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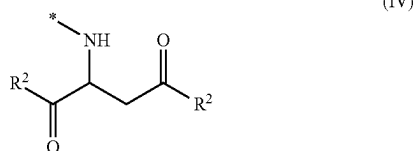
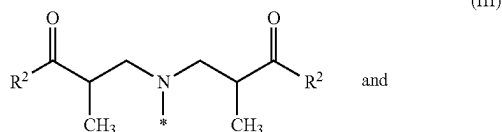
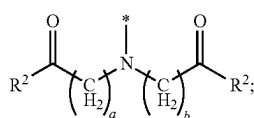
$$\text{R}^3-\text{O}-\left[\begin{array}{cc}\text{H} & \text{H} \\ | & | \\ \text{C} & -\text{C}-\text{O} \\ | & | \\ \text{R}^4 & \text{R}^5\end{array}\right]_c$$

LAUNDRY DETERGENT FORMULATION

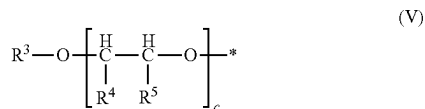
[0001] The present invention relates to a laundry detergent formulation. In particular, the present invention relates to a laundry detergent formulation, comprising a carrier, a cleaning surfactant and a cleaning booster, wherein the cleaning booster is of formula (I)



wherein A^1 is a divalent linking group having 4 to 24 carbon atoms; and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III) and formula (IV)



wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2; wherein b is 1 or 2; and wherein each R^2 is independently of formula (V)



wherein the * in formula (V) is the point of attachment to the associated base formula; wherein R^3 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^4 and R^5 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with the proviso that at least one of R^4 and R^5 is a hydrogen in each subunit c ; and wherein c is 0 to 30; and with the proviso that when the divalent linking group, A^1 , has 4 carbon atoms, the divalent linking group, A^1 , includes a cycle.

[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.

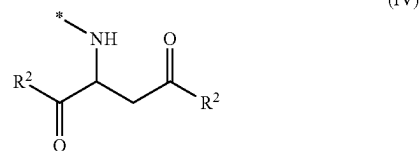
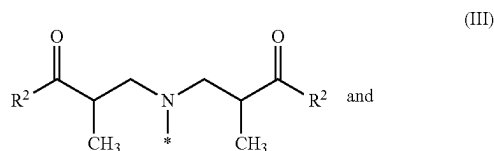
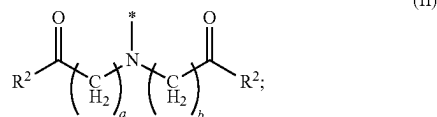
[0003] One approach for reducing the unit dose of surfactant is to incorporate polymers into the liquid detergent formulations as described by Boutique et al. in U.S. Patent Application Publication No. 20090005288. Boutique et al. disclose a graft copolymer of polyethylene, polypropylene or polybutylene 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. There is also a continuing need for new cleaning boosters with improved biodegradability according to OECD 301F protocol when compared with conventional cleaning boosters.

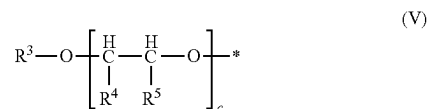
[0005] The present invention provides a laundry detergent formulation, comprising: a carrier; a cleaning surfactant; and a cleaning booster, wherein the cleaning booster is of formula (I)



wherein A^1 is a divalent linking group having 4 to 24 carbon atoms; and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III) and formula (IV)



wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2; wherein b is 1 or 2; and wherein each R^2 is independently of formula (V)



wherein the * in formula (V) is the point of attachment to the associated base formula; wherein R^3 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^4 and R^5 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with

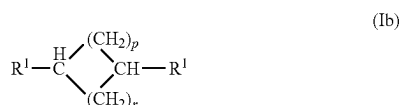
the proviso that at least one of R^4 and R^5 is a hydrogen in each subunit c; and wherein c is 0 to 30; and with the proviso that when the divalent linking group, A^1 , has 4 carbon atoms, the divalent linking group, A^1 , includes a cycle.

[0006] The present invention provides a laundry detergent formulation, comprising: a carrier; a cleaning surfactant; and a cleaning booster, wherein the cleaning booster is of formula (Ia)



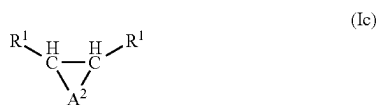
wherein n is 5 to 24; and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III) and formula (IV); wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2; wherein b is 1 or 2; and wherein each R^2 is independently of formula (V); wherein the * in formula (V) is the point of attachment to the associated base formula; wherein R^3 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^4 and R^5 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with the proviso that at least one of R^4 and R^5 is a hydrogen in each subunit c; and wherein c is 0 to 30.

