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(71) Applicants: DOW GLOBAL TECHNOLOGIES LLC

[US/US]; 2211 H.H. Dow Way, Midland, Michigan 48674 (US). ROHM AND HAAS COMPANY [US/US]; 400 Arcola Road, Collegeville, Pennsylvania 19426 (US).

(72) Inventors: PEERA, Asghar A.; 400 Arcola Road, Collegeville, Pennsylvania 19426 (US). DONOVAN, Stephen; 400 Arcola Road, Collegeville, Pennsylvania 19426 (US). CREAMER, Marianne; 400 Arcola Road, Collegeville, Pennsylvania 19426 (US).

(74) Agent: DEIBERT, Thomas S.; The Dow Chemical Company, Intellectual Property, P. O. Box 1967, Midland, Michigan 48641-1967 (US).

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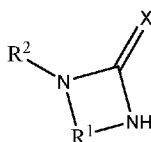
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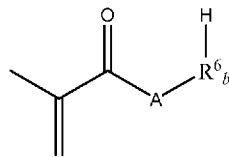
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(54) Title: LIQUID LAUNDRY DETERGENT FORMULATION

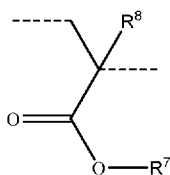
(57) Abstract: A liquid laundry detergent formulation is provided, comprising: a liquid carrier; a cleaning surfactant; and a cleaning booster polymer, wherein the cleaning booster polymer has structural units of a monoethylenically unsaturated carboxylic acid monomer; structural units of an ethylenically unsaturated monomer of formula (I); optionally, structural units of an ethylenically unsaturated monomer of formula (III); and optionally, structural units of an ethylenically unsaturated monomer of formula (IV).



formula (I)



formula (III)



formula (IV)

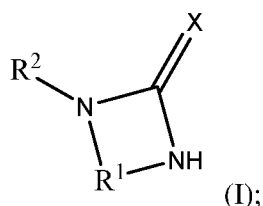


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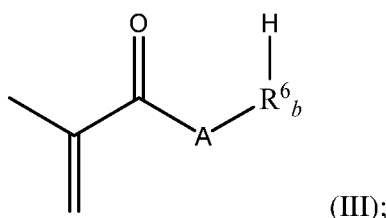
— *with international search report (Art. 21(3))*

LIQUID LAUNDRY DETERGENT FORMULATION

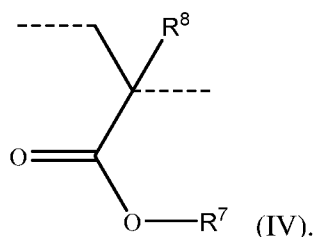
[0001] The present invention relates to a liquid laundry detergent formulation. In particular, the present invention relates to a liquid laundry detergent formulation, comprising a liquid carrier, a cleaning surfactant and a cleaning booster polymer having structural units of a monoethylenically unsaturated carboxylic acid monomer; structural units of an ethylenically unsaturated monomer of formula (I)



optionally, structural units of an ethylenically unsaturated monomer of formula (III)



and optionally, structural units of an ethylenically unsaturated monomer of formula (IV)

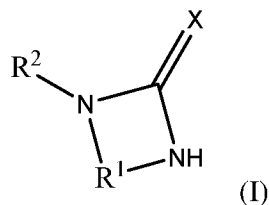


[0002] Laundry detergents in liquid and gel forms providing excellent overall cleaning are desirable to consumers. Such laundry detergents typically include surfactants among other components to deliver the consumer desired cleaning benefits. Nevertheless, increasing sensitivity for the environment and rising material costs, a move to reduce the utilization of surfactants in laundry detergents is growing. Consequently, detergent manufactures are seeking ways to reduce the amount of surfactant per unit dose of the laundry detergent while maintaining overall cleaning performance.

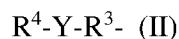
[0003] One approach for reducing the unit dose of surfactant is to incorporate polymers into the liquid detergent formulations as described by Boutique et al. in U.S. Patent Application Publication No. 20090005288. Boutique et al. disclose a graft copolymer of polyethylene, polypropylene or polybutylene oxide with vinyl acetate in a weight ratio of from about 1:0.2 to about 1:10 for use in liquid or gel laundry detergent formulations having about 2 to about 20 wt% surfactant.

[0004] Notwithstanding, there remains a continuing need for liquid laundry detergent formulations exhibiting maintained primary cleaning performance with a reduced surfactant loading; preferably, while also providing improved anti-redeposition performance.

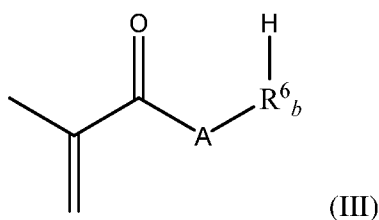
[0005] The present invention provides a liquid laundry detergent formulation, comprising: a liquid carrier; a cleaning surfactant; and a cleaning booster polymer, wherein the cleaning booster polymer, comprises: (a) 60 to 95 wt%, based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic acid monomer; (b) 5 to 40 wt%, based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (I)



wherein X is selected from the group consisting of an oxygen atom and a sulfur atom; wherein R¹ is a C₂₋₄ alkylene group; wherein R² is selected from the group consisting of a 2-(2-carboxyacrylamide)ethyl group, a vinyl group, an allyl group, an isopropenyl group, an acryloyl group, a methacryloyl group, a 2-hydroxy-3-(allyloxy)propyl group and a functional group of formula (II)

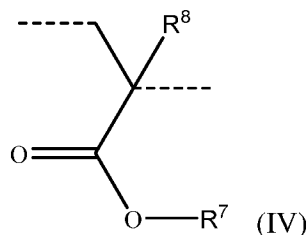


wherein R³ is a C₁₋₅ alkylene group; wherein Y is selected from the group consisting of an -O- and an -NR⁵-, where R⁵ is selected from the group consisting of a hydrogen and a C₁₋₈ alkyl group; and wherein R⁴ is selected from the group consisting of a 2-hydroxy-3-(allyloxy)propyl group, a vinyl group, a methacryloyl group, an acryloyl group and a methacryloyloxyaceto group; (c) 0 to 20 wt%, based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (III)



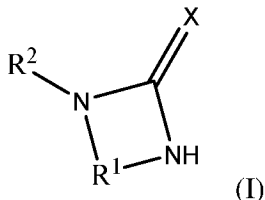
wherein A is selected from the group consisting of an -O- and an -NR⁵-; wherein each R⁶ is independently selected from the group consisting of a -CH₂CH₂O- group, a -CH₂CH(CH₃)O- group and a -CH₂CH(CH₂CH₃)O- group; and wherein b is 2 to 20; (d) 0

to 5 wt%, based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (IV)

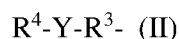


wherein each R^7 is independently selected from a -C_{1-4} alkyl group; and wherein each R^8 is independently selected from the group consisting of a hydrogen and a methyl group.

