preferred amine oxides are alkyl dimethyl amine oxide or alkyl amido propyl dimethyl amine oxide, more preferably alkyl dimethyl amine oxide and especially coco dimethyl amino oxide. Amine oxide may have a linear or mid-branched alkyl moiety. Typical linear amine oxides include water-soluble amine oxides containing one R1 C8-18 alkyl moiety and 2 R2 and R3 moieties selected from the group consisting of C1-3 alkyl groups and C1-3 hydroxyalkyl groups. Preferably amine oxide is characterized by the formula R1 - N(R2)(R3) O wherein R1 is a C8-18 alkyl and R2 and R3 are selected from the group consisting of methyl, ethyl, propyl, isopropyl, 2-hydroxethyl, 2-hydroxypropyl and 3-hydroxypropyl. The linear amine oxide surfactants in particular may include linear C10-C18 alkyl dimethyl amine oxides and linear C8-C12 alkoxy ethyl dihydroxy ethyl amine oxides. Preferred amine oxides include linear C10, linear C10-C12, and linear C12-C14 alkyl dimethyl amine oxides. As used herein "mid-branched" means that the amine oxide has one alkyl moiety having n1 carbon atoms with one alkyl branch on the alkyl moiety having n2 carbon atoms. The alkyl branch is located on the  $\alpha$  carbon from the nitrogen on the alkyl moiety. This type of branching for the amine oxide is also known in the art as an internal amine oxide. The total sum of n1 and n2 is from 10 to 24 carbon atoms, preferably from 12 to 20, and more preferably from 10 to 16. The number of carbon atoms for the one alkyl moiety (n1) should be approximately the same number of carbon atoms as the one alkyl branch (n2) such that the one alkyl moiety and the one alkyl branch are symmetric. As used herein "symmetric" means that | n1 - n2 | is less than or equal to 5, preferably 4, most preferably from 0 to 4 carbon atoms in at least 50 wt%, more preferably at least 75 wt% to 100 wt% of the mid-branched amine oxides for use herein. [0145] The amine oxide may further comprise two moieties, independently selected from a C1-3 alkyl, a C1-3 hydroxyalkyl group, or a polyethylene oxide group containing an average of from about 1 to about 3 ethylene oxide groups. Preferably the two moieties are selected from a C1-3 alkyl, more preferably both are selected as a C1 alkyl.

## Zwitterionic surfactant

[0146] Other suitable surfactants include betaines, such as alkyl betaines, alkylamidobetaine, amidazoliniumbetaine, sulfobetaine (INCI Sultaines) as well as the Phosphobetaine and preferably meets formula (I):

$$R^{1}$$
-[CO-X(CH<sub>2</sub>)<sub>n</sub>]<sub>x</sub>-N<sup>+</sup>(R<sup>2</sup>)(R<sub>3</sub>)<sub>m</sub>-(CH<sub>2</sub>)m-[CH(OH)-CH<sub>2</sub>]<sub>v</sub>-Y- (I)

wherein

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R<sup>1</sup> is a saturated or unsaturated C6-22 alkyl residue, preferably C8-18 alkyl residue, in particular a saturated C10-16 alkyl residue, for example a saturated C12-14 alkyl residue;

X is NH, NR<sup>4</sup> with C1-4 Alkyl residue R<sup>4</sup>, O or S,

n a number from 1 to 10, preferably 2 to 5, in particular 3,

x 0 or 1, preferably 1,

R<sup>2</sup>, R<sup>3</sup> are independently a C1-4 alkyl residue, potentially hydroxy substituted such as a hydroxyethyl, preferably a methyl.

m a number from 1 to 4, in particular 1, 2 or 3,

y 0 or 1 and

Y is COO, SO3, OPO(OR<sup>5</sup>)O or P(O)(OR<sup>5</sup>)O, whereby R<sup>5</sup> is a hydrogen atom H or a C1-4 alkyl residue.

**[0147]** Preferred betaines are the alkyl betaines of the formula (Ia), the alkyl amido propyl betaine of the formula (Ib), the Sulfo betaines of the formula (Ic) and the Amido sulfobetaine of the formula (Id);

$$R^{1}-N^{+}(CH_{3})_{2}-CH_{2}COO^{-}$$
 (Ia)

 $R^{1}$ -CO-NH(CH<sub>2</sub>)<sub>3</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>COO<sup>-</sup> (Ib)

 $R^{1}-N^{+}(CH_{3})_{2}-CH_{2}CH(OH)CH_{2}SO_{3}-$  (Ic)

 $R^{1}$ -CO-NH-(CH<sub>2</sub>)<sub>3</sub>-N+(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>CH(OH)CH<sub>2</sub>SO<sub>3</sub>- (Id)

in which R<sup>1</sup>1 as the same meaning as in formula I. Particularly preferred betaines are the Carbobetaine [wherein Y=COO-], in particular the Carbobetaine of the formula (Ia) and (Ib), more preferred are the Alkylamidobetaine of the formula (Ib).

[0148] Examples of suitable betaines and sulfobetaine are the following [designated in accordance with INCI]: Almondamidopropyl of betaines, Apricotam idopropyl betaines, Avocadamidopropyl of betaines, Babassuamidopropyl of betaines, Behenam idopropyl betaines, Behenyl of betaines, betaines, Canolam idopropyl betaines, Capryl/Capram idopropyl betaines, Carnitine, Cetyl of betaines, Cocamidoethyl of betaines, Cocam idopropyl betaines, Cocam idopropyl Hydroxysultaine, Coco betaines, Coco Hydroxysultaine, Coco/Oleam idopropyl betaines, Coco Sultaine, Decyl of betaines, Dihydroxyethyl Oleyl Glycinate, Dihydroxyethyl Soy Glycinate, Dihydroxyethyl Stearyl Glycinate, Dihydroxyethyl Tallow Glycinate, Dimethicone Propyl of PG-betaines, Erucam idopropyl Hydroxysultaine, Hydrogenated Tallow of betaines, Isostearam idopropyl betaines, Lauram idopropyl betaines, Lauryl of betaines, Myristam idopropyl betaines, Myristyl of betaines, Oleam idopropyl betaines, Oleam idopropyl betaines, Oleam idopropyl betaines, Palmam idopropyl betaines, Palm itam idopropyl betaines, Palmitoyl Carnitine, Palm Kernelam idopropyl betaines, Polytetrafluoroethylene Acetoxypropyl of betaines, Ricinoleam idopropyl betaines, Sesam idopropyl betaines, Soyam idopropyl betaines, Stearam idopropyl betaines, Tallow Dihydroxyethyl of betaines, Undecylenam idopropyl betaines and Wheat Germam idopropyl betaines. A preferred betaine is, for example, Cocoamidopropylbetaine.

Fatty Acid

**[0149]** Especially when in liquid form, preferably, the detergent composition comprises between 1.5% and 20%, more preferably between 2% and 15%, even more preferably between 3% and 10%, most preferably between 4% and 8% by weight of the liquid detergent composition of soap, preferably a fatty acid salt, more preferably an amine neutralized fatty acid salt, wherein preferably the amine is an alkanolamine more preferably selected from monoethanolamine, diethanolamine, triethanolamine or a mixture thereof, more preferably monoethanolamine.

