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(54) Title: DETERGENT COMPOSITION CONTAINING SUDS BOOSTING AND SUDS STABILIZING MODIFIED BIOPOLYMER

(57) Abstract: New cleaning compositions including novel suds boosting and stabilization biopolymers containing alkoxy, anionic and nitrogen containing substitution are disclosed. In particular, cleaning compositions including suds boosting and stabilization biopolymers containing modified polysaccharides having alkoxy, anionic and nitrogen containing substitution and methods of forming the same are disclosed.



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DETERGENT COMPOSITION CONTAINING SUDS BOOSTING AND SUDS STABILIZING MODIFIED BIOPOLYMER

FIELD OF THE INVENTION

The present invention relates to suds boosting and stabilizing modified biopolymers in detergent compositions. More particularly, the biopolymers in the present invention relate to detergent compositions that provide suds boosting and stabilization benefits in fabric care products, dish care products and other cleaning products or applications where cleaning of surfaces is needed.

BACKGROUND OF THE INVENTION

Although automatic mechanical washing has been widely accepted and used nowadays, there are still many situations where people need to do hand-washing, such as the washing needs for delicate garments, dishes and/or items which need special care. Indeed, in many developing countries, consumers' washing habit for laundry is to wash their garments with either non-automated top loaded washing machines (i.e. apparatus which comprises two separated tubs, one for washing or rinsing, and one for spinning), or in basins or buckets. The washing in basins or buckets and non-automated top loaded washing machines may involve the steps of washing with detergent, wringing or spinning, and rinsing one or more times with water.

Sudsing profile of a detergent composition, including but not be limited to speed and volume of suds generated upon dissolving the detergent composition in a washing solution, retention of suds during the washing cycle and ease in rinsing the suds in the rinsing cycle is highly valued by consumers doing hand-washing and non-automated top loaded laundry machine-washing. Suds are viewed by such consumers as an important signal that a detergent is 'working' and is an active driver of accomplishing their cleaning objectives. Thus, a rapidly generated high volume of suds and well retained suds during washing cycle are highly preferred. On the other hand, high volumes of suds in the washing cycle typically results in suds being carried over to the rinse bath solution and requiring additional time, energy and water to thoroughly rinse the laundered or cleaned items. Accordingly, quick collapse of suds in a rinsing solution is another preferred aspect of the sudsing profile of a detergent composition.

Also, a commonly known and widely used high suds detergent in the art typically comprises a high level of surfactant and builder, such as more than 15% of surfactant and more

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than 10% of builder. Recently, the impact of excessive use of such raw materials and their impact on the environment has become a serious concern as such materials exhaust non-renewable natural resources and may ultimately be discharged into the environment, such as into rivers and lakes. Further, there is a critical need to minimize the use of petrochemical based materials and increase the use renewable and biodegradable materials to improve the environmental impact of detergent chemicals. Hence, there is still a need for a detergent composition having reduced level of surfactant and/or builder, or even without builder. However, one difficulty in meeting this need is that the reduction of surfactant and/or builder in a detergent composition significantly deteriorates the sudsing profile of the detergent composition; for example, the suds generation speed and volume of suds generated is low, and suds are not well retained during the washing cycle, since hydrophobic soils (grease, oils) and hydrophilic soils (clay particulates) dispersed in the washing solution depress suds. Such a detergent composition with poor sudsing profile can be unacceptable to consumers who highly value the sudsing profile of the detergent composition.

Other detergent products such as, for example, hard surface cleaners, such as dish washing detergents, and those used in the health and beauty areas, including shampoos and soaps, may also benefit from products having improved sudsing properties.

Accordingly, there remains a need in the art of polymeric materials, specifically biopolymer materials, for new and improved suds or foam forming, retention, boosting and/or stabilization components in cleaning compositions. In addition, cleaning composition having improved suds boosting and stabilization such that the suds or foam levels are maintained for extended periods are also desired. Further, there remains critical need for a suds boosting and stabilizing biopolymer for a detergent composition containing a reduced level of total surfactant and/or builders while the sudsing profile of the detergent composition is not apparently deteriorated, i.e. a high volume of suds is generated quickly upon dissolving the detergent composition in a washing solution and suds is well-retained during washing cycle.

SUMMARY OF THE INVENTION

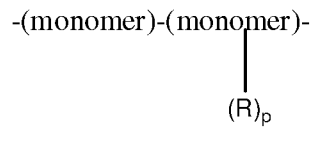
The present disclosure relates to a cleaning composition comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted linear or branched biopolymer backbone. Methods of making a cleaning composition and of treating a substrate, such as fabrics, hard surfaces, and biological surfaces are also disclosed. The present disclosure relates

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to biopolymers containing specific functional groups, where the biopolymers boost and/or stabilize suds during cleaning/treating fabrics and various other surfaces. The specific functional groups are derived from having alkoxy substitution, nitrogen containing substitution, such as amine and quaternary ammonium cation groups, and anionic substitution present with a degree of substitution (DS) from about 0.01 to about 2.0.

In particular, according to one embodiment, the present disclosure provides cleaning compositions comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted linear or branched biopolymer backbone having a structure:

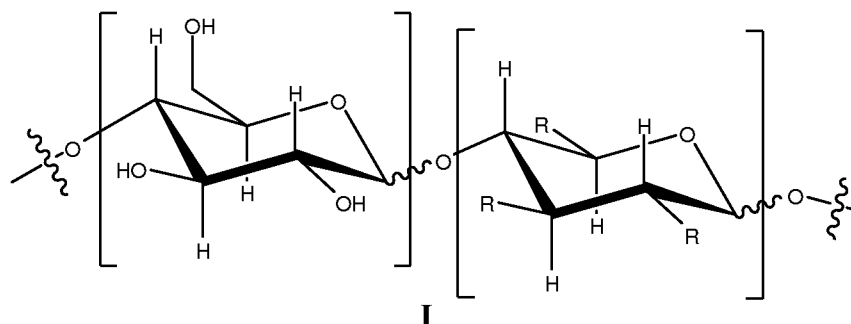


wherein the randomly substituted polymer backbone comprises the residues of at least one unsubstituted monomer and at least one substituted monomer, wherein the residues of the monomers are independently selected from the group consisting of amino acid residues, furanose residues, pyranose residues and mixtures of any thereof, and the residues of the substituted monomers further comprise -(R)_p substituent groups. Each R substituent is independently selected from an anionic substituent and a nitrogen containing substituent; or an alkoxy substituent, an anionic substituent, and a nitrogen containing substituent and p is an integer with a value from 1 to 3. The anionic substituent has a degree of substitution ranging from 0.0001 to 2.0, the nitrogen containing substituent has a degree of substitution ranging from 0.01 to 0.04, and the alkoxy substituent has a degree of substitution of 0 or ranging from 0.001 to 1.0, provided that the substituted monomer residue comprises at least one nitrogen containing substituent. The biopolymer has a ratio of the degree of substitution of the nitrogen containing substituent to the degree of substitution of the anionic substituent that ranges from 0.05:1 to 0.2:1. One embodiment of the suds boosting and stabilizing biopolymer has a weight average molecular weight ranging from 10,000 Daltons to 100,000,000 Daltons. Another embodiment of the suds boosting and stabilizing biopolymer comprises a blend of a biopolymer having a weight average molecular weight ranging from 10,000 Daltons to 1,000,000 Daltons and a biopolymer having a weight average molecular weight ranging from 1,000,000 Daltons to 100,000,000 Daltons. The nitrogen containing substituent may be either an amine substituent or a quaternary ammonium cationic substituent.

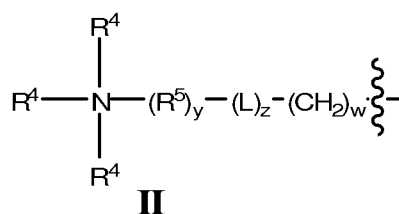
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According to another embodiment, the present disclosure provides cleaning compositions comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted polysaccharide backbone comprising unsubstituted and substituted glucopyranose residues and having a general structure according to Formula I:



wherein each substituted glucopyranose residue independently comprises from 1 to 3 R substituents, which may be the same or different on each substituted glucopyranose residue. Each R substituent is independently a substituent selected from hydroxyl, hydroxymethyl, R^1 , R^2 , R^3 and a polysaccharide branch having a general structure according to Formula I; or hydroxyl, hydroxymethyl, R^1 , R^2 and a polysaccharide branch having a general structure according to Formula I, provided that at least one R substituent comprises at least one R^1 and at least one R^2 group. Each R^1 is independently, the same or different, a first substituent group having a degree of substitution ranging from 0.01 to 0.04 and a structure according to Formula II:

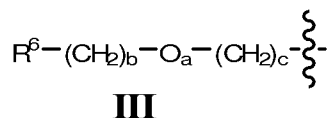


wherein each R^4 is a substituent selected from the group consisting of a lone pair of electrons; H; CH_3 ; linear or branched, saturated or unsaturated C_2 - C_{18} alkyl, provided that at least two of the R^4 groups are not a lone pair of electrons, R^5 is a linear or branched, saturated or unsaturated C_2 - C_{18} alkyl chain or a linear or branched, saturated or unsaturated secondary hydroxy(C_2 - C_{18})alkyl chain, L is a linking group selected from the group consisting of -O-, -C(O)O-, - NR^9 -, -C(O) NR^9 -, and - $NR^9C(O)NR^9$ -, and R^9 is H or C_1 - C_6 alkyl, w has a value of 0 or 1, y has a value of 0 or 1, and z has a value of 0 or 1. Each R^2 is independently, the same or different, a second

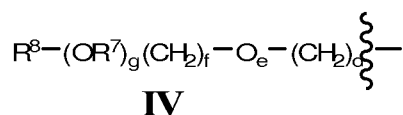
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substituent group having a degree of substitution ranging from 0.0001 to 2.0 and a structure according to Formula III:



wherein R^6 is an anionic substituent selected from the group consisting of carboxylate, carboxymethyl, succinate, sulfate, sulfonate, arylsulfonate, phosphate, phosphonate, dicarboxylate, and polycarboxylate, a has a value of 0 or 1, b is an integer from 0 to 18, and c has a value of 0 or 1. Each R^3 is independently, the same or different, a third substituent group having a degree of substitution of 0 or ranging from 0.001 to 1.0, and having a structure according to Formula IV:



wherein d has a value of 0 or 1, e has a value of 0 or 1, f is an integer from 0 to 8, g is an integer from 0 to 50, each R^7 is the group ethylene, propylene, butylene, or mixtures thereof, and R^8 is an end group selected from the group consisting of hydrogen, C_1 - C_{20} alkyl, hydroxy, $-\text{OR}^1$ and $-\text{OR}^2$. The ratio of the degree of substitution of the first substituent to the degree of substitution of the second substituent ranges from 0.05:1 to 0.2:1. One embodiment of the suds boosting and stabilizing biopolymer has a weight average molecular weight ranging from 10,000 Daltons to 100,000,000 Daltons. Another embodiment of the suds boosting and stabilizing biopolymer comprises a blend of a biopolymer having a weight average molecular weight ranging from 10,000 Daltons to 1,000,000 Daltons and a biopolymer having a weight average molecular weight ranging from 1,000,000 Daltons to 100,000,000 Daltons.

In yet another embodiment, the present disclosure provides methods for making a cleaning composition comprising adding a suds boosting and stabilizing biopolymer to the cleaning composition. The suds boosting and stabilizing biopolymer comprises a randomly substituted polysaccharide backbone comprising unsubstituted and substituted glucopyranose residues and having a general structure according to Formula I as described herein.

In a further embodiment, the present disclosure provides methods of treating a fabric comprising contacting the fabric with an effective amount of a fabric care composition comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted polysaccharide backbone comprising unsubstituted and substituted glucopyranose residues and

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having a general structure according to Formula I. The various embodiments of the present disclosure are described in greater detail herein.

In another embodiment, the present disclosure provides cleaning compositions comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted polysaccharide backbone comprising unsubstituted and substituted glucopyranose residues and having a general formula according to Formula I, wherein each substituted glucopyranose residue independently comprises from 1 to 3 R substituents, which may be the same or different on each substituted glucopyranose residue. Each R substituent is independently a substituent selected from hydroxyl, hydroxymethyl, R^2 , and a polysaccharide branch having a general structure according to Formula I, provided that at least one R substituent comprises at least one R^2 . Each R^2 is independently, the same or different a second substituent group having a degree of substitution ranging from 0.1 to 2.0 and having a structure according to Formula III. The suds boosting and stabilizing biopolymer has a weight average molecular weight ranging from 10,000 Daltons to 100,000,000 Daltons.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

As used herein, the term "cleaning composition" includes, unless otherwise indicated, detergent compositions, laundry cleaning compositions, hard surface cleaning compositions, and personal care cleaning compositions for use in the health and beauty area. Cleaning compositions include granular, powder, liquid, gel, paste, bar form and/or flake type cleaning agents, laundry detergent cleaning agents, laundry soak or spray treatments, fabric treatment compositions, dish washing detergents and soaps, shampoos, body washes and soaps, and other similar cleaning compositions. As used herein, the term "fabric treatment composition" includes, unless otherwise indicated, fabric softening compositions, fabric enhancing compositions, fabric freshening compositions and combinations thereof. Such compositions may be, but need not be, rinse added compositions.