[0006] The present invention provides a liquid laundry detergent formulation, comprising: 25 to 97.9 wt%, based on weight of the liquid laundry detergent formulation, of a liquid carrier; 2 to 60 wt%, based on weight of the liquid laundry detergent formulation, of a cleaning surfactant; and 0.1 to 15 wt%, based on weight of the liquid laundry detergent formulation, of a cleaning booster polymer, wherein the cleaning booster polymer, comprises: (a) 60 to 95 wt%, based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic acid monomer; (b) 5 to 40 wt%, based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (I)

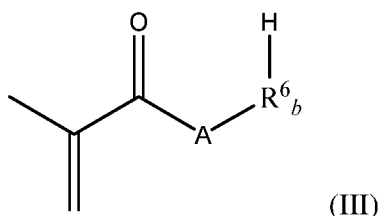


wherein X is selected from the group consisting of an oxygen atom and a sulfur atom; wherein R^1 is a C_{2-4} alkylene group; wherein R^2 is selected from the group consisting of a 2-(2-carboxyacrylamide)ethyl group, a vinyl group, an allyl group, an isopropenyl group, an acryloyl group, a methacryloyl group, a 2-hydroxy-3-(allyloxy)propyl group and a functional group of formula (II)

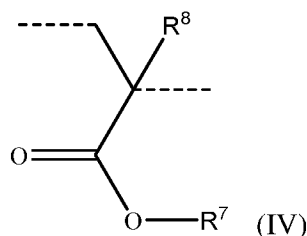


wherein R^3 is a C_{1-5} alkylene group; wherein Y is selected from the group consisting of an -O- and an $\text{-NR}^5\text{-}$, where R^5 is selected from the group consisting of a hydrogen and a C_{1-8} alkyl group; and wherein R^4 is selected from the group consisting of a 2-hydroxy-3-(allyloxy)propyl group, a vinyl group, a methacryloyl group, an acryloyl group and a methacryloyloxyaceto group; (c) 0 to 20 wt%, based on dry weight of the cleaning

booster polymer, of structural units of an ethylenically unsaturated monomer of formula (III)



wherein A is selected from the group consisting of an -O- and an -NR⁵-; wherein each R⁶ is independently selected from the group consisting of a -CH₂CH₂O- group, a -CH₂CH(CH₃)O- group and a -CH₂CH(CH₂CH₃)O- group; and wherein *b* is 2 to 20; (d) 0 to 5 wt%, based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (IV)



wherein each R⁷ is independently selected from a -C₁₋₄ alkyl group; and wherein each R⁸ is independently selected from the group consisting of a hydrogen and a methyl group.

[0007] The present invention provides a method of washing a fabric article of the present invention, comprising: providing a soiled fabric article; providing a liquid laundry detergent formulation according to claim 1; providing a wash water; and applying the wash water and the liquid laundry detergent formulation to the soiled fabric to provide a cleaned fabric article.

DETAILED DESCRIPTION

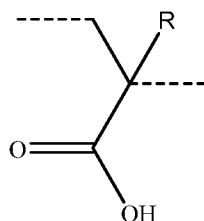
[0008] It has been surprisingly found that the liquid laundry detergent formulations with a cleaning booster polymer as described herein facilitate a significant improvement in primary cleaning performance for dust sebum, while maintaining good anti-redeposition performance for ground clay.

[0009] Unless otherwise indicated, ratios, percentages, parts, and the like are by weight. Weight percentages (or wt%) in the composition are percentages of dry weight, i.e., excluding any water that may be present in the composition.

[0010] As used herein, unless otherwise indicated, the terms "weight average molecular weight" and "M_w" are used interchangeably to refer to the weight average molecular weight as measured in a conventional manner with gel permeation chromatography (GPC) and

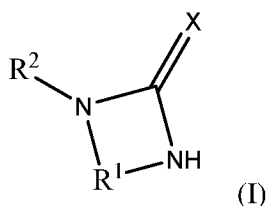
conventional standards, such as polystyrene standards. GPC techniques are discussed in detail in *Modern Size Exclusion Liquid Chromatography: Practice of Gel Permeation and Gel Filtration Chromatography*, Second Edition, Striegel, et al., John Wiley & Sons, 2009. Weight average molecular weights are reported herein in units of Daltons.

[0011] The term "structural units" as used herein and in the appended claims refers to the remnant of the indicated monomer; thus a structural unit of (meth)acrylic acid is illustrated:



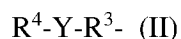
wherein the dotted lines represent the points of attachment to the polymer backbone and where R is a hydrogen for structural units of acrylic acid and a -CH₃ group for structural units of methacrylic acid.

[0012] Preferably, the liquid laundry detergent formulation of the present invention, comprises a liquid carrier (preferably, 25 to 97.9 wt% (more preferably, 50 to 94.5 wt%; still more preferably, 62.5 to 91.75 wt%; yet more preferably, 70 to 89.9 wt%; most preferably, 76 to 88 wt%), based on weight of the liquid laundry detergent formulation, of the liquid carrier); a cleaning surfactant (preferably, 2 to 60 wt% (more preferably, 5 to 40 wt%; still more preferably, 7.5 to 30 wt%; yet more preferably, 10 to 25 wt%; most preferably, 10 to 20 wt%), based on weight of the liquid laundry detergent formulation, of the cleaning surfactant); and a cleaning booster polymer (preferably, 0.1 to 15 wt% (more preferably, 0.5 to 10 wt%; still more preferably, 0.75 to 7.5 wt%; yet more preferably, 1 to 5 wt%; most preferably 2 to 4 wt%), based on weight of the liquid laundry detergent formulation, of the cleaning booster polymer), wherein the cleaning booster polymer comprises: (a) structural units of a monoethylenically unsaturated carboxylic acid monomer; (b) structural units of an ethylenically unsaturated monomer of formula (I)

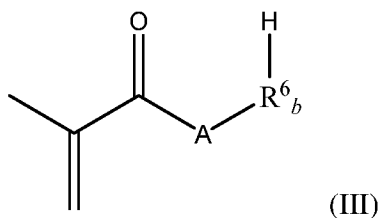


wherein X is selected from the group consisting of an oxygen atom and a sulfur atom; wherein R¹ is a C₂₋₄ alkylene group; wherein R² is selected from the group consisting of a 2-(2-carboxyacrylamide)ethyl group, a vinyl group, an allyl group, an isopropenyl group, an

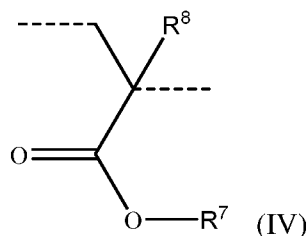
acryloyl group, a methacryloyl group, a 2-hydroxy-3-(allyloxy)propyl group and a functional group of formula (II)



wherein R^3 is a C_{1-5} alkylene group; wherein Y is selected from the group consisting of an -O- and an -NR⁵-, where R^5 is selected from the group consisting of a hydrogen and a C_{1-8} alkyl group; and wherein R^4 is selected from the group consisting of a 2-hydroxy-3-(allyloxy)propyl group, a vinyl group, a methacryloyl group, an acryloyl group and a methacryloyloxyaceto group; (c) optionally, structural units of an ethylenically unsaturated monomer of formula (III)



wherein A is selected from the group consisting of an -O- and an -NR⁵-, wherein each R^6 is independently selected from the group consisting of a -CH₂CH₂O- group, a -CH₂CH(CH₃)O- group and a -CH₂CH(CH₂CH₃)O- group; and wherein b is 2 to 20; and (d) optionally, structural units of an ethylenically unsaturated monomer of formula (IV)



wherein each R^7 is independently selected from a C_{1-4} alkyl group; and wherein each R^8 is independently selected from the group consisting of a hydrogen and a methyl group.

[0013] Preferably, the liquid laundry detergent formulation of the present invention, comprises a liquid carrier. More preferably, the liquid laundry detergent formulation of the present invention comprises 25 to 97.9 wt% (preferably, 50 to 94.5 wt%; more preferably, 62.5 to 91.75 wt%; yet more preferably, 70 to 89.9 wt%; most preferably, 76 to 88 wt%), based on weight of the liquid laundry detergent formulation, of a liquid carrier. Still more preferably, the liquid laundry detergent formulation of the present invention comprises 25 to 97.9 wt% (preferably, 50 to 94.5 wt%; more preferably, 62.5 to 91.75 wt%; yet more preferably, 70 to 89.9 wt%; most preferably, 76 to 88 wt%), based on weight of the liquid laundry detergent formulation, of a liquid carrier; wherein the liquid carrier comprises water. Most preferably, the liquid laundry detergent formulation of the present invention

comprises 25 to 97.9 wt% (preferably, 50 to 94.5 wt%; more preferably, 62.5 to 91.75 wt%; yet more preferably, 70 to 89.9 wt%; most preferably, 76 to 88 wt%), based on weight of the liquid laundry detergent formulation, of a liquid carrier; wherein the liquid carrier is water.