#### Perfume

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**[0150]** Preferred compositions of the invention comprise perfume. Typically the composition comprises a perfume that comprises one or more perfume raw materials, selected from the group as described in WO08/87497. However, any perfume useful in a detergent may be used. A preferred method of incorporating perfume into the compositions of the invention is via an encapsulated perfume particle comprising either a water-soluble hydroxylic compound or melamine-formaldehyde or modified polyvinyl alcohol. In one aspect the encapsulate comprises (a) an at least partially water-soluble solid matrix comprising one or more water-soluble hydroxylic compounds, preferably starch; and (b) a perfume oil encapsulated by the solid matrix. In a further aspect the perfume may be pre-complexed with a polyamine, preferably a polyethylenimine so as to form a Schiff base.

### **Polymers**

[0151] The detergent composition may comprise one or more polymers for example for cleaning and/or care. Examples are optionally modified carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid co-polymers and carboxylate polymers. [0152] Suitable carboxylate polymers include maleate/acrylate random copolymer or polyacrylate homopolymer. The carboxylate polymer may be a polyacrylate homopolymer having a molecular weight of from 4,000 Da to 9,000 Da, or from 6,000 Da to 9,000 Da. Other suitable carboxylate polymers are co-polymers of maleic acid and acrylic acid, and may have a molecular weight in the range of from 4,000 Da to 90,000 Da.

**[0153]** Other suitable carboxylate polymers are co-polymers comprising: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; and (iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

# formula (I):

 $\begin{array}{c}
R_0 \\
H_2C = C \\
R \\
O \\
CH_2 \\
X \\
O = F
\end{array}$ 

wherein in formula (I), R<sub>0</sub> represents a hydrogen atom or CH<sub>3</sub> group, R represents a CH<sub>2</sub> group, CH<sub>2</sub>CH<sub>2</sub> group or single bond, X represents a number 0-5 provided X represents a number 1-5 when R is a single bond, and R<sub>1</sub> is a hydrogen atom or C1 to C20 organic group;

## formula (II)

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in formula (II),  $R_0$  represents a hydrogen atom or  $CH_3$  group, R represents a  $CH_2$  group,  $CH_2CH_2$  group or single bond,  $R_1$  is a hydrogen atom or  $R_2$  to  $R_3$  group.

**[0154]** The composition may comprise one or more amphiphilic cleaning polymers such as the compound having the following general structure:  $bis((C_2H_5O)(C_2H_4O)n)(CH_3)-N^+-C_xH_{2x}-N^+-(CH_3)-bis((C_2H_5O)(C_2H_4O)n)$ , wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof. In one aspect, this polymer is sulphated or sulphonated to provide a zwitterionic soil suspension polymer.

[0155] The composition preferably comprises amphiphilic alkoxylated grease cleaning polymers which have balanced hydrophilic and properties such that they remove grease particles from fabrics and surfaces. Preferred amphiphilic alkoxylated grease cleaning polymers comprise a core structure and a plurality of alkoxylate groups attached to that core structure. These may comprise alkoxylated polyalkylenimines, preferably having an inner polyethylene oxide block and an outer polypropylene oxide block. Typically these may be incorporated into the compositions of the invention in amounts of from 0.005 to 10 wt%, generally from 0.5 to 8 wt%.

**[0156]** Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(CH_2CH_2O)_m(CH_2)_nCH_3$  wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

[0157] The composition may comprise polyethylene glycol polymers and these may be particularly preferred in compositions comprising mixed surfactant systems. Suitable polyethylene glycol polymers include random graft co-polymers comprising: (i) hydrophilic backbone comprising polyethylene glycol; and (ii) side chain(s) selected from the group consisting of: C4-C25 alkyl group, polypropylene, polybutylene, vinyl ester of a saturated C1-C6 mono-carboxylic acid, C1-C6 alkyl ester of acrylic or methacrylic acid, and mixtures thereof. Suitable polyethylene glycol polymers have a polyethylene glycol backbone with random grafted polyvinyl acetate side chains. The average molecular weight of the polyethylene glycol backbone can be in the range of from 2,000 Da to 20,000 Da, or from 4,000 Da to 8,000 Da. The molecular weight ratio of the polyethylene glycol backbone to the polyvinyl acetate side chains can be in the range of from 1:1 to 1:5, or from 1:1.2 to 1:2. The average number of graft sites per ethylene oxide units can be in the range of from 0.5 to 0.9, or the average number of graft sites per ethylene oxide units can be in the range of from 0.1 to 0.5, or from 0.2 to 0.4. A suitable polyethylene glycol polymer is Sokalan HP22.

**[0158]** Typically these polymers when present are each incorporated into the compositions of the invention in amounts from 0.005 to 10 wt%, more usually from 0.05 to 8 wt%.

**[0159]** Preferably the composition comprises one or more carboxylate polymer, such as a maleate/acrylate random copolymer or polyacrylate homopolymer. In one aspect, the carboxylate polymer is a polyacrylate homopolymer having a molecular weight of from 4,000 Da to 9,000 Da, or from 6,000 Da to 9,000 Da. Typically these are incorporated into the compositions of the invention in amounts from 0.005 to 10 wt%, or from 0.05 to 8 wt%.

[0160] Preferably the composition comprises one or more soil release polymers.

**[0161]** Suitable soil release polymers are polyester soil release polymers such as Repel-o-tex polymers, including Repel-o-tex SF, SF-2 and SRP6 supplied by Rhodia. Other suitable soil release polymers include Texcare polymers, including Texcare SRA100, SRA300, SRN100, SRN170, SRN240, SRN260, SRN300 and SRN325 supplied by Clariant. Other suitable soil release polymers are Marloquest polymers, such as Marloquest SL supplied by Sasol.

**[0162]** Preferably the composition comprises one or more cellulosic polymer, including those selected from alkyl cellulose, alkyl alkoxyalkyl cellulose, carboxyalkyl cellulose, alkyl carboxyalkyl cellulose. Preferred cellulosic polymers are selected from the group comprising carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, methyl carboxymethyl cellulose, and mixures thereof. In one aspect, the carboxymethyl cellulose has a degree of carboxymethyl substitution from 0.5 to 0.9 and a molecular weight from 100,000 Da to 300,000 Da.

**[0163]** The composition preferably comprises a cationically-modified polysaccharide polymer. Preferably, the cationic polysaccharide polymer is selected from cationically modified hydroxyethyl cellulose, cationically modified hydroxypropyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, cationically modified hydroxyethyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, or a mixture thereof.

# Fabric Shading Dye

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**[0164]** The composition preferably comprises a fabric shading agent. Suitable fabric shading agents include dyes, dye-clay conjugates, and pigments. Suitable dyes include small molecule dyes and polymeric dyes. Suitable small molecule dyes include small molecule dyes selected from the group consisting of dyes falling into the Colour Index (C.I.)

classifications of Direct Blue, Direct Red, Direct Violet, Acid Blue, Acid Red, Acid Violet, Basic Blue, Basic Violet and Basic Red, or mixtures thereof. Preferered dyes include alkoxylated azothiophenes, Solvent Violet 13, Acid Violet 50 and Direct Violet 9. Particularly preferred dyes are polymeric dyes, particularly comprising polyalkoxy, most preferably polyethoxy groups, for example:

wherein the index values x and y are independently selected from 1 to 10.