As used herein, the term "suds boosting and stabilizing" includes biopolymer and compositions that can increase the level of suds or foam produced by the cleaning composition and/or increase the duration that the suds or foam lasts by stabilizing the bubbles in the suds or foam; compared to the suds or foam of a composition that does not contain the suds boosting and stabilizing composition or biopolymer.

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As used herein, the term "personal care cleaning composition" includes shampoos, hand washing compositions, body washing compositions, hair removal compositions, etc.

As used herein, the term "comprising" means various components conjointly employed in the preparation of the compositions of the present disclosure. Accordingly, the terms "consisting essentially of" and "consisting of" are embodied in the term "comprising".

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 term "plurality" means more than one.

As used herein, the terms "residue", "monomer residue" and "residue of a monomer" when used with reference to the structure of a polymer mean the chemical structure of the monomer unit remaining after the monomer unit has been incorporated into the polymer chain by the polymerization reaction.

As used herein, the terms "fabric", "textile", and "cloth" are used non-specifically and may refer to any type of material, including natural and synthetic fibers, such as, but not limited to, cotton, polyester, nylon, silk and the like, including blends of various fabrics.

As used herein, the term "furanose" means a cyclic form of a monosaccharide having a 5-membered furan ring. As used herein, the term "pyranose" means a cyclic form of a monosaccharide having a 6-membered pyran ring. As used herein, the term "glucopyranose" means the cyclic form of glucose having a 6-membered pyran ring.

As used herein, the term "polysaccharide" means a biopolymer made primarily from saccharide monomer units, for example, but not limited to cyclic saccharide (i.e., furanose and pyranose) monomer units.

As used herein, the term "cellulose" means a polyglucopyranose biopolymer wherein the glucopyranose residues are connected by $\beta(1 \rightarrow 4)$ glycosidic linkages and containing about 7,000 to about 15,000 glucose units. As used herein, the term "hemicellulose" includes a heteropolysaccharide obtained primarily from cell walls and contains xylose, mannose, galactose, rhamnose and arabinose residues, along with glucose residues and other monomeric sugar derived residues, connected in chains of around 200 saccharide units. As used herein, the term "starch" includes various polyglucopyranose biopolymers wherein the glucopyranose residues are connected by $\alpha(1 \rightarrow 4)$ glycosidic linkages. Starch can comprise amylose and amylopectin. As used herein, the term "amylose" includes unbranched polyglucopyranose

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biopolymers wherein the glucopyranose residues are connected by $\alpha(1\rightarrow4)$ glycosidic linkages and containing from about 300 to 10,000 glucose units. As used herein, the term "amylopectin" includes branched polyglucopyranose biopolymers wherein the glucopyranose residues are connected by $\alpha(1\rightarrow4)$ glycosidic linkages with polyglucose branches connected by $\alpha(1\rightarrow6)$ glycosidic linkages occurring approximately every 24 to 30 glucose unit and containing from about 2,000 to 200,000 glucose units.

As used herein, the term "randomly substituted" means the substituents on the monomer residues in the randomly substituted biopolymer occur in a non-repeating or random fashion. That is, the substitution on a substituted monomer residue may be the same or different (i.e., substituents (which may be the same or different) on different atoms on the monomer residues) from the substitution on a second substituted monomer residue in a biopolymer, such that the overall substitution on the polymer has no pattern. Further, the substituted monomer residues occur randomly within the biopolymer (i.e., there is no pattern with the substituted and unsubstituted monomer residues within the polymer).

As used herein, the "degree of substitution" of suds boosting and stabilizing biopolymers is an average measure of the number of hydroxyl groups on each monomeric unit which are derivatized by substituent groups. For example, in polyglucan biopolymers, such as starch and cellulose, since each anhydroglucose unit has three potential hydroxyl groups available for substitution, the maximum possible degree of substitution is 3. The degree of substitution is expressed as the number of moles of substituent groups per mole of anhydroglucose unit, on a molar average basis. There are number of ways to determine degree of substitution of suds boosting and stabilizing biopolymers. The methods used will depend on the type of substituent on biopolymer. The degree of substitution can be determined using proton nuclear magnetic resonance spectroscopy (^1H NMR) methods well-known in the art. Suitable ^1H NMR techniques include those described in "Observation on NMR Spectra of Starches in Dimethyl Sulfoxide, Iodine-Complexing, and Solvating in Water-Dimethyl Sulfoxide", Qin-Ji Peng and Arthur S. Perlin, *Carbohydrate Research*, **160** (1987), 57-72; and "An Approach to the Structural Analysis of Oligosaccharides by NMR Spectroscopy", J. Howard Bradbury and J. Grant Collins, *Carbohydrate Research*, **71**, (1979), 15-25.

As used herein, the term "average molecular weight" refers to the average molecular weight of the biopolymer chains in a biopolymer composition. Average molecular weight may

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be calculated as either the weight average molecular weight (M_w) or the number average molecular weight (M_n). Weight average molecular weight may be calculated using the equation:

$$M_w = (\sum_i N_i M_i^2) / (\sum_i N_i M_i)$$

where N_i is the number of molecules having molecular weight M_i . Number average molecular weight may be calculated using the equation:

$$M_n = (\sum_i N_i M_i) / (\sum_i N_i).$$

The weight average molecular weight may be measured according to a gel permeation chromatography ("GPC") method described in U.S. Application Publication No. 2003/0154883 A1, entitled "Non-Thermoplastic Starch Fibers and Starch Composition for Making Same." In one embodiment of the invention, starch based biopolymers may be hydrolyzed to reduce the molecular weight of such starch components. The degree of hydrolysis may be measured by Water Fluidity ("WF"), which is a measure of the solution viscosity of the gelatinized starch.

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

All percentages and ratios are calculated by weight unless otherwise indicated. All percentages and ratios are calculated based on the total composition unless otherwise indicated.

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

Suds Boosting and Stabilizing Biopolymer

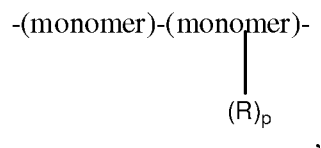
The present disclosure relates to a cleaning composition comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted linear or branched biopolymer backbone, such as a polysaccharide or polypeptide backbone. Methods of making a cleaning composition and of treating a fabric are also disclosed. The present disclosure relates to biopolymers containing specific functional groups to boost sudsing levels and/or stabilize the

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resulting suds or foam on fabrics and various surfaces, such as hard surfaces, skin, hair, and the like.

According to one embodiment, the suds boosting and stabilizing biopolymer may comprise a randomly substituted linear or branched biopolymer backbone having a structure:



wherein the randomly substituted polymer backbone comprises the residues of at least one unsubstituted monomer and at least one substituted monomer. According to certain embodiments, the residues of the substituted and unsubstituted monomers may be selected from amino acid residues, furanose residues, pyranose residues, and mixtures of any thereof. The residue of the substituted monomer may comprise -(R)_p substituent groups. According to certain embodiments, p is an integer from 1 to 3. That is, each at least one, and in specific embodiments a plurality of the residues of the monomer may be substituted monomer residues having 1, 2, or 3 substituent group R attached to the monomer residue. According to these embodiments, the randomly substituted polymer backbone must comprise at least one substituted monomer residue.

According to the various embodiments, the biopolymer is randomly substituted and may be linear or branched and each R residue on the various substituted monomer residues may be independently selected from an anionic substituent and a nitrogen containing substituent; or an alkoxy substituent, an anionic substituent and a nitrogen containing substituent. That is, according to one embodiment, the suds boosting and stabilizing biopolymer may comprise R groups selected from anionic substituents and nitrogen containing substituents; and in another embodiment, the suds boosting and stabilizing biopolymer may comprise R groups selected from alkoxy substituents, anionic substituents and nitrogen containing substituents. Various suitable structures for the alkoxy substituents, anionic substituents and the nitrogen containing substituents are described in detail herein. As used herein, the term "nitrogen containing substituents" include both quaternary ammonium cationic substituents and amine substituents (i.e., primary, secondary, and tertiary amine substituents) that may form ammonium cationic substituents after protonation, for example, under at least mildly acidic conditions.

In certain embodiments of the cleaning composition, the randomly substituted biopolymer backbone may be a randomly substituted polysaccharide backbone. For example, in

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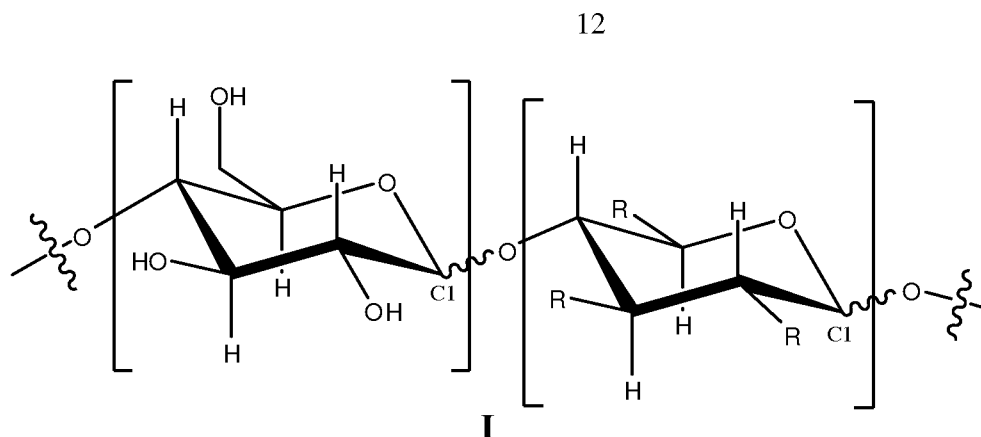
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specific embodiments, the randomly substituted polysaccharide backbone may be a randomly substituted polyglucose backbone, such that the residue of the monomer is an unsubstituted glucopyranose residue or a substituted glucopyranose residue. Examples of randomly substituted polyglucose backbones include, but are not limited to, randomly substituted cellulose backbones, randomly substituted hemicellulose backbone, a randomly substituted starch backbone (such as a randomly substituted amylose backbone or a randomly substituted amylopectin backbone, or mixtures thereof), and blends of any thereof. For example, when the polyglucose backbone is a randomly substituted hemicellulose backbone, the backbone may further comprise one or more non-glycopyranose saccharide residues, such as, but not limited to xylose, mannose, galactose, rhamnose and arabinose residues.

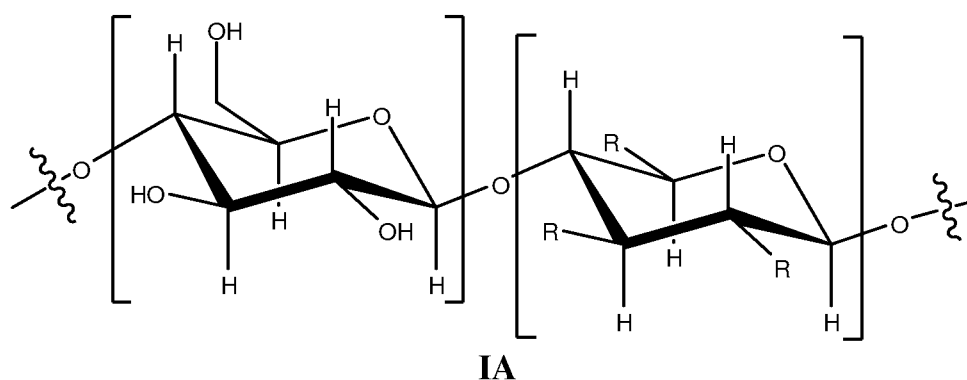
According to various embodiments of the cleaning composition, the composition may further comprise one or more additional adjuncts. For example, suitable adjuncts for a fabric care cleaning composition may include, but are not limited to, bleach activators, surfactants, builders, chelating agents, dye transfer inhibiting agents, dispersants, enzymes, enzyme stabilizers, catalytic metal complexes, polymeric dispersing agents, clay and soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, perfumes, perfume delivery systems, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids, pigments, and various combinations of any thereof. According to certain embodiments, the cleaning composition may be a fabric care composition such as a liquid laundry detergent (including, for example, a heavy duty liquid ("HDL") laundry detergent), a solid laundry detergent, a laundry soap product, or a laundry spray treatment product. In addition, the suds boosting and stabilizing biopolymer described according to the various embodiments herein, may be included in any cleaning formulation (such as a fabric care formulation, hard surface cleaning compositions, dish cleaning formulation, personal care cleaning formulation, etc.) or other formulation (such as agrochemical foaming compositions, oil-field foaming compositions and/or fire-fighting foaming compositions) in which suds boosting and stabilizing are desired.