[0014] Preferably, the liquid carrier can include water miscible liquids, such as, C₁₋₃ alkanolamines and C₁₋₃ alkanols. More preferably, the liquid carrier includes 0 to 8 wt% (preferably, 0.2 to 8 wt%; more preferably, 0.5 to 5 wt%), based on weight of the liquid carrier, of water miscible liquids; wherein the water miscible liquids are selected from the group consisting of C₁₋₃ alkanolamines, C₁₋₃ alkanols and mixtures thereof.

[0015] Preferably, the liquid laundry detergent formulation of the present invention, comprises: a cleaning surfactant. More preferably, the liquid laundry detergent formulation of the present invention, comprises: 2 to 60 wt% (more preferably, 5 to 40 wt%; still more preferably, 7.5 to 30 wt%; yet more preferably, 10 to 25 wt%; most preferably, 10 to 20 wt%), based on weight of the liquid laundry detergent formulation, of a cleaning surfactant. Still more preferably, the liquid laundry detergent formulation of the present invention, comprises: 2 to 60 wt% (more preferably, 5 to 40 wt%; still more preferably, 7.5 to 30 wt%; yet more preferably, 10 to 25 wt%; most preferably, 10 to 20 wt%), based on weight of the liquid laundry detergent formulation, of a cleaning surfactant; wherein the cleaning surfactant is selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants and mixtures thereof. Yet still more preferably, the liquid laundry detergent formulation of the present invention, comprises: 2 to 60 wt% (more preferably, 5 to 40 wt%; still more preferably, 7.5 to 30 wt%; yet more preferably, 10 to 25 wt%; most preferably, 10 to 20 wt%), based on weight of the liquid laundry detergent formulation, of a cleaning surfactant; wherein the cleaning surfactant is selected from the group consisting of a mixture including an anionic surfactant and a non-ionic surfactant. Most preferably, the liquid laundry detergent formulation of the present invention, comprises: 2 to 60 wt% (more preferably, 5 to 40 wt%; still more preferably, 7.5 to 30 wt%; yet more preferably, 10 to 25 wt%; most preferably, 10 to 20 wt%), based on weight of the liquid laundry detergent formulation, of a cleaning surfactant; wherein the cleaning surfactant includes a mixture of a linear alkyl benzene sulfonate, a sodium lauryl ethoxysulfate and a nonionic alcohol ethoxylate.

[0016] Anionic surfactants include alkyl sulfates, alkyl benzene sulfates, alkyl benzene sulfonic acids, alkyl benzene sulfonates, alkyl polyethoxy sulfates, alkoxylated alcohols, paraffin sulfonic acids, paraffin sulfonates, olefin sulfonic acids, olefin sulfonates,

alpha-sulfocarboxylates, esters of alpha-sulfocarboxylates, alkyl glyceryl ether sulfonic acids, alkyl glyceryl ether sulfonates, sulfates of fatty acids, sulfonates of fatty acids, sulfonates of fatty acid esters, alkyl phenols, alkyl phenol polyethoxy ether sulfates, 2-acryloxy-alkane-1-sulfonic acid, 2-acryloxy-alkane-1-sulfonate, beta-alkyloxy alkane sulfonic acid, beta-alkyloxy alkane sulfonate, amine oxides and mixtures thereof. Preferred anionic surfactants include C₈₋₂₀ alkyl benzene sulfates, C₈₋₂₀ alkyl benzene sulfonic acid, C₈₋₂₀ alkyl benzene sulfonate, paraffin sulfonic acid, paraffin sulfonate, alpha-olefin sulfonic acid, alpha-olefin sulfonate, alkoxyated alcohols, C₈₋₂₀ alkyl phenols, amine oxides, sulfonates of fatty acids, sulfonates of fatty acid esters, C₈₋₁₀ alkyl polyethoxy sulfates and mixtures thereof. More preferred anionic surfactants include C₁₂₋₁₆ alkyl benzene sulfonic acid, C₁₂₋₁₆ alkyl benzene sulfonate, C₁₂₋₁₈ paraffin-sulfonic acid, C₁₂₋₁₈ paraffin-sulfonate, C₁₂₋₁₆ alkyl polyethoxy sulfate and mixtures thereof.

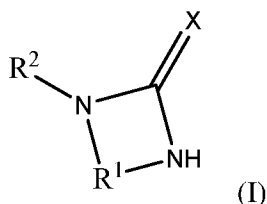
[0017] Non-ionic surfactants include alkoxyates (e.g., polyglycol ethers, fatty alcohol polyglycol ethers, alkylphenol polyglycol ethers, end group capped polyglycol ethers, mixed ethers, hydroxy mixed ethers, fatty acid polyglycol esters and mixtures thereof. Preferred non-ionic surfactants include fatty alcohol polyglycol ethers. More preferred non-ionic surfactants include secondary alcohol ethoxylates, ethoxylated 2-ethylhexanol, ethoxylated seed oils, butanol capped ethoxylated 2-ethylhexanol and mixtures thereof. Most preferred non-ionic surfactants include secondary alcohol ethoxylates.

[0018] Cationic surfactants include quaternary surface active compounds. Preferred cationic surfactants include quaternary surface active compounds having at least one of an ammonium group, a sulfonium group, a phosphonium group, an iodonium group and an arsonium group. More preferred cationic surfactants include at least one of a dialkyldimethylammonium chloride and alkyl dimethyl benzyl ammonium chloride. Still more preferred cationic surfactants include at least one of C₁₆₋₁₈ dialkyldimethylammonium chloride, a C₈₋₁₈ alkyl dimethyl benzyl ammonium chloride and dimethyl ditallow ammonium chloride. Most preferred cationic surfactant includes dimethyl ditallow ammonium chloride.

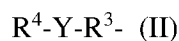
[0019] Amphoteric surfactants include betaines, amine oxides, alkylamidoalkylamines, alkyl-substituted amine oxides, acylated amino acids, derivatives of aliphatic quaternary ammonium compounds and mixtures thereof. Preferred amphoteric surfactants include derivatives of aliphatic quaternary ammonium compounds. More preferred amphoteric surfactants include derivatives of aliphatic quaternary ammonium compounds with a long chain group having 8 to 18 carbon atoms. Still more preferred amphoteric surfactants

include at least one of C₁₂₋₁₄ alkyldimethylamine oxide,
 3-(N,N-dimethyl-N-hexadecyl-ammonio)propane-1-sulfonate,
 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate. Most preferred
 amphoteric surfactants include at least one of C₁₂₋₁₄ alkyldimethylamine oxide.