# Dye Transfer Inhibitors

**[0165]** Suitable dye transfer inhibitors include polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone, polyvinyloxazolidone, polyvinylimidazole and mixtures thereof. Preferred are poly(vinyl pyrrolidone), poly(vinylpyridine betaine), poly(vinylpyridine N-oxide), poly(vinyl pyrrolidone-vinyl imidazole) and mixtures thereof. Suitable commercially available dye transfer inhibitors include PVP-K15 and K30 (Ashland), Sokalan® HP165, HP50, HP53, HP59, HP56K, HP56, HP66 (BASF), Chromabond® S-400, S403E and S-100 (Ashland).

### Chelant

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**[0166]** The composition may comprise chelant for example selected from phosphonic, sulphonic, succinic and acetic chelants or mixtures thereof. Suitable examples include HEDP, DTPA, EDTA, MGDA, GLDA, EDDS and 4,5-dihydroxy-1,3-benzenedisulfonic acids and salts thereof.

## Methods of Making the Composition

**[0167]** The present invention relates to methods of making the compositions described herein. The compositions of the invention may be solid (for example granules or tablets) or liquid form. Preferably the compositions are in liquid form. They may be made by any process chosen by the formulator, including by a batch process, a continuous loop process, or combinations thereof.

[0168] When in the form of a liquid, the compositions of the invention may be aqueous (typically above 2 wt% or even above 5 or 10 wt% total water, up to 90 or up to 80wt% or 70 wt% total water) or non-aqueous (typically below 2 wt% total water content). Typically the compositions of the invention will be in the form of an aqueous solution or uniform dispersion or suspension of optical brightener, DTI and optional additional adjunct materials, some of which may normally be in solid form, that have been combined with the normally liquid components of the composition, such as the liquid alcohol ethoxylate nonionic, the aqueous liquid carrier, and any other normally liquid optional ingredients. Such a solution, dispersion or suspension will be acceptably phase stable. When in the form of a liquid, the detergents of the invention preferably have viscosity from 1 to 1500 centipoises (1-1500 mPa\*s), more preferably from 100 to 1000 centipoises (100-1000 mPa\*s), and most preferably from 200 to 500 centipoises (200-500 mPa\*s) at 20s-1 and 21°C. Viscosity can be determined by conventional methods. Viscosity may be measured using an AR 550 rheometer from TA instruments using a plate steel spindle at 40 mm diameter and a gap size of 500 μm. The high shear viscosity at 20s-1 and low shear viscosity at 0.05-1 can be obtained from a logarithmic shear rate sweep from 0.1-1 to 25-1 in 3 minutes time at 21C. The preferred rheology described therein may be achieved using internal existing structuring with detergent ingredients or by employing an external rheology modifier. More preferably the detergents, such as detergent liquid compositions have a high shear rate viscosity of from about 100 centipoise to 1500 centipoise, more preferably from 100 to 1000 cps. Unit Dose detergents, such as detergent liquid compositions have high shear rate viscosity of from 400 to 1000cps. Detergents such as laundry softening compositions typically have high shear rate viscosity of from 10 to 1000, more preferably from 10 to 800 cps, most preferably from 10 to 500 cps. Hand dishwashing compositions have high shear rate viscosity of from 300 to 4000 cps, more preferably 300 to 1000 cps.

**[0169]** The cleaning and/or treatment compositions in the form of a liquid herein can be prepared by combining the components thereof in any convenient order and by mixing, e.g., agitating, the resulting component combination to form a phase stable liquid detergent composition. In a process for preparing such compositions, a liquid matrix is formed containing at least a major proportion, or even substantially all, of the liquid components, e.g., nonionic surfactant, the non-surface active liquid carriers and other optional liquid components, with the liquid components being thoroughly

admixed by imparting shear agitation to this liquid combination. For example, rapid stirring with a mechanical stirrer may usefully be employed. While shear agitation is maintained, substantially all of any anionic surfactants and the solid form ingredients can be added. Agitation of the mixture is continued, and if necessary, can be increased at this point to form a solution or a uniform dispersion of insoluble solid phase particulates within the liquid phase. After some or all of the solid-form materials have been added to this agitated mixture, particles of any enzyme material to be included, e.g., enzyme granulates, are incorporated. As a variation of the composition preparation procedure hereinbefore described, one or more of the solid components may be added to the agitated mixture as a solution or slurry of particles premixed with a minor portion of one or more of the liquid components. After addition of all of the composition components, agitation of the mixture is continued for a period of time sufficient to form compositions having the requisite viscosity and phase stability characteristics. Frequently this will involve agitation for a period of from about 30 to 60 minutes.

**[0170]** The adjunct ingredients in the compositions of this invention may be incorporated into the composition as the product of the synthesis generating such components, either with or without an intermediate purification step. Where there is no purification step, commonly the mixture used will comprise the desired component or mixtures thereof (and percentages given herein relate to the weight percent of the component itself unless otherwise specified) and in addition unreacted starting materials and impurities formed from side reactions and/or incomplete reaction. For example, for an ethoxylated or substituted component, the mixture will likely comprise different degrees of ethoxylation/substitution.

#### Method of Use

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**[0171]** The present invention relates to methods of using the cleaning compositions of the present invention to clean a surface, such as a textile. In general, the method includes mixing the cleaning composition as described herein with water to form an aqueous liquor and contacting a surface, preferably a textile, with the aqueous liquor in a laundering step. The target surface may include a greasy soil such as a body soil. The compositions herein, typically prepared as hereinbefore described, can be used to form aqueous washing/treatment solutions for use in the laundering/treatment of fabrics and/or hard surfaces. Generally, an effective amount of such a composition is added to water, for example in a conventional fabric automatic washing machine, to form such aqueous liquor laundering solutions. The aqueous liquor so formed is then contacted, typically under agitation, with the fabrics to be laundered/treated therewith. An effective amount of the cleaning composition herein added to water to form aqueous liquors for washing can comprise amounts sufficient to form from about 500 to 25,000 ppm, or from 500 to 15,000 ppm of composition in aqueous liquor, or from about 1,000 to 3,000 ppm of the cleaning compositions herein will be provided in aqueous liquor.

**[0172]** Typically, the aqueous liquor is formed by contacting the detergent with (wash) water in such an amount that the concentration of the cleaning composition in the aqueous liquor is from above 0.1 g/l to 5g/l, or from 1g/1, and to 4.5g/l, or to 4.0g/l, or to 3.5g/l, or to 3.0g/l, or to 2.5g/l, or even to 2.0g/l, or even to 1.5g/l. The method of laundering fabric or textile may be carried out in a top-loading or front-loading automatic washing machine, or can be used in a hand-wash laundry application. In these applications, the aqueous liquor formed and concentration of laundry detergent composition in the aqueous liquor is that of the main wash cycle. Any input of water during any optional rinsing step(s) is not included when determining the volume of the aqueous liquor.

[0173] The aqueous liquor may comprise 40 litres or less of water, or 30 litres or less, or 20 litres or less, or 10 litres or less, or 8 litres or less, or even 6 litres or less of water. The wash liquor may comprise from above 0 to 15 litres, or from 2 litres, and to 12 litres, or even to 8 litres of water. Typically from 0.01kg to 2kg of fabric per litre of aqueous liquor is dosed into said aqueous liquor. Typically from 0.01kg, or from 0.07kg, or from 0.10kg, or from 0.10kg, or from 0.10kg, or from 0.20kg, or from 0.25kg fabric per litre of aqueous liquor is dosed into said aqueous liquor. Optionally, 50g or less, or 45g or less, or 40g or less, or 35g or less, or 30g or less, or 25g or less, or 20g or less, or even 15g or less, or even 10g or less of the composition is contacted to water to form the aqueous liquor. Such compositions are typically employed at concentrations of from about 500 ppm to about 15,000 ppm in solution. When the wash solvent is water, the water temperature typically ranges from about 5 °C to about 90 °C and, when the situs comprises a fabric, the water to fabric ratio is typically from about 1:1 to about 30:1. Typically the aqueous liquor comprising the detergent of the invention has a pH of from 3 to 11.5.