According to specific embodiments, the present disclosure provides for a cleaning composition comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted polysaccharide backbone comprising unsubstituted and substituted glucopyranose residues and having a general structure according to Formula I, below:

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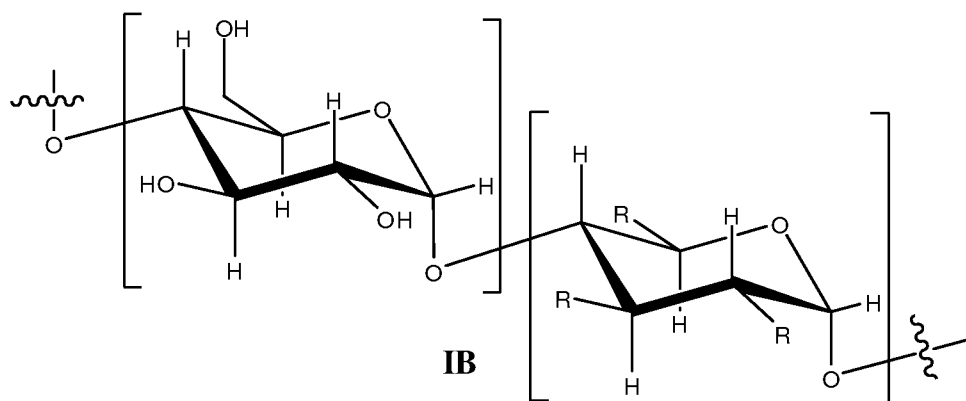
where the stereochemistry at the C1 anomeric carbon is determined, at least in part, by the source of the polysaccharide. As discussed herein, the randomly substituted polysaccharide backbone may be a randomly substituted cellulose backbone (i.e., C1 stereochemistry is β) or a randomly substituted starch backbone (i.e., C1 stereochemistry is α). According to those embodiments where the polysaccharide is a randomly substituted cellulose backbone, the randomly substituted cellulose backbone may have a general structure according to Formula IA:



According to those embodiments where the polysaccharide is a randomly substituted starch backbone, the randomly substituted starch backbone may have a general structure according to Formula IB:

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It should be noted for any of Formulae I, IA, or IB, that the structural representation depicted herein is not meant to infer any arrangement of the substituted or unsubstituted glucopyranose residues or any ratio of substituted or unsubstituted glucopyranose residues.

In these embodiments, the polysaccharide backbone, such as, the cellulose, the hemicellulose or the starch backbone, has been chemically modified to include one or more substituents on the substituted glucopyranose residues. Certain reactions suitable for modifying the starch are described in detail in the Examples section.

Referring to any of Formulae I, IA, or IB, each substituted glucopyranose residue may independently comprise from 1 to 3 -R substituents, which may be the same or different on each substituted glucopyranose residue. That is, the number and type of substituent on a substituted glucopyranose residue may be the same as or different from the other substituted glucopyranose residues in the biopolymer backbone. For example, and not to imply any particular preferred substitution pattern, one substituted glucopyranose residue may have a substituent on the C2 carbon, such as an anionic substituent, whereas another substituted glucopyranose residue in the polysaccharide may be unsubstituted at the C2 carbon, but have a nitrogen containing substituent at the C3 carbon and an alkoxy substituent at the C6 carbon.

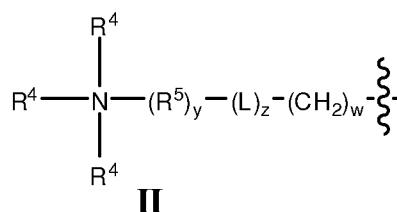
According to one embodiment, the R substituent in any of Formulae I, IA, or IB may each be independently a substituent selected from hydroxyl, hydroxymethyl, R^1 , R^2 , R^3 , and a polysaccharide branch having a general structure according to Formulae I, IA, or IB, provided that at least one of the R substituents on the substituted glucopyranose residue is R^1 , R^2 , or R^3 . In specific compositions a plurality of R substituents are R^1 , R^2 , and R^3 . In another embodiment, the R substituent in any of Formulae I, IA, or IB may each be independently a substituent selected from hydroxyl, hydroxymethyl, R^1 , R^2 , and a polysaccharide branch having a general structure according to Formulae I, IA, or IB, provided that at least one of the R

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substituents on the substituted glucopyranose residue is R^1 or R^2 . In specific compositions a plurality of R substituents are R^1 and R^2 . In those embodiments where the R substituent is a polysaccharide branch, the polysaccharide branch may be bonded to the polysaccharide backbone by a glycosidic bond formed by reaction of a hydroxyl group on a substituted glucopyranose residue in the backbone and a C1 anomeric carbon of the polysaccharide branch, such as, for example, an α or $\beta(1\rightarrow2)$ glycosidic bond, an α or $\beta(1\rightarrow3)$ glycosidic bond or an α or $\beta(1\rightarrow6)$ glycosidic bond.

In those embodiments wherein the R substituent is an R^1 substituent, R^1 may be a quaternary ammonium cationic substituent or an amine substituent that becomes cationic in mildly acidic environments (such as a primary, secondary, or tertiary amine containing substituent). For example, according to these embodiments, each R^1 may be independently, the same or different, a first substituent group having a structure according to Formula II:



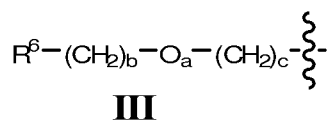
According to these embodiments, each R^4 is a substituent selected from a lone pair of electrons; H; CH_3 ; or a linear or branched, saturated or unsaturated C_2 - C_{18} alkyl. According to certain embodiments of the R^1 group, at least two of the R^4 groups of Formula II must not be a lone pair of electrons. That is, in these embodiments, one R^4 group may be a lone pair of electrons such that the nitrogen containing end group in Formula II is an amine group under neutral or basic conditions. It will be understood by one skilled in the art that the amine group may be protonated under acidic conditions to provide an ammonium cationic charge. According to other embodiments of the R^1 group, no R^4 group is a lone pair of electrons, such that the nitrogen containing end group in Formula II is an ammonium cation. Referring still to Formula II, R^5 may be a linear or branched, saturated or unsaturated C_2 - C_{18} alkyl chain or a linear or branched, saturated or unsaturated secondary hydroxy(C_2 - C_{18})alkyl chain. In various embodiments, the group L is a linking group selected from -O-, -C(=O)O-, -OC(=O)-, - NR^9 -, -C(=O)NR⁹-, - NR^9 C(=O)-, and - NR^9 C(=O)NR⁹-, where R^9 is H, or C_1 - C_6 alkyl. According to the various embodiments, w may have a value of 0 or 1, y may have a value of 0 or 1, and z may have a value of 0 or 1.

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According to certain embodiments of the suds boosting and stabilizing polysaccharide where the R substituent may comprise an R¹ first substituent group, the R¹ first substituent may have a degree of substitution ranging from 0.01 to 0.04. In other embodiments, the R¹ first substituent may have a degree of substitution ranging from 0.01 to 0.02.

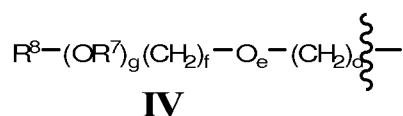
In those embodiments wherein the R substituent is an R² substituent, R² may be an anionic substituent. For example, according to these embodiments, each R² may be independently, the same or different, a second substituent group having a structure according to Formula III:



According to these embodiments, each R⁶ may be an anionic substituent selected from a carboxylate (-COO⁻), carboxymethyl (-CH₂COO⁻), succinate (-OOCCH₂CH₂COO⁻), sulfate (-OS(O₂)O⁻), sulfonate (-S(O₂)O⁻), arylsulfonate (-Ar-S(O₂)O⁻, where Ar is an aryl ring), phosphate (-OPO₂(OR') or -OPO₃²⁻, where R' is a H, alkyl, or aryl), phosphonate (-PO₂(OR') or -PO₃²⁻, where R' is a H, alkyl, or aryl), dicarboxylate (-Y(COO⁻)₂, where Y is alkyl or aryl), or polycarboxylate (-Y(COO⁻)_t, where Y is alkyl or aryl and t is greater than 2). According to the various embodiments, a may have a value of 0 or 1, b is an integer having a value from 0 to 18, and c may have a value of 0 or 1.

According to certain embodiments of the suds boosting and stabilizing polysaccharide where the R substituent may comprise an R² second substituent group, the R² second substituent may have a degree of substitution ranging from 0.0001 to 2.0. In other embodiments, the R² second substituent may have a degree of substitution ranging from 0.01 to 2.0. In other embodiments, the R² second substituent may have a degree of substitution ranging from 0.1 to 1.5. In still other embodiments, the R² second substituent may have a degree of substitution ranging from 0.5 to 1.25.

In those embodiments wherein the R substituent is an R³ substituent, R³ may be an alkoxy substituent. For example, according to these embodiments, each R³ may be independently, the same or different, a third substituent group having a structure according to Formula IV:



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According to these embodiments, each R^7 may be a group selected from ethylene, propylene, butylene, or mixtures thereof. In certain embodiments, the structure of (OR^7) may be a polyethylene oxide group, a polypropylene oxide group, a polybutylene oxide group or mixtures thereof. In specific embodiments, (OR^7) may have a structure $-O-CH(R^{10})CH_2-$, where R^{10} is methyl or ethyl (i.e., polypropylene oxide and polybutylene oxide, respectively). The structure ' OR^7 ' includes structures where the oxygen is between R^7 and R^8 and structures where the oxygen is between R^7 and $(CH_2)_f$. Each R^8 group may be an end group selected from hydrogen, C_1 - C_{20} alkyl (which may be branched or unbranched, and saturated or unsaturated), hydroxy, $-OR^1$, or $-OR^2$ (where R^1 and R^2 are as described herein). According to the various embodiments, d may have a value of 0 or 1, e may have a value of 0 or 1, f is an integer having a value from 0 to 8, and g is an integer having a value from 0 to 50.

According to certain embodiments of the suds boosting and stabilization polysaccharide where the R substituent may comprise an R^3 third substituent group, the R^3 third substituent may have a degree of substitution of 0 or ranging from 0.001 to 1.0. In other embodiments, the R^3 third substituent may have a degree of substitution ranging from 0.001 to 1.0. In other embodiments, the R^3 third substituent may have a degree of substitution ranging from 0.01 to 0.5. In still other embodiments, the R^3 third substituent may have a degree of substitution ranging from 0.01 to 0.3. In yet other embodiments, the R^3 third substituent may have a degree of substitution ranging from 0.01 to 0.1. As set forth herein, in certain embodiments of the suds boosting and stabilization biopolymer, the substituted polysaccharide may not have an alkoxy R^3 substituents. That is, in certain embodiments, the degree of substitution of R^3 is 0 and the suds boosting and stabilization biopolymer may comprise anionic and nitrogen containing substituents.

According to various embodiments described herein, the suds boosting and stabilization biopolymer may have a weight average molecular weight ranging from 10,000 Daltons to 100,000,000 Daltons. In other embodiments, the suds boosting and stabilization biopolymers described herein may comprise a blend of at least a first randomly substituted polysaccharide having a structure according to Formula I, IA, or IB and a weight average molecular weight ranging from 10,000 Daltons to 1,000,000 Daltons and a second randomly substituted polysaccharide having a structure according to Formula I, IA, or IB and a weight average molecular weight ranging from 1,000,000 Daltons to 100,000,000 Daltons.

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Specific embodiments of the substituted suds boosting and stabilization biopolymers of the present disclosure may have a specific ratio of nitrogen containing substituents to anionic substituents. For example, according to one embodiment, the substituted suds boosting and stabilizing biopolymers have a ratio of degree of substitution of the first substituent (i.e., the nitrogen containing substituent) to degree of substitution of the second substituent (i.e., the anionic substituent) ranging from 0.05:1 to 0.2:1. According to another embodiment, the ratio of degree of substitution of the first substituent (i.e., the nitrogen containing substituent) to degree of substitution of the second substituent (i.e., the anionic substituent) may range from 0.05:1 to 0.4:1. Biopolymers having substitution within these ranges show excellent suds boosting and retention/stabilization.

In another embodiment, the cleaning composition may comprise a suds boosting and stabilizing biopolymer comprising a randomly substituted polysaccharide backbone comprising unsubstituted and substituted glucopyranose residues and having a general structure represented by Formula I, IA or IB, wherein each substituted glucopyranose residue independently comprises from 1 to 3 -R residues, which may be the same or different on each substituted glucopyranose residue. Each R substituent may be independently a substituent selected from hydroxyl, hydroxymethyl, R^2 , and a polysaccharide branch having a general structure according to Formula I, IA or IB, provided that at least one R substituent comprises at least one R^2 group. R^2 may be as described herein.

In various embodiments of the randomly substituted polysaccharide, the polysaccharide backbone may be a randomly substituted starch backbone where the starch comprises amylose and/or amylopectin. Suitable sources of starch that may be chemically modified to produce the suds boosting and stabilization biopolymers described herein include corn starch, wheat starch, rice starch, waxy corn starch, oat starch, cassava starch, waxy barley starch, waxy rice starch, glutenous rice starch, sweet rice starch, potato starch, tapioca starch, sago starch, high amylose starch and mixtures of any thereof. While specific starch sources are recited herein, it is contemplated by the inventors that any source of cellulose, hemicellulose, or starch would be suited to form the randomly substituted polysaccharide suds boosting and stabilization biopolymers described herein. Other modified polysaccharides are within the scope of the present disclosure.