[0020] Preferably, the liquid laundry detergent formulation of the present invention,
 comprises: a cleaning booster polymer. More preferably, the liquid laundry detergent
 formulation of the present invention, comprises: 0.1 to 15 wt% (preferably, 0.5 to 10 wt%;
 more preferably, 0.75 to 7.5 wt%; still more preferably, 1 to 5 wt%; most preferably 2 to 4
 wt%), based on weight of the liquid laundry detergent formulation, of a cleaning booster
 polymer. Most preferably, the liquid laundry detergent formulation of the present
 invention, comprises: 0.1 to 15 wt% (preferably, 0.5 to 10 wt%; more preferably, 0.75 to
 7.5 wt%; still more preferably, 1 to 5 wt%; most preferably 2 to 4 wt%), based on weight of
 the liquid laundry detergent formulation, of a cleaning booster polymer; wherein the
 cleaning booster polymer comprises: (a) 60 to 95 wt% (preferably, 70 to 92 wt%; more
 preferably, 75 to 91 wt%; still more preferably, 80 to 90 wt%; most preferably, 83 to 87
 wt%), based on dry weight of the cleaning booster polymer, of structural units of a
 monoethylenically unsaturated carboxylic acid monomer; (b) 5 to 40 wt% (preferably, 8 to
 30 wt%; more preferably, 9 to 25 wt%; still more preferably, 10 to 20 wt%; most
 preferably, 13 to 17 wt%), based on dry weight of the cleaning booster polymer, of
 structural units of an ethylenically unsaturated monomer of formula (I)

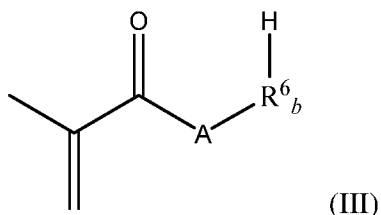


wherein X is selected from the group consisting of an oxygen atom and a sulfur atom;
 wherein R¹ is a C₂₋₄ alkylene group; wherein R² is selected from the group consisting of a
 2-(2-carboxyacrylamide)ethyl group, a vinyl group, an allyl group, an isopropenyl group, an
 acryloyl group, a methacryloyl group, a 2-hydroxy-3-(allyloxy)propyl group and a
 functional group of formula (II)

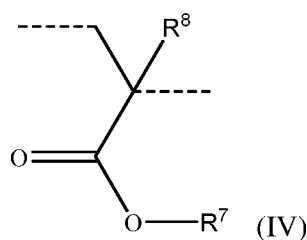


wherein R³ is a C₁₋₅ alkylene group; wherein Y is selected from the group consisting of
 an -O- and an -NR⁵-, where R⁵ is selected from the group consisting of a hydrogen and a C₁₋₈
 alkyl group; and wherein R⁴ is selected from the group consisting of a
 2-hydroxy-3-(allyloxy)propyl group, a vinyl group, a methacryloyl group, an acryloyl group

and a methacryloyloxyaceto group; (c) 0 to 20 wt% (preferably, 0 to 15 wt%; more preferably, 0 to 10 wt%; still more preferably, 0 to 5 wt%; most preferably, 0 wt%), based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (III)



wherein A is selected from the group consisting of an -O- and an -NR⁵-; wherein each R⁶ is independently selected from the group consisting of a -CH₂CH₂O- group, a -CH₂CH(CH₃)O- group and a -CH₂CH(CH₂CH₃)O- group; and wherein b is 2 to 20; (d) 0 to 5 wt% (preferably, 0 to 3 wt%; more preferably, 0 to 2 wt%; most preferably, 0 wt%), based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (IV)



wherein each R⁷ is independently selected from a -C₁₋₄ alkyl group; and wherein each R⁸ is independently selected from the group consisting of a hydrogen and a methyl group.

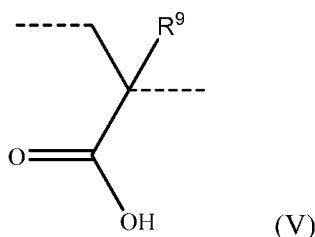
[0021] Preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention has a weight average molecular weight, M_w, of 500 to 100,000 Daltons (preferably, 2,000 to 50,000 Daltons; more preferably, 5,000 to 25,000 Daltons; most preferably, 10,000 to 20,000 Daltons).

[0022] Preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 60 to 95 wt% (preferably, 70 to 92 wt%; more preferably, 75 to 91 wt%; still more preferably, 80 to 90 wt%; most preferably, 83 to 87 wt%), based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic acid monomer. More preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 60 to 95 wt% (preferably, 70 to 92 wt%; more preferably, 75 to 91 wt%; still more preferably, 80 to 90 wt%; most preferably, 83 to 87 wt%), based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic

acid monomer; wherein the monoethylenically unsaturated carboxylic acid monomer is selected from monoethylenically unsaturated monomers that contain at least one carboxylic acid group. Still more preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 60 to 95 wt% (preferably, 70 to 92 wt%; more preferably, 75 to 91 wt%; still more preferably, 80 to 90 wt%; most preferably, 83 to 87 wt%), based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic acid monomer; wherein the monoethylenically unsaturated carboxylic acid monomer is selected from the group consisting of (meth)acrylic acid, (meth)acryloxypionic acid, itaconic acid, aconitic acid, maleic acid, maleic anhydride, fumaric acid, crotonic acid, citraconic acid, maleic anhydride, monomethyl maleate, monomethyl fumarate, monomethyl itaconate, and other derivatives such as corresponding anhydride, amides, and esters. Yet still more preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 60 to 95 wt% (preferably, 70 to 92 wt%; more preferably, 75 to 91 wt%; still more preferably, 80 to 90 wt%; most preferably, 83 to 87 wt%), based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic acid monomer; wherein the monoethylenically unsaturated carboxylic acid monomer is selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof. Still yet more preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 60 to 95 wt% (preferably, 70 to 92 wt%; more preferably, 75 to 91 wt%; still more preferably, 80 to 90 wt%; most preferably, 83 to 87 wt%), based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic acid monomer; wherein the monoethylenically unsaturated carboxylic acid core monomer includes acrylic acid. Most preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 60 to 95 wt% (preferably, 70 to 92 wt%; more preferably, 75 to 91 wt%; still more preferably, 80 to 90 wt%; most preferably, 83 to 87 wt%), based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic acid monomer; wherein the monoethylenically unsaturated carboxylic acid core monomer is acrylic acid.

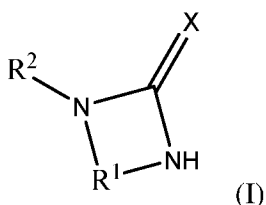
[0023] Preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 60 to 95 wt% (preferably, 70 to 92 wt%; more preferably, 75 to 91 wt%; still more preferably, 80 to 90 wt%; most preferably, 83 to 87 wt%), based on dry weight of the cleaning booster polymer, of structural units of a

monoethylenically unsaturated carboxylic acid monomer; wherein the structural units of the monoethylenically unsaturated carboxylic acid monomer are structural units of formula (V)



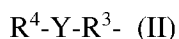
wherein each R^9 is independently selected from a hydrogen and a $-CH_3$ group (preferably, a hydrogen). Most preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention, comprises: 60 to 95 wt% (preferably, 70 to 92 wt%; more preferably, 75 to 91 wt%; still more preferably, 80 to 90 wt%; most preferably, 83 to 87 wt%), based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic acid monomer; wherein the structural units of the monoethylenically unsaturated monocarboxylic acid monomer are structural units of formula (V), wherein each R^9 is independently selected from a hydrogen and a $-CH_3$ group; wherein R^9 is a hydrogen in 50 to 100 mol% (preferably, 75 to 100 mol%; more preferably, 90 to 100 mol%; still more preferably, 98 to 100 mol%; most preferably, 100 mol%) of the structural units of formula (V) in the cleaning booster polymer.