**[0174]** In one aspect, such method comprises the steps of optionally washing and/or rinsing said surface or fabric, contacting said surface or fabric with any composition disclosed in this specification then optionally washing and/or rinsing said surface or fabric is disclosed, with an optional drying step.

[0175] Drying of such surfaces or fabrics may be accomplished by any one of the common means employed either in domestic or industrial settings: machine drying or open-air drying. The fabric may comprise any fabric capable of being laundered in normal consumer or institutional use conditions, and the invention is particularly suitable for synthetic textiles such as polyester and nylon and especially for treatment of mixed fabrics and/or fibres comprising synthetic and cellulosic fabrics and/or fibres. As examples of synthetic fabrics are polyester, nylon, these may be present in mixtures with cellulosic fibres, for example, polycotton fabrics. The solution typically has a pH of from 7 to 11, more usually 8 to 10.5. The compositions are typically employed at concentrations from 500 ppm to 5,000 ppm in solution. The water

temperatures typically range from about 5 °C to about 90 °C. The water to fabric ratio is typically from about 1:1 to about 30:1.

### Use of a Mannanase Enzyme

**[0176]** The present invention further relates to a use of a mannanase enzyme as defined above, to enhance the greasy-stain removal of an amine, such as an etheramine (e.g., a polyetheramine) as described herein.

#### Use of an Amine

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**[0177]** The present invention further relates to a use of an amine, such as an etheramine (e.g., a polyetheramine) to enhance the malodor-reducing benefits of a mannanase enzyme as defined herein.

#### **TEST METHODS**

Enzymatic activity towards xyloglucan substrates

**[0178]** An enzyme is deemed to have activity towards xyloglucan if the pure enzyme has a specific activity of greater than 50000 XyloU/g according to the following assay at pH 7.5.

[0179] The xyloglucanase activity is measured using AZCL-xyloglucan from Megazyme, Ireland as substrate (blue substrate).

**[0180]** A solution of 0.2% of the blue substrate is suspended in a 0.1M phosphate buffer pH 7.5, 20°C under stirring in a 1.5ml Eppendorf tubes (0.75ml to each), 50 microlitres enzyme solution is added and they are incubated in an Eppendorf Thermomixer for 20 minutes at 40°C, with a mixing of 1200 rpm. After incubation the coloured solution is separated from the solid by 4 minutes centrifugation at 14,000 rpm and the absorbance of the supernatant is measured at 600nm in a 1cm cuvette using a spectrophotometer. One XyloU unit is defined as the amount of enzyme resulting in an absorbance of 0.24 in a 1cm cuvette at 600nm.

**[0181]** Only absorbance values between 0.1 and 0.8 are used to calculate the XyloU activity. If an absorbance value is measured outside this range, optimization of the starting enzyme concentration should be carried out accordingly.

### Enzymatic activity towards amorphous cellulose substrates

**[0182]** An enzyme is deemed to have activity towards amorphous cellulose if the pure enzyme has a specific activity of greater than 20000 EBG/g according to the following assay at pH 7.5. Chemicals used as buffers and substrates were commercial products of at least reagent grade. Endoglucanase Activity Assay Materials:

- 0.1M phosphate buffer pH 7.5
- Cellazyme C tablets, supplied by Megazyme International, Ireland.
- Glass microfiber filters, GF/C, 9cm diameter, supplied by Whatman.

#### Method:

[0183] In test tubes, mix 1ml pH 7.5 buffer and 5ml deionised water.

**[0184]** Add 100 microliter of the enzyme sample (or of dilutions of the enzyme sample with known weight:weight dilution factor). Add 1 Cellazyme C tablet into each tube, cap the tubes and mix on a vortex mixer for 10 seconds. Place the tubes in a thermostated water bath, temperature 40°C. After 15,30 and 45 minutes, mix the contents of the tubes by inverting the tubes, and replace in the water bath. After 60 minutes, mix the contents of the tubes by inversion and then filter through a GF/C filter. Collect the filtrate in a clean tube.

**[0185]** Measure Absorbance (Aenz) at 590nm, with a spectrophotometer. A blank value, Awater, is determined by adding  $100\mu l$  water instead of 100 microliter enzyme dilution.

## Calculate Adelta = Aenz - Awater.

[0186] Adelta must be <0.5. If higher results are obtained, repeat with a different enzyme dilution factor. Determine DFO.1, where DFO.1 is the dilution factor needed to give Adelta = 0.1. Unit Definition: 1 Endo-Beta-Glucanase activity unit (1 EBG) is the amount of enzyme that gives Adelta = 0.10, under the assay conditions specified above. Thus, for example, if a given enzyme sample, after dilution by a dilution factor of 100, gives Adelta = 0.10, then the enzyme sample

has an activity of 100 EBG/g.

## **EXAMPLES**

<sup>5</sup> **[0187]** The following are illustrative examples of cleaning compositions according to the present invention and are not intended to be limiting.

Examples 1 to 18: Unit Dose Compositions.

10 [0188] These examples provide various formulations for unit dose laundry detergents and comprise double compartment unit dose products comprising one powder and one liquid compartment. The film used to encapsulate the compositions in PVA. Each example is prepared by combining a liquid compartment composition selected from compositions A-E with a powder compartment composition selected from compositions F-K.

Example	1	2	3	4	5	6
Liquid composition	20g A	25g A	20g A	15g A	20g B	20g B
Solid composition	15g F	12g G	12g H	12g I	15g J	15g K

Example	7	8	9	10	11	12
Liquid composition	15g B	17g B	20g C	19g C	15g C	25g C
Solid composition	15g L	14g F	15g G	18g H	15g I	12g J

Example	13	14	15	16	17	18
Liquid composition	20g D	18g D	22g D	32g E	32g E	27g E
Solid composition	20g K	13g L	15g F	17g G	12g H	18g I

Ingradianta	Α	В	С	D	E			
<u>Ingredients</u>	% weight of compartment							
LAS	19.09	16.76	8.59	6.56	3.44			
AE3S	1.91	0.74	0.18	0.46	0.07			
AE7	14.00	17.50	26.33	28.08	31.59			
Citric Acid	0.6	0.6	0.6	0.6	0.6			
C12-15 Fatty Acid	14.8	14.8	14.8	14.8	14.8			
Polymer 3	4.0	4.0	4.0	4.0	4.0			
Chelant 2	1.2	1.2	1.2	1.2	1.2			
Optical Brightener 1	0.20	0.25	0.01	0.01	0.50			
Optical Brightener 2	0.20	-	0.25	0.03	0.01			
Optical Brightener 3	0.18	0.09	0.30	0.01	-			
DTI 1	0.10	-	0.20	0.01	0.05			
DTI 2	-	0.10	0.20	0.25	0.05			
Glycerol	6.1	6.1	6.1	6.1	6.1			
Monoethanol amine	8.0	8.0	8.0	8.0	8.0			

(continued)