In specific embodiments of the suds boosting and stabilization compositions, the randomly substituted starch backbone may be derived from a high amylose starch. For example,

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in one embodiment the starch may have an amylose content ranging from about 20% to about 90% by weight of the total modified polysaccharide. In another embodiment, the starch may have an amylose content ranging from about 50% to about 85% by weight. In still another embodiment, the starch may have an amylose content ranging from about 50% to about 70% by weight. According to these embodiments, at least a portion of the remaining starch may be derived from amylopectin. Suitable techniques for measuring percentage amylose by weight of the starch include the methods described by the following: "Determination of Amylose in Cereal and Non-Cereal Starches by a Colorimetric Assay: Collaborative Study," C. Martinez and J. Prodolliet, *Starch*, 48 (1996), 81-85; and "An Improved Colorimetric Procedure for Determining Apparent and Total Amylose in Cereal and Other Starches", W. R. Morrison and B. Laignelet, *Journal Of Cereal Science*, 1 (1983).

In other embodiments, the cleaning composition may comprise a suds boosting and stabilization biopolymer that comprises a randomly substituted starch backbone that comprises a randomly substituted amylopectin backbone. According to these embodiments, the amylopectin backbone may comprise at least one $\alpha(1\rightarrow6)$ polyglucopyranose branch where a hydroxyl group at the C6 position on a glucopyranose monomer residue on the starch backbone has reacted to form a glycosidic bond with a C1 carbon of a polyglucopyranose branch which comprises unsubstituted and substituted glucopyranose residues. The polyglucopyranose branch may have a structure according to Formula I, IA, or IB. In other embodiments, the amylopectin back bone may comprise a plurality of $\alpha(1\rightarrow6)$ polyglucopyranose branches occurring at approximately every 24 to 30 glucopyranose residues in the amylopectin starch backbone.

In one embodiment of the present disclosure, the modified starch based biopolymers may be hydrolyzed to reduce the molecular weight of such starch components. The degree of hydrolysis may be measured by Water Fluidity (WF), which is a measure of the solution viscosity of the gelatinized starch. A suitable method for determining WF is described at columns 8-9 of U.S. Patent No. 4,499,116. One skilled in the art will readily appreciate that starch biopolymers that have a relatively high degree of hydrolysis will have low solution viscosity or a high water fluidity value. According to one embodiment, the modified starch based biopolymer may comprise a viscosity having a WF value from about 40 to about 84. Suitable methods of hydrolyzing starch include, but are not limited to, those described by U.S. Patent No. 4,499,116, with specific mention to column 4.

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In other embodiments of the cleaning compositions, the polysaccharide backbone may be a randomly substituted hemicellulose backbone. The randomly substituted hemicellulose backbone may comprise at least one unsubstituted or substituted carbohydrate residue, such as, for example, an unsubstituted or substituted xylose residue, an unsubstituted or substituted mannose residue, an unsubstituted or substituted galactose residue, an unsubstituted or substituted rhamnose residue, an unsubstituted or substituted arabinose residue, and combinations of any thereof. According to certain embodiments, the substituted carbohydrate residue comprises at least one R^1 substituent or at least one R^2 substituent and may optionally comprise one or more R^3 substituent.

The suds boosting and stabilization biopolymers according to the various embodiments described herein may be incorporated into the cleaning composition in an amount necessary to provide the improved sudsing characteristics for the cleaning composition. In certain embodiments, the suds boosting and stabilization biopolymers may comprise from 0.1% to 20.0% by weight of the cleaning composition. In other embodiments, the suds boosting and stabilization biopolymers may comprise from 0.1% to 10.0% by weight of the cleaning composition. In still other embodiments, the suds boosting and stabilization biopolymers may comprise from 0.5% to 5.0% by weight of the cleaning composition.

Cleaning Compositions

Still further embodiments of the present disclosure provide for methods of making a cleaning composition, such as, for example, a fabric care composition, a dish cleaning composition, a shampoo, or the like. According to specific embodiments, the methods may comprise the steps of adding a suds boosting and stabilization biopolymer to the cleaning composition. The suds boosting and stabilization biopolymer may comprise a randomly substituted biopolymer such as the randomly substituted polysaccharide backbones, as described in detail herein. In certain embodiments, such as, but not limited to, those methods for making a fabric care composition, the method may further comprise adding at least one or more adjuncts, such as a bleach activator, a surfactant, a builder, a chelating agent, a dye transfer inhibiting agent, a dispersant, an enzyme, an enzyme stabilizer, a catalytic metal complex, a polymeric dispersing agent, a clay and soil removal/anti-redeposition agent, a brightener, a suds suppressor, a dye, a perfume, a perfume delivery system, a structure elasticizing agent, a fabric softener, a carrier, a hydrotrope, a processing aid, a pigments, and combinations of any thereof, to the cleaning composition.

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Still other embodiments of the present disclosure provide methods of treating a fabric comprising contacting the fabric with an effective amount of the fabric care composition comprising the suds boosting and stabilization biopolymer as described herein. Contacting the fabric may be as a pre-treatment or contacting during a cleaning process, such as, during a wash cycle or rinse cycle.

In those aspects of the cleaning composition where the composition is a fabric care composition, the fabric care compositions may take the form of liquid laundry detergent compositions. In one aspect, such compositions may be a heavy duty liquid (HDL) composition. Such compositions may comprise a sufficient amount of a surfactant to provide the desired level of one or more cleaning properties, typically by weight of the total composition, from about 5% to about 90%, from about 5% to about 70% or even from about 5% to about 40%, and the suds boosting and stabilization biopolymer of the present disclosure, to provide a suds boosting and stabilization benefit to fabric treated in a solution containing the detergent. Typically the detergent is used in the wash solution at a level of from about 0.0001% to about 0.05%, or even from about 0.001% to about 0.01% by weight of the wash solution.

The liquid fabric care compositions may additionally comprise an aqueous, non-surface active liquid carrier. Generally, the amount of the aqueous, non-surface active liquid carrier employed in the compositions herein will be effective to solubilize, suspend or disperse the composition components. For example, the compositions may comprise, by weight, from about 5% to about 90%, from about 10% to about 70%, or even from about 20% to about 70% of an aqueous, non-surface active liquid carrier.

The most cost effective type of aqueous, non-surface active liquid carrier may be water. Accordingly, the aqueous, non-surface active liquid carrier component may be generally mostly, if not completely, water. While other types of water-miscible liquids, such alkanols, diols, other polyols, ethers, amines, and the like, have been conventionally added to liquid detergent compositions as co-solvents or stabilizers, in certain embodiments of the present disclosure, the utilization of such water-miscible liquids may be minimized to hold down composition cost. Accordingly, the aqueous liquid carrier component of the liquid detergent products herein will generally comprise water present in concentrations ranging from about 5% to about 90%, or even from about 20% to about 70%, by weight of the composition.

The liquid detergent compositions herein may take the form of an aqueous solution or uniform dispersion or suspension of surfactant, suds boosting and stabilization biopolymer, and

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certain optional adjunct ingredients, some of which may normally be in solid form, that have been combined with the normally liquid components of the composition, such as the liquid alcohol ethoxylate nonionic, the aqueous liquid carrier, and any other normally liquid optional ingredients. Such a solution, dispersion or suspension will be acceptably phase stable and will typically have a viscosity which ranges from about 100 to 600 cps, more preferably from about 150 to 400 cps. For purposes of this disclosure, viscosity may be measured with a Brookfield LV DV-II+ viscometer apparatus using a #21 spindle.

Suitable surfactants may be anionic, nonionic, cationic, zwitterionic and/or amphoteric surfactants. In one aspect, the detergent composition comprises anionic surfactant, nonionic surfactant, or mixtures thereof.

Suitable anionic surfactants may be any of the conventional anionic surfactant types typically used in liquid detergent products. Such surfactants include the alkyl benzene sulfonic acids and their salts as well as alkoxylated or non-alkoxylated alkyl sulfate materials. Exemplary anionic surfactants are the alkali metal salts of C₁₀-C₁₆ alkyl benzene sulfonic acids, preferably C₁₁-C₁₄ alkyl benzene sulfonic acids. In one aspect, the alkyl group is linear. Such linear alkyl benzene sulfonates are known as "LAS". Such surfactants and their preparation are described for example in U.S. Patent Nos. 2,220,099 and 2,477,383. Especially preferred are the sodium and potassium linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14. Sodium C₁₁-C₁₄, e.g., C₁₂ LAS is a specific example of such surfactants.

Another exemplary type of anionic surfactant comprises ethoxylated alkyl sulfate surfactants. Such materials, also known as alkyl ether sulfates or alkyl polyethoxylate sulfates, are those which correspond to the formula: R'-O-(C₂H₄O)_n-SO₃M wherein R' is a C₈-C₂₀ alkyl group, n is from about 1 to 20, and M is a salt-forming cation. In a specific embodiment, R' is C₁₀-C₁₈ alkyl, n is from about 1 to 15, and M is sodium, potassium, ammonium, alkylammonium, or alkanolammonium. In more specific embodiments, R' is a C₁₂-C₁₆, n is from about 1 to 6, and M is sodium.

The alkyl ether sulfates will generally be used in the form of mixtures comprising varying R' chain lengths and varying degrees of ethoxylation. Frequently such mixtures will inevitably also contain some non-ethoxylated alkyl sulfate materials, i.e., surfactants of the above ethoxylated alkyl sulfate formula wherein n = 0. Non-ethoxylated alkyl sulfates may also be added separately to the compositions of this disclosure and used as or in any anionic

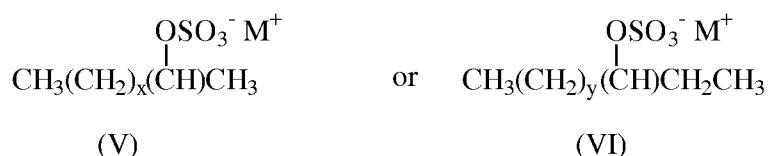
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surfactant component which may be present. Specific examples of non-alkoxylated, e.g., non-ethoxylated, alkyl ether sulfate surfactants are those produced by the sulfation of higher C₈-C₂₀ fatty alcohols. Conventional primary alkyl sulfate surfactants have the general formula:

R'OSO₃⁻M⁺ wherein R' is typically a linear C₈-C₂₀ hydrocarbyl group, which may be straight chain or branched chain, and M is a water-solubilizing cation. In specific embodiments, R' is a C₁₀-C₁₅ alkyl, and M is alkali metal, more specifically R' is C₁₂-C₁₄ and M is sodium.

Specific, non-limiting examples of anionic surfactants useful herein include: a) C₁₁-C₁₈ alkyl benzene sulfonates (LAS); b) C₁₀-C₂₀ primary, branched-chain and random alkyl sulfates (AS); c) C₁₀-C₁₈ secondary (2,3)-alkyl sulfates having formulae (V) and (VI):



wherein M in formulae (V) and (VI) is hydrogen or a cation which provides charge neutrality, and all M units, whether associated with a surfactant or adjunct ingredient, can either be a hydrogen atom or a cation depending upon the form isolated by the artisan or the relative pH of the system wherein the compound is used, with non-limiting examples of preferred cations including sodium, potassium, ammonium, and mixtures thereof, and x is an integer of at least about 7, preferably at least about 9, and y is an integer of at least 8, preferably at least about 9; d) C₁₀-C₁₈ alkyl alkoxy sulfates (AE_xS) wherein preferably x is from 1-30; e) C₁₀-C₁₈ alkyl alkoxy carboxylates preferably comprising 1-5 ethoxy units; f) mid-chain branched alkyl sulfates as discussed in U.S. Patent Nos. 6,020,303 and 6,060,443; g) mid-chain branched alkyl alkoxy sulfates as discussed in U.S. Patent Nos. 6,008,181 and 6,020,303; h) 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; i) methyl ester sulfonate (MES); and j) alpha-olefin sulfonate (AOS).

Suitable nonionic surfactants useful herein can comprise any of the conventional nonionic surfactant types typically used in liquid detergent products. These include alkoxylated fatty alcohols and amine oxide surfactants. Preferred for use in the liquid detergent products herein are those nonionic surfactants which are normally liquid. Suitable nonionic surfactants for use herein include the alcohol alkoxy nonionic surfactants. Alcohol alkoxyates are materials which correspond to the general formula: R¹¹(C_mH_{2m}O)_nOH wherein R¹¹ is a C₈-C₁₆ alkyl group, m is from 2 to 4, and n ranges from about 2 to 12. Preferably R¹¹ is an alkyl group,

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which may be primary or secondary, that contains from about 9 to 15 carbon atoms, more preferably from about 10 to 14 carbon atoms. In one embodiment, the alkoxyated fatty alcohols will also be ethoxylated materials that contain from about 2 to 12 ethylene oxide moieties per molecule, more preferably from about 3 to 10 ethylene oxide moieties per molecule.