[0024] Preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 5 to 40 wt% (preferably, 8 to 30 wt%; more preferably, 9 to 25 wt%; still more preferably, 10 to 20 wt%; most preferably, 13 to 17 wt%), based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (I)



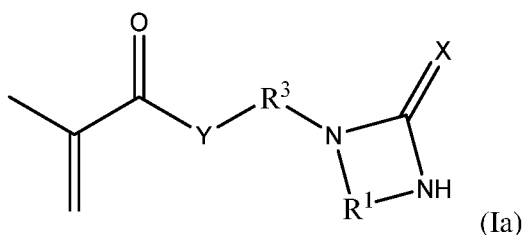
wherein X is selected from the group consisting of an oxygen atom and a sulfur atom (preferably, an oxygen atom); wherein R^1 is a C_{2-4} alkylene group (preferably, R^1 is selected from the group consisting of a $-CH_2CH_2CH_2-$ group, a $-CH(CH_3)CH_2-$ group, and a $-CH_2CH_2-$ group; more preferably, R^1 is a $-CH_2CH_2-$ group); wherein R^2 is selected from the group consisting of a 2-(2-carboxyacrylamide)ethyl group, a vinyl group, an allyl group,

an isopropenyl group, an acryloyl group, a methacryloyl group, a 2-hydroxy-3-(allyloxy)propyl group and a functional group of formula (II)



wherein R^3 is a C_{1-5} alkylene group (preferably, a C_{2-4} alkylene group; more preferably, R^3 is selected from the group consisting of a $-\text{CH}_2\text{CH}_2\text{CH}_2-$ group, a $-\text{CH}(\text{CH}_3)\text{CH}_2-$ group, and a $-\text{CH}_2\text{CH}_2-$ group; most preferably, R^3 is a $-\text{CH}_2\text{CH}_2-$ group); wherein Y is selected from the group consisting of an $-\text{O}-$ and an $-\text{NR}^5-$ (preferably, $-\text{O}-$), where R^5 is selected from the group consisting of a hydrogen and a C_{1-8} alkyl group (preferably, a C_{1-4} alkyl group; more preferably, a C_{1-2} alkyl group; most preferably, a methyl group); and wherein R^4 is selected from the group consisting of a 2-hydroxy-3-(allyloxy)propyl group, a vinyl group, a methacryloyl group, an acryloyl group and a methacryloyloxyaceto group.

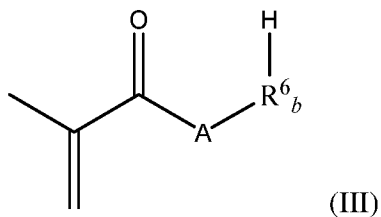
[0025] Preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 5 to 40 wt% (preferably, 8 to 30 wt%; more preferably, 9 to 25 wt%; still more preferably, 10 to 20 wt%; most preferably, 13 to 17 wt%), based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (I); wherein the structural units of the ethylenically unsaturated monomer of formula (I) are of formula (Ia)



wherein Y is selected from the group consisting of an $-\text{O}-$ and an $-\text{NR}^5-$ (preferably, an $-\text{O}-$), where R^5 is selected from the group consisting of a hydrogen and a C_{1-8} alkyl group (preferably, a C_{1-4} alkyl group; more preferably, a C_{1-2} alkyl group; most preferably, a methyl group); wherein R^1 is selected from the group consisting of a $-\text{CH}_2\text{CH}_2\text{CH}_2-$ group, a $-\text{CH}(\text{CH}_3)\text{CH}_2-$ group, and a $-\text{CH}_2\text{CH}_2-$ group (preferably, a $-\text{CH}_2\text{CH}_2-$ group); wherein R^3 is a C_{1-5} alkylene group (preferably, a C_{2-4} alkylene group; more preferably, R^3 is selected from the group consisting of a $-\text{CH}_2\text{CH}_2\text{CH}_2-$ group, a $-\text{CH}(\text{CH}_3)\text{CH}_2-$ group, and a $-\text{CH}_2\text{CH}_2-$ group; most preferably, R^3 is a $-\text{CH}_2\text{CH}_2-$ group); and wherein X is selected from the group consisting of an oxygen atom and a sulfur atom (preferably, an oxygen atom).

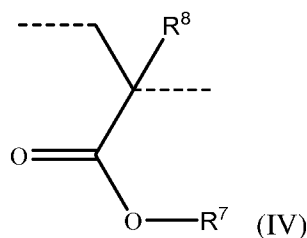
[0026] Preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 0 to 20 wt% (preferably, 0 to 15 wt%;

more preferably, 0 to 10 wt%; still more preferably, 0 to 5 wt%; most preferably, 0 wt%), based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (III)



wherein A is selected from the group consisting of an -O- and an -NR⁵- (preferably, an -O-), where R⁵ is selected from the group consisting of a hydrogen and a C₁₋₈ alkyl group (preferably, a C₁₋₄ alkyl group; more preferably, a C₁₋₂ alkyl group; most preferably, a methyl group); wherein each R⁶ is independently selected from the group consisting of a -CH₂CH₂O- group, a -CH₂CH(CH₃)O- group and a -CH₂CH(CH₂CH₃)O- group (preferably, a -CH₂CH₂O- group and a -CH₂CH(CH₃)O- group; most preferably, a -CH₂CH₂O- group); and wherein b is 2 to 20 (preferably, 2 to 10; more preferably, 2 to 7; most preferably, 2 to 4).

[0027] Preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 0 to 5 wt% (preferably, 0 to 3 wt%; more preferably, 0 to 2 wt%; most preferably, 0 wt%), based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (IV)



wherein each R⁷ is independently selected from a -C₁₋₄ alkyl group (preferably, a methyl group, an ethyl group and a butyl group; more preferably, an ethyl group and a butyl group; most preferably, an ethyl group) and wherein each R⁸ is independently selected from the group consisting of a hydrogen and a methyl group (preferably, a hydrogen). More preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention comprises: 0 to 5 wt% (preferably, 0 to 3 wt%; more preferably, 0 to 2 wt%; most preferably, 0 wt%), based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (IV), wherein R⁷ is an ethyl group in 75 to 100 mol% (preferably, 90 to 100 mol%; more preferably, 98 to 100

mol%; most preferably, 100 mol%) of the structural units of formula (IV) in the cleaning booster polymer and wherein R⁸ is a hydrogen in 75 to 100 mol% (preferably, 90 to 100 mol%; more preferably, 98 to 100 mol%; most preferably, 100 mol%) of the structural units of formula (IV) in the cleaning booster polymer.

[0028] Preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention contains < 1 wt% (preferably, < 0.5 wt%; more preferably, < 0.2 wt%; still more preferably, < 0.1 wt%; yet still more preferably, < 0.01 wt%; most preferably, < the detectable limit), based on the dry weight of the liquid laundry additive, of a vinyl alcohol polymer (PVA). More preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention contains < 1 wt% (preferably, < 0.5 wt%; more preferably, < 0.2 wt%; still more preferably, < 0.1 wt%; yet still more preferably, < 0.01 wt%; most preferably, < the detectable limit), based on the dry weight of the liquid laundry additive, of a vinyl alcohol polymer (PVA); wherein the vinyl alcohol polymer has a degree of saponification of 80 to 100 mol% (determined using the method specified in JIS K 6726 (1994)). Most preferably, the cleaning booster polymer used in the liquid laundry detergent formulation of the present invention contains < 1 wt% (preferably, < 0.5 wt%; more preferably, < 0.2 wt%; still more preferably, < 0.1 wt%; yet still more preferably, < 0.01 wt%; most preferably, < the detectable limit), based on the dry weight of the liquid laundry additive, of a vinyl alcohol polymer (PVA); wherein the vinyl alcohol polymer may include modified vinyl alcohol polymer. Modified vinyl alcohol polymer includes anion-modified PVA (e.g., sulfonic acid group modified PVA and carboxylic acid group-modified PVA); cation-modified PVA (e.g., quaternary amine group-modified PVA); amide-modified PVA; acetoacetyl group-modified PVAs; diacetone acrylamide-modified PVA and ethylene-modified PVA.