[0007] The present invention provides a laundry detergent formulation, comprising: a carrier; a cleaning surfactant; and a cleaning booster, wherein the cleaning booster is of formula (Ib)



wherein p and r are independently 1 to 4; and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III) and formula (IV); wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2; wherein b is 1 or 2; and wherein each R^2 is independently of formula (V); wherein the * in formula (V) is the point of attachment to the associated base formula; wherein R^3 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^4 and R^5 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with the proviso that at least one of R^4 and R^5 is a hydrogen in each subunit c; and wherein c is 0 to 30.

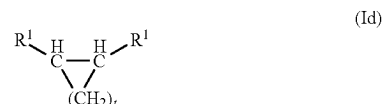
[0008] The present invention provides a laundry detergent formulation, comprising: a carrier; a cleaning surfactant; and a cleaning booster, wherein the cleaning booster is of formula (Ic)



wherein A^2 is a divalent linking group having 2 to 22 carbon atoms; and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III) and formula (IV); wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2; wherein b is 1 or 2; and wherein each

R^2 is independently of formula (V); wherein the * in formula (V) is the point of attachment to the associated base formula; wherein R^3 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^4 and R^5 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with the proviso that at least one of R^4 and R^5 is a hydrogen in each subunit c; and wherein c is 0 to 30.

[0009] The present invention provides a laundry detergent formulation, comprising: a carrier; a cleaning surfactant; and a cleaning booster, wherein the cleaning booster is of formula (Id)



wherein t is 2 to 10; and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III) and formula (IV); wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2; wherein b is 1 or 2; and wherein each R^2 is independently of formula (V); wherein the * in formula (V) is the point of attachment to the associated base formula; wherein R^3 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^4 and R^5 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with the proviso that at least one of R^4 and R^5 is a hydrogen in each subunit c; and wherein c is 0 to 30.

[0010] The present invention provides a method of washing a fabric article, comprising: providing a soiled fabric article; providing a laundry detergent formulation according to the present invention; providing a wash water; and applying the wash water and the laundry detergent formulation to the soiled fabric to provide a cleaned fabric article.

DETAILED DESCRIPTION

[0011] It has been surprisingly found that the laundry detergent formulations with a cleaning booster as described herein facilitate improvement in primary cleaning performance for sebum soil removal, while imparting good anti-redeposition performance for dust sebum and clay; and also exhibiting desirable biodegradability profiles according to OECD 301F protocol.

[0012] 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.

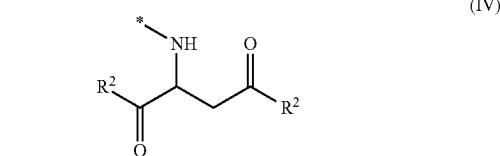
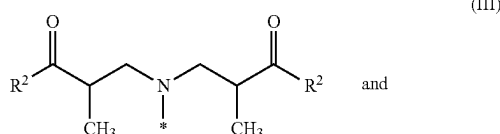
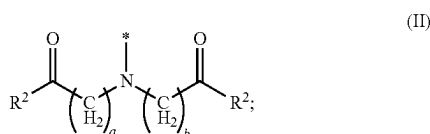
[0013] Preferably, the laundry detergent formulation of the present invention can be formulated in any typical form, e.g., as a tablet, powder, monodose, sachet, paste, liquid or gel. More preferably, the laundry detergent formulation of the present invention is a liquid or gel. Most preferably, the laundry detergent formulation of the present invention is an aqueous liquid detergent formulation.

[0014] Preferably, the laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulations) comprises: a carrier (preferably, a liquid carrier); a cleaning surfactant; and a cleaning booster, wherein the cleaning

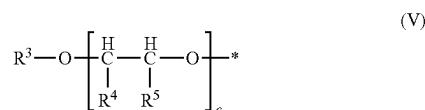
booster is of formula (I) (preferably, wherein formula (I) is selected from the group consisting of formula (Ia), formula (Ib), formula (Ic) and formula (Id) (preferably, formula (Ia) and formula (Ib))



wherein A^1 is a divalent linking group having 4 to 24 carbon atoms (preferably, wherein the divalent linking group, A^1 , is a divalent cyclic or acyclic, linear or branched, aliphatic hydrocarbon having 4 to 24 carbon atoms (preferably, 4 to 12 carbon atoms)); and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III) and formula (IV) (preferably, formula (II) and formula (III); most preferably, formula (III))



wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2 (preferably, 1); wherein b is 1 or 2 (preferably, 1); (preferably, wherein $a=b$) and wherein each R^2 is independently of formula (V) (i.e., the individual occurrences of R^2 in formula (II), formula (III) and formula (IV) can be the same or different from one another)



wherein the * in formula (V) is the point of attachment to the associated base formula (i.e., formula (II), formula (III) or formula (IV)); wherein R^3 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group (preferably, a hydrogen and a C_{1-5} alkyl group; more preferably, a methyl group, an ethyl group and a butyl group; still more preferably, a methyl group and an n-butyl group; most preferably, an n-butyl group); wherein each R^4 and R^5 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with the proviso that at least one of R^4 and R^5 is a hydrogen in each subunit c ; and wherein c is 0 to 30 (preferably, with the proviso that c is 2 to 30 (preferably, 2 to 25; more preferably, 2 to 17; most preferably, 4 to 12) in 70 to 100 mol % (preferably, 80 to 100 mol %; more preferably, 90 to 100 mol %; most preferably, 95 to 100 mol

%) of the occurrences of formula (V) in the cleaning booster); and with the proviso that when the divalent linking group, A^1 , has 4 carbon atoms, the divalent linking group, A^1 , includes a cycle (preferably, with the proviso that when the divalent linking group, A^1 , has 4 carbon atoms, the cleaning booster of formula (I) is selected from the group consisting of formula (Ib), formula (Ic) and formula (Id)).