The alkoxyated fatty alcohol materials useful in the liquid detergent compositions herein will frequently have a hydrophilic-lipophilic balance (HLB) which ranges from about 3 to 17. More preferably, the HLB of this material will range from about 6 to 15, most preferably from about 8 to 15. Alkoxyated fatty alcohol nonionic surfactants have been marketed under the tradename NEODOL® by the Shell Chemical Company.

Another suitable type of nonionic surfactant useful herein comprises the amine oxide surfactants. Amine oxides are materials which are often referred to in the art as "semi-polar" nonionics. Amine oxides have the formula: $R'(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2 \cdot qH_2O$. In this formula, R' is a relatively long-chain hydrocarbyl moiety which can be saturated or unsaturated, linear or branched, and can contain from 8 to 20, preferably from 10 to 16 carbon atoms, and is more preferably C_{12} - C_{16} primary alkyl. R is a short-chain moiety, preferably selected from hydrogen, methyl and $-CH_2OH$. When $x + y + z$ is different from 0, EO is ethyleneoxy, PO is propyleneoxy and BO is butyleneoxy. Amine oxide surfactants are illustrated by C_{12} - C_{14} alkyl dimethyl amine oxide.

Non-limiting examples of nonionic surfactants include: a) C_{12} - C_{18} alkyl ethoxylates, such as, NEODOL® nonionic surfactants; b) C_6 - C_{12} alkyl phenol alkoxyates wherein the alkoxyate units are a mixture of ethyleneoxy and propyleneoxy units; c) C_{12} - C_{18} alcohol and C_6 - C_{12} alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as PLURONIC® from BASF; d) C_{14} - C_{22} mid-chain branched alcohols, BA, as discussed in U.S. Patent No. 6,150,322; e) C_{14} - C_{22} mid-chain branched alkyl alkoxyates, BAE_x, wherein x is 1-30, as discussed in U.S. Patent Nos. 6,153,577; 6,020,303; and 6,093,856; f) alkyl polysaccharides as discussed in U.S. Patent No. 4,565,647; specifically alkyl polyglycosides as discussed in U.S. Patent Nos. 4,483,780 and 4,483,779; g) polyhydroxy fatty acid amides as discussed in U.S. Patent No. 5,332,528; WO 92/06162; WO 93/19146; WO 93/19038; and WO 94/09099; and h) ether capped poly(oxyalkylated) alcohol surfactants as discussed in U.S. Patent No. 6,482,994 and WO 01/42408.

In the fabric care compositions herein, the deterative surfactant component may comprise combinations of anionic and nonionic surfactant materials. When this is the case, the weight

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ratio of anionic to nonionic will typically range from 10:90 to 90:10, more typically from 30:70 to 70:30.

Cationic surfactants are well known in the art and non-limiting examples of these include quaternary ammonium surfactants, which can have up to 26 carbon atoms. Additional examples include a) alkoxyate quaternary ammonium (AQA) surfactants as discussed in U.S. Patent No. 6,136,769; b) dimethyl hydroxyethyl quaternary ammonium as discussed in U.S. Patent No. 6,004,922; c) polyamine cationic surfactants as discussed in WO 98/35002; WO 98/35003; WO 98/35004; WO 98/35005; and WO 98/35006; d) cationic ester surfactants as discussed in U.S. Patent Nos. 4,228,042; 4,239,660; 4,260,529; and 6,022,844; and e) amino surfactants as discussed in U.S. Patent No. 6,221,825 and WO 00/47708, specifically amido propyldimethyl amine (APA).

Non-limiting 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; betaine, including alkyl dimethyl betaine and cocodimethyl amidopropyl betaine, C₈-C₁₈ (preferably C₁₂-C₁₈) amine oxides and sulfo and hydroxy betaines, such as N-alkyl-N,N-dimethylammino-1-propane sulfonate where the alkyl group can be C₈-C₁₈, preferably C₁₀-C₁₄.

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 contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 at column 19, lines 18-35, for examples of ampholytic surfactants.

In another aspect of the present disclosure, the fabric care compositions disclosed herein, may take the form of granular laundry detergent compositions. Such compositions comprise the suds boosting and stabilization biopolymer of the present disclosure to provide soil and stain removal benefits along with acceptable sudsing levels when a fabric is washed in a solution containing the detergent. Typically, the granular laundry detergent compositions are used in

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washing solutions at a level of from about 0.0001% to about 0.05%, or even from about 0.001% to about 0.01% by weight of the washing solution.

Granular detergent compositions of the present disclosure may include any number of conventional detergent ingredients. For example, the surfactant system of the detergent composition may include anionic, nonionic, zwitterionic, ampholytic and cationic classes and compatible mixtures thereof. Detergent surfactants for granular compositions are described in U.S. Patent Nos. 3,664,961 and 3,919,678. Cationic surfactants include those described in U.S. Patent Nos. 4,222,905 and 4,239,659.

Non-limiting examples of surfactant systems include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-C₁₈ glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the surfactant system. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. See WO 92/06154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

The detergent composition can, and preferably does, include a detergent builder. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metals, especially sodium, salts of the above.

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Preferred for use herein are the phosphates, carbonates, silicates, C₁₀-C₁₈ fatty acids, polycarboxylates, and mixtures thereof. More preferred are sodium tripolyphosphate, tetrasodium pyrophosphate, citrate, tartrate mono- and di-succinates, sodium silicate, and mixtures thereof.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphates. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane-1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Patent Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176; and 3,400,148. Examples of non-phosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicates having a weight ratio of SiO₂ to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Water-soluble, non-phosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Polymeric polycarboxylate builders are set forth in U.S. Patent No. 3,308,067. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid. Some of these materials are useful as the water-soluble anionic polymer as hereinafter described, but only if in intimate admixture with the non-soap anionic surfactant. Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent Nos. 4,144,226 and 4,246,495.

Water-soluble silicate solids represented by the formula SiO₂•M₂O, M being an alkali metal, and having a SiO₂:M₂O weight ratio of from about 0.5 to about 4.0, are useful salts in the detergent granules of this disclosure at levels of from about 2% to about 15% on an anhydrous weight basis. Anhydrous or hydrated particulate silicate can be utilized, as well.

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Any number of additional ingredients can also be included as components in the granular detergent composition. These include other detergency builders, bleaches, bleach activators, suds boosters or suds suppressors, anti-tarnish and anti-corrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, smectite clays, enzymes, enzyme-stabilizing agents and perfumes. See U.S. Patent No. 3,936,537.

Bleaching agents and activators are described in U.S. Patent Nos. 4,412,934 and 4,483,781. Chelating agents are also described in U.S. Patent No. 4,663,071 from column 17, line 54 through column 18, line 68. Suds modifiers are also optional ingredients and are described in U.S. Patent Nos. 3,933,672 and 4,136,045. Suitable smectite clays for use herein are described in U.S. Patent No. 4,762,645 column 6, line 3 through column 7, line 24. Suitable additional detergency builders for use herein are enumerated in U.S. Patent No. 3,936,537 at column 13, line 54 through column 16, line 16, and in U.S. Patent No. 4,663,071.

In yet another aspect of the present disclosure, the fabric care compositions disclosed herein, may take the form of rinse added fabric conditioning compositions. Such compositions may comprise a fabric softening active and the suds boosting and stabilization biopolymer of the present disclosure, to provide a sudsing benefits when treating fabric with the composition, typically from about 0.00001 wt. % (0.1 ppm) to about 1 wt. % (10,000 ppm), or even from about 0.0003 wt. % (3 ppm) to about 0.03 wt. % (300 ppm) based on total rinse added fabric conditioning composition weight. In another specific embodiment, the compositions are rinse added fabric conditioning compositions. Examples of typical rinse added conditioning composition can be found in U.S. Provisional Patent Application Serial No. 60/687,582 filed on October 8, 2004.

Adjunct Materials

While not essential for the purposes of the present disclosure, the non-limiting list of adjuncts illustrated hereinafter are suitable for use in the fabric care compositions and may be desirably incorporated in certain embodiments of the disclosure, for example to assist or enhance performance, for treatment of the substrate to be cleaned, or to modify the aesthetics of the composition as is the case with perfumes, colorants, dyes or the like. It is understood that such adjuncts are in addition to the components that were previously listed for any particular embodiment. The total amount of such adjuncts may range from about 0.1% to about 50%, or even from about 1% to about 30%, by weight of the fabric care composition.

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The precise nature of these additional components, and levels of incorporation thereof, will depend on the physical form of the composition and the nature of the operation for which it is to be used. Suitable adjunct materials include, but are not limited to, polymers, for example cationic polymers, surfactants, builders, chelating agents, dye transfer inhibiting agents, dispersants, enzymes, and enzyme stabilizers, catalytic materials, bleach activators, polymeric dispersing agents, clay soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, additional perfume and perfume delivery systems, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids and/or pigments. In addition to the disclosure below, suitable examples of such other adjuncts and levels of use are found in U.S. Patent Nos. 5,576,282; 6,306,812; and 6,326,348.

As stated, the adjunct ingredients are not essential to the fabric care compositions. Thus, certain embodiments of the compositions do not contain one or more of the following adjunct materials: bleach activators, surfactants, builders, chelating agents, dye transfer inhibiting agents, dispersants, enzymes, and enzyme stabilizers, catalytic metal complexes, polymeric dispersing agents, clay and soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, additional perfumes and perfume delivery systems, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids and/or pigments. However, when one or more adjuncts are present, such one or more adjuncts may be present as detailed below:

Surfactants - The compositions according to the present disclosure can comprise a surfactant or surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic surfactants and/or ampholytic and/or zwitterionic and/or semi-polar nonionic surfactants. The surfactant is typically present at a level of from about 0.1%, from about 1%, or even from about 5% by weight of the cleaning compositions to about 99.9%, to about 80%, to about 35%, or even to about 30% by weight of the cleaning compositions.

Builders - The compositions of the present disclosure can comprise one or more detergent builders or builder systems. When present, the compositions will typically comprise at least about 1% builder, or from about 5% or 10% to about 80%, 50%, or even 30% by weight, of said builder. Builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates, alkali metal silicates, alkaline earth and alkali metal carbonates, aluminosilicate builders polycarboxylate compounds, ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1,3,5-trihydroxybenzene-2,4,6-trisulphonic acid, and carboxymethyl-oxysuccinic acid, the

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various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Chelating Agents - The compositions herein may also optionally contain one or more copper, iron and/or manganese chelating agents. If utilized, chelating agents will generally comprise from about 0.1% by weight of the compositions herein to about 15%, or even from about 3.0% to about 15% by weight of the compositions herein.

Dye Transfer Inhibiting Agents - The compositions of the present disclosure may also include one or more dye transfer inhibiting agents. Suitable polymeric dye transfer inhibiting agents include, but are not limited to, polyvinylpyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof. When present in the compositions herein, the dye transfer inhibiting agents are present at levels from about 0.0001%, from about 0.01%, from about 0.05% by weight of the cleaning compositions to about 10%, about 2%, or even about 1% by weight of the cleaning compositions.

Dispersants - The compositions of the present disclosure can also contain dispersants. Suitable water-soluble organic materials are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid may comprise at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Enzymes - The compositions can comprise one or more detergent enzymes which provide cleaning performance and/or fabric care benefits. Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidas, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, and amylases, or mixtures thereof. A typical combination is a cocktail of conventional applicable enzymes like protease, lipase, cutinase and/or cellulase in conjunction with amylase.

Enzyme Stabilizers - Enzymes for use in compositions, for example, detergents can be stabilized by various techniques. The enzymes employed herein can be stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions that provide such ions to the enzymes.

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Catalytic Metal Complexes - The compositions may include catalytic metal complexes. One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium, tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequester having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Patent No. 4,430,243.

If desired, the compositions herein can be catalyzed by means of a manganese compound. Such compounds and levels of use are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Patent No. 5,576,282.

Cobalt bleach catalysts useful herein are known, and are described, for example, in U.S. Patent Nos. 5,597,936 and 5,595,967. Such cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. Patent Nos. 5,597,936, and 5,595,967.

Compositions herein may also suitably include a transition metal complex of a macropolycyclic rigid ligand ("MRL"). As a practical matter, and not by way of limitation, the compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the benefit agent MRL species in the aqueous washing medium, and may provide from about 0.005 ppm to about 25 ppm, from about 0.05 ppm to about 10 ppm, or even from about 0.1 ppm to about 5 ppm, of the MRL in the wash liquor.

Preferred transition-metals in the instant transition-metal bleach catalyst include manganese, iron and chromium. Preferred MRLs herein are a special type of ultra-rigid ligand that is cross-bridged such as 5,12-diethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane. Suitable transition metal MRLs are readily prepared by known procedures, such as taught, for example, in WO 00/32601, and U.S. Patent No. 6,225,464.

Processes of Making Cleaning Compositions

The cleaning compositions of the present disclosure 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; 5,489,392; and 5,486,303.

