



- (51) International Patent Classification:  
*C11D 3/37* (2006.01) *C11D 1/02* (2006.01)
- (21) International Application Number:  
PCT/US2015/033866
- (22) International Filing Date:  
3 June 2015 (03.06.2015)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
62/008,530 6 June 2014 (06.06.2014) US
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- (81) Designated States (*unless otherwise indicated, for every  
kind of national protection available*): AE, AG, AL, AM,  
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,  
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,  
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,  
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,  
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,  
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,  
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,  
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,  
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (*unless otherwise indicated, for every  
kind of regional protection available*): ARIPO (BW, GH,  
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,  
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,  
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,  
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,  
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,  
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments (Rule 48.2(h))

(54) Title: DETERGENT COMPOSITION COMPRISING POLYALKYLENEIMINE POLYMERS

(57) Abstract: Detergent compositions comprising anionic surfactant and a carboxymethylated polyalkyleneimine, where the deter-  
gent compositions are substantially free of bleach. Methods of using such compositions, for example, to treat a surface.



## DETERGENT COMPOSITION COMPRISING POLYALKYLENEIMINE POLYMERS

## FIELD OF THE INVENTION

5           The present disclosure relates to detergent compositions, and more specifically, to detergent compositions comprising carboxymethylated polyalkyleneimines. The present disclosure also relates to methods of using the disclosed detergent compositions.

## BACKGROUND OF THE INVENTION

10           Today's consumers demand a broad spectrum of performance benefits from laundry detergents. Detergent formulators are therefore continuously seeking to provide multiple benefits, such as whitening and stain removal. Detergent ingredients that have multiple functions and/or can provide more than one benefit are especially preferred, as they give formulation flexibility and help to keep costs down.

15           Although bleaching agents are known to provide whitening and stain removal benefits, bleaching agents may present certain disadvantages in detergent compositions. For example, bleaching agents may be difficult to formulate into detergent, as they may be incompatible with other components of the detergent. Furthermore, certain bleaching agents, such as peroxide bleaches, may be unstable in detergent formulations, as metal ions present in the compositions or  
20           on the target fabric may contribute to decomposition of the bleaching agent.

          Chelating agents may be added to bleach-containing compositions to stabilize the bleach. It is believed that chelating agents bind to metal ions present in the detergent, in the wash liquor, or on the target fabric, resulting in a decreased rate of bleach decomposition. Known chelating agents include: phosphonate chelants, such as ethydrionic acid and hydroxy-ethane diphosphonic acid (HEDP); polyfunctionally-substituted aromatic chelants, such as 1,2-dihydroxy-3,5-  
25           disulfobenzene (TIRON®); succinate chelants, such as ethylenediamine N,N'-disuccinic acid (EDDS); amino carboxylate chelants, such as diethylene triamine pentaacetate (DTPA) and propylene diamine tetracetic acid (PDTA); polycarboxylic acids of pyridine, such as dipicolinic acid; and others, including malonic acid and hydroxy-pyridine-N-oxides, e.g., 2-hydroxy-  
30           pyridine-1-oxide.

          However, even when a bleaching agent is stabilized with the use of a chelating agent, formulation difficulties persist. Therefore, there is a need to produce a detergent composition – which is substantially free of bleach – that provides whitening and stain removal benefits, particularly on bleachable stains.

It has surprisingly been discovered that detergent compositions, which are substantially free of bleach, that comprise carboxymethylated polyethyleneimine compounds provide unexpected whiteness and stain removal benefits.

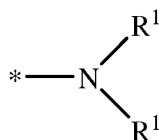
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## SUMMARY OF THE INVENTION

In some aspects, the present disclosure relates to a detergent composition comprising anionic surfactant and a carboxymethylated polyethyleneimine, where the detergent composition is substantially free of bleach, preferably substantially free of peroxide bleach.

In some aspects, the present disclosure relates to a detergent composition comprising:  
 10 anionic surfactant; and a carboxymethylated polyalkyleneimine; where the detergent composition is substantially free of bleach; and where the carboxymethylated polyalkyleneimine comprises moieties selected from the following:

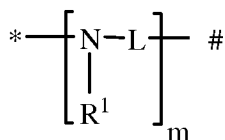
- (a) chain initiating groups A of Formula I:



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Formula I;

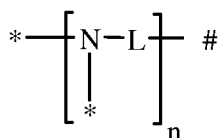
- (b) chain propagating groups Q of Formula II:



Formula II;

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- (c) chain branching groups Q' of Formula III:

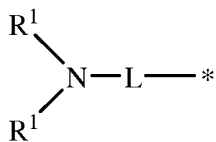


Formula III;

25

- (d) chain terminating groups T of Formula IV:

3



Formula IV;

and mixtures thereof, where each  $\text{R}^1$  is independently selected from H,  $\text{CH}_2\text{COOM}$ , or (poly) alkylene oxide of formula  $(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$ , where each M is independently selected from H or a suitable charge balancing counterion, and where x is independently from about 1 to about 20, and where the molar ratio of (H moieties +  $\text{CH}_2\text{COOM}$  moieties) : ((poly)alkylene oxide moieties) is greater than about 10:1, where each L is a linking group independently selected from a substituted or unsubstituted  $\text{C}_2$  or  $\text{C}_3$  alkylene group; where the asterisk (\*) represents a point of attachment to the L of any Q, Q' or T group; where the number sign (#) represents a point of attachment to the N of any A, Q, or Q' group; and where m and n are integers selected such that the weight average molecular weight of the carboxymethylated polyalkyleneimine is from about 1,500 to about 100,000.

#### DETAILED DESCRIPTION OF THE INVENTION

As used herein, the articles including “the”, “a” and “an” when used in a claim or in the specification, 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.

As used herein, the terms “fabric”, “textile”, and “cloth” are used non-specifically and may refer to any type of flexible material consisting of a network of natural or artificial fibers, including natural, artificial, and synthetic fibers, such as, but not limited to, cotton, linen, wool, polyester, nylon, silk, acrylic, and the like, including blends of various fabrics or fibers.

As used herein, the phrase “detergent composition” includes compositions and formulations designed for treating, including cleaning, textiles, fabric, and hard surfaces. Such compositions include but are not limited to, laundry cleaning compositions and laundry detergents, fabric softening compositions, fabric enhancing compositions, fabric freshening compositions, laundry pre-wash compositions, laundry pre-treat compositions, laundry additives, a fabric treatment composition, a dry cleaning composition, a laundry soak or spray treatment, a laundry rinse additive, a wash additive, a post-rinse fabric treatment, an ironing aid, a liquid hand dishwashing composition, an automatic dishwashing detergent, and a hard surface cleaner. A

detergent composition may be in the form of granules (e.g., powder), a liquid (including heavy duty liquid (“HDL”) detergents), a gel, a paste, a bar, a single-phase or a multi-phase unit dose composition, a detergent contained in a single-phase or multi-phase or multi-compartment water soluble pouch, a detergent contained on or in a porous substrate or nonwoven sheet, a flake formulation, a spray product, or a delayed delivery formulation. In the context of laundry, such compositions may be used as a pre-laundering treatment, a post-laundering treatment, or may be added during the rinse or wash cycle of the laundering operation. In some aspects, the composition is in a unit dose form, where the composition is encapsulated in a water-soluble film or pouch; in some aspects, the water-soluble film or pouch comprises polyvinyl alcohol, polyvinyl acetate, or mixtures thereof. Suitable films are described in more detail below. In some aspects, the unit dose form comprises at least two compartments, or at least three compartments. In some aspects, at least one compartment may be superimposed on another compartment.

“Substantially free” of a particular ingredient(s), as used herein, is to be understood to mean that specifically none, or alternatively no functionally useful amount, of the specific ingredient(s) is purposefully added to the composition. It is understood to one of ordinary skill in the art that trace amounts of various ingredient(s) may be present as impurities or contaminants.

5 Alternatively, “substantially free” can be taken to mean that the composition contains less than about 0.5%, alternatively less than about 0.1%, or alternatively less than about 0.01%, or even 0.0%, by weight of the composition of an indicated ingredient. It is understood to one of ordinary skill in the art that certain ingredients, whether purposefully added or present as impurities, may decompose over time or react with other ingredients so that the final product may  
10 contain minimal concentrations, including 0%, of such ingredients. For the avoidance of doubt, to determine whether a composition is “substantially free” of an ingredient, measurements of the ingredient’s percentage by weight may be taken, for example, immediately after the composition has been manufactured, when the composition is packaged and/or shipped for sale, when the composition is obtained by a consumer, or after the composition has been stored by the  
15 consumer.

#### Detergent Composition

The compositions of the present invention comprise surfactant and a carboxymethylated polyethyleneimine polymer, are substantially free of peroxide bleach, and may optionally contain  
20 hueing dye and/or other additional laundry adjuncts. These components are described in more detail below.

### Surfactant

The cleaning compositions comprise a surfactant system in an amount sufficient to provide desired cleaning properties. In some embodiments, the cleaning composition comprises, by weight of the composition, from about 1% to about 70% of a surfactant system. In other embodiments, the liquid cleaning composition comprises, by weight of the composition, from about 2% to about 60% of the surfactant system. In further embodiments, the cleaning composition comprises, by weight of the composition, from about 5% to about 30% of the surfactant system. In some aspects, the cleaning composition comprises, by weight of the composition, from about 20% to about 60%, or from about 30% to about 50% of the surfactant system. The surfactant system may comprise a deterative surfactant selected from anionic surfactants, nonionic surfactants, cationic surfactants, zwitterionic surfactants, amphoteric surfactants, ampholytic surfactants, and mixtures thereof. Those of ordinary skill in the art will understand that a deterative surfactant encompasses any surfactant or mixture of surfactants that provide cleaning, stain removing, or laundering benefit to soiled material.

### Anionic Surfactants

In some examples, the surfactant system of the cleaning composition may comprise from about 1% to about 70%, by weight of the surfactant system, of one or more anionic surfactants. In other examples, the surfactant system of the cleaning composition may comprise from about 2% to about 60%, by weight of the surfactant system, of one or more anionic surfactants. In further examples, the surfactant system of the cleaning composition may comprise from about 5% to about 30%, by weight of the surfactant system, of one or more anionic surfactants. In further examples, the surfactant system may consist essentially of, or even consist of one or more anionic surfactants.

Specific, non-limiting examples of suitable anionic surfactants include any conventional anionic surfactant. This may include a sulfate deterative surfactant, for e.g., alkoxyated and/or non-alkoxyated alkyl sulfate materials, and/or sulfonic deterative surfactants, e.g., alkyl benzene sulfonates.

Alkoxyated alkyl sulfate materials comprise ethoxyated alkyl sulfate surfactants, also known as alkyl ether sulfates or alkyl polyethoxylate sulfates. Examples of ethoxyated alkyl sulfates include water-soluble salts, particularly the alkali metal, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure

an alkyl group containing from about 8 to about 30 carbon atoms and a sulfonic acid and its salts. (Included in the term “alkyl” is the alkyl portion of acyl groups. In some examples, the alkyl group contains from about 15 carbon atoms to about 30 carbon atoms. In other examples, the alkyl ether sulfate surfactant may be a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of about 12 to 30 carbon atoms, and in some examples an average carbon chain length of about 25 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from about 1 mol to 4 mols of ethylene oxide, and in some examples an average (arithmetic mean) degree of ethoxylation of 1.8 mols of ethylene oxide. In further examples, the alkyl ether sulfate surfactant may have a carbon chain length between about 10 carbon atoms to about 18 carbon atoms, and a degree of ethoxylation of from about 1 to about 6 mols of ethylene oxide.

Non-ethoxylated alkyl sulfates may also be added to the disclosed cleaning compositions and used as an anionic surfactant component. Examples of non-alkoxylated, e.g., non-ethoxylated, alkyl sulfate surfactants include those produced by the sulfation of higher C<sub>8</sub>-C<sub>20</sub> fatty alcohols. In some examples, primary alkyl sulfate surfactants have the general formula: ROSO<sub>3</sub><sup>-</sup> M<sup>+</sup>, wherein R is typically a linear C<sub>8</sub>-C<sub>20</sub> hydrocarbyl group, which may be straight chain or branched chain, and M is a water-solubilizing cation. In some examples, R is a C<sub>10</sub>-C<sub>15</sub> alkyl, and M is an alkali metal. In other examples, R is a C<sub>12</sub>-C<sub>14</sub> alkyl and M is sodium.

Other useful anionic surfactants can include the alkali metal salts of alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain (linear) or branched chain configuration, e.g. those of the type described in U.S. Pat. Nos. 2,220,099 and 2,477,383. In some examples, the alkyl group is linear. Such linear alkylbenzene sulfonates are known as “LAS.” In other examples, the linear alkylbenzene sulfonate may have an average number of carbon atoms in the alkyl group of from about 11 to 14. In a specific example, the linear straight chain alkyl benzene sulfonates may have an average number of carbon atoms in the alkyl group of about 11.8 carbon atoms, which may be abbreviated as C<sub>11.8</sub> LAS. Such surfactants and their preparation are described for example in U.S. Pat. Nos. 2,220,099 and 2,477,383.

Other anionic surfactants useful herein are the water-soluble salts of: paraffin sulfonates and secondary alkane sulfonates containing from about 8 to about 24 (and in some examples about 12 to 18) carbon atoms; alkyl glyceryl ether sulfonates, especially those ethers of C<sub>8-18</sub> alcohols (e.g., those derived from tallow and coconut oil). Mixtures of the alkylbenzene

sulfonates with the above-described paraffin sulfonates, secondary alkane sulfonates and alkyl glyceryl ether sulfonates are also useful. Further suitable anionic surfactants useful herein may be found in U.S. Patent No. 4,285,841, Barrat et al., issued August 25, 1981, and in U.S. Patent No. 3,919,678, Laughlin, et al., issued December 30, 1975, both of which are herein incorporated by reference.

#### Nonionic surfactants

The surfactant system of the cleaning composition may comprise a nonionic surfactant. In some examples, the surfactant system comprises up to about 25%, by weight of the surfactant system, of one or more nonionic surfactants, e.g., as a co-surfactant. In some examples, the cleaning compositions comprises from about 0.1% to about 15%, by weight of the surfactant system, of one or more nonionic surfactants. In further examples, the cleaning compositions comprises from about 0.3% to about 10%, by weight of the surfactant system, of one or more nonionic surfactants.

Suitable nonionic surfactants useful herein can comprise any conventional nonionic surfactant. These can include, for e.g., alkoxyated fatty alcohols and amine oxide surfactants. In some examples, the cleaning compositions may contain an ethoxylated nonionic surfactant. These materials are described in U.S. Pat. No. 4,285,841, Barrat et al, issued Aug. 25, 1981. The nonionic surfactant may be selected from the ethoxylated alcohols and ethoxylated alkyl phenols of the formula  $R(OC_2H_4)_nOH$ , wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of  $n$  is from about 5 to about 15. These surfactants are more fully described in U.S. Pat. No. 4,284,532, Leikhim et al, issued Aug. 18, 1981. In one example, the nonionic surfactant is selected from ethoxylated alcohols having an average of about 24 carbon atoms in the alcohol and an average degree of ethoxylation of about 9 moles of ethylene oxide per mole of alcohol.

Other non-limiting examples of nonionic surfactants useful herein include:  $C_{12}$ - $C_{18}$  alkyl ethoxylates, such as, NEODOL<sup>®</sup> nonionic surfactants from Shell;  $C_6$ - $C_{12}$  alkyl phenol alkoxyates wherein the alkoxyate units are a mixture of ethyleneoxy and propyleneoxy units;  $C_{12}$ - $C_{18}$  alcohol and  $C_6$ - $C_{12}$  alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic<sup>®</sup> from BASF;  $C_{14}$ - $C_{22}$  mid-chain branched alcohols, BA, as discussed in US 6,150,322;  $C_{14}$ - $C_{22}$  mid-chain branched alkyl alkoxyates, BAE<sub>x</sub>, wherein  $x$  is from 1 to 30, as discussed in U.S. 6,153,577, U.S. 6,020,303 and U.S. 6,093,856; Alkylpolysaccharides as



discussed in U.S. 4,565,647 to Llenado, issued January 26, 1986; specifically alkylpolyglycosides as discussed in U.S. 4,483,780 and U.S. 4,483,779; Polyhydroxy fatty acid amides as discussed in U.S. 5,332,528, WO 92/06162, WO 93/19146, WO 93/19038, and WO 94/09099; and ether capped poly(oxyalkylated) alcohol surfactants as discussed in U.S. 6,482,994 and WO 01/42408.