[0029] Preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises a structurant. More preferably, the liquid laundry detergent formulation of the present invention, further comprises 0 to 2 wt% (preferably, 0.05 to 0.8 wt%; more preferably, 0.1 to 0.4 wt%), based on weight of the liquid laundry detergent formulation, of a structurant. Most preferably, the liquid laundry detergent formulation of the present invention, further comprises 0 to 2 wt% (preferably, 0.05 to 0.8 wt%; more preferably, 0.1 to 0.4 wt%), based on weight of the liquid laundry detergent formulation, of a structurant; wherein the structurant is a non-polymeric, crystalline hydroxy-functional materials capable of forming thread like structuring systems throughout the liquid laundry detergent formulation when crystallized in situ.

[0030] Preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises a hydrotrope. More preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises: 0 to 10 wt% (preferably, 0.1 to 7.5 wt%; more preferably, 0.2 to 5 wt%; most preferably, 0.5 to 2.5 wt%), based on the weight of the liquid laundry detergent formulation, of a hydrotrope. More preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises: 0 to 10 wt% (preferably, 0.1 to 7.5 wt%; more preferably, 0.2 to 5 wt%; most preferably, 0.5 to 2.5 wt%), based on the weight of the liquid laundry detergent formulation, of a hydrotrope; wherein the hydrotrope is selected from the group consisting of alkyl hydroxides; glycols; urea; monoethanolamine; diethanolamine; triethanolamine; calcium, sodium, potassium, ammonium and alkanol ammonium salts of xylene sulfonic acid, toluene sulfonic acid, ethylbenzene sulfonic acid, naphthalene sulfonic acid and cumene sulfonic acid; salts thereof and mixtures thereof. Most preferably, the liquid laundry detergent formulation of the present invention, further comprises: 0 to 10 wt% (preferably, 0.1 to 7.5 wt%; more preferably, 0.2 to 5 wt%; most preferably, 0.5 to 2.5 wt%), based on the weight of the liquid laundry detergent formulation, of a hydrotrope; wherein the hydrotrope is selected from the group consisting of ethanol, propylene glycol, sodium toluene sulfonate, potassium toluene sulfonate, sodium xylene sulfonate, ammonium xylene sulfonate, potassium xylene sulfonate, calcium xylene sulfonate, sodium cumene sulfonate, ammonium cumene sulfonate and mixtures thereof.

[0031] Preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises a fragrance. More preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises: 0 to 10 wt% (preferably, 0.001 to 5 wt%; more preferably, 0.005 to 3 wt%; most preferably, 0.01 to 2.5 wt%), based on the weight of the liquid laundry detergent formulation, of a fragrance.

[0032] Preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises a builder. More preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises: 0 to 50 wt% (preferably, 5 to 50 wt%; more preferably, 7.5 to 30 wt%), based on the weight of the liquid laundry detergent formulation, of a builder. Most preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises: 0 to 50 wt% (preferably, 5 to 50 wt%; more preferably, 7.5 to 30 wt%), based on the weight of the liquid laundry detergent formulation, of a builder; wherein the builder is selected from the group consisting of inorganic builders (e.g., tripolyphosphate, pyrophosphate); alkali

metal carbonates; borates; bicarbonates; hydroxides; zeolites; citrates (e.g., sodium citrate); polycarboxylates; monocarboxylates; aminotris(methylenephosphonic acid); salts of aminotris(methylenephosphonic acid); hydroxyethanediphosphonic acid; salts of hydroxyethanediphosphonic acid; diethylenetriaminepenta(methylenephosphonic acid); salts of diethylenetriaminepenta(methylenephosphonic acid); ethylenediaminetetraethylphosphonic acid; salts of ethylenediaminetetraethylphosphonic acid; oligomeric phosphonates; polymeric phosphonates; mixtures thereof.

[0033] Preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises a fabric softener. More preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises: 0 to 10 wt% (preferably, 0.5 to 10 wt%), based on the weight of the liquid laundry detergent formulation, of a fabric softener. Most preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises: 0 to 10 wt% (preferably, 0.5 to 10 wt%), based on the weight of the liquid laundry detergent formulation, of a fabric softener; wherein the fabric softener is a cationic coacervating polymer (e.g., cationic hydroxyl ethyl cellulose; polyquaternium polymers and combinations thereof).

[0034] Preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises a pH adjusting agent. More preferably, the liquid laundry detergent formulation of the present invention, optionally further comprises a pH adjusting agent; wherein the liquid laundry detergent formulation has a pH from 6 to 12.5 (preferably, 6.5 to 11; more preferably, 7.5 to 10). Bases for adjusting pH include mineral bases such as sodium hydroxide (including soda ash) and potassium hydroxide; sodium bicarbonate; sodium silicate; ammonium hydroxide; and organic bases (e.g., mono-, di- or tri-ethanolamine; and 2-dimethylamino-2-methyl-1-propanol (DMAMP)). Acids to adjust the pH include mineral acids (e.g., hydrochloric acid, phosphorus acid and sulfuric acid) and organic acids (e.g., acetic acid).

[0035] Preferably, the liquid laundry detergent formulation of the present invention contains < 1 wt% (preferably, < 0.5 wt%; more preferably, < 0.2 wt%; still more preferably, < 0.1 wt%; yet still more preferably, < 0.01 wt%; most preferably, < the detectable limit), based on the dry weight of the liquid laundry additive, of a vinyl alcohol polymer (PVA).

[0036] Preferably, the method of washing a fabric article of the present invention, comprises: providing a soiled fabric article (preferably, wherein the soiled fabric article is soiled with at least one of clay and used motor oil; more preferably, wherein the soiled fabric article is soiled with used motor oil)(preferably, wherein the soiled fabric article is a

stained cotton; more preferably, wherein the soiled fabric article is cotton stained with used motor oil); providing a liquid laundry detergent formulation of the present invention; providing a wash water; and applying the wash water and the liquid laundry detergent formulation to the soiled fabric to provide a cleaned fabric article. More preferably, the method of washing a fabric article of the present invention, comprises: providing a soiled fabric article (preferably, wherein the soiled fabric article is soiled with at least one of clay and used motor oil; more preferably, wherein the soiled fabric article is soiled with used motor oil)(preferably, wherein the soiled fabric article is a stained cotton; more preferably, wherein the soiled fabric article is cotton stained with used motor oil); providing a liquid laundry detergent formulation of the present invention; providing a wash water; providing a rinse water; applying the wash water and the liquid laundry detergent formulation to the soiled fabric to provide a cleaned fabric article; and then applying the rinse water to the cleaned fabric article to remove the liquid laundry detergent formulation from the cleaned fabric article.

[0037] Some embodiments of the present invention will now be described in detail in the following **Examples**.

Synthesis S1: Polymer 1

[0038] A two liter round bottom flask, equipped with a mechanical stirrer, heating mantle, thermocouple, condenser and inlets for the addition of monomer(s), initiator and chain regulator was charged with deionized water (206.25 g). The flask contents were then stirred and heated to 72 °C. Once the flask contents reached reaction temperature of 72 °C, a 0.15% aqueous iron sulfate heptahydrate promoter solution (2.5 g) was added, followed by sodium metabisulfite (SMBS) (0.84 g) dissolved in deionized water (5.25 g) as a pre-charge. Then, separate feeds were made to the flask as follows:

Initiator co-feed: sodium persulfate (0.96 g) dissolved in deionized water (22.5 g) was fed to the flask over 95 minutes.

Chain Transfer Agent (CTA) co-feed: sodium metabisulfite (19.42 g) dissolved in deionized water (45 g) was fed to the flask over 80 minutes.