In one aspect, the liquid detergent compositions disclosed herein may be prepared by combining the components thereof in any convenient order and by mixing, e.g., agitating, the

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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 liquid components, e.g., nonionic surfactant, the non-surface active liquid carriers and other optional liquid components, with the liquid components being thoroughly admixed by imparting shear agitation to this liquid combination. For example, rapid stirring with a mechanical stirrer may usefully be employed. While shear agitation is maintained, substantially all of any anionic surfactant and the solid 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 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.

In another aspect of producing liquid detergents, the suds boosting and stabilization biopolymer is first combined with one or more liquid components to form a suds boosting and stabilization biopolymer premix, and this suds boosting and stabilization biopolymer premix is added to a composition formulation containing a substantial portion, for example more than 50% by weight, more than 70% by weight, or even more than 90% by weight, of the balance of components of the laundry detergent composition. For example, in the methodology described above, both the suds boosting and stabilization biopolymer premix and the enzyme component may be added at a final stage of component additions. In another aspect, the suds boosting and stabilization biopolymer is encapsulated prior to addition to the detergent composition, the encapsulated biopolymer is suspended in a structured liquid, and the suspension is added to a composition formulation containing a substantial portion of the balance of components of the laundry detergent composition.

Various techniques for forming detergent compositions in such solid forms are well known in the art and may be used herein. In one aspect, when the fabric care composition is in the form of a granular particle, the suds boosting and stabilization biopolymer is provided in

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particulate form, optionally including additional but not all components of the laundry detergent composition. The suds boosting and stabilization biopolymer particulate is combined with one or more additional particulates containing a balance of components of the laundry detergent composition. Further, the suds boosting and stabilization biopolymer, optionally including additional but not all components of the laundry detergent composition may be provided in an encapsulated form, and the suds boosting and stabilization biopolymer encapsulate is combined with particulates containing a substantial balance of components of the laundry detergent composition.

Methods of Using Fabric Care Compositions

The fabric care compositions disclosed in the present specification may be used to clean or treat a fabric or other textile. Typically at least a portion of the fabric is contacted with an embodiment of the aforementioned fabric care compositions, in neat form or diluted in a liquor, for example a wash liquor, and then the fabric may be optionally washed and/or rinsed. In one aspect, a fabric is optionally washed and/or rinsed, contacted with an embodiment of the aforementioned fabric care compositions and then optionally washed and/or rinsed. For purposes of the present disclosure, washing includes but is not limited to, scrubbing, and mechanical agitation. The fabric may comprise most any fabric capable of being laundered or treated.

The fabric care compositions disclosed in the present specification can be used to form aqueous washing solutions having acceptable sudsing levels for use in the laundering of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine or manual washing process, to form such aqueous laundering solutions. The aqueous washing solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered therewith. An effective amount of the fabric care composition, such as the liquid detergent compositions disclosed in the present specification, may be added to water to form aqueous laundering solutions that may comprise from about 500 to about 7,000 ppm or even from about 1,000 to about 3,000 pm of fabric care composition.

In one aspect, the fabric care compositions may be employed as a laundry additive, a pre-treatment composition and/or a post-treatment composition.

While various specific embodiments have been described in detail herein, the present disclosure is intended to cover various different combinations of the disclosed embodiments and

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is not limited to those specific embodiments described herein. The various embodiments of the present disclosure may be better understood when read in conjunction with the following representative examples. The following representative examples are included for purposes of illustration and not limitation.

Test Method

Sudsing Profile Test Methods:

The sudsing profile of the detergent composition herein can be measured by employing a suds cylinder tester (SCT). The SCT has a set of 8 cylinders. Each cylinder is typically 30 cm long and 9 cm in diameter and may be independently rotated at a rate of 20-22 revolutions per minute (rpm). A water solution of a detergent composition to be tested is prepared by dissolving 3.4 g detergent composition into 1000 ml water having water hardness of 10 gpg. The water solution in the cylinder has a height of 16 cm which is deemed to be a constant during the whole test. A scale is attached on the external wall of each cylinder with 0 starting from the top surface of the cylinder bottom. The SCT rotates at 22 rpm for a time period as specified below, the rotation is stopped and the suds height read, which is the number of the top layer of suds minus the water solution height, 16 cm. The height of the top layer of suds should be the line which crosses the interface of air and dense suds and is vertical to the cylinder wall. Scattered bubbles clinging to the interior surface of the cylinder wall are not counted in reading the suds height. The SCT first rotates at 22 rpm for 3 minutes, the rotation is stopped and 640 μ l artificial soil is added (purchased from Equest, USA) to each cylinder. The SCT rotates at 22 rpm, rotation is stopped and the suds height read every 1 minute for ten times. The average of the ten records is recorded as the suds height of generation 1 (Gen. 1). After taking the ten records of the suds height of generation 1, 320 μ l artificial soil is added to each cylinder, the SCT rotates at about 22 rpm, rotation is stopped and the suds height read every 1 minutes for ten times. The average number of the 10 records is recorded as the suds height of generation 2 (Gen. 2). Another 320 μ l artificial soil is added to each cylinder and the steps of rotating the SCT and reading the suds height every 1 minute for ten times are repeated. The average number of the 10 records is recorded as the suds height of generation 3 (Gen. 3). Such a test may be used to simulate the initial sudsing profile of a composition, as well as its sudsing profile in a washing cycle, as more soils dissolve into the water solution from the fabrics being washed.

EXAMPLES

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Example 1

Synthesis methods:

Synthesis of carboxymethyl quaternary ammonium starch:

To a 2 L flask is charged corn starch (45 g) and methanol (75 mL). The solution is stirred for 10 minutes after which time NaOH (26.5g of a 50% w/w solution) is added over 5 minutes. After stirring an additional 2 hrs, (3-chloro-2-hydroxypropyl) trimethylammonium chloride (2.4 g) is added over 5 minutes after which the reaction is heated to 60 °C for three hours. Next, monochloroacetic acid (19 g of an 80% aqueous solution) is added slowly and the resulting solution heated at 60 °C for 3 hours. After cooling, the reaction was slurried in 200 mL isopropanol and the solids are removed by filtration, washed with methanol (200 mL) and dried under vacuum to yield the desired modified starch.

Cationic polysaccharide:

In one aspect of the invention, cationic polysaccharides refer to polysaccharides that have been chemically modified to provide the polysaccharides with a positive charge in aqueous solution, such as by substitution with a quaternary ammonium substituent or an amine substituent that may become cationic under mildly acidic conditions. This chemical modification includes, but is not limited to, the addition of amino and/or ammonium group(s) into the biopolymer molecules. Non-limiting examples of these ammonium groups may include substituents such as trimethylhydroxypropyl ammonium chloride, dimethylstearylhydroxypropyl ammonium chloride, or dimethyldodecylhydroxypropyl ammonium chloride. See Solarek, D. B., *Cationic Starches in Modified Starches: Properties and Uses*, Wurzburg, O. B., Ed., CRC Press, Inc., Boca Raton, Florida 1986, pp 113-125.

Anionic polysaccharide modification:

In another aspect of the present disclosure, anionic polysaccharides refer to polysaccharides that have been chemically modified to provide the polysaccharides with a negative charge in aqueous solution. This chemical modification includes, but is not limited to, the addition of an anionic group(s) to the dispersant polymer, such as, for example, carboxylate ($-\text{COO}^-$), carboxymethyl ($-\text{CH}_2\text{COO}^-$), succinate ($-\text{OOCCH}_2\text{CH}_2\text{COO}^-$), sulfate ($-\text{OS}(\text{O}_2)\text{O}^-$), sulfonate ($-\text{S}(\text{O}_2)\text{O}^-$), arylsulfonate ($-\text{Ar-S}(\text{O}_2)\text{O}^-$, where Ar is an aryl ring), phosphate ($-\text{OPO}_2(\text{OR}')^-$ or $-\text{OPO}_3^{2-}$, where R' is a H, alkyl, or aryl), phosphonate ($-\text{PO}_2(\text{OR}')^-$ or $-\text{PO}_3^{2-}$, where R' is a H, alkyl, or aryl), dicarboxylate ($-\text{Y}(\text{COO}^-)_2$, where Y is alkyl or aryl), or polycarboxylate

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(-Y(COO⁻)_t, where Y is alkyl or aryl and t is greater than 2). Such derivatization reactions are known in the art, for example, carboxymethylated polysaccharides may be made according to the procedure set forth in Hofreiter, B. T., *Carboxymethyl Starches in Modified Starches: Properties and Uses*, Wurzburg, O. B., Ed., CRC Press, Inc., Boca Raton, Florida 1986, pp 185-188.; direct oxidation of the C6 carbon on the polysaccharide to give the C6 carboxylate (or carboxylic acid derivative) or aldehyde may be performed according to procedures set forth in U.S. Patent Nos. 5,501,814 and 5,565,556, U.S. Application Publication No. 2007/0015678 A1, or Bragd, P.L., et al., "TEMPO-mediated oxidation of polysaccharides: survey of methods and applications," *Topics in Catalysis*, 27, 2004, 49-66; and succinates and alkenyl succinates may be made according to the procedures set forth in Trubiano, P. C., *Succinate and Substituted Succinate Derivatives of Starch: Properties and Uses*, Wurzburg, O. B., Ed., CRC Press, Inc., Boca Raton, Florida 1986, pp 131-147 or U.S. Application Publication No. 2006/0287519 A1. Alkoxy polysaccharide modification:

In another aspect of the present disclosure, alkoxy polysaccharides refer to polysaccharides that have been chemically modified to provide the polysaccharides with an alkoxy substitution. This chemical modification includes, but is not limited to, the substitution of a hydroxyethyl group (-CH₂CH₂OH), hydroxypropyl group (-CH₂CH(CH₃)OH), hydroxybutyl group (-CH₂CH(CH₂CH₃)OH), polyethyleneoxy groups, polypropyleneoxy groups and polybutyleneoxy groups onto a free hydroxyl group on the polysaccharide backbone. Such derivatization reactions are known in the art, for example, hydroxypropylated polysaccharides may be made according to the procedure set forth in Tuschhoff, J. V., *Hydroxypropylated Starches in Modified Starches: Properties and Uses*, Wurzburg, O. B., Ed., CRC Press, Inc., Boca Raton, Florida 1986, pp 79-95. Hydroxyethylated polysaccharides and hydroxybutylated polysaccharides are made using a similar method except using ethylene oxide and butylenes oxide, respectively, instead of propylene oxide.

Example 2—Cleaning Composition Formulation

Sample formulations are prepared utilizing modified polysaccharides suds boosting and stabilizing biopolymer according to one aspect of the present disclosure. The formulations are prepared using standard industry practice to mix the ingredients. Formulations I, II, III and IV include 1% by weight of the modified polysaccharide suds boosting and stabilizing polymer whereas Formulation V includes 3% by weight of the modified polysaccharide suds boosting

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and stabilizing polymer. The compositions of the five formulations are set forth in Table 1. The example cleaning composition formulations are examined to establish their ability to promote improved suds boosting and stabilizing benefits during a washing process.

Table 1: Cleaning Composition Formulations

Ingredients	Formulation I	Formulation II	Formulation III	Formulation IV	Formulation V
Sodium alkylbenzenesulfonate	16.0000	14.0000	12.0000	12.0000	7.9
Sodium alkyl alcohol ethoxylate (3) sulfate	-	-	-	-	4.73
Sodium mid-cut alkyl sulfate		1.5000	1.5000	1.5000	-
Alkyl Dimethyl hydroxyethyl quaternary amine (Chloride)	-	-	-	-	0.5
Alkyl ethoxylate	1.3000	1.3000	1.3000	1.3000	--
Polyamine ¹	-	-	-	-	0.79
Nonionic Polymer ²	1.0000	1.0000	1.0000	1.0000	1.0
Carboxymethylcellulose	0.2000	0.2000	0.2000	0.2000	1.0
Sodium polyacrylate	--	--	--	--	--
Sodium polyacrylate/maleate polymer	0.7000	0.7000	0.7000	0.7000	3.5
Modified Polysaccharides ³	1.0000	1.0000	1.0000	1.0000	3.0000
Sodium tripolyphosphate	10.0000	5.0000	3.0000	--	--
Zeolite	16.0000	16.0000	16.0000	16.0000	--
Citric Acid	--	--	--	--	5.0
Sodium Carbonate	12.5000	12.5000	12.5000	12.5000	25.0
Sodium Silicate	4.0	4.0	4.0	4.0	--
Enzymes ³	0.30	0.30	0.30	0.30	0.5
Minors including moisture ⁴	balance	balance	balance	balance	balance

1. Hexamethylenediamine ethoxylated to 24 units for each hydrogen atom bonded to a nitrogen, quaternized.
2. Comb polymer of polyethylene glycol and polyvinylacetate.
3. Enzyme cocktail selected from known detergent enzymes including amylase, cellulase, protease, lipase.
4. Balance to 100% can, for example, include minors like optical brightener, perfume, suds suppresser, soil dispersant, soil release polymer, chelating agents, bleach additives and boosters, dye transfer inhibiting agents, aesthetic enhancers (example: Speckles), additional water, and fillers, including sulfate, CaCO₃, talc, silicates, etc.
- 5a. Undegraded cationized carboxymethyl tapioca or corn starch where cationic group is trimethyl hydroxypropyl ammonium chloride with DS= 0.003 and carboxymethyl group DS= 0.44.
- 5b. Degraded cationized carboxymethyl tapioca or corn starch to about MW ~ 500,000 Dalton where cationic group is trimethyl hydroxypropyl ammonium chloride with DS= 0.003 and carboxymethyl group DS=0.44.
- 5c. Undegraded hydroxypropyl corn starches with DS= 0.15 of hydroxylalkyl group.
- 5d. Hydroxylbutyl corn starches with DS= 0.15 of hydroxylalkyl group MW~ 1.7k Dalton.