#### Anionic/Nonionic Combinations

The surfactant system may comprise combinations of anionic and nonionic surfactant materials. In some examples, the weight ratio of anionic surfactant to nonionic surfactant is at least about 2:1. In other examples, the weight ratio of anionic surfactant to nonionic surfactant is at least about 5:1. In further examples, the weight ratio of anionic surfactant to nonionic surfactant is at least about 10:1.

#### Cationic Surfactants

The surfactant system may comprise a cationic surfactant. In some aspects, the surfactant system comprises from about 0% to about 7%, or from about 0.1% to about 5%, or from about 1% to about 4%, by weight of the surfactant system, of a cationic surfactant, e.g., as a co-surfactant. In some aspects, the cleaning compositions of the invention are substantially free of cationic surfactants and surfactants that become cationic below a pH of 7 or below a pH of 6.

Non-limiting examples of cationic include: the quaternary ammonium surfactants, which can have up to 26 carbon atoms include: alkoxyate quaternary ammonium (AQA) surfactants as discussed in US 6,136,769; dimethyl hydroxyethyl quaternary ammonium as discussed in 6,004,922; dimethyl hydroxyethyl lauryl ammonium chloride; polyamine cationic surfactants as discussed in WO 98/35002, WO 98/35003, WO 98/35004, WO 98/35005, and WO 98/35006; cationic ester surfactants as discussed in US Patents Nos. 4,228,042, 4,239,660 4,260,529 and US 6,022,844; and amino surfactants as discussed in US 6,221,825 and WO 00/47708, specifically amido propyldimethyl amine (APA).

#### Zwitterionic Surfactants

Examples of zwitterionic surfactants include: derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants; betaines, including alkyl dimethyl betaine and cocodimethyl amidopropyl betaine, C<sub>8</sub> to C<sub>18</sub> (for example from C<sub>12</sub> to C<sub>18</sub>) amine oxides (e.g., C<sub>12-14</sub> dimethyl amine oxide) and sulfo

and hydroxy betaines, such as N-alkyl-N,N-dimethylammino-1-propane sulfonate where the alkyl group can be C<sub>8</sub> to C<sub>18</sub> and in certain embodiments from C<sub>10</sub> to C<sub>14</sub>.

#### Ampholytic Surfactants

5           Specific, non-limiting examples of ampholytic surfactants include: aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents may contain at least about 8 carbon atoms, for example from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 at column 19, lines 18-35, for suitable  
10           examples of ampholytic surfactants.

#### Amphoteric Surfactants

          Examples of amphoteric surfactants include: aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the  
15           aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. Examples of compounds falling within this definition are sodium 3-(dodecylamino)propionate, sodium 3-(dodecylamino) propane-1-sulfonate, sodium 2-(dodecylamino)ethyl sulfate, sodium 2-  
20           (dimethylamino) octadecanoate, disodium 3-(N-carboxymethyldodecylamino)propane 1-sulfonate, disodium octadecyl-imminodiacetate, sodium 1-carboxymethyl-2-undecylimidazole, and sodium N,N-bis (2-hydroxyethyl)-2-sulfato-3-dodecoxypropylamine. See U.S. Pat. No. 3,929,678 to Laughlin et al., issued Dec. 30, 1975 at column 19, lines 18-35, for examples of amphoteric surfactants.

25           In one aspect, the surfactant system comprises an anionic surfactant and, as a co-surfactant, a nonionic surfactant, for example, a C<sub>12</sub>-C<sub>18</sub> alkyl ethoxylate. In another aspect, the surfactant system comprises C<sub>10</sub>-C<sub>15</sub> alkyl benzene sulfonates (LAS) and, as a co-surfactant, an anionic surfactant, e.g., C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates (AE<sub>x</sub>S), where x is from 1-30. In another aspect, the surfactant system comprises an anionic surfactant and, as a co-surfactant, a cationic  
30           surfactant, for example, dimethyl hydroxyethyl lauryl ammonium chloride.

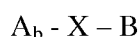
#### Branched Surfactants

          Suitable branched deterative surfactants include anionic branched surfactants selected from branched sulphate or branched sulphonate surfactants, e.g., branched alkyl sulphate,

branched alkyl alkoxyated sulphate, and branched alkyl benzene sulphonates, comprising one or more random alkyl branches, e.g., C<sub>1-4</sub> alkyl groups, typically methyl and/or ethyl groups.

In some aspects, the branched deterative surfactant is a mid-chain branched deterative surfactant, typically, a mid-chain branched anionic deterative surfactant, for example, a mid-chain branched alkyl sulphate and/or a mid-chain branched alkyl benzene sulphonate. In some aspects, the deterative surfactant is a mid-chain branched alkyl sulphate. In some aspects, the mid-chain branches are C<sub>1-4</sub> alkyl groups, typically methyl and/or ethyl groups.

In some aspects, the branched surfactant comprises a longer alkyl chain, mid-chain branched surfactant compound of the formula:



where:

(a) A<sub>b</sub> is a hydrophobic C<sub>9</sub> to C<sub>22</sub> (total carbons in the moiety), typically from about C<sub>12</sub> to about C<sub>18</sub>, mid-chain branched alkyl moiety having: (1) a longest linear carbon chain attached to the - X - B moiety in the range of from 8 to 21 carbon atoms; (2) one or more C<sub>1</sub> - C<sub>3</sub> alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 2 carbon (counting from carbon #1 which is attached to the - X - B moiety) to position ω - 2 carbon (the terminal carbon minus 2 carbons, i.e., the third carbon from the end of the longest linear carbon chain); and (4) the surfactant composition has an average total number of carbon atoms in the A<sub>b</sub>-X moiety in the above formula within the range of greater than 14.5 to about 17.5 (typically from about 15 to about 17);

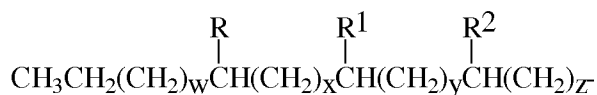
b) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene (such as polyoxyethylene and polyoxypropylene), alkoxyated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccaminates, polyalkoxyated carboxylates, glucamides, taurinates, sarcosinates, glycinate, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxyated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxyalkylated quats, alkylated/polyhydroxyated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids (it is to be noted that more than one hydrophobic moiety may be attached to B, for example as in (A<sub>b</sub>-X)<sub>z</sub>-B to give dimethyl quats); and

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(c) X is selected from -CH<sub>2</sub>- and -C(O)-.

Generally, in the above formula the A<sub>b</sub> moiety does not have any quaternary substituted carbon atoms (i.e., 4 carbon atoms directly attached to one carbon atom). Depending on which hydrophilic moiety (B) is selected, the resultant surfactant may be anionic, nonionic, cationic, zwitterionic, amphoteric, or ampholytic. In some aspects, B is sulfate and the resultant surfactant is anionic.

In some aspects, the branched surfactant comprises a longer alkyl chain, mid-chain branched surfactant compound of the above formula wherein the A<sub>b</sub> moiety is a branched primary alkyl moiety having the formula:



wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula (including the R, R<sup>1</sup>, and R<sup>2</sup> branching) is from 13 to 19; R, R<sup>1</sup>, and R<sup>2</sup> are each independently selected from hydrogen and C1-C3 alkyl (typically methyl), provided R, R<sup>1</sup>, and R<sup>2</sup> are not all hydrogen and, when z is 0, at least R or R<sup>1</sup> is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and w + x + y + z is from 7 to 13.

In certain aspects, the branched surfactant comprises a longer alkyl chain, mid-chain branched surfactant compound of the above formula wherein the A<sub>b</sub> moiety is a branched primary alkyl moiety having the formula selected from:



or mixtures thereof; wherein a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further

when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;

when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;

when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;

when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;

when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12;

12

when  $a + b = 15$ ,  $a$  is an integer from 2 to 14 and  $b$  is an integer from 1 to 13;

when  $a + b = 16$ ,  $a$  is an integer from 2 to 15 and  $b$  is an integer from 1 to 14;

when  $d + e = 8$ ,  $d$  is an integer from 2 to 7 and  $e$  is an integer from 1 to 6;

when  $d + e = 9$ ,  $d$  is an integer from 2 to 8 and  $e$  is an integer from 1 to 7;

5 when  $d + e = 10$ ,  $d$  is an integer from 2 to 9 and  $e$  is an integer from 1 to 8;

when  $d + e = 11$ ,  $d$  is an integer from 2 to 10 and  $e$  is an integer from 1 to 9;

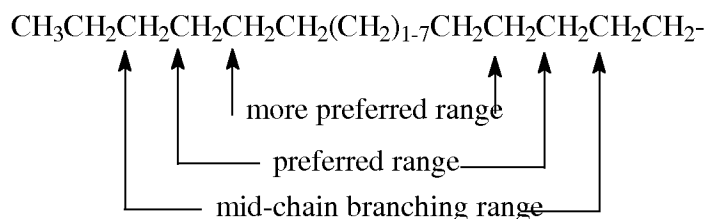
when  $d + e = 12$ ,  $d$  is an integer from 2 to 11 and  $e$  is an integer from 1 to 10;

when  $d + e = 13$ ,  $d$  is an integer from 2 to 12 and  $e$  is an integer from 1 to 11;

when  $d + e = 14$ ,  $d$  is an integer from 2 to 13 and  $e$  is an integer from 1 to 12.

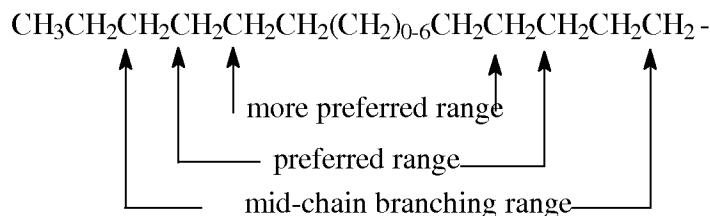
10 In the mid-chain branched surfactant compounds described above, certain points of branching (e.g., the location along the chain of the  $R$ ,  $R^1$ , and/or  $R^2$  moieties in the above formula) are preferred over other points of branching along the backbone of the surfactant. The formula below illustrates the mid-chain branching range (i.e., where points of branching occur), preferred mid-chain branching range, and more preferred mid-chain branching range for mono-

15 methyl branched alkyl  $A^b$  moieties.



For mono-methyl substituted surfactants, these ranges exclude the two terminal carbon atoms of the chain and the carbon atom immediately adjacent to the  $-X-B$  group.

20 The formula below illustrates the mid-chain branching range, preferred mid-chain branching range, and more preferred mid-chain branching range for di-methyl substituted alkyl  $A^b$  moieties.



Additional suitable branched surfactants are disclosed in US 6008181, US 6060443, US 6020303, US 6153577, US 6093856, US 6015781, US 6133222, US 6326348, US 6482789, US 6677289, US 6903059, US 6660711, US 6335312, and WO 9918929. Yet other suitable branched surfactants include those described in WO9738956, WO9738957, and WO0102451.

In some aspects, the branched anionic surfactant comprises a branched 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.

5 In some aspects, the branched anionic surfactant comprises a C12/13 alcohol-based surfactant comprising a methyl branch randomly distributed along the hydrophobe chain, e.g., Safol®, Marlipal® available from Sasol.

Further suitable branched anionic deterative surfactants include surfactants derived from alcohols branched in the 2-alkyl position, such as those sold under the trade names  
10 Isalchem®123, Isalchem®125, Isalchem®145, Isalchem®167, which are derived from the oxo process. Due to the oxo process, the branching is situated in the 2-alkyl position. These 2-alkyl branched alcohols are typically in the range of C11 to C14/C15 in length and comprise structural isomers that are all branched in the 2-alkyl position. These branched alcohols and surfactants are described in US20110033413.

15 Other suitable branched surfactants include those disclosed in US6037313 (P&G), WO9521233 (P&G), US3480556 (Atlantic Richfield), US6683224 (Cognis), US20030225304A1 (Kao), US2004236158A1 (R&H), US6818700 (Atofina), US2004154640 (Smith et al), EP1280746 (Shell), EP1025839 (L'Oreal), US6765119 (BASF), EP1080084 (Dow), US6723867 (Cognis), EP1401792A1 (Shell), EP1401797A2 (Degussa AG), US2004048766 (Raths et al),  
20 US6596675 (L'Oreal), EP1136471 (Kao), EP961765 (Albemarle), US6580009 (BASF), US2003105352 (Dado et al), US6573345 (Cryovac), DE10155520 (BASF), US6534691 (du Pont), US6407279 (ExxonMobil), US5831134 (Peroxid-Chemie), US5811617 (Amoco), US5463143 (Shell), US5304675 (Mobil), US5227544 (BASF), US5446213A (MITSUBISHI KASEI CORPORATION), EP1230200A2 (BASF), EP1159237B1 (BASF),  
25 US20040006250A1 (NONE), EP1230200B1 (BASF), WO2004014826A1 (SHELL), US6703535B2 (CHEVRON), EP1140741B1 (BASF), WO2003095402A1 (OXENO), US6765106B2 (SHELL), US20040167355A1 (NONE), US6700027B1 (CHEVRON), US20040242946A1 (NONE), WO2005037751A2 (SHELL), WO2005037752A1 (SHELL), US6906230B1 (BASF), WO2005037747A2 (SHELL) OIL COMPANY.

30 Additional suitable branched anionic deterative surfactants include surfactant derivatives of isoprenoid-based polybranched detergent alcohols, as described in US 2010/0137649.

Isoprenoid-based surfactants and isoprenoid derivatives are also described in the book entitled “Comprehensive Natural Products Chemistry: Isoprenoids Including Carotenoids and Steroids (Vol. two)”, Barton and Nakanishi, © 1999, Elsevier Science Ltd and are included in the structure E, and are hereby incorporated by reference.

5 Further suitable branched anionic deterative surfactants include those derived from anteiso and iso-alcohols. Such surfactants are disclosed in WO2012009525.

Additional suitable branched anionic deterative surfactants include those described in US Patent Application Nos. 2011/0171155A1 and 2011/0166370A1.

Suitable branched anionic surfactants also include Guerbet-alcohol-based surfactants.

10 Guerbet alcohols are branched, primary monofunctional alcohols that have two linear carbon chains with the branch point always at the second carbon position. Guerbet alcohols are chemically described as 2-alkyl-1-alkanols. Guerbet alcohols generally have from 12 carbon atoms to 36 carbon atoms. The Guerbet alcohols may be represented by the following formula: (R1)(R2)CHCH<sub>2</sub>OH, where R1 is a linear alkyl group, R2 is a linear alkyl group, the sum of the  
15 carbon atoms in R1 and R2 is 10 to 34, and both R1 and R2 are present. Guerbet alcohols are commercially available from Sasol as Isofol® alcohols and from Cognis as Guerbetol.

The surfactant system disclosed herein may comprise any of the branched surfactants described above individually or the surfactant system may comprise a mixture of the branched surfactants described above. Furthermore, each of the branched surfactants described above may include a bio-based content.

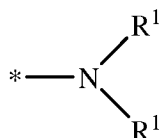
20 In some aspects, the branched surfactant has a bio-based content of at least about 50%, at least about 60%, at least about 70%, at least about 80%, at least about 90%, at least about 95%, at least about 97%, or about 100%.

#### Carboxymethylated Polyalkyleneimine

25 The compositions of the present invention comprise carboxymethylated polyalkyleneimines, sometimes also referred to as carboxymethylated polyalkyleneamines, described further below. The carboxymethylated polyalkyleneimine may be water soluble or water dispersible.

In some aspects, the carboxymethylated polyalkyleneimine comprises moieties selected  
30 from the following:

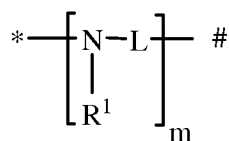
(a) chain initiating groups A of Formula I:



15

Formula I;

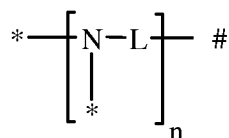
(b) chain propagating groups Q of Formula II:



5

Formula II;

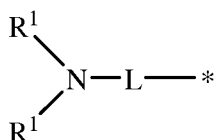
(c) chain branching groups Q' of Formula III:



Formula III;

10

(d) chain terminating groups T of Formula IV:



Formula IV;

15

or mixtures thereof, where each  $\text{R}^1$  is independently selected from H,  $\text{CH}_2\text{COOM}$  (where each M is independently selected from H or a suitable charge balancing counterion), or (poly) alkylene oxide of formula  $(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$ , , and where x is independently from about 1 to about 20, or from about 1 to about 10, or from about 1 to about 4, and where the molar ratio of (H moieties +  $\text{CH}_2\text{COOM}$  moieties) : ((poly)alkylene oxide moieties) is greater than about 10:1, or greater than about 20:1; where each L is a linking group independently selected from a substituted or unsubstituted alkylene group, typically from a substituted or unsubstituted  $\text{C}_2$  or  $\text{C}_3$  alkylene group, or from a substituted or unsubstituted  $\text{C}_2$  alkylene group, or from an unsubstituted  $\text{C}_2$  alkylene group; where the asterisk (\*) represents a point of attachment to the L of any Q, Q' or T group; where the number sign (#) represents a point of attachment to the N of any A, Q, or Q' group; and where m and n are integers selected such that the weight average molecular weight of the carboxymethylated polyalkyleneimine is from about 1,500 to about 100,000 daltons.