Ingradianta	Α	В	С	D	Е			
<u>Ingredients</u>	% weight of compartment							
Tri-isopropanol amine	-	-	2.0	-	-			
Tri-ethanol amine	-	2.0	-	-	-			
Cumene sulfonate	-	-	-	-	2.0			
Protease	0.80	0.60	0.07	1.00	1.50			
Galactanase	0.07	0.05	-	0.10	-			
Amylase 1	0.20	0.11	0.30	0.50	0.05			
Amylase 2	0.11	0.20	0.10	1	0.50			
Polishing enzyme	0.005	0.05	-	-	-			
Mannanase	0.005	0.05	0.005	0.010	0.005			
Dispersin B	0.010	0.05	0.005		-			
Cyclohexyl dimethanol	-	-	-	2.0	-			
Acid violet 50	0.03	0.02						
Violet DD			0.01	0.05	0.02			
Structurant	0.14	0.14	0.14	0.14	0.14			
Perfume	1.9	1.9	1.9	1.9	1.9			
Water, solvents and miscellaneous		ı	To 100%					
pH	7.5-8.2							

Ingradient	F	G	Н	ı	J	K		
Ingredient	% weight							
Sodium carbonate	20.0	35.0	30.0	29.0	28.0	18.0		
Carboxymethyl cellulose	2.0	1.0	-	-	2.5	0.6		
Sodium silicate 2R	5.0	-	5.0	3.2	20.0	-		
Tetraacetyl ethylenediamine	20.0	15.0	18.0	15.0	-	25.0		
Sodium percarbonate	50.0	44.0	45.0	45.0	29.0	50.0		
Polyetheramine	0.5	2	0.5	1	0.5	4		
Sulfate/ Water & Miscellaneous	Balance							

[0189] Based on total cleaning and/or treatment composition/compartment weight. Enzyme levels are reported as raw material.

# Examples 19 to 24

**[0190]** Granular laundry detergent compositions for hand washing or washing machines, typically top-loading washing machines.

Ingredient	19	20	21	22	23	24		
ingredient	% weight							
LAS	11.33	10.81	7.04	4.20	3.92	2.29		

(continued)

lu ava dia ut	19	20	21	22	23	24
Ingredient			% we	ight		
Quaternary ammonium	0.70	0.20	1.00	0.60	-	-
AE3S	0.51	0.49	0.32	-	0.08	0.10
AE7	8.36	11.50	12.54	11.20	16.00	21.51
Sodium Tripolyphosphate	5.0	-	4.0	9.0	2.0	-
Zeolite A	-	1.0	-	1.0	4.0	1.0
Sodium silicate 1.6R	7.0	5.0	2.0	3.0	3.0	5.0
Sodium carbonate	20.0	17.0	23.0	14.0	14.0	16.0
Polyacrylate MW 4500	1.0	0.6	1.0	1.0	1.5	1.0
Polymer 6	0.1	0.2	-	-	0.1	-
Carboxymethyl cellulose	1.0	0.3	1.0	1.0	1.0	1.0
Acid Violet 50	0.05	-	0.02	-	0.04	-
Violet DD	-	0.03	-	0.03	-	0.03
Protease 2	0.10	0.10	0.10	0.10	-	0.10
Amylase	0.03	-	0.03	0.03	0.03	0.03
Lipase	0.03	0.07	0.30	0.10	0.07	0.40
Polishing enzyme	0.002	-	0.05	-	0.02	-
Galactanase	0.001	0.0005	-	-	0.001	0.01
Mannanase	0.001	0.001	0.01	0.05	0.002	0.02
Dispersin B	0.001	0.001	0.05	-	0.001	-
Optical Brightener 1	0.200	0.001	0.300	0.650	0.050	0.001
Optical Brightener 2	0.060	-	0.650	0.180	0.200	0.060
Optical Brightener 3	0.100	0.060	0.050	-	0.030	0.300
Chelant 1	0.60	0.80	0.60	0.25	0.60	0.60
DTI 1	0.32	0.15	0.15	1	0.10	0.10
DTI 2	0.32	0.15	0.30	0.30	0.10	0.20
Sodium Percarbonate	4.6	5.2	5.0	5.7	4.5	7.3
Nonanoyloxybenzensulfonate	1.9	0.0	1.66	0.0	0.33	0.75
Tetraacetylethylenediamine	0.58	1.2	0.51	0.0	0.015	0.28
Photobleach	0.0030	0.0	0.0012	0.0030	0.0021	-
S-ACMC	0.1	0.0	0.0	0.0	0.06	0.0
Polyetheramine	0.5	2	0.5	1	0.5	4
Sulfate/Moisture			Bala	nce		1

# Examples 25-30

[0191] Granular laundry detergent compositions typically for front-loading automatic washing machines.

Ingredient	25	26	27	28	29	30
ingredient			% we	eight		
LAS	6.08	5.05	4.27	3.24	2.30	1.09
AE3S	-	0.90	0.21	0.18	-	0.06
AS	0.34	-	-	-	-	-
AE7	4.28	5.95	6.72	7.98	9.20	10.35
Quaternary ammonium	0.5	-	-	0.3	-	-
Crystalline layered silicate	4.1	-	4.8	-	-	-
Zeolite A	5.0	-	2.0	-	2.0	2.0
Citric acid	3.0	4.0	3.0	4.0	2.5	3.0
Sodium carbonate	11.0	17.0	12.0	15.0	18.0	18.0
Sodium silicate 2R	0.08	-	0.11	-	-	-
Optical Brightener 1	-	0.25	0.05	0.01	0.10	0.02
Optical Brightener 2	-	-	0.25	0.20	0.01	0.08
Optical Brightener 3	-	0.06	0.04	0.15	-	0.05
DTI 1	0.08	-	0.04	-	0.10	0.01
DTI 2	0.08	-	0.04	0.10	0.10	0.02
Soil release agent	0.75	0.72	0.71	0.72	-	-
Acrylic /maleic acid copolymer	1.1	3.7	1.0	3.7	2.6	3.8
Carboxymethyl cellulose	0.2	1.4	0.2	1.4	1.0	0.5
Protease 3	0.20	0.20	0.30	0.15	0.12	0.13
Amylase 3	0.20	0.15	0.20	0.30	0.15	0.15
Lipase	0.05	0.15	0.10	-	-	-
Amylase 2	0.03	0.07	-	-	0.05	0.05
Cellulase 2	-	-	-	-	0.10	0.10
Polishing enzyme	0.003	0.005	0.020	-	-	-
Galactanase	0.001	0.002	-	0.010	-	0.001
Mannanase	0.002	0.010	0.020	0.020	0.010	0.003
Dispersin B	0.002	0.010	0.020	0.020	-	0.002
Tetraacetylehtylenediamine	3.6	4.0	3.6	4.0	2.2	1.4
Sodium percabonate	13.0	13.2	13.0	13.2	16.0	14.0
Chelant 3	-	0.2	-	0.2	-	0.2
Chelant 2	0.2	-	0.2	-	0.2	0.2
MgSO <sub>4</sub>	-	0.42	-	0.42	-	0.4
Perfume	0.5	0.6	0.5	0.6	0.6	0.6
Suds suppressor agglomerate	0.05	0.10	0.05	0.10	0.06	0.05
Soap	0.45	0.45	0.45	0.45	-	-
Acid Violet 50	0.04	-	0.05	-	0.04	-
Violet DD	_	0.04	_	0.05	-	0.04

(continued)

Ingredient	25	26	27	28	29	30			
<u>ingredient</u>	% weight								
S-ACMC	0.01	0.01	-	0.01	-	1			
Direct Violet 9 (active)	-	-	0.0001	0.0001	-				
Polyetheramine	0.5	2	0.5	1	0.5	4			
Sulfate/ Water & Miscellaneous	Balance								

# Examples 31-37

[0192] Heavy Duty Liquid laundry detergent compositions.