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5e. Octenyl succinate tapioca or waxy corn Starch with 6 wt% bound OSA WF=40.

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".

All documents cited in the Detailed Description of the Disclosure are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present disclosure. To the extent that any meaning or definition of a term in this document conflicts with any meaning 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 invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

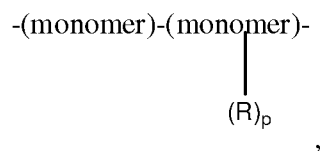
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CLAIMS

What is claimed is:

1. A cleaning composition comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted linear or branched biopolymer backbone having a structure:



wherein the randomly substituted polymer backbone comprises the residues of at least one unsubstituted monomer and at least one substituted monomer, wherein the residues of monomers are independently selected from the group consisting of amino acid residues, furanose residues, pyranose residues, and mixtures of any thereof, and the residue of the substituted monomer further comprises -(R)_p substituent groups,

where each R substituent is independently selected from an anionic substituent and a nitrogen containing substituent; or an alkoxy substituent, an anionic substituent and a nitrogen containing substituent,

where the anionic substituent has a degree of substitution ranging from 0.0001 to 2.0, the nitrogen containing substituent has a degree of substitution ranging from 0.01 to 0.04, the alkoxy substituent has a degree of substitution of 0 or ranging from 0.001 to 1.0, p is an integer from 1 to 3, and the ratio of the degree of substitution of the nitrogen containing substituent to the degree of substitution of the anionic substituent ranges from 0.05:1 to 0.2:1, and

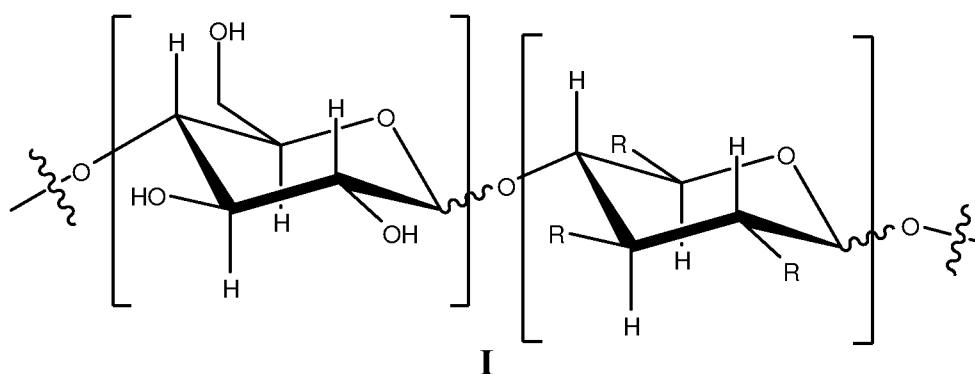
wherein the suds boosting and stabilizing biopolymer has a weight average molecular weight ranging from 10,000 Daltons to 100,000,000 Daltons.

2. The cleaning composition of claim 1, wherein the randomly substituted biopolymer backbone is a randomly substituted polysaccharide backbone.
3. The cleaning composition of claim 2, wherein the randomly substituted polysaccharide backbone comprises a randomly substituted polyglucose backbone and the residues of the monomers comprise substituted and unsubstituted glucopyranose residues.

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4. The cleaning composition of claim 3, wherein the randomly substituted polyglucose backbone is selected from the group consisting of a randomly substituted cellulose backbone, a randomly substituted hemicellulose backbone, a randomly substituted starch backbone and blends thereof.
5. The cleaning composition of claim 1, further comprising at least one or more adjuncts selected from the group consisting of bleach activators, surfactants, builders, chelating agents, dye transfer inhibiting agents, dispersants, enzymes, enzyme stabilizers, catalytic metal complexes, polymeric dispersing agents, clay and soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, perfumes, perfume delivery systems, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids, and pigments.
6. The cleaning composition of claim 1, wherein the cleaning composition is a fabric care product selected from the group consisting of liquid laundry detergents, solid laundry detergents, laundry soap products, laundry spray treatment products, a dish washing detergent, a beauty care detergent, a shampoo, and a household cleaning detergent.
7. A cleaning composition comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted polysaccharide backbone comprising unsubstituted and substituted glucopyranose residues and having a general structure according to Formula I:



wherein each substituted glucopyranose residue independently comprises from 1 to 3 R substituents, which may be the same or different on each substituted glucopyranose residue, and

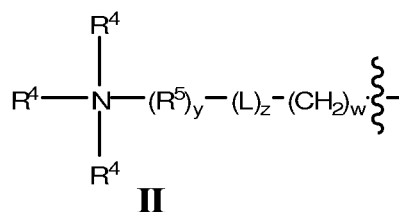
wherein each R substituent is independently a substituent selected from hydroxyl, hydroxymethyl, R^1 , R^2 , R^3 and a polysaccharide branch having a general structure according to

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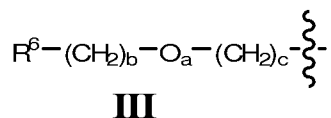
Formula I; or hydroxyl, hydroxymethyl, R^1 , R^2 , and a polysaccharide branch having a general structure according to Formula I, provided that at least one R substituent comprises at least one R^1 and at least one R^2 ,

wherein each R^1 is independently, the same or different, a first substituent group having a degree of substitution ranging from 0.01 to 0.04 and a structure according to Formula II:



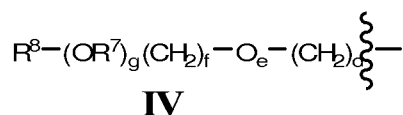
wherein each R^4 is a substituent selected from the group consisting of a lone pair of electrons; H; CH_3 ; linear or branched, saturated or unsaturated C_2 - C_{18} alkyl, provided that at least two of the R^4 groups are not a lone pair of electrons, R^5 is a linear or branched, saturated or unsaturated C_2 - C_{18} alkyl chain or a linear or branched, saturated or unsaturated secondary hydroxy(C_2 - C_{18})alkyl chain, L is a linking group selected from the group consisting of -O-, -C(O)O-, - NR^9 -, -C(O) NR^9 -, and - $NR^9C(O)NR^9$ -, and R^9 is H or C_1 - C_6 alkyl, w has a value of 0 or 1, y has a value of 0 or 1, and z has a value of 0 or 1,

each R^2 is independently, the same or different, a second substituent group having a degree of substitution ranging from 0.0001 to 2.0 and a structure according to Formula III:



wherein R^6 is an anionic substituent selected from the group consisting of carboxylate, carboxymethyl, succinate, sulfate, sulfonate, arylsulfonate, phosphate, phosphonate, dicarboxylate, and polycarboxylate, a has a value of 0 or 1, b is an integer from 0 to 18, and c has a value of 0 or 1,

each R^3 is independently, the same or different, a third substituent group having a degree of substitution of 0 or ranging from 0.001 to 1.0, and having a structure according to Formula IV:



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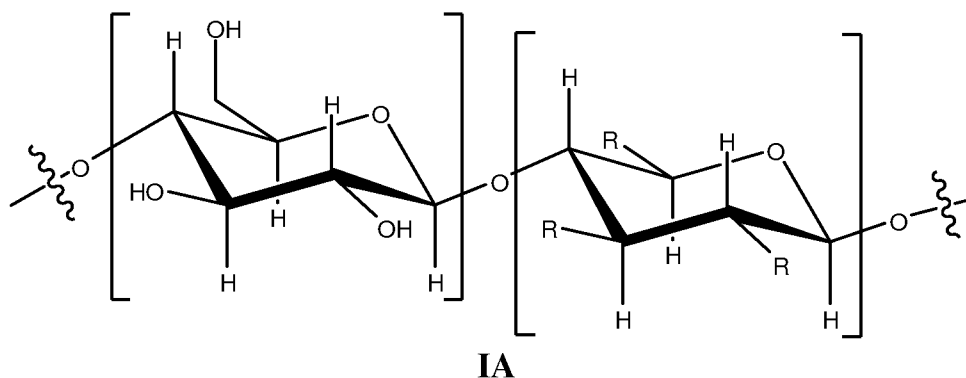
wherein d has a value of 0 or 1, e has a value of 0 or 1, f is an integer from 0 to 8, g is an integer from 0 to 50, each R^7 is the group ethylene, propylene, butylene, or mixtures thereof, and R^8 is an end group selected from the group consisting of hydrogen, C_1 - C_{20} alkyl, hydroxy, $-OR^1$ and $-OR^2$, and

wherein the ratio of the degree of substitution of the first substituent to the degree of substitution of the second substituent ranges from 0.05:1 to 0.2:1, and the suds boosting and stabilizing biopolymer has a weight average molecular weight ranging from 10,000 Daltons to 100,000,000 Daltons.

8. The cleaning composition of claim 7, wherein (OR^7) has a structure $-O-CH(R^{10})CH_2-$, wherein R^{10} is methyl or ethyl.

9. The cleaning composition of claim 7, wherein the suds boosting and stabilizing biopolymer comprises a blend of at least a first randomly substituted polysaccharide having a structure according to Formula I and a weight average molecular weight ranging from 10,000 Daltons to 1,000,000 Daltons and a second randomly substituted polysaccharide having a structure according to Formula I and a weight average molecular weight ranging from 1,000,000 Daltons to 100,000,000 Daltons.

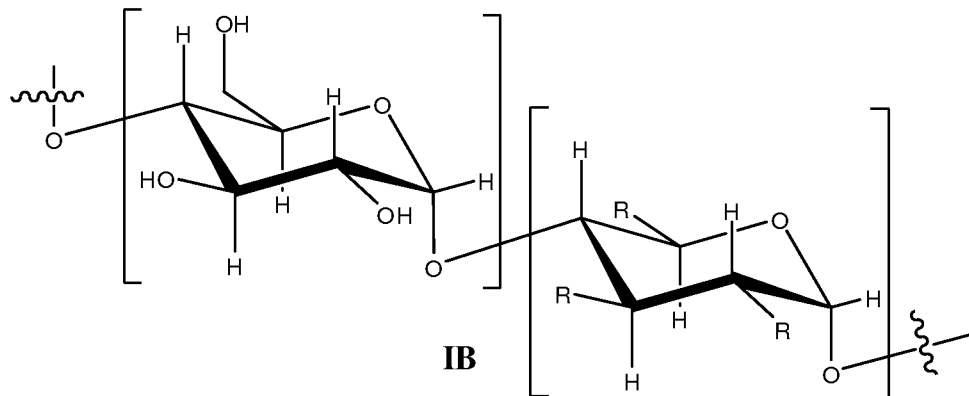
10. The cleaning composition of claim 7, wherein the randomly substituted polysaccharide backbone is a randomly substituted cellulose backbone having the general structure according to Formula IA:



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11. The cleaning composition of claim 7, wherein the randomly substituted polysaccharide backbone is a randomly substituted starch backbone having the general structure according to Formula IB:



12. The cleaning composition of claim 11, wherein the randomly substituted starch backbone is derived from a starch selected from corn starch, wheat starch, rice starch, waxy corn starch, oat starch, cassava starch, waxy barley starch, waxy rice starch, glutenous rice starch, sweet rice starch, potato starch, tapioca starch, sago starch, high amylose starch, or mixtures of any thereof.

13. The cleaning composition of claim 12, wherein the randomly substituted starch backbone is derived from a high amylose starch having an amylose content of from about 30% to about 90% by weight.

14. The cleaning composition of claim 11, wherein the randomly substituted starch backbone is a randomly substituted amylopectin backbone, further comprising at least one $\alpha(1\rightarrow6)$ polyglucopyranose branch, wherein the polyglucopyranose branch comprises unsubstituted and substituted glucopyranose residues.