25



Typically, at least one  $R^1$  is  $CH_2COOM$ . In some aspects,  $R^1$  is independently selected from H or  $CH_2COOM$ . The carboxymethylated polyalkyleneimine may be substantially free of (poly)alkylene oxide moieties, or of ethoxylation and/or of propoxylation groups. Substituted L groups may independently comprise  $C_1$ - $C_4$  alkyls, typically  $C_1$ - $C_4$  linear alkyls.

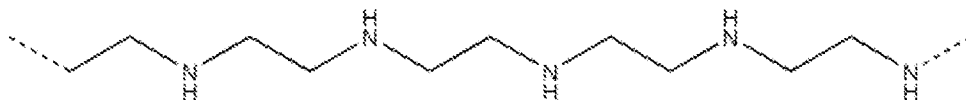
5        Suitable charge balancing counterions that may be selected for M include alkali metal ions, alkali earth metal ions, ammonium ions, or mixtures thereof. Suitable charge balancing counter ions include  $Na^+$ ,  $Li^+$ ,  $K^+$ ,  $\frac{1}{2} Mg^{2+}$ ,  $\frac{1}{2} Ca^{2+}$ , ammonium, substituted ammonium, such as  $C_1$ - $C_6$  alkanolammonium, mono-ethanolamine (MEA), tri-ethanolamine (TEA), di-ethanolamine (DEA), or any mixture thereof. In some aspects, in solution, the charge balancing  
10        counterion may be dissociated from the methylcarboxy ( $CH_2COO^-$ ) group.

In some aspects,  $m + n \geq 1$ . Typically, m and n are both equal to or greater than 1.

The carboxymethylated polyalkyleneimine compounds of the present invention may have a weight average molecular weight of from about 1500 to about 100,000, or from 5000 to about 75,000, or from about 20,000 to about 60,000, or of from about 40,000 to about 55,000 daltons.

15        In some aspects, the indices m and n, as described above, are integers selected such that the weight average molecular weight of the carboxymethylated polyalkyleneimine falls within any of the disclosed molecular weight ranges.

The carboxymethylated polyalkyleneimine compounds comprise a polyalkyleneimine backbone. The backbone may be linear (*e.g.*, the polyalkyleneimine comprises Q groups but no Q' groups) or branched (*e.g.*, the polyalkyleneimine comprises at least one Q' group). In some  
20        aspects, the ratio of m : n (where m and n are defined above) is from about 95 : 5 to about 5 : 95, or from about 80 : 20 to about 20 : 80, or from about 70 : 30 to about 30 : 70, or from about 70 : 30 to about 50 : 50, or from about 60 : 40 to about 50 : 50. In some aspects, the polyalkyleneimine backbone is a polyethyleneimine (PEI) backbone, preferably a branched PEI  
25        backbone. Suitable polyalkyleneimine backbones may, for example, be polyethyleneimines of the following general structure:



The above structure is unsubstituted, and it is recognized that each of the H groups shown above independently represents a possible point of branching, carboxymethylation, or other  
30        substitution. Furthermore, in some aspects, each of the H groups shown above may be substituted with a suitable charge-balancing cation, including  $Na^+$ ,  $Li^+$ ,  $K^+$ ,  $\frac{1}{2} Mg^{2+}$ ,  $\frac{1}{2} Ca^{2+}$ , substituted ammonium, such as  $C_1$ - $C_6$  alkanolammonium, mono-ethanolamine (MEA), tri-

ethanolamine (TEA), di-ethanolamine (DEA), or any mixture thereof. In some aspects, in solution, the cation may be dissociated from the polyamine.

The polyalkyleneimine compounds may be described by a degree of substitution, which may be represented by a percentage. For example, carboxymethylated PEIs having a degree of substitution of about 70% means that about 70% of the hydrogens of the primary or secondary amines of the parent PEI have been substituted with carboxymethyl groups. In some aspects, the polyalkyleneimine compounds of the present invention have degrees of substitution ranging from about 30% to about 99%, or from about 50% to about 98%, or from about 60% to about 98%, or from about 60% to about 85%, or from about 85% to about 95%. In some aspects, when the weight average molecular weight of the polyalkyleneimine backbone is relatively low (for example, from about 500 to about 10,000), the degree of substitution may be relatively high (for example, from about 85% to about 98%).

The degree of substitution may also be represented by the ratio of N-CH<sub>2</sub>COOM groups to N-H groups. In some aspects, when the polyalkyleneimine comprises R<sup>1</sup> groups, the degree of substitution may be represented as the ratio of the number of R<sup>1</sup> groups that are CH<sub>2</sub>COOM compared to the number of R<sup>1</sup> groups that are H. In some aspects, the degree of substitution, when described as a ratio, may be from about 30:70 to about 99:1, or from about 50:50 to about 98:2, or from about 60:40 to about 98:2, or from about 60:40 to about 85:15, or from about 70:30 to about 90:10, or from about 85:15 to about 98:2.

A polyalkyleneimine compound may be described by the molecular weight of its unsubstituted backbone. For example, a polyalkyleneimine with a polyethyleneimine (PEI) backbone of weight average molecular weight 25,000 daltons may be described as PEI 25,000. Polyalkyleneimines of the present disclosure may have a backbone with a weight average molecular weight of from about 500 to about 50,000, or from about 500 to about 30,000, or from about 500 to about 25,000, or from about 5,000 to about 25,000, or from about 20,000 to about 25,000 Daltons.

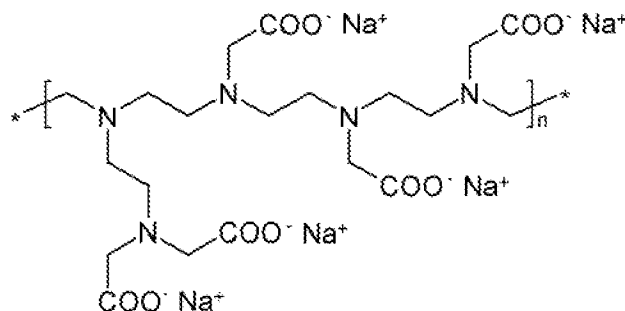
A polyalkyleneimine compound may also be described by its own molecular weight. Polyalkyleneimine compounds of the present disclosure may have weight average molecular weights of from about 1000 to about 100,000 daltons, or from about 5000 to about 75,000 daltons, or from about 25,000 to about 50,000 daltons.

In some aspects, the composition comprises a carboxymethylated polyalkyleneimine characterized by a degree of substitution of from about 30% to about 75%, or from about 50% to about 70%, or from about 55% to about 65%, and, optionally, a weight average molecular weight of from about 25,000 daltons to about 75,000 daltons. Compositions comprising such

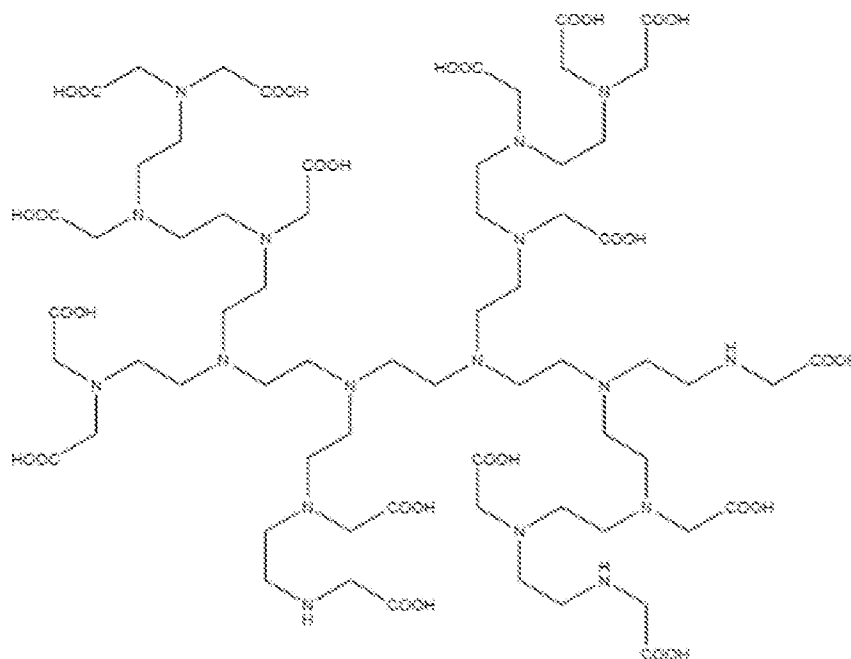
carboxymethylated polyalkyleneimines may be particularly useful in whitening particular fabrics, especially those previously treated with a fabric enhancer.

In some aspects, the composition comprises a carboxymethylated polyalkyleneimine characterized by a weight average molecular weight of from about 1000 daltons, or from about 1500 daltons, or from about 2000 daltons, or from about 5000 daltons, to about 45,000 daltons, or to about 30,000 daltons, or to about 20,000 daltons, or to about 15,000 daltons, and, optionally, a degree of substitution of from about 80%, or from about 85%, or from about 90%, to about 99%, or to about 97%, or to about 95%. Such carboxymethylated polyalkyleneimines may be particularly useful in compact detergent compositions that have relatively high surfactant levels and/or low water levels, such as in a unit dose article.

Suitable carboxymethylated polyalkyleneimine compounds include compounds comprising the following general structure:



A nonlimiting example of a suitable carboxymethylated polyalkyleneimine is shown below, having a molecular weight of about 1600, an 88% degree of substitution, and a ratio of N-CH<sub>2</sub>COOM groups to N-H of 8:1.



The compositions of the present invention may comprise from about 0.05% to about 5%, of from about 0.1% to about 2.5%, or from about 0.2% to about 1%, or from about 0.3% to about 0.6%, by weight of the composition, carboxymethylated polyalkyleneimine.

Polyalkyleneimine compounds are well-known in the art, and methods of synthesis and substitution may be found, for example, in WO1997040087A1, US Patent Number 3424790, and J. Inorg. Nucl. Chem., Volume 40, 199-201 (1978). Carboxymethylated polyalkyleneimine compounds suitable for the present invention are commercially available from BASF (Ludwigshafen, Germany), for example under the trade name TRILON® P.

### Bleach

In some aspects, the compositions are substantially free of bleach. The compositions may be substantially free of peroxide bleach. The surfactant composition may contain from about 0%, including 0%, to about 0.01% by weight of the composition peroxide bleach. In some aspects, the composition comprises less than 0.1% peroxide bleach.

As used herein, the term peroxide bleach may include hydrogen peroxide, sources of peroxide, or a mixture thereof. As used herein, a source of peroxide refers to a compound or system that produces and/or generates peroxide ions in solution. Sources of peroxide include percarbonates, persilicate, persulphate such as monopersulfate, perborates (including any hydrate thereof, including the mono- or tetra-hydrate), peroxyacids such as diperoxydodecanedioic acid

(DPDA), magnesium perphthalic acid, dialkylperoxides, diacylperoxides, preformed percarboxylic acids (including monopercarboxylic acids), perbenzoic and alkylperbenzoic acids, organic and inorganic peroxides and/or hydroperoxides or mixtures thereof. Additionally, hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms.

In some aspects, the composition is substantially free of, or contains less than 0.1%, non-peroxide bleach. Examples of non-peroxide bleach include hypohalite bleaches and sources thereof. Non-limiting examples of hypohalite bleaches or sources thereof include a simple hypochlorite salt, such as those of the alkali or alkaline earth metals, or a compound which produces hypochlorite on hydrolysis, such as organic N-chloro compounds. Other hypohalites may include hypobromite, which may be provided *in situ* from a bromide salt and a suitable strong oxidant such as hypochlorite.

#### Hueing Agent

The compositions may comprise a fabric hueing agent (sometimes referred to as shading, bluing or whitening agents). Typically the hueing agent provides a blue or violet shade to fabric. Hueing agents can be used either alone or in combination to create a specific shade of hueing and/or to shade different fabric types. This may be provided for example by mixing a red and green-blue dye to yield a blue or violet shade. Hueing agents may be selected from any known chemical class of dye, including but not limited to acridine, anthraquinone (including polycyclic quinones), azine, azo (e.g., monoazo, disazo, trisazo, tetrakisazo, polyazo), including premetallized azo, benzodifurane and benzodifuranone, carotenoid, coumarin, cyanine, diazahemicyanine, diphenylmethane, formazan, hemicyanine, indigoids, methane, naphthalimides, naphthoquinone, nitro and nitroso, oxazine, phthalocyanine, pyrazoles, stilbene, styryl, triarylmethane, triphenylmethane, xanthenes and mixtures thereof.

Suitable fabric hueing agents include dyes, dye-clay conjugates, and organic and inorganic pigments. Suitable dyes include small molecule dyes and polymeric dyes. Small molecule dyes include small molecule dyes selected from the group consisting of dyes falling into the Colour Index (C.I.) classifications of Direct, Basic, Reactive or hydrolysed Reactive, Solvent or Disperse dyes for example that are classified as Blue, Violet, Red, Green or Black, and provide the desired shade either alone or in combination. In another aspect, suitable small molecule dyes include small molecule dyes selected from the group consisting of Colour

Index (Society of Dyers and Colourists, Bradford, UK) numbers Direct Violet dyes such as 9, 35, 48, 51, 66, and 99, Direct Blue dyes such as 1, 71, 80 and 279, Acid Red dyes such as 17, 73, 52, 88 and 150, Acid Violet dyes such as 15, 17, 24, 43, 49 and 50, Acid Blue dyes such as 15, 17, 25, 29, 40, 45, 75, 80, 83, 90 and 113, Acid Black dyes such as 1, Basic Violet dyes such as 1, 3, 4, 10 and 35, Basic Blue dyes such as 3, 16, 22, 47, 66, 75 and 159, Disperse or Solvent dyes such as those described in EP1794275 or EP1794276, or dyes as disclosed in US 7208459 B2, and mixtures thereof. In another aspect, suitable small molecule dyes include small molecule dyes selected from the group consisting of C. I. numbers Acid Violet 17, Direct Blue 71, Direct Violet 51, Direct Blue 1, Acid Red 88, Acid Red 150, Acid Blue 29, Acid Blue 113 or mixtures thereof.

Suitable polymeric dyes include polymeric dyes selected from the group consisting of polymers containing covalently bound (sometimes referred to as conjugated) chromogens, (dye-polymer conjugates), for example polymers with chromogens co-polymerized into the backbone of the polymer and mixtures thereof. Polymeric dyes include those described in WO2011/98355, WO2011/47987, US2012/090102, WO2010/145887, WO2006/055787 and WO2010/142503. In another aspect, suitable polymeric dyes include polymeric dyes selected from the group consisting of fabric-substantive colorants sold under the name of Liquitint® (Milliken, Spartanburg, South Carolina, USA), dye-polymer conjugates formed from at least one reactive dye and a polymer selected from the group consisting of polymers comprising a moiety selected from the group consisting of a hydroxyl moiety, a primary amine moiety, a secondary amine moiety, a thiol moiety and mixtures thereof. In still another aspect, suitable polymeric dyes include polymeric dyes selected from the group consisting of Liquitint® Violet CT, carboxymethyl cellulose (CMC) covalently bound to a reactive blue, reactive violet or reactive red dye such as CMC conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC, alkoxylated triphenyl-methane polymeric colourants, alkoxylated thiophene polymeric colourants, and mixtures thereof.

Preferred hueing dyes include the whitening agents found in WO 08/87497 A1, WO2011/011799 and WO2012/054835. Preferred hueing agents for use in the present invention may be the preferred dyes disclosed in these references, including those selected from Examples 1-42 in Table 5 of WO2011/011799. Other preferred dyes are disclosed in US 8138222. Other preferred dyes are disclosed in WO2009/069077.