[0015] Preferably, the laundry detergent formulation of the present invention is a liquid laundry detergent formulation, comprising: a liquid carrier (preferably, 25 to 97.9 wt % (more preferably, 30 to 95.5 wt %; still more preferably, 40 to 93 wt %; yet more preferably, 45 to 90.5 wt %; most preferably, 50 to 87.5 wt %), based on weight of the laundry detergent formulation, of the liquid carrier); a cleaning surfactant (preferably, 2 to 60 wt % (more preferably, 4 to 50 wt %; still more preferably, 6 to 40 wt %; yet more preferably, 7.5 to 35 wt %; most preferably, 10 to 30 wt %), based on weight of the laundry detergent formulation, of the cleaning surfactant); and a cleaning booster (preferably, 0.1 to 15 wt % (more preferably, 0.5 to 12 wt %; still more preferably, 1 to 10 wt %; yet more preferably, 2 to 8 wt %; most preferably 2.5 to 7.5 wt %), based on weight of the laundry detergent formulation, of the cleaning booster), wherein the cleaning booster is of formula (I) (preferably, wherein formula (I) is selected from the group consisting of formula (Ia), formula (Ib), formula (Ic) and formula (Id) (preferably, formula (Ia) and formula (Ib)); wherein A^1 is a divalent linking group having 4 to 24 carbon atoms (preferably, wherein the divalent linking group, A^1 , is a divalent cyclic or acyclic, linear or branched, aliphatic hydrocarbon having 4 to 24 carbon atoms (preferably, 4 to 12 carbon atoms)); and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III) and formula (IV) (preferably, formula (II) and formula (III); most preferably, formula (III)); wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2 (preferably, 1); wherein b is 1 or 2 (preferably, 1); (preferably, wherein $a=b$) and wherein each R^2 is independently of formula (V) (i.e., the individual occurrences of R^2 in formula (II), formula (III) and formula (IV) can be the same or different from one another); wherein the * in formula (V) is the point of attachment to the associated base formula (i.e., formula (II), formula (III) or formula (IV)); wherein R^3 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group (preferably, a hydrogen and a C_{1-5} alkyl group; more preferably, a methyl group, an ethyl group and a butyl group; still more preferably, a methyl group and an n-butyl group; most preferably, an n-butyl group); wherein each R^4 and R^5 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with the proviso that at least one of R^4 and R^5 is a hydrogen in each subunit c ; and wherein c is 0 to 30 (preferably, with the proviso that c is 2 to 30 (preferably, 2 to 25; more preferably, 2 to 17; most preferably, 4 to 12) in 70 to 100 mol % (preferably, 80 to 100 mol %; more preferably, 90 to 100 mol %; most preferably, 95 to 100 mol %) of the occurrences of formula (V) in the cleaning booster); and with the proviso that when the divalent linking group, A^1 , has 4 carbon atoms, the divalent linking group, A^1 , includes a cycle (preferably, with the proviso that when the divalent linking group, A^1 , has 4 carbon atoms, the cleaning booster of formula (I) is selected from the group consisting of formula (Ib), formula (Ic) and formula (Id)).

[0016] Preferably, the laundry detergent formulation of the present invention comprises a carrier, wherein the carrier is selected from solid and liquid carriers. More preferably, the laundry detergent formulation of the present invention is a liquid laundry detergent formulation; wherein the carrier is a liquid carrier. Still more preferably, the laundry detergent formulation of the present invention is a liquid laundry detergent formulation comprising 25 to 97.9 wt % (preferably, 30 to 95.5 wt %; more preferably, 40 to 93 wt %; still more preferably, 45 to 90.5 wt %; most preferably, 50 to 87.5 wt %), based on weight of the laundry detergent formulation, of a liquid carrier. Yet more preferably, the laundry detergent formulation of the present invention is a liquid laundry detergent formulation comprising 25 to 97.9 wt % (preferably, 25 to 97.9 wt % (more preferably, 30 to 95.5 wt %; still more preferably, 40 to 93 wt %; yet more preferably, 45 to 90.5 wt %; most preferably, 50 to 87.5 wt %), based on weight of the laundry detergent formulation, of a liquid carrier; wherein the liquid carrier comprises water. Most preferably, the laundry detergent formulation of the present invention is a liquid laundry detergent formulation comprising 25 to 97.9 wt % (preferably, 25 to 97.9 wt % (more preferably, 30 to 95.5 wt %; still more preferably, 40 to 93 wt %; yet more preferably, 45 to 90.5 wt %; most preferably, 50 to 87.5 wt %), based on weight of the laundry detergent formulation, of a liquid carrier; wherein the liquid carrier is water.