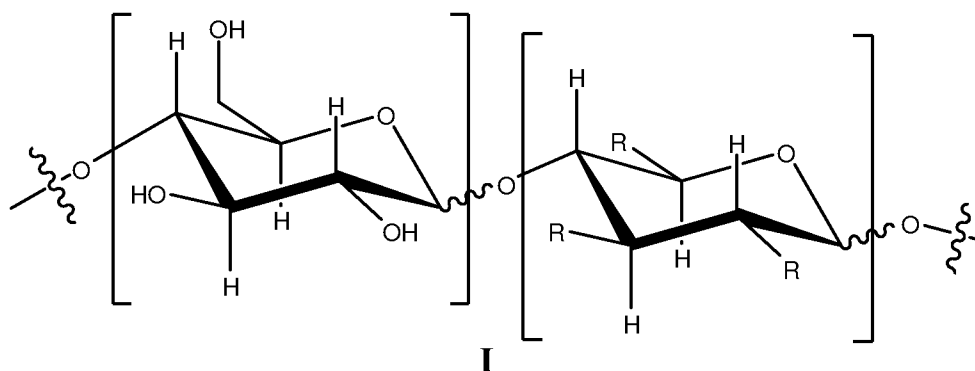
15. The cleaning composition of claim 7, wherein the polysaccharide backbone is a randomly substituted hemicellulose backbone further comprising at least one unsubstituted or substituted carbohydrate residue selected from the group consisting of an unsubstituted or substituted xylose residue, an unsubstituted or substituted mannose residue, an unsubstituted or substituted galactose residue, an unsubstituted or substituted rhamnose residue, an unsubstituted or substituted arabinose residue, and combinations of any thereof,

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wherein the substituted carbohydrate residue comprises at least one R^1 substituent or R^2 substituent and may optionally comprise one or more R^3 substituent.

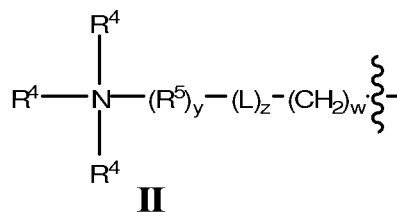
16. A method for making a cleaning composition comprising:
 adding a suds boosting and stabilizing biopolymer to the cleaning composition,
 wherein the suds boosting and stabilizing biopolymer comprises a randomly substituted polysaccharide backbone comprising unsubstituted and substituted glucopyranose residues and having a general structure according to Formula I:



wherein each substituted glucopyranose residue independently comprises from 1 to 3 R substituents, which may be the same or different on each substituted glucopyranose residue, and

wherein each R substituent is independently a substituent selected from hydroxyl, hydroxymethyl, R^1 , R^2 , R^3 and a polysaccharide branch having a general structure according to Formula I; or hydroxyl, hydroxymethyl, R^1 , R^2 , and a polysaccharide branch having a general structure according to Formula I, provided that at least one R substituent comprises at least one R^1 and at least one R^2 ,

wherein each R^1 is independently, the same or different, a first substituent group having a degree of substitution ranging from 0.01 to 0.04 and a structure according to Formula II:



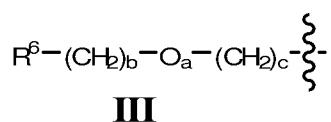
wherein each R^4 is a substituent selected from the group consisting of a lone pair of electrons; H; CH_3 ; linear or branched, saturated or unsaturated C_2 - C_{18} alkyl, provided that at least two of the

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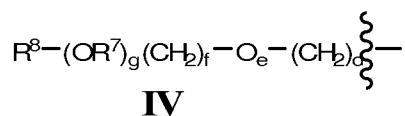
R^4 groups are not a lone pair of electrons, R^5 is a linear or branched, saturated or unsaturated C_2 - C_{18} alkyl chain or a linear or branched, saturated or unsaturated secondary hydroxy(C_2 - C_{18})alkyl chain, L is a linking group selected from the group consisting of -O-, -C(O)O-, -NR⁹-, -C(O)NR⁹-, and -NR⁹C(O)NR⁹-, and R^9 is H or C_1 - C_6 alkyl, w has a value of 0 or 1, y has a value of 0 or 1, and z has a value of 0 or 1,

each R^2 is independently, the same or different, a second substituent group having a degree of substitution ranging from 0.0001 to 2.0 and a structure according to Formula III:



wherein R^6 is an anionic substituent selected from the group consisting of carboxylate, carboxymethyl, succinate, sulfate, sulfonate, arylsulfonate, phosphate, phosphonate, dicarboxylate, and polycarboxylate, a has a value of 0 or 1, b is an integer from 0 to 18, and c has a value of 0 or 1,

each R^3 is independently, the same or different, a third substituent group having a degree of substitution of 0 or ranging from 0.001 to 1.0, and having a structure according to Formula IV:



wherein d has a value of 0 or 1, e has a value of 0 or 1, f is an integer from 0 to 8, g is an integer from 0 to 50, each R^7 is the group ethylene, propylene, butylene, or mixtures thereof, and R^8 is an end group selected from the group consisting of hydrogen, C_1 - C_{20} alkyl, hydroxy, -OR¹ and -OR², and

wherein the ratio of the degree of substitution of the first substituent to the degree of substitution of the second substituent ranges from 0.05:1 to 0.2:1, and the suds boosting and stabilizing biopolymer has a weight average molecular weight ranging from 10,000 Daltons to 100,000,000 Daltons.

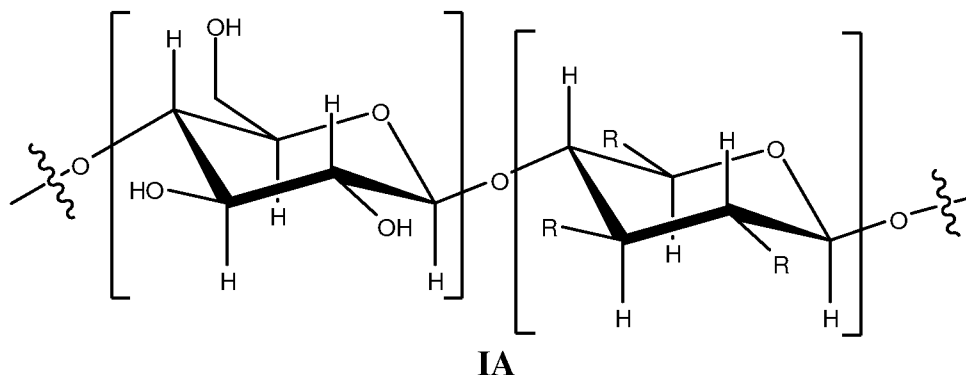
17. The method of claim 16, wherein the suds boosting and stabilizing biopolymer comprises a blend of at least a first randomly substituted polysaccharide having a structure according to Formula I and a weight average molecular weight ranging from 10,000 Daltons to 1,000,000 Daltons and a second randomly substituted polysaccharide having a structure according to

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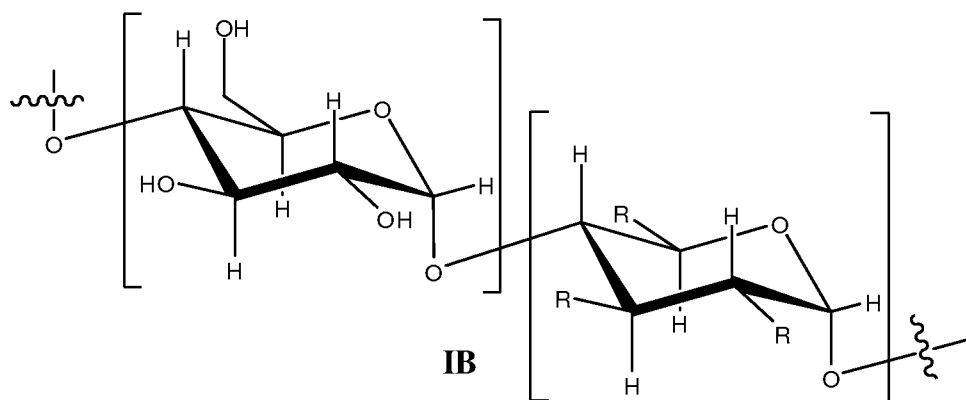
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Formula I and a weight average molecular weight ranging from 1,000,000 Daltons to 100,000,000 Daltons.

18. The method of claim 16, wherein the randomly substituted polysaccharide backbone is a randomly substituted cellulose backbone having the general structure according to Formula IA:



19. The method of claim 16, wherein the randomly substituted polysaccharide backbone is a randomly substituted starch backbone having the general structure according to Formula IB:



20. The method of claim 19, wherein the randomly substituted starch backbone is derived from a starch selected from corn starch, wheat starch, rice starch, waxy corn starch, oat starch, cassava starch, waxy barley starch, waxy rice starch, glutenous rice starch, sweet rice starch, potato starch, tapioca starch, sago starch, high amylose starch, or mixtures of any thereof.

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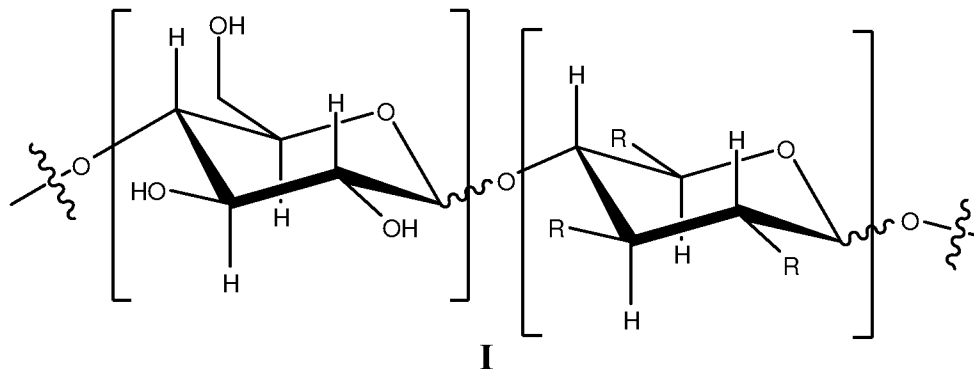
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21. The method of claim 20, wherein the randomly substituted starch backbone is derived from a high amylose starch having an amylose content of from about 30% to about 90% by weight.
22. The cleaning composition of claim 19, wherein the randomly substituted starch backbone is a randomly substituted amylopectin backbone, further comprising at least one $\alpha(1\rightarrow6)$ polyglucopyranose branch, wherein the polyglucopyranose branch comprises unsubstituted and substituted glucopyranose residues.
23. The method of claim 16, wherein the polysaccharide backbone is a randomly substituted hemicellulose backbone further comprising at least one unsubstituted or substituted carbohydrate residue selected from the group consisting of an unsubstituted or substituted xylose residue, an unsubstituted or substituted mannose residue, an unsubstituted or substituted galactose residue, an unsubstituted or substituted rhamnose residue, an unsubstituted or substituted arabinose residue, and combinations of any thereof,
wherein the substituted carbohydrate residue comprises at least one R^1 substituent or R^2 substituent and may optionally comprise one or more R^3 substituent.
24. The method of claim 16, further comprising:
adding at least one or more adjuncts selected from the group consisting of bleach activators, surfactants, builders, chelating agents, dye transfer inhibiting agents, dispersants, enzymes, enzyme stabilizers, catalytic metal complexes, polymeric dispersing agents, clay and soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, perfumes, perfume delivery systems, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids, and pigments to the fabric care composition.
25. A method of treating a fabric comprising:
contacting the fabric with an effective amount of a fabric care composition comprising the cleaning composition according to claim 7.

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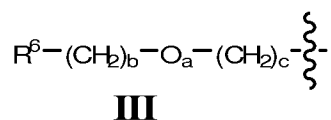
26. A cleaning composition comprising a suds boosting and stabilizing biopolymer comprising a randomly substituted polysaccharide backbone comprising unsubstituted and substituted glucopyranose residues and having a general structure according to Formula I:



wherein each substituted glucopyranose residue independently comprises from 1 to 3 R substituents, which may be the same or different on each substituted glucopyranose residue, and

wherein each R substituent is independently a substituent selected from hydroxyl, hydroxymethyl, R^2 , and a polysaccharide branch having a general structure according to Formula I, provided that at least one R substituent comprises at least one R^2 ,

wherein each R^2 is independently, the same or different, a second substituent group having a degree of substitution ranging from 0.1 to 2.0 and a structure according to Formula III:



wherein R^6 is an anionic substituent selected from the group consisting of carboxylate, carboxymethyl, succinate, sulfate, sulfonate, arylsulfonate, phosphate, phosphonate, dicarboxylate, and polycarboxylate, a has a value of 0 or 1, b is an integer from 0 to 18, and c has a value of 0 or 1, and

wherein the suds boosting and stabilizing biopolymer has a weight average molecular weight ranging from 10,000 Daltons to 100,000,000 Daltons.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/057379

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D3/37 C11D3/00 C11D11/00

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 practical, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99/14245 A1 (PROCTER & GAMBLE [US]; LEUPIN JENNIFER ANN [US]; BOYER STANTON LANE [U] 25 March 1999 (1999-03-25) page 1, paragraph 1; claims 1-4; example III	1-11, 16, 18-19, 24-26
X	GB 699 530 A (SCHOLTEN CHEMISCHE FAB) 11 November 1953 (1953-11-11) claims 1, 6, 7, 13; examples 1, 3-5	26
X,P	WO 2009/010911 A2 (PROCTER & GAMBLE [US]; TANG MING [CN]; SUN YONGMEI [CN]; PRICE KENNETH) 22 January 2009 (2009-01-22) page 14, line 6 - page 15, line 4; claims 1, 11-13; example 2; table 2	26

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

7 January 2010

Date of mailing of the international search report

20/01/2010

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Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2009/057379

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 2009010911	A2	22-01-2009	AR 067616 A1 14-10-2009
			US 2009023625 A1 22-01-2009