In much discrete	1	2	3	4	5	6	7
<u>Ingredients</u>			(	% weight			
AE <sub>1.8</sub> S	6.77	5.16	1.36	1.30	-	-	-
AE <sub>3</sub> S	-	-	-	-	0.45	-	-
LAS	0.86	2.06	2.72	0.68	0.95	1.56	3.55
HSAS	1.85	2.63	1.02	-	-	-	-
AE9	6.32	9.85	10.20	7.92			
AE8							35.45
AE7					8.40	12.44	
C <sub>12-14</sub> dimethyl Amine Oxide	0.30	0.73	0.23	0.37	-	-	-
C <sub>12-18</sub> Fatty Acid	0.80	1.90	0.60	0.99	1.20	-	15.00
Citric Acid	2.50	3.96	1.88	1.98	0.90	2.50	0.60
Optical Brightener 1	1.00	0.80	0.10	0.30	0.05	0.50	0.001
Optical Brightener 3	0.001	0.05	0.01	0.20	0.50	-	1.00
Sodium formate	1.60	0.09	1.20	0.04	1.60	1.20	0.20
DTI 1	0.32	0.05	-	0.60	0.10	0.60	0.01
DTI 2	0.32	0.10	0.60	0.60	0.05	0.40	0.20
Sodium hydroxide	2.30	3.80	1.70	1.90	1.70	2.50	2.30
Monoethanolamine	1.40	1.49	1.00	0.70	-	-	-
Diethylene glycol	5.50	-	4.10	-	-	-	-
Chelant 1	0.15	0.15	0.11	0.07	0.50	0.11	0.80
4-formyl-phenylboronic acid	-		-	1	0.05	0.02	0.01
Sodium tetraborate	1.43	1.50	1.10	0.75	-	1.07	-
Ethanol	1.54	1.77	1.15	0.89	-	3.00	7.00
Polymer 1	0.10	-	-	-	-	-	2.00
Polymer 2	0.30	0.33	0.23	0.17	-	-	-
Polymer 3	-	-	-	-	-	-	0.80
Polymer 4	0.80	0.81	0.60	0.40	1.00	1.00	-
1,2-Propanediol	-	6.60	ı	3.30	0.50	2.00	8.00

(continued)

Ingradianta	1	2	3	4	5	6	7
<u>Ingredients</u>			(	% weight			
Structurant	0.10	-	-	-	-	-	0.10
Perfume	1.60	1.10	1.00	0.80	0.90	1.50	1.60
Perfume encapsulate	0.10	0.05	0.01	0.02	0.10	0.05	0.10
Protease	0.80	0.60	0.70	0.90	0.70	0.60	1.50
Galactanase	0.03	0.01	-	0.01	0.02	0.002	ı
Amylase 1	0.30	-	0.30	0.10	-	0.40	0.10
Amylase 2	-	0.20	0.10	0.15	0.07	-	0.10
Xyloglucannase	0.20	0.10	-	-	0.05	0.05	0.20
Lipase	0.40	0.20	0.30	0.10	0.20	_	-
Polishing enzyme	-	0.04	-	-	-	0.004	-
Mannanase of SEQ ID NO: 1	0.05	0.03	0.01	0.03	0.03	0.003	0.003
Dispersin B	-	-	-	0.05	0.03	0.001	0.001
Acid Violet 50	0.05	-	-	-	-	-	0.005
Direct Violet 9	-	-	-	-	-	0.05	-
Violet DD	-	0.035	0.02	0.037	0.04	_	-
Alkoxylated polyaryl/polyalkyl phenol	0.8	1.0	1.2	0.9	0.5	2.2	3.1
Water, dyes & minors				Balance			
рН				8.2			

[0193] Based on total cleaning and/or treatment composition weight. Enzyme levels are reported as raw material.

35	AE1.8S	is C <sub>12-15</sub> alkyl ethoxy (1.8) sulfate
•	AE3S	is C <sub>12-15</sub> alkyl ethoxy (3) sulfate

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AE7 is  $C_{12-15}$  alkyl ethoxy (3) suitate

AE7 is  $C_{12-13}$  alcohol ethoxylate, with an average degree of ethoxylation of 7

AE8 is  $C_{12-13}$  alcohol ethoxylate, with an average degree of ethoxylation of 8

AE9 is  $C_{12-13}$  alcohol ethoxylate, with an average degree of ethoxylation of 9

Amylase 1 is Stainzyme®, 15 mg active/g
Amylase 2 is Natalase®, 29 mg active/g
Amylase 3 is Stainzyme® Plus, 20 mg active/g,

AS is C<sub>12-14</sub> alkylsulfate

Cellulase 2 is Celluclean™, 15.6 mg active/g
Xyloglucanase is Whitezyme®, 20mg active/g
Chelant 1 is diethylene triamine pentaacetic acid
Chelant 2 is 1-hydroxyethane 1,1-diphosphonic acid

Chelant 3 is sodium salt of ethylenediamine-N,N'-disuccinic acid, (S,S) isomer (EDDS)

Dispersin B is a glycoside hydrolase, reported as 1000mg active/g

50 DTI 1 is poly(4-vinylpyridine-1-oxide) (such as Chromabond S-403E®),
DTI 2 is poly(1-vinylpyrrolidone-co-1-vinylimidazole) (such as Sokalan

HSAS HP56®). is mid-branched alkyl sulfate as disclosed in US 6,020,303 and US6,060,443 LAS is linear alkylbenzenesulfonate having an average aliphatic carbon chain length  $C_9$ - $C_{15}$  (HLAS

is acid form).

Galactanase is SEQ ID NO: 9, as active protein.

Mannanase is SEQ ID NO:1, as active protein

Lipase is Lipex®, 18 mg active/g
Mannanase is Mannaway®, 25 mg active/g

Optical Brightener 1 is disodium 4,4'-bis{[4-anilino-6-morpholino-s-triazin-2-yl]-amino}-2,2'-stilbenedisulfonate

Optical Brightener 2 is disodium 4,4'-bis-(2-sulfostyryl)biphenyl (sodium salt)

Optical Brightener 3 is Optiblanc SPL10® from 3V Sigma

Perfume encapsulate is a core-shell melamine formaldehyde perfume microcapsules

5 Photobleach is a sulfonated zinc phthalocyanine

Polishing enzyme is Para-nitrobenzyl esterase, reported as 1000mg active/g

Polyetheramine as described in present invention.

Polymer 1 is  $bis((C_2H_5O)(C_2H_4O)n)(CH_3)-N^+-C_xH_{2x}-N^+-(CH_3)-bis((C_2H_5O)(C_2H_4O)n)$ , wherein n=1

20-30,x = 3 to 8 or sulphated or sulfonated variants thereof

10 Polymer 2 is ethoxylated (EO<sub>15</sub>) tetraethylene pentamine

Polymer 3 is ethoxylated polyethylenimine
Polymer 4 is ethoxylated hexamethylene diamine
Polymer 5 is Acusol 305, provided by Rohm&Haas

Polymer 6 is a polyethylene glycol polymer grafted with vinyl acetate side chains, provided by BASF.