Suitable dye clay conjugates include dye clay conjugates selected from the group comprising at least one cationic/basic dye and a smectite clay, and mixtures thereof. In another

aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of one cationic/basic dye selected from the group consisting of C.I. Basic Yellow 1 through 108, C.I. Basic Orange 1 through 69, C.I. Basic Red 1 through 118, C.I. Basic Violet 1 through 51, C.I. Basic Blue 1 through 164, C.I. Basic Green 1 through 14, C.I. Basic Brown 1 through 23, CI Basic Black 1 through 11, and a clay selected from the group consisting of Montmorillonite clay, Hectorite clay, Saponite clay and mixtures thereof. In still another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of: Montmorillonite Basic Blue B7 C.I. 42595 conjugate, Montmorillonite Basic Blue B9 C.I. 52015 conjugate, Montmorillonite Basic Violet V3 C.I. 42555 conjugate, Montmorillonite Basic Green G1 C.I. 42040 conjugate, Montmorillonite Basic Red R1 C.I. 45160 conjugate, Montmorillonite C.I. Basic Black 2 conjugate, Hectorite Basic Blue B7 C.I. 42595 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Green G1 C.I. 42040 conjugate, Hectorite Basic Red R1 C.I. 45160 conjugate, Hectorite C.I. Basic Black 2 conjugate, Saponite Basic Blue B7 C.I. 42595 conjugate, Saponite Basic Blue B9 C.I. 52015 conjugate, Saponite Basic Violet V3 C.I. 42555 conjugate, Saponite Basic Green G1 C.I. 42040 conjugate, Saponite Basic Red R1 C.I. 45160 conjugate, Saponite C.I. Basic Black 2 conjugate and mixtures thereof.

Suitable pigments include pigments selected from the group consisting of flavanthrone, indanthrone, chlorinated indanthrone containing from 1 to 4 chlorine atoms, pyranthrone, dichloropyranthrone, monobromodichloropyranthrone, dibromodichloropyranthrone, tetrabromopyranthrone, perylene-3,4,9,10-tetracarboxylic acid diimide, wherein the imide groups may be unsubstituted or substituted by C1-C3 -alkyl or a phenyl or heterocyclic radical, and wherein the phenyl and heterocyclic radicals may additionally carry substituents which do not confer solubility in water, anthrapyrimidinecarboxylic acid amides, violanthrone, isoviolanthrone, dioxazine pigments, copper phthalocyanine which may contain up to 2 chlorine atoms per molecule, polychloro-copper phthalocyanine or polybromochloro-copper phthalocyanine containing up to 14 bromine atoms per molecule and mixtures thereof.

In another aspect, suitable pigments include pigments selected from the group consisting of Ultramarine Blue (C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15) and mixtures thereof.

The aforementioned fabric hueing agents can be used in combination (any mixture of fabric hueing agents can be used).

#### Adjunct Cleaning Additives

The cleaning compositions of the invention may also contain adjunct cleaning additives. Suitable adjunct cleaning additives include builders, structurants or thickeners, clay soil removal/anti-redeposition agents, polymeric soil release agents, polymeric dispersing agents, polymeric grease cleaning agents, enzymes, enzyme stabilizing systems, bleaching compounds, 5 bleaching agents, bleach activators, bleach catalysts, brighteners, dyes, hueing agents, dye transfer inhibiting agents, chelating agents, suds suppressors, softeners, and perfumes.

### Enzymes

The cleaning compositions described herein may comprise one or more enzymes which provide cleaning performance and/or fabric care benefits. Examples of suitable enzymes include, 10 but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, mannanases, pectate lyases, keratinases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, and amylases, or mixtures thereof. A typical combination is an enzyme cocktail that may 15 comprise, for example, a protease and lipase in conjunction with amylase. When present in a consumer product, 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 consumer product.

In one aspect preferred enzymes would include a protease. Suitable proteases include 20 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 25 microbial protease or/and a trypsin-type protease. Examples of suitable neutral or alkaline proteases include:

- (a) subtilisins (EC 3.4.21.62), including those derived from *Bacillus*, such as *Bacillus lentus*, *B. alkalophilus*, *B. subtilis*, *B. amyloliquefaciens*, *Bacillus pumilus* and *Bacillus gibsonii* described in US 6,312,936 B1, US 5,679,630, US 4,760,025, US 7,262,042 and WO 09/021867. 30
- (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 *Cellulomonas* described in WO 05/052161 and WO 05/052146.



(c) metalloproteases, including those derived from *Bacillus amyloliquefaciens* described in WO 07/044993A2.

Preferred proteases include those derived from *Bacillus gibsonii* or *Bacillus Lentus*.

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 + S101R + 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.

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* *Stearothermophilus* or a truncated version thereof.

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 Wehlstrasse 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, Chuo-ku Tokyo 103-8210, Japan). In one aspect, suitable amylases include NATALASE®, STAINZYME® and STAINZYME PLUS® and mixtures thereof.

In one aspect, such enzymes may be selected from the group consisting of: lipases, including “first cycle lipases” such as those described in U.S. Patent 6,939,702 B1 and US PA 2009/0217464. In one aspect, the lipase is a first-wash lipase, preferably a variant 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 O59952 (derived from *Thermomyces* *lanuginosus* (*Humicola* *lanuginosa*)). Preferred lipases would include those sold under the tradenames Lipex® and Lipolex®.

In one aspect, 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 7,141,403B2) and mixtures thereof. Suitable endoglucanases are sold under the tradenames Celluclean® and Whitezyme® (Novozymes A/S, Bagsvaerd, Denmark).

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).

5        Enzyme Stabilizing System

The enzyme-containing compositions described herein may optionally comprise from about 0.001% to about 10%, in some examples from about 0.005% to about 8%, and in other examples, from about 0.01% to about 6%, by weight of the composition, of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergent enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, chlorine bleach scavengers and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the cleaning composition. *See* U.S. Pat. No. 4,537,706 for a review of borate stabilizers.

Builders

The cleaning compositions of the present invention may optionally comprise a builder. Built cleaning compositions typically comprise at least about 1% builder, based on the total weight of the composition. Liquid cleaning compositions may comprise up to about 10% builder, and in some examples up to about 8% builder, of the total weight of the composition. Granular cleaning compositions may comprise up to about 30% builder, and in some examples up to about 5% builder, by weight of the composition.

Builders selected from aluminosilicates and silicates assist in controlling mineral hardness in wash water, especially calcium and/or magnesium, or to assist in the removal of particulate soils from surfaces. Suitable builders may be selected from the group consisting of phosphates polyphosphates, especially sodium salts thereof; carbonates, bicarbonates, sesquicarbonates, and carbonate minerals other than sodium carbonate or sesquicarbonate; organic mono-, di-, tri-, and tetracarboxylates, especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylate,s including aliphatic and aromatic types; and phytic acid. These may be

complemented by borates, e.g., for pH-buffering purposes, or by sulfates, especially sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or builder-containing cleaning compositions. Other builders can be selected from the polycarboxylate builders, for example, copolymers of acrylic acid, copolymers of acrylic acid and maleic acid, and copolymers of acrylic acid and/or maleic acid, and other suitable ethylenic monomers with various types of additional functionalities. Also suitable for use as builders herein are synthesized crystalline ion exchange materials or hydrates thereof having chain structure and a composition represented by the following general anhydride form:  $x(M_2O) \cdot ySiO_2 \cdot zM'O$  wherein M is Na and/or K, M' is Ca and/or Mg;  $y/x$  is 0.5 to 2.0; and  $z/x$  is 0.005 to 1.0 as taught in U.S. Pat. No. 5,427,711.

Structurant / Thickeners

## i. Di-benzylidene Polyol Acetal Derivative

The fluid detergent composition may comprise from about 0.01% to about 1% by weight of a dibenzylidene polyol acetal derivative (DBPA), or from about 0.05% to about 0.8%, or from about 0.1% to about 0.6%, or even from about 0.3% to about 0.5%. Non-limiting examples of suitable DBPA molecules are disclosed in US 61/167604. In one aspect, the DBPA derivative may comprise a dibenzylidene sorbitol acetal derivative (DBS). Said DBS derivative may be selected from the group consisting of: 1,3:2,4-dibenzylidene sorbitol; 1,3:2,4-di(p-methylbenzylidene) sorbitol; 1,3:2,4-di(p-chlorobenzylidene) sorbitol; 1,3:2,4-di(2,4-dimethyldibenzylidene) sorbitol; 1,3:2,4-di(p-ethylbenzylidene) sorbitol; and 1,3:2,4-di(3,4-dimethyldibenzylidene) sorbitol or mixtures thereof. These and other suitable DBS derivatives are disclosed in US 6,102,999, column 2 line 43 to column 3 line 65.

## ii. Bacterial Cellulose

The fluid detergent composition may also comprise from about 0.005 % to about 1 % by weight of a bacterial cellulose network. The term “bacterial cellulose” encompasses any type of cellulose produced via fermentation of a bacteria of the genus *Acetobacter* such as CELLULON® by CPKelco U.S. and includes materials referred to popularly as microfibrillated cellulose, reticulated bacterial cellulose, and the like. Some examples of suitable bacterial cellulose can be found in US 6,967,027; US 5,207,826; US 4,487,634; US 4,373,702; US 4,863,565 and US 2007/0027108. In one aspect, said fibres have cross sectional dimensions of 1.6 nm to 3.2 nm by 5.8 nm to 133 nm. Additionally, the bacterial cellulose fibres have an average microfibre length of at least about 100 nm, or from about 100 to about 1,500 nm. In one aspect, the bacterial cellulose microfibrils have an aspect ratio, meaning the average microfibre length divided by the widest cross sectional microfibre width, of from about 100:1 to about 400:1, or even from about 200:1 to about 300:1.

## iii. Coated Bacterial Cellulose

In one aspect, the bacterial cellulose is at least partially coated with a polymeric thickener. The at least partially coated bacterial cellulose can be prepared in accordance with the methods disclosed in US 2007/0027108 paragraphs 8 to 19. In one aspect the at least partially coated bacterial cellulose comprises from about 0.1 % to about 5 %, or even from about 0.5 % to about 3 %, by weight of bacterial cellulose; and from about 10 % to about 90 % by weight of the polymeric thickener. Suitable bacterial cellulose may include the bacterial cellulose described above and suitable polymeric thickeners include: carboxymethylcellulose, cationic hydroxymethylcellulose, and mixtures thereof.

iv. Cellulose fibers non-bacterial cellulose derived

In one aspect, the composition may further comprise from about 0.01 to about 5% by weight of the composition of a cellulosic fiber. Said cellulosic fiber may be extracted from vegetables, fruits or wood. Commercially available examples are Avicel® from FMC, Citri-Fi from Fiberstar or Betafib from Cosun.

v. Non-Polymeric Crystalline Hydroxyl-Functional Materials

In one aspect, the composition may further comprise from about 0.01 to about 1% by weight of the composition of a non-polymeric crystalline, hydroxyl functional structurant. Said non-polymeric crystalline, hydroxyl functional structurants generally may comprise a crystallizable glyceride which can be pre-emulsified to aid dispersion into the final fluid detergent composition. In one aspect, crystallizable glycerides may include hydrogenated castor oil or "HCO" or derivatives thereof, provided that it is capable of crystallizing in the liquid detergent composition.

vi. Polymeric Structuring Agents

Fluid detergent compositions of the present invention may comprise from about 0.01 % to about 5 % by weight of a naturally derived and/or synthetic polymeric structurant. Examples of naturally derived polymeric structurants of use in the present invention include: hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, carboxymethyl cellulose, polysaccharide derivatives and mixtures thereof. Suitable polysaccharide derivatives include: pectine, alginate, arabinogalactan (gum Arabic), carrageenan, gellan gum, xanthan gum, guar gum and mixtures thereof. Examples of synthetic polymeric structurants of use in the present invention include: polycarboxylates, polyacrylates, hydrophobically modified ethoxylated urethanes, hydrophobically modified non-ionic polyols and mixtures thereof. In one aspect, said polycarboxylate polymer is a polyacrylate, polymethacrylate or mixtures thereof. In another aspect, the polyacrylate is a copolymer of unsaturated mono- or di-carbonic acid and C<sub>1</sub>-C<sub>30</sub> alkyl ester of the (meth)acrylic acid. Said copolymers are available from Noveon inc under the tradename Carbopol Aqua 30.

vii. Di-amido-gellants

In one aspect, the external structuring system may comprise a di-amido gellant having a molecular weight from about 150 g/mol to about 1,500 g/mol, or even from about 500 g/mol to about 900 g/mol. Such di-amido gellants may comprise at least two nitrogen atoms, wherein at least two of said nitrogen atoms form amido functional substitution groups. In one aspect, the amido groups are different. In another aspect, the amido functional groups are the same. The di-amido gellant has the following formula:

30



wherein:

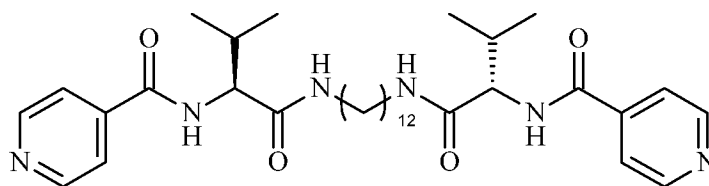
$R_1$  and  $R_2$  is an amino functional end-group, or even amido functional end-group, in one aspect  $R_1$  and  $R_2$  may comprise a pH-tuneable group, wherein the pH tuneable amido-gellant may have a pKa of from about 1 to about 30, or even from about 2 to about 10. In one aspect, the pH tuneable group may comprise a pyridine. In one aspect,  $R_1$  and  $R_2$  may be different. In another aspect, may be the same.

L is a linking moiety of molecular weight from 14 to 500 g/mol. In one aspect, L may comprise a carbon chain comprising between 2 and 20 carbon atoms. In another aspect, L may comprise a pH-tuneable group. In one aspect, the pH tuneable group is a secondary amine.

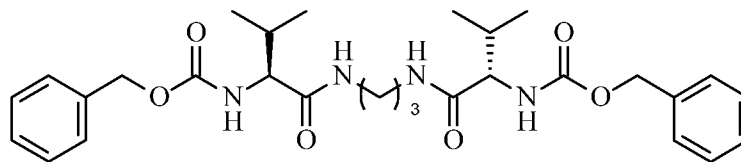
In one aspect, at least one of  $R_1$ ,  $R_2$  or L may comprise a pH-tuneable group.

Non-limiting examples of di-amido gellants are:

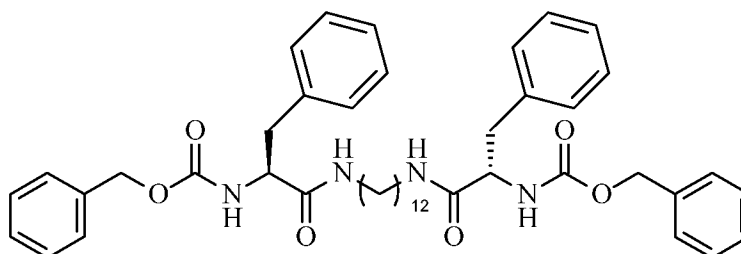
*N,N'*-(2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide



dibenzyl (2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)dicarbamate



dibenzyl (2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)dicarbamate



### Polymeric Dispersing Agents

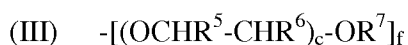
5           The consumer product may comprise one or more polymers. Examples are carboxymethylcellulose, poly(vinyl-pyrrolidone), poly(ethylene glycol), poly(vinyl alcohol), poly(vinylpyridine-N-oxide), poly(vinylimidazole), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid co-polymers.

10           The consumer product may comprise one or more amphiphilic cleaning polymers such as the compound having the following general structure:  $\text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3)\text{-N}^+\text{-C}_x\text{H}_{2x}\text{-N}^+\text{-(CH}_3\text{)-bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)$ , wherein  $n$  = from 20 to 30, and  $x$  = from 3 to 8, or sulphated or sulphonated variants thereof.

15           The consumer product may comprise amphiphilic alkoxyated grease cleaning polymers which have balanced hydrophilic and hydrophobic properties such that they remove grease particles from fabrics and surfaces. Specific embodiments of the amphiphilic alkoxyated grease cleaning polymers of the present invention comprise a core structure and a plurality of alkoxyate groups attached to that core structure. These may comprise alkoxyated polyalkylenimines, preferably having an inner polyethylene oxide block and an outer polypropylene oxide block.

20           Carboxylate polymer - The consumer products of the present invention may also include one or more carboxylate polymers 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.