Monomer co-feed 1: A monomer solution containing glacial acrylic acid (240 g) and of poly-ethylene glycol methacrylate (PEGMA 360) (30 g) was fed to the flask over 90 minutes.

Monomer co-feed 2: Dimethylaminoethyl methacrylate (DMAEMA) (30 g) was fed to the flask over 90 minutes.

Upon completion of the co-feeds, deionized water (17 g) was added as a rinse. The flask contents were held at 72 °C for 10 minutes. At completion of the hold, two sequential chase solutions were added to the flask with a 5 minute hold between the chase additions. Both chases comprised sodium persulfate (0.39 g) in deionized water (5.25 g) and were added over 10 minutes. After the second chase addition, the flask contents were then held at 72 °C for 20 minutes. At the completion of the final hold the flask contents were cooled to below 50 °C. Then a 50% aqueous sodium hydroxide solution (110 g) was added to the flask contents slowly through an addition funnel while maintaining the temperature below 60 °C. After addition of the aqueous sodium hydroxide solution, a 35% aqueous hydrogen peroxide scavenger solution (2.9 g) was added to the flask contents. With no residual bisulfite detected, a 50% aqueous sodium hydroxide solution (100 g) was added to the flask contents, keeping the temperature below 60 °C. A final rinse of deionized water (20 g) was then added through the addition funnel to the flask contents. The flask contents were then cooled to < 35 °C. The product polymer had a solids content of 45.1%, pH was 6.46, Brookfield viscosity of 1,030 cps. Residual monomer measured at below 25 ppm. Final weight average molecular weight, M_w , as measured by Gel Permeation Chromatography was 6,783 Daltons.

Synthesis S2: Polymer 2

[0039] A two liter round bottom flask, equipped with a mechanical stirrer, heating mantle, thermocouple, condenser and inlets for the addition of monomer(s), initiator and chain regulator was charged with deionized water (206.25 g). The flask contents were then set to stir and heated to 72 °C. Once the flask contents reached reaction temperature of 72 °C, a 0.15% aqueous iron sulfate heptahydrate promoter solution (2.5 g) was added to the flask contents, followed by the addition of sodium metabisulfite (SMBS) (1.13 g) dissolved in deionized water (5.25 g) as pre-charge. Then, separate feeds were made to the flask as follows:

Initiator co-feed: sodium persulfate (1.55 g) dissolved in deionized water (30 g) was fed to the flask over 95 minutes.

Chain Transfer Agent (CTA) co-feed: sodium metabisulfite (25.87 g) dissolved in deionized water (60 g) was fed to the flask over 80 minutes.

Monomer co-feed: A monomer solution containing glacial acrylic acid (255 g) and of 2-(2-oxoimidazolidin-1-yl)ethyl methacrylate (90 g) was fed to the flask over 90 minutes.

Upon completion of the co-feeds, deionized water (15 g) was added as a rinse. The flask contents were held at 72 °C for 10 minutes. At completion of the hold, two sequential chase solutions were added to the flask with a 5 minute hold between the chase additions. Both chases comprised sodium persulfate (0.39 g) in deionized (8.0 g) and were added over 10 minutes. After the second chase addition, the flask contents were then held at 72 °C for 20 minutes. At the completion of the final hold the flask contents were cooled to below 50 °C. Then a 50% aqueous sodium hydroxide solution (105 g) was added to the flask contents slowly through an addition funnel while maintaining the temperature below 60 °C. After addition of the aqueous sodium hydroxide solution, a 30% aqueous hydrogen peroxide scavenger solution (5.2 g) was added to the flask contents. With no residual bisulfite detected, a 50% aqueous sodium hydroxide solution (106 g) was added to the flask contents, keeping the temperature below 60 °C. A final rinse of deionized water (15 g) was then added to through the addition funnel to the flask contents. The flask contents were then cooled to < 35 °C. The product polymer had a solids content of 42.5%, pH was 6.16, Brookfield viscosity of 1,170 cps. Residual monomer measured at below 50 ppm. Final weight average molecular weight, M_w , as measured by Gel Permeation Chromatography was 15,488 Daltons; and the number average molecular weight, M_n , was 4,520 Daltons.

Comparative Examples C1-C2 and Example 1: Liquid Laundry Detergent

[0040] The liquid laundry detergent formulations used in the cleaning tests in the subsequent Examples were prepared having the generic formulation as described in **TABLE 1** with the cleaning booster polymer as noted in **TABLE 2** and were prepared by standard liquid laundry formulation preparation procedures.

TABLE 1

<u>Ingredient</u>	<u>Commercial Name</u>	<u>wt%</u>
Linear alkyl benzene sulfonate	Nacconal 90G*	8.0
Sodium lauryl ethoxysulfate	Steol CS-460*	2.0
Non-ionic surfactant	Biosoft N25-7*	4.0
Cleaning Booster polymer	--	3.0
Deionized water	--	QS to 100
* available from Stepan Company		

TABLE 2

<u>Example</u>	<u>Cleaning Booster Polymer</u>
Comparative Example C1	ethoxylated poly(ethyleneimine) ¹
Comparative Example C2	Polymer 1
1	Polymer 2
¹ available from BASF under the tradename Sokolan™ HP-20	

Primary Cleaning Performance

[0041] The primary cleaning performance of the liquid laundry detergent formulations of **Comparative Examples C1-C2** and **Example 1** were assessed in a Terg-o-tometer Model TOM-52-A available from SR Lab Instruments (6 x 1 L wells) agitated at 90 cycles per minute with the conditions noted in **TABLE 3**.

TABLE 3

<u>Parameter</u>	<u>Setting</u>
Temperature	15 °C
Water hardness	200 ppm, Ca/Mg = 2/1
Fabric Types (3 in each well)	Stained Cotton 400
Stains	Clay, Motor Oil and Dust Sebum (Bought from Scientific Services S/D, Inc.)
Wash time	16 minutes
Rinse time	3 minutes
Liquid laundry detergent dosage	0.5 g/L

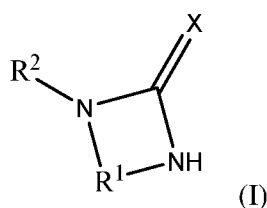
[0042] The soil removal index (SRI) was calculated using ASTM Method D4265-14. The ΔSRI was determined in reference to a control detergent with the same surfactant concentrations absent cleaning booster. The results are provided in **TABLE 4**.

TABLE 4

<u>Example</u>	<u>Stain ΔSRI</u>		
	<u>Ground Clay</u>	<u>Motor Oil</u>	<u>Dust Sebum</u>
Comp. Ex. C1	+8	+5	+1
Comp. Ex. C2	+8	+5	+3
Ex. 1	+7	+1	+5

We claim:

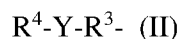
1. A liquid laundry detergent formulation, comprising:
 - a liquid carrier;
 - a cleaning surfactant; and
 - a cleaning booster polymer, wherein the cleaning booster polymer, comprises:
 - (a) 60 to 95 wt%, based on dry weight of the cleaning booster polymer, of structural units of a monoethylenically unsaturated carboxylic acid monomer;
 - (b) 5 to 40 wt%, based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (I)



wherein X is selected from the group consisting of an oxygen atom and a sulfur atom;

wherein R¹ is a C₂₋₄ alkylene group;

wherein R² is selected from the group consisting of a 2-(2-carboxyacrylamide)ethyl group, a vinyl group, an allyl group, an isopropenyl group, an acryloyl group, a methacryloyl group, a 2-hydroxy-3-(allyloxy)propyl group and a functional group of formula (II)