[0017] Preferably, the liquid carrier optionally includes a water miscible liquid, such as, C_{1-3} alkanols, C_{1-3} alkanediols and mixtures thereof. More preferably, the liquid carrier optionally includes 0 to 10 wt % (preferably, 0.2 to 8 wt %; more preferably, 0.5 to 7.5 wt %), based on weight of the liquid carrier, of water miscible liquids; wherein the water miscible liquids are selected from the group consisting of C_{1-3} alkanols, C_{1-3} alkanediols (e.g., propylene glycol) and mixtures thereof. Most preferably, the liquid carrier optionally includes 0 to 10 wt % (preferably, 0.2 to 8 wt %; more preferably, 0.5 to 7.5 wt %), based on weight of the liquid carrier, of water miscible liquids; wherein the water miscible liquids are selected from the group consisting of ethanol, propylene glycol and mixtures thereof.

[0018] Preferably, the laundry detergent formulation of the present invention, comprises: a cleaning surfactant. More preferably, the laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation) comprises: 2 to 60 wt % (preferably, 4 to 50 wt %; more preferably, 6 to 40 wt %; yet more preferably, 7.5 to 35 wt %; most preferably, 10 to 30 wt %), based on weight of the laundry detergent formulation, of a cleaning surfactant. Still more preferably, the laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation), comprises: 2 to 60 wt % (preferably, 4 to 50 wt %; more preferably, 6 to 40 wt %; yet more preferably, 7.5 to 35 wt %; most preferably, 10 to 30 wt %), based on weight of the 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 laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation), comprises: 2 to 60 wt % (preferably, 4 to 50 wt %; more

preferably, 6 to 40 wt %; yet more preferably, 7.5 to 35 wt %; most preferably, 10 to 30 wt %), based on weight of the 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 laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation), comprises: 2 to 60 wt % (preferably, 4 to 50 wt %; more preferably, 6 to 40 wt %; yet more preferably, 7.5 to 35 wt %; most preferably, 10 to 30 wt %), based on weight of the 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.

[0019] Anionic surfactants include alkyl sulfates, alkyl benzene sulfates, alkyl benzene sulfonic acids, alkyl benzene sulfonates, alkyl polyethoxy sulfates, alkoxyated 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 C_{8-20} alkyl benzene sulfates, C_{8-20} alkyl benzene sulfonic acid, C_{8-20} alkyl benzene sulfonate, paraffin sulfonic acid, paraffin sulfonate, alpha-olefin sulfonic acid, alpha-olefin sulfonate, alkoxyated alcohols, C_{8-20} alkyl phenols, amine oxides, sulfonates of fatty acids, sulfonates of fatty acid esters, C_{8-10} alkyl polyethoxy sulfates and mixtures thereof. More preferred anionic surfactants include C_{12-16} alkyl benzene sulfonic acid, C_{12-16} alkyl benzene sulfonate, C_{12-18} paraffin-sulfonic acid, C_{12-18} paraffin-sulfonate, C_{12-16} alkyl polyethoxy sulfate and mixtures thereof.

[0020] 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.

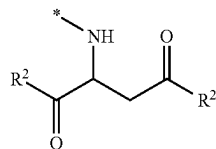
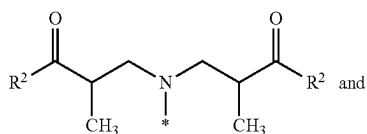
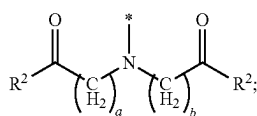
[0021] Cationic surfactants include quaternary surface active compounds. Preferred cationic surfactants include quaternary surface active compounds having at least one of an ammonium group, a sulfonium group, a phosphonium group, an iodonium group and an arsonium group. More preferred cationic surfactants include at least one of a dialkyldimethylammonium chloride and alkyl dimethyl benzyl ammonium chloride. Still more preferred cationic surfactants include at least one of C_{16-18} dialkyldimethylammonium chloride, a C_{8-18} alkyl dimethyl benzyl ammonium chloride di-tallow dimethyl ammonium chloride and di-tallow dimethyl ammonium chloride. Most preferred cationic surfactant includes di-tallow dimethyl ammonium chloride.

[0022] 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.