25           Soil release polymer - The consumer products of the present invention may also include one or more soil release polymers having a structure as defined by one of the following structures (I), (II) or (III):





wherein:

a, b and c are from 1 to 200;

d, e and f are from 1 to 50;

5 Ar is a 1,4-substituted phenylene;

sAr is 1,3-substituted phenylene substituted in position 5 with SO<sub>3</sub>Me;

Me is Li, K, Mg/2, Ca/2, Al/3, ammonium, mono-, di-, tri-, or tetraalkylammonium

wherein the alkyl groups are C<sub>1</sub>-C<sub>18</sub> alkyl or C<sub>2</sub>-C<sub>10</sub> hydroxyalkyl, or mixtures thereof;

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are independently selected from H or C<sub>1</sub>-C<sub>18</sub> n- or iso-alkyl; and

10 R<sup>7</sup> is a linear or branched C<sub>1</sub>-C<sub>18</sub> alkyl, or a linear or branched C<sub>2</sub>-C<sub>30</sub> alkenyl, or a cycloalkyl group with 5 to 9 carbon atoms, or a C<sub>8</sub>-C<sub>30</sub> aryl group, or a C<sub>6</sub>-C<sub>30</sub> arylalkyl group.

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,  
15 SRN170, SRN240, SRN300 and SRN325 supplied by Clariant. Other suitable soil release polymers are Marloquest polymers, such as Marloquest SL supplied by Sasol.

Cellulosic polymer - The consumer products of the present invention may also include one or more cellulosic polymers including those selected from alkyl cellulose, alkyl alkoxyalkyl cellulose, carboxyalkyl cellulose, alkyl carboxyalkyl cellulose. In one aspect, the cellulosic  
20 polymers are selected from the group comprising carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, methyl carboxymethyl cellulose, and mixtures 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.

Examples of polymeric dispersing agents are found in U.S. Pat. No. 3,308,067, European Patent  
25 Application No. 66915, EP 193,360, and EP 193,360.

### Additional Amines

Additional amines may be used in the cleaning compositions described herein for added removal of grease and particulates from soiled materials. The cleaning compositions described herein may comprise from about 0.1% to about 10%, in some examples, from about 0.1% to about 4%, and in other examples, from about 0.1% to about 2%, by weight of the cleaning composition, of additional amines. Non-limiting examples of additional amines may include, but are not limited to, polyamines, oligoamines, triamines, diamines, pentamines, tetraamines, or combinations thereof. Specific examples of suitable additional amines include tetraethylenepentamine, triethylenetetraamine, diethylenetriamine, or a mixture thereof

For example, alkoxyated polyamines may be used for grease and particulate removal. Such compounds may include, but are not limited to, ethoxylated polyethyleneimine, ethoxylated hexamethylene diamine, and sulfated versions thereof. Polypropoxylated derivatives may also be included. A wide variety of amines and polyaklyeneimines can be alkoxyated to various degrees. A useful example is 600g/mol polyethyleneimine core ethoxylated to 20 EO groups per NH and is available from BASF. The cleaning compositions described herein may comprise from about 0.1% to about 10%, and in some examples, from about 0.1% to about 8%, and in other examples, from about 0.1% to about 6%, by weight of the cleaning composition, of alkoxyated polyamines.

Alkoxyated polycarboxylates may also be used in the cleaning compositions herein to provide grease removal. 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  $-(\text{CH}_2\text{CH}_2\text{O})_m (\text{CH}_2)_n \text{CH}_3$  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 may be in the range of about 2000 to about 50,000. The cleaning compositions described herein may comprise from about 0.1% to about 10%, and in some examples, from about 0.25% to about 5%, and in other examples, from about 0.3% to about 2%, by weight of the cleaning composition, of alkoxyated polycarboxylates.

### Bleaching Compounds, Bleaching Agents, Bleach Activators, and Bleach Catalysts

The cleaning compositions described herein may contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. Bleaching agents may be present at levels of from about 1% to about 30%, and in some examples from about 5%

to about 20%, based on the total weight of the composition. If present, the amount of bleach activator may be from about 0.1% to about 60%, and in some examples from about 0.5% to about 40%, of the bleaching composition comprising the bleaching agent plus bleach activator.

Examples of bleaching agents include oxygen bleach, perborate bleach, percarboxylic acid bleach and salts thereof, peroxygen bleach, persulfate bleach, percarbonate bleach, and mixtures thereof. Examples of bleaching agents are disclosed in U.S. Pat. No. 4,483,781, U.S. patent application Ser. No. 740,446, European Patent Application 0,133,354, U.S. Pat. No. 4,412,934, and U.S. Pat. No. 4,634,551.

Examples of bleach activators (e.g., acyl lactam activators) are disclosed in U.S. Pat. Nos. 4,915,854; 4,412,934; 4,634,551; 4,634,551; and 4,966,723.

In some examples, cleaning compositions may also include a transition metal bleach catalyst. In other examples, the transition metal bleach catalyst may be encapsulated. The transition metal bleach catalyst may comprise a transition metal ion, which may be selected from the group consisting of Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cu(III), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(V), W(VI), Pd(II), Ru(II), Ru(III), and Ru(IV). The transition metal bleach catalyst may comprise a ligand, such as a macropolycyclic ligand or a cross-bridged macropolycyclic ligand. The transition metal ion may be coordinated with the ligand. The ligand may comprise at least four donor atoms, at least two of which are bridgehead donor atoms. Suitable transition metal bleach catalysts are described in U.S. 5,580,485, U.S. 4,430,243; U.S. 4,728,455; U.S. 5,246,621; U.S. 5,244,594; U.S. 5,284,944; U.S. 5,194,416; U.S. 5,246,612; U.S. 5,256,779; U.S. 5,280,117; U.S. 5,274,147; U.S. 5,153,161; U.S. 5,227,084; U.S. 5,114,606; U.S. 5,114,611, EP 549,271 A1; EP 544,490 A1; EP 549,272 A1; and EP 544,440 A2. Another suitable transition metal bleach catalyst is a manganese-based catalyst, as is disclosed in U.S. 5,576,282. Suitable cobalt bleach catalysts are described, for example, in U.S. 5,597,936 and U.S. 5,595,967. Such cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. 5,597,936, and U.S. 5,595,967. A suitable transition metal bleach catalyst is a transition metal complex of ligand such as bispidones described in WO 05/042532 A1.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized in cleaning compositions. They include, for example, photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines described in U.S. Pat. No. 4,033,718, or pre-formed organic peracids, such as peroxydicarboxylic acid or salt thereof, or a

peroxysulphonic acid or salt thereof. A suitable organic peracid is phthaloylimidoperoxypropionic acid. If used, the cleaning compositions described herein will typically contain from about 0.025% to about 1.25%, by weight of the composition, of such bleaches, and in some examples, of sulfonate zinc phthalocyanine.

5           Brighteners

Optical brighteners or other brightening or whitening agents may be incorporated at levels of from about 0.01% to about 1.2%, by weight of the composition, into the cleaning compositions described herein. Commercial optical brighteners, which may be used herein, can be classified into subgroups, which include, but are not necessarily limited to, derivatives of  
10   stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphen-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents," M. Zahradnik, John Wiley & Sons, New York (1982). Specific, non-limiting examples of optical brighteners which may be useful in the present compositions are those identified in  
15   U.S. Pat. No. 4,790,856 and U.S. Pat. No. 3,646,015.

Dye Transfer Inhibiting Agents

Fabric cleaning compositions may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents may include polyvinyl pyrrolidone polymers, polyamine N-  
20   oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents may be used at a concentration of about 0.01% to about 10%, by weight of the composition, in some examples, from about 0.01% to about 5%, by weight of the composition, and in other examples, from about 0.05% to about 2% by weight of the composition.

25           Chelating Agents

The detergent compositions described herein may also contain one or more metal ion chelating agents. Suitable molecules include copper, iron and/or manganese chelating agents and mixtures thereof. Such chelating agents can be selected from the group consisting of phosphonates, amino carboxylates, amino phosphonates, succinates, polyfunctionally-substituted  
30   aromatic chelating agents, 2-pyridinol-N-oxide compounds, hydroxamic acids, carboxymethyl inulins and mixtures thereof. Chelating agents can be present in the acid or salt form including alkali metal, ammonium, and substituted ammonium salts thereof, and mixtures thereof. Non-

limiting examples of chelants of use in the present invention are found in U.S. Patent 7445644, U.S. Patent 7585376 and U.S. Publication 2009/0176684A1.

Aminocarboxylates useful as chelating agents include, but are not limited to ethylenediaminetetracetates (EDTA); N-(hydroxyethyl)ethylenediaminetriacetates (HEDTA);  
5 nitrilotriacetates (NTA); ethylenediamine tetrapropionates; triethylenetetraaminehexacetates, diethylenetriamine-pentaacetates (DTPA); methylglycinediacetic acid (MGDA); Glutamic acid diacetic acid (GLDA); ethanoldiglycines; triethylenetetraaminehexaactic acid (TTHA); N-hydroxyethyliminodiacetic acid (HEIDA); dihydroxyethylglycine (DHEG); ethylenediaminetetrapropionic acid (EDTP) and derivatives thereof.

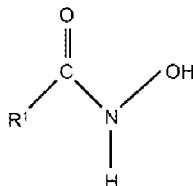
10 Phosphorus containing chelants include, but are not limited to diethylene triamine penta (methylene phosphonic acid) (DTPMP CAS 15827-60-8); ethylene diamine tetra(methylene phosphonic acid) (EDTMP CAS 1429-50-1); 2-Phosphonobutane 1,2,4-tricarboxylic acid (Bayhibit® AM); hexamethylene diamine tetra(methylene phosphonic acid) (CAS 56744-47-9); hydroxy-ethane diphosphonic acid (HEDP CAS 2809-21-4); hydroxyethane dimethylene  
15 phosphonic acid; 2-phosphono- 1,2,4-Butanetricarboxylic acid (CAS 37971-36-1); 2-hydroxy-2-phosphono-Acetic acid (CAS 23783-26-8); Aminotri(methylenephosphonic acid) (ATMP CAS 6419-19-8); P,P'-(1,2-ethanediyl)bis-Phosphonic acid (CAS 6145-31-9); P,P'-methylenebis-Phosphonic acid (CAS 1984-15-2); Triethylenediaminetetra(methylene phosphonic acid) (CAS 28444-52-2); P-(1-hydroxy-1-methylethyl)-Phosphonic acid (CAS 4167-10-6);  
20 bis(hexamethylene triamine penta(methylenephosphonic acid)) (CAS 34690-00-1); N2,N2,N6,N6-tetrakis(phosphonomethyl)-Lysine (CAS 194933-56-7, CAS 172780-03-9), salts thereof, and mixtures thereof. Preferably, these aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

A biodegradable chelator that may also be used herein is ethylenediamine disuccinate  
25 ("EDDS"). In some examples, but of course not limited to this particular example, the [S,S] isomer as described in U.S. Patent 4,704,233 may be used. In other examples, the trisodium salt of EDDA may be used, though other forms, such as magnesium salts, may also be useful.

Polyfunctionally-substituted aromatic chelating agents may also be used in the cleaning compositions. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Compounds of  
30 this type in acid form are dihydroxydisulfobenzenes, such as 1,2-dihydroxy-3,5-disulfobenzene, also known as Tiron. Other sulphonated catechols may also be used. In addition to the disulfonic acid, the term "tiron" may also include mono- or di-sulfonate salts of the acid, such as, for example, the disodium sulfonate salt, which shares the same core molecular structure with the disulfonic acid.

The detergent composition according to the present invention may comprise a substituted or unsubstituted 2-pyridinol-N-oxide compound or a salt thereof, as a chelating agent. Included within the scope of this invention are tautomers of this compound, e.g., 1-Hydroxy-2(1H)-pyridinone, as chelating agents. In certain aspects, the detergent composition comprises a 2-pyridinol-N-oxide compound selected from the group consisting of: 2-hydroxypyridine-1-oxide; 3-pyridinecarboxylic acid, 2-hydroxy-, 1-oxide; 6-hydroxy-3-pyridinecarboxylic acid, 1-oxide; 2-hydroxy-4-pyridinecarboxylic acid, 1-oxide; 2-pyridinecarboxylic acid, 6-hydroxy-, 1-oxide; 6-hydroxy-3-pyridinesulfonic acid, 1-oxide; and mixtures thereof. In certain aspects, the detergent composition comprises a 1-Hydroxy-2(1H)-pyridinone compound selected from the group consisting of: 1-Hydroxy-2(1H)-pyridinone (CAS 822-89-9); 1,6-dihydro-1-hydroxy-6-oxo-3-Pyridinecarboxylic acid (CAS 677763-18-7); 1,2-dihydro-1-hydroxy-2-oxo-4-Pyridinecarboxylic acid (CAS 119736-22-0); 1,6-dihydro-1-hydroxy-6-oxo-2-Pyridinecarboxylic acid (CAS 94781-89-2); 1-hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)-2(1H)-Pyridinone (CAS 50650-76-5); 6-(cyclohexylmethyl)-1-hydroxy-4-methyl-2(1H)-Pyridinone (CAS 29342-10-7); 1-hydroxy-4,6-dimethyl-2(1H)-Pyridinone (CAS 29342-02-7); 1-Hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)-2-pyridone monoethanolamine (CAS 68890-66-4); 1-hydroxy-6-(octyloxy)-2(1H)-Pyridinone (CAS 162912-64-3); 1-Hydroxy-4-methyl-6-cyclohexyl-2-pyridinone ethanolamine salt (CAS 41621-49-2); 1-Hydroxy-4-methyl-6-cyclohexyl-2-pyridinone (CAS 29342-05-0); 6-ethoxy-1,2-dihydro-1-hydroxy-2-oxo-4-Pyridinecarboxylic acid, methyl ester (CAS 36979-78-9); 1-hydroxy-5-nitro -2(1H)-Pyridinone (CAS 45939-70-6); and mixtures thereof. These compounds are commercially available from, for example, Sigma-Aldrich (St. Louis, MO), Princeton Building Blocks (Monmouth Junction, NJ), 3B Scientific Corporation (Libertyville, IL), SynFine Research (Richmond Hill, ON), Ryan Scientific, Inc. (Mt. Pleasant, SC), and/or Aces Pharma (Branford, CT).

Hydroxamic acids are a class of chemical compounds in which a hydroxylamine is inserted into a carboxylic acid and be used as chelating agents. A general structure of a hydroxamic acid is the following:



The preferred hydroxamates are those where R<sup>1</sup> is C4 to C14 alkyl, preferably normal alkyl, most preferably saturated, salts thereof and mixtures thereof. When the C8 material is used, it called octyl hydroxamic acid.

Other suitable chelating agents for use herein are the commercial DEQUEST series, and  
5 chelants from Monsanto, Akzo-Nobel, DuPont, Dow, BASF, and Nalco.

The chelant may be present in the detergent compositions disclosed herein at from about 0.005% to about 15% by weight, about 0.01% to about 5% by weight, about 0.1% to about 3.0% by weight, or from about 0.2% to about 0.7% by weight, or from about 0.3% to about 0.6% by weight of the detergent compositions disclosed herein.

#### 10 Suds Suppressors

Compounds for reducing or suppressing the formation of suds can be incorporated into the cleaning compositions described herein. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. Pat. No. 4,489,455, 4,489,574, and in front-loading style washing machines.

15 A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). Examples of suds suppressors include monocarboxylic fatty acid and soluble salts therein, high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides),  
20 fatty acid esters of monovalent alcohols, aliphatic C<sub>18</sub>-C<sub>40</sub> ketones (e.g., stearone), N-alkylated amino triazines, waxy hydrocarbons preferably having a melting point below about 100 °C, silicone suds suppressors, and secondary alcohols. Suds suppressors are described in U.S. Pat. No. 2,954,347; 4,265,779; 4,265,779; 3,455,839; 3,933,672; 4,652,392; 4,978,471; 4,983,316; 5,288,431; 4,639,489; 4,749,740; and 4,798,679; 4,075,118; European Patent Application No.  
25 89307851.9; EP 150,872; and DOS 2,124,526.

The cleaning compositions herein may comprise from 0% to about 10%, by weight of the composition, of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts thereof, may be present in amounts of up to about 5% by weight of the cleaning composition, and in some examples, from about 0.5% to about 3% by weight of the cleaning  
30 composition. Silicone suds suppressors may be utilized in amounts of up to about 2.0% by weight of the cleaning composition, although higher amounts may be used. Monostearyl phosphate suds suppressors may be utilized in amounts ranging from about 0.1% to about 2% by weight of the cleaning composition. Hydrocarbon suds suppressors may be utilized in amounts

ranging from about 0.01% to about 5.0% by weight of the cleaning composition, although higher levels can be used. Alcohol suds suppressors may be used at a concentration ranging from about 0.2% to about 3% by weight of the cleaning composition.