Protease is Purafect Prime®, 40.6 mg active/g
Protease 2 is Savinase®, 32.89 mg active/g
Protease 3 is Purafect®, 84 mg active/g

Quaternary ammonium  $\,$  is  $C_{12-14}$  Dimethylhydroxyethyl ammonium chloride

S-ACMC is Reactive Blue 19 Azo-CM-Cellulose provided by Megazyme

20 Soil release agent is Repel-o-tex® SF2, supplied by Solvay

Structurant is Hydrogenated Castor Oil

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Violet DD is a thiophene azo polymeric hueing dye provided by Milliken

[0194] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

# SEQUENCE LISTING

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25	Trp As	p Glu Asp 35	Ala Asp	Thr Val	l Ser Leu	Thr Phe	Thr Ser 45	Asp Ala						
30	Thr Ly	s Leu Tyr	Asp Val	Lys Ile 55	e Arg Tyr	Ser Gly 60	Pro Tyr	Gly Ser						
35	Lys Ty 65	r Thr Arg	Ile Ser 70	Tyr Ası	n Gly Ala	Thr Gly 75	Gly Asp	Ile Ser 80						
	Leu Pr	o Glu Thr	Thr Glu 85	Trp Ala	a Thr Val 90	Asn Ala	Gly Gln	Ala Leu 95						
40	Leu As	n Ala Gly 100		Thr Ile	Lys Leu 105	His Asn	Asn Trp	Gly Trp						
45	Tyr Le	u Ile Asp 115	Ala Val	Ile Let		Ser Val	Pro Arg 125	Pro Pro						
50	His Gl 13	n Val Thr O	Asp Ala	Leu Val	L Asn Thr	Asn Ser 140	Asn Ala	Val Thr						
	Lys Gl 145	n Leu Met	Lys Phe 150		l Ser Lys	Tyr His 155	Lys Ala	Tyr Ile 160						
55	Thr Gl	y Gln Gln	Glu Leu 165	His Ala	a His Gln 170	_	Glu Lys	Asn Val 175						

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5	Ser	Arg	Val 195	Glu	Phe	Gly	Thr	Thr 200	Ser	Gln	Ala	Val	Glu 205	Gln	Ala	Ile
10	Asp	Phe 210	Asp	Lys	Arg	Gly	Gly 215	Ile	Val	Thr	Phe	Ala 220	Trp	His	Trp	Asn
	Ala 225	Pro	Ser	Gly	Leu	Ile 230	Asn	Thr	Pro	Gly	Ser 235	Glu	Trp	Trp	Arg	Gly 240
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	Arg	Pro 290	Leu	His	Glu	Ala	Glu 295	Gly	Gly	Trp	Phe	Trp 300	Trp	Gly	Ala	Lys
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	Ala	Lys	Asp	Trp 340	Tyr		_	Asp	Glu 3 <b>4</b> 5	Ile	Val	Asp	Val	Leu 350	Ser	Phe
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45	Tyr	<b>A</b> sn 370	Ala	Leu	Val	Glu	Leu 375	Gly	Lys	Asp	Lys	<b>Lys</b> 380	Leu	Ile	Ala	Ala
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20		hr Pro 50	Ser	Ala	Thr	Thr 455	Thr	Ser	Ser	Thr	Thr 460	Thr	Pro	Ser	Ala
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	Ser Arg Val Glu Tyr	Gly Ala Val Gly Ser	Thr Val Pro Asp Ala Ile

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45	Gly Ala Cys Se 65	r Thr Asn 70	Thr Tyr Asn	Gly Ser Ser 75	Met Val Val Ser 80
50	Ser Ser Ile Ly	s Pro Ser 85	Arg Gln Val	Asp Gly Tyr 90	Trp Leu Asp Trp 95
	Ala Ser Thr As		Ser Ser Ser 105	Trp Asn Trp	Asn Val Asp Ala 110
55	Asn Gln Arg Al 115	a Met Leu	Gln Lys Ala 120	Lys Ala Asn	Gly Ala Asn Ile 125

	Phe	Glu 130	Leu	Phe	Ser	Asn	Ser 135	Pro	Met	Trp	Trp	Met 140	Cys	Leu	Asn	His
5	Asn 145	Pro	Ser	Gly	Ser	Gly 150	Ser	Ser	Asp	Asn	Leu 155	Gln	Ser	Trp	Asn	Tyr 160
10	Gln	Asn	His	Ala	Val 165	Tyr	Leu	Ala	Asn	Ile 170	Ala	Gln	His	Ala	Gln 175	Gln
45	Asn	Trp	Gly	Ile 180	Gln	Phe	Gln	Ser	Val 185	Glu	Ala	Phe	Asn	Glu 190	Pro	Ser
15	Ser	Gly	Trp 195	Gly	Pro	Thr	Gly	Thr 200	Gln	Glu	Gly	Cys	His 205	Phe	Ala	Val
20	Ser	Thr 210	Met	Ala	Thr	Val	Ile 215	Gly	Tyr	Leu	Asn	Thr 220	Glu	Leu	Ala	Gln
25	Arg 225	Gly	Leu	Ser	Ser	Phe 230	Ile	Ser	Ala	Ser	Asp 235	Glu	Thr	Ser	Tyr	Asp 240
	Leu	Ala	Ile	Ser	Thr 245	Trp	Gln	Gly	Leu	Gly 250	Ser	Ser	Ala	Gln	<b>As</b> n 255	Ala
30	Val	Lys	Arg	Val 260	Asn	Val	His	Gly	Tyr 265	Gln	Gly	Gly	Gly	Gly 270	Arg	Arg
35	Asp	Thr	Leu 275	Tyr	Ser	Leu	Val	Ser 280	Gln	Ala	Gly	Lys	Arg 285	Leu	Trp	Asn
40	Ser	Glu 290	Tyr	Gly	Asp	Ala				Gly	_	Ser 300	Met	Tyr	Thr	Asn
	<b>Leu</b> 305	Leu	Leu	Asp	Phe	Thr 310	Trp	Leu	His	Pro	Thr 315	Ala	Trp	Val	Tyr	Trp 320
45	Gln	Ala	Ile	Asp	Gly 325	Ser	Gly	Trp	Gly	Leu 330	Ile	Val	Gly	Asp	Asn 335	Asp
50	Gln	Leu	Thr	Leu 340	Ser	Ser	Ala	Ser	Thr 345	Lys	Tyr	Phe	Val	Leu 350	Ala	Gln
	Leu	Thr	<b>Arg</b> 355	His	Ile	Arg	Pro	Gly 360	Met	Gln	Ile	Leu	Thr 365	Thr	Pro	Asp
55	Gly	Asn 370	Thr	Val	Ala	Ala	Tyr 375	Asp	Ser	Gly	Ser	Gln 380	Lys	Leu	Val	Ile