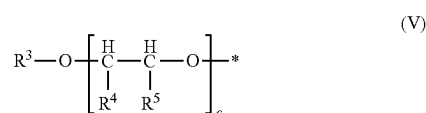
[0023] Preferably, the laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation), comprises: 0.1 to 15 wt % (preferably, 0.5 to 12 wt %; more preferably, 1 to 10 wt %; yet more preferably, 2 to 8 wt %; most preferably 2.5 to 7.5 wt %), based on weight of the laundry detergent formulation, of the cleaning booster; wherein the cleaning booster is of formula (I) (preferably, wherein formula (I) is selected from the group consisting of formula (Ia), formula (Ib), formula (Ic) and formula (Id) (preferably, formula (Ia) and formula (Ib))



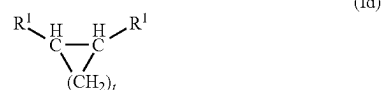
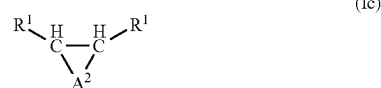
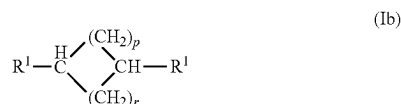
wherein A¹ is a divalent linking group having 4 to 24 carbon atoms (preferably, wherein the divalent linking group, A¹, is a divalent cyclic or acyclic, linear or branched, aliphatic hydrocarbon having 4 to 24 carbon atoms (preferably, 4 to 12 carbon atoms)); and wherein each R¹ is independently selected from the group consisting of formula (II), formula (III) and formula (IV) (preferably, formula (II) and formula (III); most preferably, formula (III))



wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2 (preferably, 1); wherein b is 1 or 2 (preferably, 1); (preferably, wherein a=b) and wherein each R² is independently of formula (V) (i.e., the individual occurrences of R² in formula (II), formula (III) and formula (IV) can be the same or different from one another)



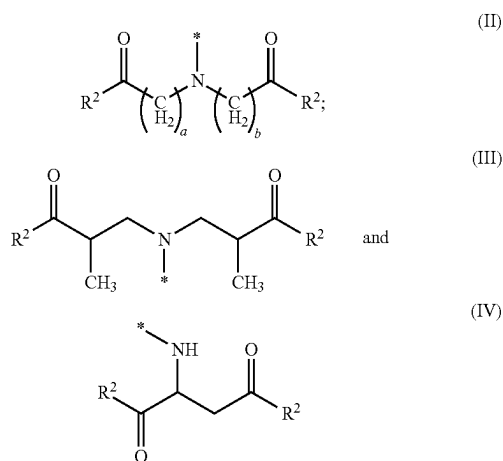
wherein the * in formula (V) is the point of attachment to the associated base formula (i.e., formula (II), formula (III) or formula (IV)); wherein R³ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group (preferably, a hydrogen and a C₁₋₅ alkyl group; more preferably, a methyl group, an ethyl group and a butyl group; still more preferably, a methyl group and an n-butyl group; most preferably, an n-butyl group); wherein each R⁴ and R⁵ is independently selected from the group consisting of a hydrogen and a C₁₋₂₅ alkyl group, with the proviso that at least one of R⁴ and R⁵ is a hydrogen in each subunit c; and wherein c is 0 to 30 (preferably, with the proviso that c is 2 to 30 (preferably, 2 to 25; more preferably, 2 to 17; most preferably, 4 to 12) in 70 to 100 mol % (preferably, 80 to 100 mol %; more preferably, 90 to 100 mol %; most preferably, 95 to 100 mol %) of the occurrences of formula (V) in the cleaning booster); and with the proviso that when the divalent linking group, A¹, has 4 carbon atoms, the divalent linking group, A¹, includes a cycle (preferably, with the proviso that when the divalent linking group, A¹, has 4 carbon atoms, the cleaning booster of formula (I) is selected from the group consisting of formula (Ib), formula (Ic) and formula (Id)). More preferably, the laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation), comprises: 0.1 to 15 wt % (preferably, 0.5 to 12 wt %; more preferably, 1 to 10 wt %; yet more preferably, 2 to 8 wt %; most preferably 2.5 to 7.5 wt %), based on weight of the laundry detergent formulation, of the cleaning booster; wherein the cleaning booster is of formula (I); wherein formula (I) is selected from the group consisting of formula (Ia), formula (Ib), formula (Ic) and formula (Id) (preferably, formula (Ia) and formula (Ib))



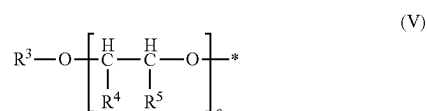
wherein n is 5 to 24 (preferably, 5 to 12); wherein p and r are independently t to 4 (preferably, 1 to 2; more preferably, wherein p and r are 2)(preferably, wherein the sum of p+r is 2 to 6 (preferably, 2 to 5; more preferably, 4)); wherein A² is a divalent linking group having 2 to 22 carbon atoms (preferably, wherein the divalent linking group, A², is a divalent, cyclic or acyclic, linear or branched, aliphatic

hydrocarbon having 2 to 22 carbon atoms (preferably, 2 to 10 carbon atoms; more preferably, 3 to 6 carbon atoms; most preferably, 4 carbon atoms); more preferably, wherein the divalent linking group, A², is an alkanediyl having 2 to 22 carbon atoms (preferably, 2 to 10 carbon atoms; more preferably, 3 to 6 carbon atoms; still more preferably, 3 to 5; most preferably, 4 carbon atoms); and wherein t is 2 to 10 (preferably, 3 to 6; more preferably, 3 to 5; most preferably, 4).