#### Suds Boosters

5 If high sudsing is desired, suds boosters such as the C<sub>10</sub>-C<sub>16</sub> alkanolamides may be incorporated into the cleaning compositions at a concentration ranging from about 1% to about 10% by weight of the cleaning composition. Some examples include the C<sub>10</sub>-C<sub>14</sub> monoethanol and diethanol amides. If desired, water-soluble magnesium and/or calcium salts such as MgCl<sub>2</sub>, MgSO<sub>4</sub>, CaCl<sub>2</sub>, CaSO<sub>4</sub>, and the like, may be added at levels of about 0.1% to about 2% by weight  
10 of the cleaning composition, to provide additional suds and to enhance grease removal performance.

#### Fabric Softeners

Various through-the-wash fabric softeners, including the impalpable smectite clays of U.S. Pat. No. 4,062,647 as well as other softener clays known in the art, may be used at levels of  
15 from about 0.5% to about 10% by weight of the composition, to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Pat. No. 4,375,416, and U.S. Pat. No. 4,291,071. Cationic softeners can also be used without clay softeners.

#### Encapsulates

20

The compositions may comprise an encapsulate. In some aspects, the encapsulate comprises a core, a shell having an inner and outer surface, where the shell encapsulates the core.

In certain aspects, the encapsulate comprises a core and a shell, where the core comprises a material selected from perfumes; brighteners; dyes; insect repellants; silicones; waxes; flavors; vitamins; fabric softening agents; skin care agents, e.g., paraffins; enzymes; anti-bacterial agents;  
25 bleaches; sensates; or mixtures thereof; and where the shell comprises a material selected from polyethylenes; polyamides; polyvinylalcohols, optionally containing other co-monomers; polystyrenes; polyisoprenes; polycarbonates; polyesters; polyacrylates; polyolefins; polysaccharides, e.g., alginate and/or chitosan; gelatin; shellac; epoxy resins; vinyl polymers;  
30 water insoluble inorganics; silicone; aminoplasts, or mixtures thereof. In some aspects, where the shell comprises an aminoplast, the aminoplast comprises polyurea, polyurethane, and/or



polyureaurethane. The polyurea may comprise polyoxymethyleneurea and/or melamine formaldehyde.

In some aspects, the encapsulate comprises a core, and the core comprises a perfume. In certain aspects, the encapsulate comprises a shell, and the shell comprises melamine formaldehyde and/or cross linked melamine formaldehyde. In some aspects, the encapsulate comprises a core comprising a perfume and a shell comprising melamine formaldehyde and/or cross linked melamine formaldehyde

Suitable encapsulates may comprise a core material and a shell, where the shell at least partially surrounds the core material. At least 75%, or at least 85%, or even at least 90% of the encapsulates may have a fracture strength of from about 0.2 MPa to about 10 MPa, from about 0.4 MPa to about 5MPa, from about 0.6 MPa to about 3.5 MPa, or even from about 0.7 MPa to about 3MPa; and a benefit agent leakage of from 0% to about 30%, from 0% to about 20%, or even from 0% to about 5%.

In some aspects, at least 75%, 85% or even 90% of said encapsulates may have a particle size of from about 1 microns to about 80 microns, about 5 microns to 60 microns, from about 10 microns to about 50 microns, or even from about 15 microns to about 40 microns.

In some aspects, at least 75%, 85% or even 90% of said encapsulates may have a particle wall thickness of from about 30 nm to about 250 nm, from about 80 nm to about 180 nm, or even from about 100 nm to about 160 nm.

In some aspects, the core of the encapsulate comprises a material selected from a perfume raw material and/or optionally a material selected from vegetable oil, including neat and/or blended vegetable oils including castor oil, coconut oil, cottonseed oil, grape oil, rapeseed, soybean oil, corn oil, palm oil, linseed oil, safflower oil, olive oil, peanut oil, coconut oil, palm kernel oil, castor oil, lemon oil and mixtures thereof; esters of vegetable oils, esters, including dibutyl adipate, dibutyl phthalate, butyl benzyl adipate, benzyl octyl adipate, tricresyl phosphate, trioctyl phosphate and mixtures thereof; straight or branched chain hydrocarbons, including those straight or branched chain hydrocarbons having a boiling point of greater than about 80 °C; partially hydrogenated terphenyls, dialkyl phthalates, alkyl biphenyls, including monoisopropylbiphenyl, alkylated naphthalene, including dipropyl naphthalene, petroleum spirits, including kerosene, mineral oil or mixtures thereof; aromatic solvents, including benzene, toluene or mixtures thereof; silicone oils; or mixtures thereof.

In some aspects, the wall of the encapsulate comprises a suitable resin, such as the reaction product of an aldehyde and an amine. Suitable aldehydes include formaldehyde. Suitable amines include melamine, urea, benzoguanamine, glycoluril, or mixtures thereof.

Suitable melamines include methylol melamine, methylated methylol melamine, imino melamine and mixtures thereof. Suitable ureas include, dimethylol urea, methylated dimethylol urea, urea-resorcinol, or mixtures thereof.

In some aspects, suitable formaldehyde scavengers may be employed with the encapsulates, for example, in a capsule slurry and/or added to a composition before, during, or after the encapsulates are added to such composition.

Suitable capsules are disclosed in USPA 2008/0305982 A1; and/or USPA 2009/0247449 A1. Alternatively, suitable capsules can be purchased from Appleton Papers Inc. of Appleton, Wisconsin USA.

In addition, the materials for making the aforementioned encapsulates can be obtained from Solutia Inc. (St Louis, Missouri U.S.A.), Cytec Industries (West Paterson, New Jersey U.S.A.), sigma-Aldrich (St. Louis, Missouri U.S.A.), CP Kelco Corp. of San Diego, California, USA; BASF AG of Ludwigshafen, Germany; Rhodia Corp. of Cranbury, New Jersey, USA; Hercules Corp. of Wilmington, Delaware, USA; Agrium Inc. of Calgary, Alberta, Canada, ISP of New Jersey U.S.A., Akzo Nobel of Chicago, IL, USA; Stroeever Shellac Bremen of Bremen, Germany; Dow Chemical Company of Midland, MI, USA; Bayer AG of Leverkusen, Germany; Sigma-Aldrich Corp., St. Louis, Missouri, USA.

#### Perfumes

- 5 Perfumes and perfumery ingredients may be used in the cleaning compositions described herein. Non-limiting examples of perfume and perfumery ingredients include, but are not limited to, aldehydes, ketones, esters, and the like. Other examples include various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like.
- 10 Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes may be included at a concentration ranging from about 0.01% to about 2% by weight of the cleaning composition.

#### Fillers and Carriers

- Fillers and carriers may be used in the cleaning compositions described herein. As used
- 15 herein, the terms “filler” and “carrier” have the same meaning and can be used interchangeably.

Liquid cleaning compositions and other forms of cleaning compositions that include a liquid component (such as liquid-containing unit dose cleaning compositions) may contain water and other solvents as fillers or carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols

may be used in some examples for solubilizing surfactants, and polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) may also be used. Amine-containing solvents may also be used.

5           The cleaning compositions may contain from about 5% to about 90%, and in some examples, from about 10% to about 50%, by weight of the composition, of such carriers. For compact or super-compact heavy duty liquid or other forms of cleaning compositions, the use of water may be lower than about 40% by weight of the composition, or lower than about 20%, or lower than about 5%, or less than about 4% free water, or less than about 3% free water, or less  
10       than about 2% free water, or substantially free of free water (i.e., anhydrous).

          For powder or bar cleaning compositions, or forms that include a solid or powder component (such as powder-containing unit dose cleaning composition), suitable fillers may include, but are not limited to, sodium sulfate, sodium chloride, clay, or other inert solid ingredients. Fillers may also include biomass or decolorized biomass. Fillers in granular, bar, or  
15       other solid cleaning compositions may comprise less than about 80% by weight of the cleaning composition, and in some examples, less than about 50% by weight of the cleaning composition. Compact or supercompact powder or solid cleaning compositions may comprise less than about 40% filler by weight of the cleaning composition, or less than about 20%, or less than about 10%.

          For either compacted or supercompacted liquid or powder cleaning compositions, or other  
20       forms, the level of liquid or solid filler in the product may be reduced, such that either the same amount of active chemistry is delivered to the wash liquor as compared to noncompacted cleaning compositions, or in some examples, the cleaning composition is more efficient such that less active chemistry is delivered to the wash liquor as compared to noncompacted compositions. For example, the wash liquor may be formed by contacting the cleaning composition to water in  
25       such an amount so that the concentration of cleaning composition in the wash liquor is from above 0g/l to 4g/l. In some examples, the concentration may be from about 1g/l to about 3.5g/l, or to about 3.0g/l, or to about 2.5g/l, or to about 2.0g/l, or to about 1.5g/l, or from about 0g/l to about 1.0g/l, or from about 0g/l to about 0.5g/l. These dosages are not intended to be limiting, and other dosages may be used that will be apparent to those of ordinary skill in the art.

### 30    Buffer System

          The cleaning compositions described herein may be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 7.0 and about 12,

and in some examples, between about 7.0 and about 11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, or acids, and are well known to those skilled in the art. These include, but are not limited to, the use of sodium carbonate, citric acid or sodium citrate, monoethanol amine or other amines, boric acid or borates, and other pH-adjusting compounds well known in the art.

The cleaning compositions herein may comprise dynamic in-wash pH profiles. Such cleaning compositions may use wax-covered citric acid particles in conjunction with other pH control agents such that (i) about 3 minutes after contact with water, the pH of the wash liquor is greater than 10; (ii) about 10 minutes after contact with water, the pH of the wash liquor is less than 9.5; (iii) about 20 minutes after contact with water, the pH of the wash liquor is less than 9.0; and (iv) optionally, wherein, the equilibrium pH of the wash liquor is in the range of from about 7.0 to about 8.5.

#### Other Adjunct Ingredients

A wide variety of other ingredients may be used in the cleaning compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, and solid or other liquid fillers, erythrosine, colloidal silica, waxes, probiotics, surfactin, aminocellulosic polymers, Zinc Ricinoleate, perfume microcapsules, rhamnolipids, sophorolipids, glycopeptides, methyl ester sulfonates, methyl ester ethoxylates, sulfonated estolides, cleavable surfactants, biopolymers, silicones, modified silicones, aminosilicones, deposition aids, locust bean gum, cationic hydroxyethylcellulose polymers, cationic guar, hydrotropes (especially cumenesulfonate salts, toluenesulfonate salts, xylenesulfonate salts, and naphalene salts), antioxidants, BHT, PVA particle-encapsulated dyes or perfumes, pearlescent agents, effervescent agents, color change systems, silicone polyurethanes, opacifiers, tablet disintegrants, biomass fillers, fast-dry silicones, glycol distearate, hydroxyethylcellulose polymers, hydrophobically modified cellulose polymers or hydroxyethylcellulose polymers, starch perfume encapsulates, emulsified oils, bisphenol antioxidants, microfibrinous cellulose structurants, properfumes, styrene/acrylate polymers, triazines, soaps, superoxide dismutase, benzophenone protease inhibitors, functionalized TiO<sub>2</sub>, dibutyl phosphate, silica perfume capsules, and other adjunct ingredients, diethylenetriaminepentaacetic acid, Tiron (1,2-dihydroxybenzene-3,5-disulfonic acid), hydroxyethanedimethylenephosphonic acid, methylglycinediacetic acid, choline oxidase, pectate lyase, triarylmethane blue and violet basic dyes, methine blue and violet basic dyes, anthraquinone blue and violet basic dyes, azo dyes basic blue 16, basic blue 65, basic blue 66

basic blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48, oxazine dyes, basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141, Nile blue A and xanthene dye basic violet 10, an alkoxyated triphenylmethane polymeric colorant; an alkoxyated thiopene polymeric colorant; thiazolium dye, mica, titanium dioxide coated mica, bismuth oxychloride, paraffin waxes, sucrose esters, aesthetic dyes, hydroxamate chelants, and other actives.

The cleaning compositions described herein may also contain vitamins and amino acids such as: water soluble vitamins and their derivatives, water soluble amino acids and their salts and/or derivatives, water insoluble amino acids viscosity modifiers, dyes, nonvolatile solvents or diluents (water soluble and insoluble), pearlescent aids, foam boosters, additional surfactants or nonionic cosurfactants, pediculocides, pH adjusting agents, perfumes, preservatives, chelants, proteins, skin active agents, sunscreens, UV absorbers, vitamins, niacinamide, caffeine, and minoxidil.

The cleaning compositions of the present invention may also contain pigment materials such as nitroso, monoazo, disazo, carotenoid, triphenyl methane, triaryl methane, xanthene, quinoline, oxazine, azine, anthraquinone, indigoid, thionindigoid, quinacridone, phthalocyanine, botanical, and natural colors, including water soluble components such as those having C.I. Names. The cleaning compositions of the present invention may also contain antimicrobial agents.

## Water

In some aspects, the compositions comprise from about 50% to about 95%, or from about 60% to about 90%, or from about 65% to about 81%, by weight of the composition, water. In some aspects, the compositions comprise at least 50%, or at least 60%, or at least 70%, or at least 75%, or at least 80%, or at least 85% water. When the composition is in concentrated or unit dose form, the composition may comprise less than about 50% water, or less than 30% water, or less than 20% water, or less than 10% water, or less than 5% water. In some aspects, the composition comprises from about 1% to about 40%, or from about 2% to about 25%, or from about 3% to about 20%, or from about 4% to about 15%, or from about 5% to about 10%, by weight of the composition, water.

## Viscosity

The detergent compositions of the present disclosure may be in gel, pourable gel, non-pourable gel, liquid, or heavy duty liquid form. In some aspects, the compositions have viscosities of from about 150 cps to about 10,000 cps, or from about 200 cps to about 1500 cps,

or from about 225 cps to about 1200 cps, or from about 250 cps to about 800 cps. Unless specifically indicated to the contrary, all stated viscosities are those measured at a shear rate of  $20 \text{ s}^{-1}$  at a temperature of  $21.1^\circ\text{C}$ . Viscosity herein can be measured with any suitable viscosity-measuring instrument, *e.g.*, a Carrimed CSL2 Rheometer at a shear rate of  $20 \text{ sec}^{-1}$ .

5 Phase

In some aspects, the composition is present in a single phase after storage for four weeks at  $22^\circ\text{C}$ . Additionally, the disclosed compositions may be isotropic at  $22^\circ\text{C}$ . By "isotropic," it means a clear mixture, having a % transmittance of greater than 50% at a wavelength of 570 nm measured via a standard 10 mm pathlength cuvette with a Beckman DU spectrophotometer, in  
10 the absence of dyes and/or opacifiers.

Water-Soluble Film

The compositions of the present invention may also be encapsulated within a water-soluble film, for example to form a unit dose article. Preferred film materials are preferably polymeric materials. The film material can, for example, be obtained by casting, blow-moulding,  
15 extrusion or blown extrusion of the polymeric material, as known in the art.

Preferred polymers, copolymers or derivatives thereof suitable for use as pouch material are selected from polyvinyl alcohols, polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts, polyaminoacids or peptides, polyamides, polyacrylamide,  
20 copolymers of maleic/acrylic acids, polysaccharides including starch and gelatine, natural gums such as xanthum and carragum. More preferred polymers are selected from polyacrylates and water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose sodium, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltodextrin, polymethacrylates, and most preferably selected from polyvinyl alcohols, polyvinyl alcohol  
25 copolymers and hydroxypropyl methyl cellulose (HPMC), blends of polyvinyl alcohols, and combinations thereof. Preferably, the level of polymer in the pouch material, for example a PVA polymer, is at least 60%. The polymer can have any weight average molecular weight, preferably from about 1000 to 1,000,000, more preferably from about 10,000 to 300,000 yet more preferably from about 20,000 to 150,000. Mixtures of polymers can also be used as the  
30 pouch material.

Naturally, different film material and/or films of different thickness may be employed in making the compartments of the present invention. A benefit in selecting different films is that the resulting compartments may exhibit different solubility or release characteristics.

Most preferred film materials are PVA films known under the MonoSol (Merrillville, Indiana, USA) trade reference M8630, M8900, H8779, and those described in US 6 166 117, US 6 787 512, and USPA 2011/0188784A1, and PVA films of corresponding solubility and deformability characteristics.