Val Ala Ala Asn Trp Gly Ser Ala Gln Thr Ile Thr Phe Asp Leu Thr 385 390 395 400

Arg Ala Lys Thr Ala Gly Ser Asn Gly Ala Thr Val Pro Arg Trp Ser 405 410 415

Thr Gln Thr Ser Gly Gly Asp Gln Tyr Lys Ser Tyr Ser Asp Thr Lys
420 425 430

Ile Asn Asn Gly Lys Phe Ser Val Ser Phe Ser Thr Gly Gln Val Gln 435 440 445

Thr Phe Glu Ile Ser Gly Val Val Leu Lys 450 455

# Claims

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- 1. A cleaning composition comprising a mannanase enzyme comprising a polypeptide having mannan endo-1,4-beta-mannosidase activity (EC 3.2.1 .78) that catalyzes the hydrolysis of 1 ,4-3-D-mannosidic linkages in mannans, galactomannans and/or glucomannans; and an amine selected from the group consisting of etheramines, cyclic amines, polyamines, oligoamines, and combinations thereof.
- **2.** A cleaning composition according to claim 1 wherein the mannansase enzyme is a member of glycoside hydrolase family 26.
- 3. A cleaning composition comprising a mannanase enzyme having at least 60% sequence identity to SEQ ID NO:1, and/or having at least 81% sequence identity to SEQ ID NO: 2 and/or having at least 75% identity to SEQ ID NO: 3, and/or having at least 65% identity to SEQ ID NO: 4, and/or having at least 75% identity to SEQ ID NO: 5; and an amine selected from the group consisting of etheramines, cyclic amines, polyamines, oligoamines, and combinations thereof.
- **4.** A cleaning composition according to any preceding claim, wherein the composition further comprises a β-N-acetylglu-cosaminidase enzyme from E.C. 3.2.1.52, preferably an enzyme having at least 70% identity to SEQ ID NO:11.
- **5.** A cleaning composition according to any preceding claim, wherein the amine is selected from the group consisting of oligoamines, etheramines, cyclic amines, and combinations thereof, more preferably wherein the amine is an etheramine, more preferably wherein the etheramine is a polyetheramine.
- **6.** A cleaning composition according to claim 5, wherein the polyetheramine is selected from the group consisting of poly etheramines of Formula (I), Formula (II), and mixtures thereof:

$$Z_{1}-A_{1} + OA_{2} + OA_{3} + OA_{3$$

Formula (I)

$$\begin{array}{c} (A_{7}O) \xrightarrow{(x_{1}-1)+(y_{1}-1)+1} (A_{8}O) \xrightarrow{(x_{1}-1)+(y_{1}-1)+1} A_{9}-Z_{4} \\ R_{7} \xrightarrow{Z_{3}} O \xrightarrow{R_{12}} R_{11} \\ R_{8} \xrightarrow{R_{9}} R_{10}^{R_{11}} \end{array}$$

# Formula (II)

wherein each of  $R_1$ - $R_{12}$  is independently selected from H, alkyl, cycloalkyl, aryl, alkylaryl, or arylalkyl, wherein at least one of  $R_1$ - $R_6$  and at least one of  $R_7$ - $R_{12}$  is different from H, each of  $A_1$ - $A_9$  is independently selected from linear or branched alkylenes having about 2 to about 18 carbon atoms, each of  $Z_1$ - $Z_4$  is independently selected from OH or NH<sub>2</sub>, wherein at least one of  $Z_1$ - $Z_2$  and at least one of  $Z_3$ - $Z_4$  is NH<sub>2</sub>, wherein the sum of x+y is in the range of about 2 to about 200, wherein  $x_1 \ge 1$  and  $x_2 \ge 1$  and  $x_3 \ge 1$  and  $x_4 \ge 1$ ;

Formula (III)

# wherein

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R is selected from H or a C1-C6 alkyl group, each of  $k_1$ ,  $k_2$ , and  $k_3$  is independently selected from 0, 1, 2, 3, 4, 5, or 6, each of  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$ ,  $A_5$ , and  $A_6$  is independently selected from a linear or branched alkylene group having from about 2 to about 18 carbon atoms or mixtures thereof,  $x \ge 1$ ,  $y \ge 1$ , and  $z \ge 1$ , and the sum of  $z \ge 1$ , and the sum of  $z \ge 1$  is in the range of from about 3 to about 100, each of  $z \ge 1$ , and  $z \ge 1$ ,

- and the polyetheramine has a weight average molecular weight of from about 150 to about 1000 grams/mole.
- 7. A composition according to claim 6, wherein in said polyetheramine of Formula (I) or Formula (II), each of A<sub>1</sub>-A<sub>9</sub> is independently selected from ethylene, propylene, or butylene, preferably each of A<sub>1</sub>-A<sub>9</sub> is propylene.
- **8.** A composition according to claim 6 or claim 7, wherein in said polyetheramine of Formula (I) or Formula (II), each of R<sub>1</sub>, R<sub>2</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>11</sub>, and R<sub>12</sub> is H and each of R<sub>3</sub>, R<sub>4</sub>, R<sub>9</sub>, and R<sub>10</sub> is independently selected from a methyl group, an ethyl group, a propyl group, a butyl group, or a phenyl group.
- 9. A composition according to any of claims 6 to 8, wherein in said polyetheramine of Formula (I) or Formula (II), each of R<sub>3</sub> and R<sub>9</sub> is an ethyl group, each of R<sub>4</sub> and R<sub>10</sub> is a butyl group, and each of R<sub>1</sub>, R<sub>2</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>11</sub>, and R<sub>12</sub> is H.
  - 10. A composition according to claim 6, wherein the polyetheramine of Formula (I) has a structure according to Formula C:

# Formula C

 $\bigcap_{n} \bigcap_{n} \bigcap_{n$ 

wherein n+m is from about 0 to about 8, preferably about 0 to about 6.

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- 11. A composition according to claim 6, wherein in said polyetheramine of Formula (III), R is H or an alkyl group selected from methyl, ethyl, or propyl; each of k1, k2, and k3 is independently selected from 0, 1, or 2, preferably at least two of k1, k2, and k3 are 1; at least one of A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub>, A<sub>5</sub>, and A<sub>6</sub> is a linear or branched butylene group and the sum of x+y+z is in the range of from about 3 to about 30.
- **12.** A composition according to claim 9, wherein the polyetheramine of Formula (III) is selected from the group consisting of Formula D, Formula E, Formula F, and mixtures thereof:

# Formula D

$$H_2N$$
 $O$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 

wherein the average n is from about 0.5 to about 5;

# Formula E Formula F $H_2N \longrightarrow O \longrightarrow NH_2 \longrightarrow NH_2$ $H_2N \longrightarrow O \longrightarrow NH_2 \longrightarrow NH_2 \longrightarrow NH_2$

- **13.** A method of cleaning a surface, preferably a textile, comprising mixing the cleaning composition according to any preceding claim with water to form an aqueous liquor and contacting a surface, preferably a textile, with the aqueous liquor in a laundering step, optionally wherein prior to the laundering step, the surface comprises a greasy soil.
- 14. Use of a mannanase enzyme comprising a polypeptide having mannan endo-1,4-beta-mannosidase activity (EC 3.2.1 .78) that catalyzes the hydrolysis of 1 ,4-3-D-mannosidic linkages in mannans, galactomannans and/or glucomannans, and/or optionally having at least 60% sequence identity to SEQ ID NO:1 or having at least 81% sequence identity to SEQ ID NO: 2 and/or having at least 75% identity to SEQ ID NO: 3, and/or having at least 65% identity

to SEQ ID NO: 4, and/or having at least 75% identity to SEQ ID NO: 5; and an amine, such as an etheramine (e.g., a polyethermine), to enhance the stain-removal and/or malodor-reducing benefits preferably to enhance greasy-stain removal benefits.

5	<b>15.</b> Use according to claim 14 wherein the mannansase enzyme is a member of glycoside hydrolase family 26.
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Category

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