[0024] Preferably, the laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation), comprises: 0.1 to 15 wt % (preferably, 0.5 to 12 wt %; more preferably, 1 to 10 wt %; yet more preferably, 2 to 8 wt %; most preferably 2.5 to 7.5 wt %), based on weight of the laundry detergent formulation, of the cleaning booster; wherein the cleaning booster is of formula (I) (preferably, wherein formula (I) is selected from the group consisting of formula (Ia), formula (Ib), formula (Ic) and formula (Id) (preferably, formula (Ia) and formula (Ib)); wherein each R¹ is independently selected from the group consisting of formula (II), formula (III) and formula (IV) (preferably, formula (II) and formula (III); most preferably, formula (III))



wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2 (preferably, 1); wherein b is 1 or 2 (preferably, 1); (preferably, wherein a=b) and wherein each R² is independently of formula (V) (i.e., the individual occurrences of R² in formula (II), formula (III) and formula (IV) can be the same or different from one another);



wherein the * in formula (V) is the point of attachment to the associated base formula (i.e., formula (II), formula (III) or formula (IV)); wherein R³ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group (preferably, a hydrogen and a C₁₋₅ alkyl group; more preferably, a methyl

group, an ethyl group and a butyl group; still more preferably, a methyl group and an n-butyl group; most preferably, an n-butyl group); wherein each R⁴ and R⁵ is independently selected from the group consisting of a hydrogen and a C₁₋₂ alkyl group, with the proviso that at least one of R⁴ and R⁵ is a hydrogen in each subunit c; and wherein c is 0 to 30 (preferably, with the proviso that c is 2 to 30 (preferably, 2 to 25; more preferably, 2 to 17; most preferably, 4 to 12) in 70 to 100 mol % (preferably, 80 to 100 mol %; more preferably, 90 to 100 mol %; most preferably, 95 to 100 mol %) of the occurrences of formula (V) in the cleaning booster).

[0025] Preferably, the laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation), comprises: 0.1 to 15 wt % (preferably, 0.5 to 12 wt %; more preferably, 1 to 10 wt %; yet more preferably, 2 to 8 wt %; most preferably 2.5 to 7.5 wt %), based on weight of the laundry detergent formulation, of the cleaning booster; wherein the cleaning booster is of formula (I) (preferably, wherein formula (I) is selected from the group consisting of formula (Ia), formula (Ib), formula (Ic) and formula (Id) (preferably, formula (Ia) and formula (Ib)); wherein c is 2 to 30 for an average of 70 to 100 mol % (preferably, 80 to 100 mol %; more preferably, 90 to 100 mol %; most preferably, 95 to 100 mol %) of the R² groups of formula (V). More preferably, the laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation), comprises: 0.1 to 15 wt % (preferably, 0.5 to 12 wt %; more preferably, 1 to 10 wt %; yet more preferably, 2 to 8 wt %; most preferably 2.5 to 7.5 wt %), based on weight of the laundry detergent formulation, of the cleaning booster; wherein the cleaning booster is of formula (I) (preferably, wherein formula (I) is selected from the group consisting of formula (Ia), formula (Ib), formula (Ic) and formula (Id) (preferably, formula (Ia) and formula (Ib)); wherein an average of 70 to 100 mol % (preferably, 80 to 100 mol %; more preferably, 90 to 100 mol %; most preferably, 95 to 100 mol %) of the R² groups of formula (V) are of formula (Va)



wherein the * in formula (Va) is the point of attachment to the associated base formula (i.e., formula (II), formula (III) or formula (IV)); wherein R⁶ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group (preferably, a hydrogen and a C₁₋₅ alkyl group; more preferably, a methyl group, an ethyl group and a butyl group; still more preferably, a methyl group and an n-butyl group; most preferably, an n-butyl group); wherein each R⁷ is independently selected from the group consisting of a hydrogen and a C₁₋₂ alkyl group; and wherein y is 2 to 30. Most preferably, the laundry detergent formulation of the present invention (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation), comprises: 0.1 to 15 wt % (preferably, 0.5 to 12 wt %; more preferably, 1 to 10 wt %; yet more preferably, 2 to 8 wt %; most preferably 2.5 to 7.5 wt %), based on weight of the laundry detergent formulation, of the cleaning booster; wherein the cleaning booster is of formula (I) (preferably, wherein formula (I) is selected from the group consisting of formula (Ia), formula (Ib), formula (Ic) and formula (Id) (preferably, formula (Ia) and formula (Ib)); wherein an average of 70 to 100 mol % (preferably, 80

to 100 mol %; more preferably, 90 to 100 mol %; most preferably, 95 to 100 mol %) of the R² groups of formula (V) are of formula (Vb)



wherein the * in formula (Vb) is the point of attachment to the associated base formula (i.e., formula (II), formula (III) or formula (IV)); wherein R⁸ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group (preferably, a hydrogen and a Cis alkyl group; more preferably, a methyl group, an ethyl group and a butyl group; still more preferably, a methyl group and an n-butyl group; most preferably, an n-butyl group); wherein EO is an ethylene oxide group; wherein PO is a propylene oxide group; wherein h is 0 to 30 (preferably, 0 to 1); wherein i is 0 to 30 (preferably, 2 to 5); wherein j is 0 and 30 (preferably, 2 to 6); and wherein h+i+j is 2 to 30 (preferably, 4 to 12).