5       The film material herein can also comprise one or more additive ingredients. For example, it can be beneficial to add surfactants and/or plasticisers, for example glycerol, ethylene glycol, diethyleneglycol, propylene glycol, sorbitol and mixtures thereof. Other additives include functional detergent additives to be delivered to the wash water, for example organic polymeric dispersants, etc.

#### 10       Method of Making

The detergent compositions of the present invention can be formulated into any suitable form and prepared by any process chosen by the formulator, non-limiting examples of which are described in U.S. Patent Nos. 5,879,584; 5,691,297; 5,574,005; 5,569,645; 5,565,422; 5,516,448;  
15   5,489,392; and 5,486,303.

In one aspect, the detergent compositions disclosed herein may 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 one aspect, a liquid matrix is formed containing at least a major proportion, or even substantially all, of the  
20   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, the carboxymethylated polyethyleneimine compound and substantially all of any anionic surfactant and the solid  
25   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  
30   prills, are incorporated. As a variation of the composition preparation procedure described above, 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.

#### Method of Using

5           The present disclosure also relates to a method of treating a surface, wherein the method comprises the step of contacting a surface with the detergent composition described herein. The detergent compositions of the present disclosure may be used to clean, treat, and/or pretreat a surface, such as a fabric. Typically at least a portion of the surface is contacted with the  
10           aforementioned detergent compositions, in neat form or diluted in a liquor, e.g., a wash liquor, and then the surface fabric may be optionally washed and/or rinsed. In one aspect, a surface is optionally washed and/or rinsed, contacted with the aforementioned detergent compositions and then optionally washed and/or rinsed. In another aspect, the detergent composition is applied onto a surface, e.g., a soiled fabric, and left to act on the surface before the surface is washed. The composition may remain in contact with the surface until dry or for a longer period of time,  
15           or for a period of 1 minute to 24 hours, or 1 minute to 1 hour, or 5 minutes to 30 minutes. For purposes of the present invention, washing includes, but is not limited to, scrubbing, brushing, and mechanical agitation. Typically after washing and/or rinsing, the surface is dried. The surface may be a fabric that comprises most any fabric capable of being laundered or treated.

          The detergent compositions of the present disclosure may be used to form aqueous  
20           washing solutions for use in the laundering of fabrics. Generally, an effective amount of such compositions is added to water, for example in a conventional fabric laundering automatic washing machine or by a hand washing method, to form such aqueous laundering solutions. The aqueous washing solution so formed is then contacted, sometimes under agitation, with the fabrics to be laundered therewith. An effective amount of the detergent composition, such as the  
25           HDL detergent compositions of the present disclosure, may be added to water to form aqueous laundering solutions that may comprise from about 200 to about 15,000 ppm or even from about 300 to about 7,000 pm of detergent composition.

          In some aspects, the carboxymethylated polyalkylenimines described herein may be used as a whitening agent. In some aspects, the carboxymethylated polyalkylenimines described  
30           herein may be used as cleaning agent.

#### EXAMPLES

          The following examples illustrate compositions of the present disclosure. It will be appreciated that other modifications of the present disclosure within the skill of those in the art



can be undertaken without departing from the spirit and scope of this disclosure. All of the formulations exemplified hereinafter are prepared via conventional formulation and mixing methods unless specific methods are given.

All parts, percentages, and ratios herein are by weight unless otherwise specified. Some components may come from suppliers as dilute solutions. The levels given reflect the weight percent of the active material, unless otherwise specified. Carriers and other materials are included as “Minors”.

#### Example 1. Whiteness benefits

For the whiteness benefit test, the following laundry detergent composition is provided in Table 1.1.

Table 1.1.

<b>Ingredient</b>	<b>%</b>
LAS	11.3
AE1.8S	23.8
Dimethylhydroxyethyl lauryl ammonium chloride	1.3
NI 24-9	1.6
HSAS	3.8
Protease - Purafect® (84 mg active/g)	0.12
Amylase - Natalase® (8.65 mg active/g)	0.03
Ethoxylated Polyethylenimine	2.9
Zwitterionic ethoxylated quaternized sulfated hexamethylene diamine	4.9
Grease Cleaning Alkoxylated Polyalkylenimine Polymer	2.9
Fluorescent Whitening Agent 15	0.4
Water, Solvents, Stabilizers	Balance

Test preparation:

The following fabrics are provided for the whiteness benefit test:

Polyester 1: Polyester 854, available from Reichenbach (Wirkstoffe, Germany)

Polyester 2: PW19, available from Empirical Manufacturing Company (Cincinnati, OH, USA).

Knitted Cotton 1: CW120, available from Empirical Manufacturing Company (Cincinnati, OH, USA).

“Washed and FE Treated” fabrics were prepared according to the following method: 400g fabrics are washed in a WE Miniwasher (3.5 litre water) twice using the short program (45 minute wash cycle followed by three rinse cycles; total program is 90 minutes) at 60°C with 18.6g Ariel Compact powder detergent, twice using the short program, at 60°C nil detergent, and then three times using the short program at 40°C with 8.2 g Lenor Concentrate (a fabric enhancer) into each main wash. Fabrics are then dried in a tumble dryer on extra dry until dry.

“Washed” fabrics were prepared according to the following method: 400g fabrics are washed in a WE Miniwasher (3.5 litre water) twice using the short program (45 minute wash cycle followed by three rinse cycles; total program is 90 minutes) at 60°C with 18.6g Ariel Compact powder detergent and twice using the short program, at 60°C nil detergent. Fabrics are then dried in a tumble dryer on extra dry until dry.

#### Test Method:

Four fabric samples are prepared: Polyester 1, washed and FE treated; Polyester 2, washed and FE treated; Knitted Cotton 1, washed and FE treated; Knitted Cotton 2, washed.

Each sample is run in a 96 well plate simulated washing system that uses magnetized bearings to simulate the agitation of a typical full scale washing machine according to the following conditions: 375 ppm detergent concentration, 150 µL water per well, 25°C, water hardness of 1.0 mM (2:1 Ca<sup>2+</sup>:Mg<sup>2+</sup> molar ratio), wash pH of 8, 3000 ppm Arizona test dust (supplied PTI, Powder Technology Inc) and 2000 ppm of an oil-artificial body soil mixture as a soil stress. The composition of the oil-artificial body soil mixture is 76% propylene glycol, 12% cooking oil and 12% artificial body soil (Empirical Manufacturing Company Cincinnati, OH, USA)

Each polymer (Polymers 1-5 and Polymer 6/Trilon® P) listed in Table 1 is added at 100 ppm of the wash solution. Ethylenediamine-N,N'-diacetic acid (EDDA) is a non-polymeric chelant used as a reference (also added at 100 ppm of the wash solution). Each fabric is washed for 60 minutes and dried in the dark under ambient conditions. For each wash condition, there are two 96 well plates, and eight internal replicates per 96 well plate, for a total of 16 replicates per wash condition.

When the samples are dry, L\*, a\*, b\* and CIE WI are measured on each 96 well plate spot using a Spectrolino imaging system (Gretag Macbeth, Spectro Scan 3.273). For each treatment, the average CIE WI is determined. Delta CIE WI, as reported in Table 1.2 below, is the difference of the average CIE WI of the sample vs. the average CIE WI of a control sample without the tested chelant / polymer.

Table 1.2 – Whiteness benefits of carboxymethylated polyethyleneimines

Component A	MW of PEI backbone	Degree of Substi- tution (%)	Delta CIE WI			
			Polyester 1, washed and FE treated	Polyester 2, washed and FE treated	Knitted Cotton 1, washed and FE treated	Knitted Cotton 1, washed
<b>EDDA</b>	--	--	-2.0	-1.2	-0.9	0.0
<b>Polymer 1</b>	25000	83%	4.6	4.5	11.0	2.0
<b>Polymer 2</b>	25000	73%	6.2	5.7	11.3	2.8
<b>Polymer 3</b>	25000	63%	4.9	4.1	13.6	2.1
<b>Polymer 4</b>	5000	90%	4.4	4.3	7.6	2.4
<b>Polymer 5</b>	800	95%	3.2	2.6	3.8	1.2
<b>Polymer 6 (TRILON® P)<sup>1</sup></b>	--	--	5.3	5.4	9.4	2.8
<b>LSD (95)</b>			1.7	1.6	1.3	1.2

<sup>1</sup> TRILON P is commercially available from BASF (Ludwigshafen, Germany)

Table 1 shows that a detergent composition comprising EDDA, a non-polymeric chelant, does not significantly improve the CIE WI vs. a detergent composition control, which does not comprise EDDA. However, compositions comprising carboxymethylated polyethyleneimines such as Trilon P and Polymers 1–5 significantly improve the CIE WI across nearly all four fabrics compared to detergent composition controls, which do not comprise carboxymethylated PEIs. A difference of +2 CIE WI units is significantly noticeable by the human eye.

#### Example 2. Stain removal benefits

The laundry detergent composition in Table 2.1 is created for testing and dosed at a wash concentration of 5988 ppm.

Table 2.1.

Ingredient	%
LAS	6.0
AE3S	2.6
Fatty Acid C1218	3.1

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NI 45-7	4.4
Citric Acid	3.2
Zwitterionic ethoxylated quaternized sulfated hexamethylene diamine	1.4
PEG-PVAc Polymer	0.5
Fluorescent Whitening Agent 36	1.2
Water, Solvents, Stabilizers, Enzymes	Balance

The Stain Removal Index (SRI) is measured using a modified version of the “Standard Guide for Evaluating Stain Removal Performance in Home Laundering” (ASTM D4265-98) with modifications as noted. Four external replicates and two internal replicates are tested for each experimental condition. The tested stains were applied to white knitted cotton fabric and are supplied by Warwick Equest (Consett, UK).

Washing takes place in a Miele W1714 frontloading washing machine. Both the detergent and chelants (DTPMP and Trilon P, each at a dose of 25 ppm of the wash solution) are dosed to the machine in a plastic cup. 2.5 kg of ballast is added to each wash load, comprising a 50:50 mixture of towels and bedsheets without a fabric softener history. The machine is set to the Cotton Cycle, Short Program, 30°C with a 1600 rpm Spin. Four SBL2004 Soil Sheets (WFK, Brüggem-Bracht, Germany) are added as a soil stress and the water hardness is 20.8 grains per gallon. Fabrics are then dried in ambient conditions. Image analysis is conducted pre- and post-wash to calculate the stain removal index (SRI). The SRI for Products 1, 2, and 3 are reported in Table 2.2, as well as the Delta SRI of Products 2 and 3 as compared to Product 1.

Table 2.2 – Stain removal benefits

	<b>Product 1: Detergent from Table 2.1</b>	<b>Product 2: Detergent from Table 2.1 + 25 ppm DTPMP</b>		<b>Product 3: Detergent from Table 2.1 + 25 ppm Trilon® P</b>		
<b>Soil</b>	<b>SRI</b>	<b>SRI</b>	<b>Delta SRI</b>	<b>SRI</b>	<b>Delta SRI</b>	<b>HSD</b>
Blueberry	44.2	56.6	12.4 <sup>#</sup>	64.4	20.2 <sup>*</sup>	6.43

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Coffee	63.1	67.0	3.9	70.3	7.2 <sup>#</sup>	5.28
Gravy	54.7	59.8	5.1	65.9	11.2 <sup>#</sup>	6.62
Red Wine	48.6	57.3	8.7 <sup>#</sup>	61.0	12.4 <sup>#</sup>	6.33
Scrubbed Grass Medium	67.1	72.8	5.7	77.0	9.9 <sup>#</sup>	9.43
Tea	20.2	22.5	2.3	28.3	8.1	10.95
Vinaigrette	88.9	90.0	1.1	92.0	3.1 <sup>#</sup>	2.80

# Significant vs. Product 1

\*Significant vs. Products 1 and 2

The results show that detergents comprising Trilon® P provides significant stain removal benefits across a wide variety of stains vs. detergent alone. Furthermore, the results show that at equal ppm, Trilon® P provides increased stain removal across a wide variety of stains as compared to DTPMP.

### Example 3. Formulations

Table 3 – Granular laundry detergent compositions

Ingredient	1 (wt %)	2 (wt %)	3 (wt %)	4 (wt %)	5 (wt %)	6 (wt %)
Carboxymethylated polyalkyleneimine (e.g., Trilon P)	0.1	0.5	0.5	1	1	2
LAS	20	8	20	15	19.5	20
C <sub>12-14</sub> Dimethylhydroxyethyl ammonium chloride	4	0.2	1	0.6	0.0	0
AES	0.9	1	0.9	0.0	4	0.9
AE	0.0	0.0	0.0	1	0.1	4
Sodium tripolyphosphate	5	0.0	4	9	2	0.0
Zeolite A	0.0	1	0.0	1	4	1
1.6R Silicate (SiO <sub>2</sub> :Na <sub>2</sub> O at ratio 1.6:1)	10	5	2	3	3	5
Sodium carbonate	25	20	25	15	18	30

Acrylate Polymer	1	0.6	4	1	1.5	1
PEG-PVAc Polymer	0.1	0.2	0.0	4	0.05	0.0
Carboxymethyl cellulose	1	0.3	1	1	1	2
Stainzyme® (20 mg active/g)	0.1	0.2	0.1	0.2	0.1	0.1
Protease (Savinase®, 32.89 mg active/g)	0.1	0.1	0.1	0.1	0.4	0.1
Amylase - Natalase® (8.65 mg active /g)	0.2	0.0	0.1	0.0	0.1	0.1
Lipase - Lipex® (18 mg active /g)	0.03	0.07	0.3	0.1	0.07	1.0
Fluorescent Brightener	0.06	0.0	0.18	0.4	0.1	0.06
Chelant	0.6	1.0	0.6	0.2	0.6	0.6
MgSO <sub>4</sub>	1	1	1	0.5	1	1
Sulphonated zinc phthalocyanine	0.1	0.0	0.0012	0.01	0.0021	0.0
Hueing Agent	0.0	0.0	0.0003	0.001	0.01	0.1
Sulfate/ Water & Miscellaneous	Balance					

Table 4 – Granular laundry detergent compositions

Ingredient	7 (wt%)	8 (wt%)	9 (wt%)	10 (wt%)	11 (wt%)	12 (wt%)	13 (wt%)
Carboxymethylated polyalkyleneimine (e.g., Trilon P)	0.1	0.5	0.5	1	1	2	0.5
LAS	8	7.1	15	6.5	7.5	7.5	2.0
AES	0	4.8	1.0	5.2	4	4	2.5
AS	1	0	1	0	0	0	0.5
AE	2.2	0	2.2	0	0	0	6.5
C <sub>10-12</sub> Dimethyl hydroxyethylammonium chloride	0.5	1	4	1	0	0	0

Crystalline layered silicate ( $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$ )	4	0	5	0	10	0	0
Zeolite A	5	0	5	0	2	2	0.5
Citric Acid	3	5	3	4	2.5	3	2.5
Sodium Carbonate	15	20	14	20	23	30	23
Silicate 2R ( $\text{SiO}_2:\text{Na}_2\text{O}$ at ratio 2:1)	0.08	0	1	0	10	0	0
Soil release agent	2	0.72	0.71	0.72	0	0	0
Acrylate Polymer	1.1	3.7	1.0	3.7	2.6	3.8	4
Carboxymethylcellulose	0.15	1.4	0.2	2	1	0.5	0.5
Protease - Purafect® (84 mg active/g)	0.2	0.2	0.4	0.15	0.1	0.13	0.13
Amylase – Stainzyme Plus® (20 mg active/g)	0.2	0.15	0.2	0.3	0.15	0.15	0.15
Lipase - Lipex® (18.00 mg active/g)	0.05	0.15	0.1	0	0	0	0
Amylase - Natalase® (8.65 mg active/g)	0.1	0.2	0	0	0.15	0.15	0.15
Cellulase - Celluclean™ (15.6 mg active/g)	0	0	0	0	0.1	0.1	0.2
Chelant	0.2	0.5	1	0.2	0.2	0.4	0.2
$\text{MgSO}_4$	0.42	0.42	0.42	0.42	0.4	0.4	0.4
Perfume	0.1	0.6	0.5	0.6	0.6	0.6	1.0
Suds suppressor agglomerate	0.05	0.1	0	0.1	0.06	0.05	0.05
Soap	0.45	0.45	0.45	1	0	0	0
Sulphonated zinc phthalocyanine	0.0007	0.0012	0.0007	0.1	0.001	0	0
Hueing Agent	0	0.03	0.0001	0.0001	0	0	0.1
Sulfate/ Water & Miscellaneous	Balance						