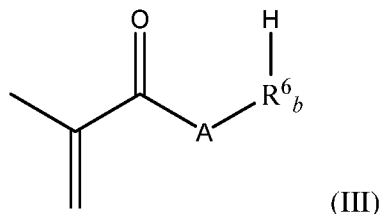


wherein R³ is a C₁₋₅ alkylene group;

wherein Y is selected from the group consisting of an -O- and an -NR⁵-, where R⁵ is selected from the group consisting of a hydrogen and a C₁₋₈ alkyl group; and

wherein R⁴ is selected from the group consisting of a 2-hydroxy-3-(allyloxy)propyl group, a vinyl group, a methacryloyl group, an acryloyl group and a methacryloyloxyaceto group;

- (c) 0 to 20 wt%, based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (III)

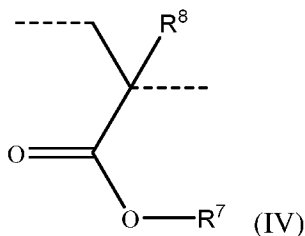


wherein A is selected from the group consisting of an -O- and an -NR⁵-;

wherein each R⁶ is independently selected from the group consisting of a -CH₂CH₂O- group, a -CH₂CH(CH₃)O- group and a -CH₂CH(CH₂CH₃)O- group; and

wherein *b* is 2 to 20;

(d) 0 to 5 wt%, based on dry weight of the cleaning booster polymer, of structural units of an ethylenically unsaturated monomer of formula (IV)



wherein each R⁷ is independently selected from a -C₁₋₄ alkyl group; and

wherein each R⁸ is independently selected from the group consisting of a hydrogen and a methyl group.

2. The liquid laundry detergent formulation, of claim 1, wherein the liquid laundry detergent formulation comprises

25 to 97.9 wt%, based on weight of the liquid laundry detergent formulation, of the liquid carrier;

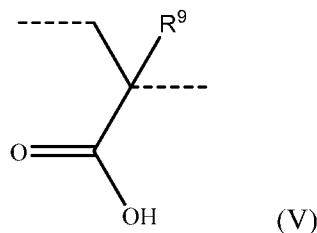
2 to 60 wt%, based on weight of the liquid laundry detergent formulation, of the cleaning surfactant; and

0.1 to 15 wt%, based on weight of the liquid laundry detergent formulation, of the cleaning booster polymer.

3. The liquid laundry detergent formulation of claim 1, wherein the liquid carrier comprises water.

4. The liquid laundry detergent formulation of claim 3, wherein the cleaning booster polymer has a weight average molecular weight, M_w, of 500 to 100,000 Daltons.

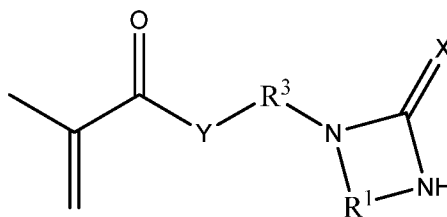
5. The liquid laundry detergent formulation of claim 4, wherein the structural units of monoethylenically unsaturated carboxylic acid monomer are structural units of formula (V)



wherein each R^9 is independently selected from a hydrogen and a $-CH_3$ group.

6. The liquid laundry detergent formulation of claim 5, wherein each R^9 is a hydrogen in 50 to 100 mol% of the structural units of formula (V) in the cleaning booster polymer.

7. The liquid laundry detergent formulation of claim 6, wherein the ethylenically unsaturated monomer of formula (I) is of formula (Ia)



wherein Y is selected from the group consisting of an $-O-$ and an $-NR^5-$; wherein R^1 is selected from the group consisting of a $-CH_2CH_2CH_2-$ group, a $-CH(CH_3)CH_2-$ group, and a $-CH_2CH_2-$ group; wherein R^3 is a C_{1-5} alkylene group; and wherein X is selected from the group consisting of an oxygen atom and a sulfur atom.

8. The liquid laundry detergent formulation of claim 7, wherein Y is an $-O-$; wherein R^1 is a $-CH_2CH_2-$ group; wherein R^3 is a C_{2-4} alkylene group and wherein X is an oxygen.

9. The liquid laundry detergent formulation of claim 8, wherein R^3 is a $-CH_2CH_2-$ group.

10. A method of washing a fabric article of the present invention, comprising: providing a soiled fabric article; providing a liquid laundry detergent formulation according to claim 1; providing a wash water; and applying the wash water and the liquid laundry detergent formulation to the soiled fabric to provide a cleaned fabric article.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2020/034799

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D3/37 C11D3/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/005288 A1 (BOUTIQUE JEAN-POL [BE] ET AL) 1 January 2009 (2009-01-01) cited in the application claims examples page 1, paragraph 3 - paragraph 5 -----	1-10
A	US 5 071 902 A (LANGERBEINS KLAUS [DE] ET AL) 10 December 1991 (1991-12-10) claims examples column 1, line 63 - column 2, line 20 column 3, line 64 - column 4, line 37 column 5, line 59 - line 66 ----- -/--	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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Date of the actual completion of the international search

14 July 2020

Date of mailing of the international search report

18/08/2020

Name and mailing address of the ISA/

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

Authorized officer

Neys, Patricia

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/034799

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2002/065208 A1 (AUBAY ERIC [FR] ET AL) 30 May 2002 (2002-05-30) claims examples page 3, paragraphs 58,63 page 2, paragraph 41 - paragraph 45 -----	1-10
A	US 2003/130160 A1 (EASON MICHAEL DOUGLAS [GB] ET AL) 10 July 2003 (2003-07-10) claims examples -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2020/034799

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009005288	A1	01-01-2009	AR 067365 A1 07-10-2009
			BR PI0813289 A2 30-12-2014
			BR PI0813361 A2 12-07-2016
			CA 2687981 A1 08-01-2009
			CA 2688014 A1 08-01-2009
			CN 101688160 A 31-03-2010
			EP 2160454 A1 10-03-2010
			EP 2164942 A1 24-03-2010
			JP 5535903 B2 02-07-2014
			JP 2010530926 A 16-09-2010
			JP 2010531384 A 24-09-2010
			US 2009005287 A1 01-01-2009
			US 2009005288 A1 01-01-2009
			US 2011143990 A1 16-06-2011
			WO 2009004555 A1 08-01-2009
			WO 2009005737 A1 08-01-2009
			ZA 200908757 B 29-09-2010
			ZA 200908791 B 25-08-2010
US 5071902	A	10-12-1991	AT 89295 T 15-05-1993
			CA 2008566 A1 25-07-1990
			DE 3902067 A1 26-07-1990
			EP 0384125 A1 29-08-1990
			JP 2918052 B2 12-07-1999
			JP H02233711 A 17-09-1990
			US 5071902 A 10-12-1991
US 2002065208	A1	30-05-2002	AR 030477 A1 20-08-2003
			AU 8415101 A 13-03-2002
			BR 0113381 A 10-06-2003
			CA 2420351 A1 07-03-2002
			EP 1366083 A2 03-12-2003
			FR 2813313 A1 01-03-2002
			JP 2004512431 A 22-04-2004
			KR 20030029147 A 11-04-2003
			US 2002065208 A1 30-05-2002
			US 2004038851 A1 26-02-2004
			US 2006211594 A1 21-09-2006
			US 2009165216 A1 02-07-2009
			WO 0218451 A2 07-03-2002
US 2003130160	A1	10-07-2003	AR 037926 A1 22-12-2004
			AU 2002352215 A1 09-07-2003
			BR 0214505 A 03-11-2004
			CA 2467680 A1 03-07-2003
			CN 1606577 A 13-04-2005
			EP 1456261 A2 15-09-2004
			US 2003130160 A1 10-07-2003
			WO 03054044 A2 03-07-2003
			ZA 200403331 B 27-07-2005