[0026] Preferably, the laundry detergent formulation of the present invention, optionally further comprises a structurant (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). More preferably, the 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 laundry detergent formulation, of a structurant (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). Most preferably, the 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 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 laundry detergent formulation when crystallized in situ (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation).

[0027] Preferably, the laundry detergent formulation of the present invention, optionally further comprises a hydrotrope (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). More preferably, the laundry detergent formulation of the present invention, optionally further comprises: 0 to 15 wt % (preferably, 0.1 to 12 wt %; more preferably, 0.2 to 10 wt %; most preferably, 0.5 to 7.5 wt %), based on the weight of the laundry detergent formulation, of a hydrotrope (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). More preferably, the laundry detergent formulation of the present invention, optionally further comprises: 0 to 15 wt % (preferably, 0.1 to 12 wt %; more preferably, 0.2 to 10 wt %; most preferably, 0.5 to 7.5 wt %), based on the weight of the 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 (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). Most preferably, the laundry detergent formulation of the present invention, further comprises: 0 to 15 wt % (preferably, 0.1 to 12 wt %; more preferably, 0.2 to 10 wt %; most preferably, 0.5 to 7.5 wt %), based on the weight of the 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 (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation).

[0028] Preferably, the laundry detergent formulation of the present invention, optionally further comprises a fragrance (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). More preferably, the 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 laundry detergent formulation, of a fragrance (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation).

[0029] Preferably, the laundry detergent formulation of the present invention, optionally further comprises a builder (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). More preferably, the 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 laundry detergent formulation, of a builder (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). Most preferably, the 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 laundry detergent formulation, of a builder; wherein the 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); ethylenediaminetetraethylenephosphonic acid; salts of ethylenediaminetetraethylenephosphonic acid; oligomeric phosphonates; polymeric phosphonates; mixtures thereof (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation).

[0030] Preferably, the laundry detergent formulation of the present invention, optionally further comprises a fabric softener (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). More preferably, the 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 laundry detergent formulation, of a fabric softener (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). Most preferably, the 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 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)

(preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation).

[0031] Preferably, the laundry detergent formulation of the present invention, optionally further comprises a pH adjusting agent (preferably, wherein the laundry detergent formulation is a liquid laundry detergent formulation). More preferably, the laundry detergent formulation of the present invention is a liquid laundry detergent formulation, optionally further comprising 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).

[0032] 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 sebum oil, dust and clay soil; more preferably, wherein the soiled fabric article is soiled with sebum oils and clay soil)(preferably, wherein the soiled fabric article is selected from the group consisting of stained cotton fabric, stained cotton interlock fabric, stained cotton terry fabric, stained polyester cotton blend fabric, stained polyester knit fabric, stained polyester woven fabric and mixtures thereof; more preferably, wherein the soiled fabric article is at least one of stained cotton fabric and stained cotton interlock fabric); 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 sebum oil, dust and clay soil; more preferably, wherein the soiled fabric article is soiled with sebum oils and clay soil)(preferably, wherein the soiled fabric article is selected from the group consisting of stained cotton fabric, stained cotton interlock fabric, stained cotton terry fabric, stained polyester cotton blend fabric, stained polyester knit fabric, stained polyester woven fabric and mixtures thereof; more preferably, wherein the soiled fabric article is at least one of stained cotton fabric and stained cotton interlock fabric); 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.

[0033] Some embodiments of the present invention will now be described in detail in the following Examples.

Synthesis S1: Michael Addition of 1,3-Diaminopropane to Dimethyl Maleate

[0034] A 250 mL 3-necked, glass, round bottom flask equipped with a magnetic stir bar was charged with 1,3-diaminopropane (15.217 g, 202 mmol, from TCI America >98.0%) and ethanol (64 mL). Gentle mixing was