Table 5 – Heavy Duty Liquid laundry detergent

	14 (wt%)	15 (wt%)	16 (wt%)	17 (wt%)	18 (wt%)	19 (wt%)	20 (wt%)
Carboxymethylated polyalkyleneimine (e.g., Trilon P)	0.1	0.5	0.5	1	1	2	0.5

AES	17	10	4	6.32	1	6	0
LAS	1.4	4	8	3.3	5	8	19
HSAS	2	5.1	3	0	0	0	0
AE	0.4	0.6	0.3	1.5	2.4	60	20.0
Lauryl Trimethyl Ammonium Chloride	0	1	0.5	0	0.25	0	0
C <sub>12-14</sub> dimethyl Amine Oxide	0.3	1	0.23	0.37	0	0	0
Sodium formate	1.6	0.09	1.2	0	1.6	0	0.2
Calcium formate	0	0	0	0.04	0	0.13	0
Calcium Chloride	0.01	0.08	0	0	0	0	0
Monoethanolamine	1.4	1.0	4.0	0.5	0	0	To pH 8.2
Diethylene glycol	5.5	0.0	4.1	0.0	0.7	0	0
Chelant	0.15	0.15	0.11	0.07	0.5	0.11	0.8
Citric Acid	2.5	3.96	1.88	1.98	0.9	2.5	0.6
C <sub>12-18</sub> Fatty Acid	0.8	3.5	0.6	0.99	1.2	0	15.0
4-formyl-phenylboronic acid	0	0	0	0	0.1	0.02	0.01
Borax	1.43	2.1	1.1	0.75	0	1.07	0
Ethanol	1.54	2	1.15	0.89	0	3	7
Ethoxylated Polyethylenimine	0	1.4	0	2.5	0	0	0.8
Zwitterionic ethoxylated quaternized sulfated hexamethylene diamine	2.1	0	0.7	1.6	0.3	1.6	0
PEG-PVAc Polymer	0.1	0.2	0.0	4	0.05	0.0	1
Grease Cleaning Alkoxylated Polyalkylenimine Polymer	1	2	0	0	1.5	0	0
1,2-Propanediol	0.0	6.6	0.0	3.3	0.5	2	8.0
Cumene sulphonate	0.0	0.0	0.5	1	2	0	0
Fluorescent Brightener	0.2	0.1	0.05	0.3	0.15	0.3	0.2
Hydrogenated castor oil derivative structurant	0.1	0	0.4	0	0	0	0.1
Perfume	1.6	1.1	1.0	0.1	0.9	1.5	1.6
Core Shell Melamine-formaldehyde encapsulate of	0.5	0.05	0.00	0.02	0.1	0.05	0.1



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perfume							
Protease (40.6 mg active/g)	0.8	0.6	0.7	0.9	0.7	0.2	1.5
Mannanase: Mannaway® (25 mg active/g)	0.07	0.05	0	0.06	0.04	0.045	0.1
Amylase: Stainzyme® (15 mg active/g)	0.3	0	0.3	0.1	0	0.6	0.1
Amylase: Natalase® (29 mg active/g)	0	0.6	0.1	0.15	0.07	0	0.1
Xyloglucanase (Whitezyme®, 20mg active/g)	0.2	0.1	0	0	0.05	0.05	0.2
Lipex® (18 mg active/g)	0.4	0.2	0.3	0.1	0.2	0	0
*Water, dyes & minors	Balance						

\*Based on total cleaning and/or treatment composition weight

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Table 6 – Unit Dose Compositions

The following compositions are encapsulated in a single- or multi-compartment pouch formed by water-soluble film, for example M8630 film, available from MonoSol (Merrillville, Indiana, USA), or film according to US Patent Application 2011/0188784A1.

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<b><u>Ingredient</u></b>	<b>21</b>	<b>22</b>	<b>23</b>	<b>24</b>	<b>25</b>
Carboxymethylated polyalkyleneimine (e.g., Trilon P)	0.1	0.5	1	2	4
LAS	22.6	20.0	14.5	14.5	14.5
AES	7.5	16.0	7.5	7.5	7.5
AE	13.0	3.0	16.0	4.0	13.0
Citric Acid	1	0.6	0.6	1.56	0.6
C <sub>12-18</sub> Fatty Acid	4.5	10	4.5	14.8	4.5
Enzymes	1.0	1.7	1.7	2.0	1.7
Ethoxylated Polyethylenimine	1.4	1.4	4.0	6.0	4.0
Chelant	0.6	0.6	1.2	1.2	3.0
PEG-PVAc Polymer	4	2.5	4	2.5	1.5

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Fluorescent Brightener	0.15	0.4	0.3	0.3	0.3
1,2 propanediol	6.3	13.8	13.8	13.8	13.8
Glycerol	12.0	5.0	6.1	6.1	6.1
Monoethanolamine	9.8	8.0	8.0	8.0	9.8
TIPA	-	-	2.0	-	-
Triethanolamine	-	2.0	-	-	-
Cumene sulphonate	-	-	-	-	2.0
Cyclohexyl dimethanol	-	-	-	2.0	-
Water	12	10	10	10	10
Structurant	0.1	0.14	0.14	0.1	0.14
Perfume	0.2	1.9	1	1.9	1.9
Hueing Agent	0	0.1	0.001	0.0001	0
Buffers (monoethanolamine)	To pH 8.0				
Solvents (1,2 propanediol, ethanol)	To 100%				

Table 7 – Laundry Additive Detergent Formulations

Ingredients	<b>26</b>	<b>27</b>	<b>28</b>	<b>29</b>	<b>30</b>	<b>31</b>
Carboxymethylated polyalkyleneimine (e.g., Trilon P)	0.1	0.5	1	2	4	1
AES	11.3	6.0	15.4	16.0	12.0	10.0
LAS	25.6	12.0	4.6	-	-	26.1
HSAS	-	-	-	3.5	-	-
Chelant	2.5	-	1.5	-	-	4.0
1,2-propandiol	-	10	-	-	-	15
Soil release agent	2.0					
Ethoxylated Polyethylenimine		1.8				
Acrylate Polymer			2.9			
Acusol 880 (Hydrophobically Modified Non-Ionic Polyol)				2.0	1.8	2.9
Protease (55mg/g active)	-	-	-	-	0.1	0.1
Amylase (30mg/g active)	-	-	-	-	-	0.02

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Perfume	-	0.2	0.03	0.17	-	0.15
Fluorescent Brightener	0.21	-	-	0.15	-	0.18
Water, other optional agents/components*	to 100% balance	to 100% balance	to 100% balance	to 100% balance	to 100% balance	to 100% balance

\*Other optional agents/components include suds suppressors, structuring agents such as those based on Hydrogenated Castor Oil (preferably Hydrogenated Castor Oil, Anionic Premix), solvents and/or Mica pearlescent aesthetic enhancer.

#### 5 Raw Materials and Notes For Composition Examples

LAS is linear alkylbenzenesulfonate having an average aliphatic carbon chain length C<sub>9</sub>-C<sub>15</sub> supplied by Stepan, Northfield, Illinois, USA or Huntsman Corp. (HLAS is acid form).

AES is selected from C<sub>12-15</sub> alkyl ethoxy (3) sulfate supplied by Stepan, Northfield, Illinois, USA and AES is C<sub>10-18</sub> alkyl ethoxy (1.8) sulfate supplied by Shell Chemicals.

- 10 AE is selected from C<sub>12-13</sub> with an average degree of ethoxylation of 6.5, C<sub>11-16</sub> with an average degree of ethoxylation of 7, C<sub>12-14</sub> with an average degree of ethoxylation of 7 and C<sub>14-15</sub> with an average degree of ethoxylation of 7, all supplied by Huntsman, Salt Lake City, Utah, USA

AS is a C<sub>12-14</sub> Alkylsulfate, supplied by Stepan, Northfield, Illinois, USA

HSAS is mid-branched alkyl sulfate as disclosed in US 6,020,303 and US 6,060,443

- 15 C<sub>12-14</sub> Dimethylhydroxyethyl ammonium chloride, supplied by Clariant GmbH, Germany  
C<sub>12-14</sub> dimethyl Amine Oxide is supplied by Procter & Gamble Chemicals, Cincinnati, USA  
Sodium tripolyphosphate is supplied by Rhodia, Paris, France  
Zeolite A is supplied by Industrial Zeolite (UK) Ltd, Grays, Essex, UK  
1.6R Silicate is supplied by Koma, Nestemica, Czech Republic

- 20 Sodium Carbonate is supplied by Solvay, Houston, Texas, USA

Acrylate Polymer can be selected from Polyacrylate MW 4500, Acrylic Acid/Maleic Acid Copolymer of 70,000 and acrylate:maleate ratio 70:30 supplied by BASF, Ludwigshafen, Germany or modified acrylate polymers disclosed in Acrylic Acid/Maleic Acid Copolymer of 70,000 and acrylate:maleate ratio 70:30, supplied by BASF, Ludwigshafen, Germany

- 25 PEG-PVAc raft copolymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is about 6000 and the weight ratio of the polyethylene oxide

to polyvinyl acetate is about 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units. Available from BASF (Ludwigshafen, Germany).

Ethoxylated Polyethylenimine is a 600 g/mol molecular weight polyethylenimine core with 20 ethoxylate groups per -NH. Available from BASF (Ludwigshafen, Germany)

- 5 Zwitterionic ethoxylated quaternized sulfated hexamethylene diamine is described in WO 01/05874 and available from BASF (Ludwigshafen, Germany)

Grease Cleaning Alkoxylated Polyalkylenimine Polymer is a 600 g/mol molecular weight polyethylenimine core with 24 ethoxylate groups per -NH and 16 propoxylate groups per -NH. Available from BASF (Ludwigshafen, Germany)

- 10 Carboxymethyl cellulose is Finnfix® V supplied by CP Kelco, Arnhem, Netherlands  
Savinase®, Natalase®, Stainzyme®, Lipex®, Celluclean™, Mannaway® and Whitezyme® are all products of Novozymes, Bagsvaerd, Denmark. Proteases may be supplied by Genencor International, Palo Alto, California, USA (e.g. Purafect Prime®) or by Novozymes, Bagsvaerd, Denmark (e.g. Liquanase®, Coronase®). All enzyme levels are expressed as % enzyme raw  
15 material.

Fluorescent Brightener is selected from Tinopal® AMS and Tinopal® CBS-X supplied by BASF, Ludwigshafen, Germany.

- Chelant is selected from, diethylenetetraamine pentaacetic acid (DTPA) supplied by Dow Chemical, Midland, Michigan, USA, hydroxyethane di phosphonate (HEDP) supplied by Solutia,  
20 St Louis, Missouri, USA; Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer (EDDS) supplied by Octel, Ellesmere Port, UK, Diethylenetriamine penta methylene phosphonic acid (DTPMP) supplied by Thermphos and 1,2-dihydroxybenzene-3,5-disulfonic acid supplied by Future Fuels Batesville, Arkansas, USA

Sulphonated zinc phthalocyanine is supplied by BASF, Ludwigshafen, Germany.

- 25 Hueing agents such as Direct Violet 9 and Direct Violet 99 may be supplied by BASF, Ludwigshafen, Germany. Those described in US Patent Applications 2012/0101018A1 and 2012/0304402A1 may be supplied by Milliken.

Soil release agent is Repel-o-tex® PF, supplied by Rhodia, Paris, France

Suds suppressor agglomerate is supplied by Dow Corning, Midland, Michigan, USA

- 30 Acusol 880 is supplied by Dow Chemical, Midland, Michigan, USA

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.”

5 Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning  
10 or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present disclosure have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the disclosure. It is  
15 therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this disclosure.

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CLAIMS

What is claimed is:

1. A detergent composition comprising:  
anionic surfactant; and  
a carboxymethylated polyalkyleneimine;  
wherein the detergent composition is substantially free of bleach.
2. The composition according to claim 1, wherein the carboxymethylated polyalkyleneimine has a weight average molecular weight of from 1500 to 100,000 daltons, preferably from 20,000 to 60,000 daltons.
3. The composition according to any preceding claim, wherein the carboxymethylated polyalkyleneimine comprises a polyethyleneimine (PEI) backbone, preferably wherein the polyethyleneimine (PEI) backbone, when unsubstituted, has a weight average molecular weight of from 500 to 50,000 daltons, more preferably from 5000 to 25,000 daltons.
4. The composition according to any preceding claim, wherein the carboxymethylated polyalkyleneimine has a degree of substitution of from 30% to 99%, preferably from 60% to 98%.
5. The composition according to any preceding claim, wherein the composition comprises from 0.05% to 5% by weight of the composition of carboxymethylated polyalkyleneimine.
6. The composition according to any preceding claim, wherein the composition comprises from 1% to 75% by weight of the composition anionic surfactant, preferably wherein the anionic surfactant comprises linear alkyl benzene sulfonate and alkyl ether sulfate.
7. The composition according to any preceding claim, wherein the composition further comprises a fabric hueing agent, preferably wherein the fabric hueing agent is selected from the group consisting of anthraquinone dyes, azine dyes, azo dyes, and mixtures thereof.
8. The composition according to any preceding claim, wherein the composition further comprises nonionic surfactant.

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9. The composition according to any preceding claim, wherein the composition is encapsulated in a water-soluble film or pouch.

10. The composition according to any preceding claim, wherein the carboxymethylated polyalkyleneimine is characterized by a degree of substitution of from 30% to 75%, and, optionally, a weight average molecular weight of from 25,000 daltons to 75,000 daltons.

11. The composition according to any preceding claim, wherein the carboxymethylated polyalkyleneimine is characterized by a weight average molecular weight of from 1000 daltons to 45,000 daltons, and, optionally, a degree of substitution of from 80% to 99%.

12. A method of treating a surface, wherein the method comprises the step of contacting a surface with the detergent composition of any preceding claim.

13. A detergent composition comprising:

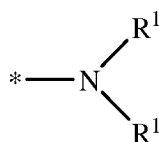
anionic surfactant; and

a carboxymethylated polyalkyleneimine;

wherein the detergent composition is substantially free of bleach;

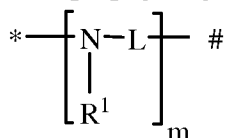
and wherein the carboxymethylated polyalkyleneimine comprises moieties selected from the following:

(a) chain initiating groups A of Formula I:



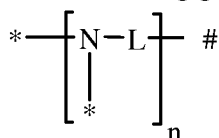
Formula I;

(b) chain propagating groups Q of Formula II:



Formula II;

(c) chain branching groups Q' of Formula III:

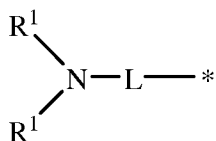


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Formula III;

(d) chain terminating groups T of Formula IV:



Formula IV;

and mixtures thereof, where each  $\text{R}^1$  is independently selected from H,  $\text{CH}_2\text{COOM}$ , or (poly)alkylene oxide of formula  $(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$ , preferably wherein each  $\text{R}^1$  is independently selected from H or  $\text{CH}_2\text{COOM}$ , where each M is independently selected from H or a suitable charge balancing counterion, and where x is independently from 1 to 20, and where the molar ratio of (H moieties +  $\text{CH}_2\text{COOM}$  moieties) : ((poly)alkylene oxide moieties) is greater than 10:1, where each L is a linking group independently selected from a substituted or unsubstituted  $\text{C}_2$  or  $\text{C}_3$  alkylene group, preferably an unsubstituted  $\text{C}_2$  alkylene group; where the asterisk (\*) represents a point of attachment to the L of any Q, Q' or T group; where the number sign (#) represents a point of attachment to the N of any A, Q, or Q' group; and where m and n are integers selected such that the weight average molecular weight of the carboxymethylated polyalkyleneimine is from 1,500 to 100,000 daltons.

14. The composition according to claim 13, wherein the weight average molecular weight of the carboxymethylated polyalkyleneimine is from 20,000 to 60,000 daltons.

15. The composition according to any of claims 13-14, wherein the composition further comprises a fabric hueing agent.



## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2015/033866

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C11D3/37 C11D1/02  
ADD.

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

## B. FIELDS SEARCHED

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

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

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

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 650 962 A (WERDEHAUSEN ACHIM ET AL) 21 March 1972 (1972-03-21) claim 1; table IV	1-15
A	----- EP 2 650 352 A1 (BASF SE [DE]) 16 October 2013 (2013-10-16) claims 1-15	1-15
A	----- WO 2006/029793 A1 (BASF AG [DE]; BECKER HEIKE [DE]; BALDENIUS KAI-UWE [DE]; HARTMANN MARK) 23 March 2006 (2006-03-23) claims 1-13; tables 1-3 -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 October 2015

Date of mailing of the international search report

14/10/2015

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Authorized officer

Richards, Michael

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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