initiated, and the flask was equipped with a cold-water condenser connected to an oil bubbler. The condenser was sealed to the center neck with silicone grease and the flask was further sealed with 2 rubber septa. The flask was then cooled by submerging in an ice water bath to absorb the heat of reaction. A thermocouple was inserted into one septum to track temperature during reaction. To the contents of the flask was slowly added dimethyl maleate (60.263 g, 404 mmol, from TCI America 97%) via a syringe over 22 minutes. A large exotherm was observed during the addition of dimethyl maleate. Once the temperature had stopped increasing, the flask was then placed on a reaction block heater and stirred at 60° C. for 4.5 hours. Progress of the reaction was monitored by ¹H and ¹³C NMR spectroscopy. Upon complete conversion of amine to disubstituted adduct, ethanol was distilled off in a rotary evaporator to yield a slightly viscous light yellow adduct. ¹H NMR (500 MHz, methanol-d₄) δ 3.75 (s, 6H), 3.70 (s, 6H), 2.74 (m, 6.5H), 2.58 (m, 2.3H), 1.65 (p, 2.2H), 1.3 (m, 1H); ¹³C NMR (500 MHz, CDCl₃) δ: 175.1 (2C), 172.8 (2C), 58.7 (1C), 58.6 (1C); 52.6 (2C), 52.3 (2C), 47.2 (1C), 47.0 (1C), 38.2 (1C) 38.1 (1C).

Synthesis S2: Michael Addition of 1,6-Diaminohexane to Dimethyl Maleate

[0035] A 100 mL 3-necked, glass, round bottom flask equipped with a magnetic stir bar was charged with 1,6-diaminohexane (1.776 g, 15.1 mmol, from Sigma Aldrich ≥99%) and ethanol (16 mL). Gentle mixing was initiated, and the flask was equipped with a cold-water condenser connected to an oil bubbler. The condenser was sealed to the center neck with silicone grease and the flask was further sealed with 2 rubber septa. The flask was then cooled by submerging in an ice water bath to absorb the heat of reaction. A thermocouple was inserted into one septum to track temperature during reaction. To the contents of the flask was slowly added dimethyl maleate (4.445 g, 29.9 mmol, from TCI America 97%) via a syringe over 2 minutes. An exotherm was observed during the addition of dimethyl maleate and 3 minutes after. Once the temperature had stopped increasing, the flask was then placed on a reaction block heater and stirred at 60° C. for 7 hours. Progress of the reaction was monitored by ¹H and ¹³C NMR spectroscopy. Upon complete conversion of amine to disubstituted adduct, ethanol was distilled off in a rotary evaporator to yield a slightly viscous light yellow adduct. ¹H NMR (500 MHz, CDCl₃) δ 3.65 (s, 6H), 3.60 (s, 7H), 3.58-3.48 (m, 2H), 2.64 (dd, J=15.8, 6.0 Hz, 2H), 2.59-2.47 (m, 5H), 2.40 (ddd, J=11.1, 7.9, 6.3 Hz, 2H), 1.35 (p, J=6.2 Hz, 5H), 1.28-1.06 (m, 7H); ¹³C NMR (500 MHz, CDCl₃) δ: 174.1 (2C), 171.2 (2C), 57.6 (2C), 52.2 (2C), 51.7 (2C), 47.9 (2C), 37.7 (2C), 29.9 (2C), 26.9 (2C).

Synthesis S3: Michael Addition of 1,12-Diaminododecane to Dimethyl Maleate

[0036] A 250 mL 3-necked, glass, round bottom flask equipped with a magnetic stir bar was charged with 1,12-diaminododecane (6.861 g, 34.2 mmol, from TCI America 99.8%) and ethanol (32 mL). Gentle mixing was initiated, and the flask was equipped with a cold-water condenser connected to an oil bubbler. The condenser was sealed to the center neck with silicone grease and the flask was further sealed with 2 rubber septa. The flask was then cooled by

submerging in an ice water bath to absorb the heat of reaction. A thermocouple was inserted into one septum to track temperature during reaction. To the contents of the flask was slowly added dimethyl maleate (10.148 g, 68.3 mmol, from TCI America 97%) via a syringe over 7 minutes. An exothermic event was observed during the addition of dimethyl maleate and 4 minutes after. Once the temperature had stopped increasing, the flask was then placed on a reaction block heater and stirred at 60° C. for 4 hours. Progress of the reaction was monitored by ¹H and ¹³C NMR spectroscopy. Upon complete conversion of amine to disubstituted adduct, ethanol was distilled off in a rotary evaporator to yield a slightly viscous light yellow adduct. ¹H NMR (500 MHz, CDCl₃) δ 3.64 (s, 6H), 3.59 (s, 6H), 3.61-3.50 (m, 3H), 2.63 (dd, J=15.8, 6.1 Hz, 2H), 2.60-2.49 (m, 5H), 2.39 (ddd, J=11.1, 8.0, 6.3 Hz, 2H), 1.41-1.28 (m, 5H), 1.20 (s, 2H), 1.21-1.08 (m, 18H); ¹³C NMR (500 MHz, CDCl₃) δ: 174.1 (2C), 171.2 (2C), 57.6 (2C), 51.9 (2C), 51.6 (2C), 48.0 (2C), 37.6 (2C), 29.9 (2C), 29.4 (m, 6C), 27.0 (2C).

Synthesis S4: Michael Addition of Trans-1,4-diaminocyclohexane to Dimethyl Maleate

[0037] A 250 mL 3-necked, glass, round bottom flask equipped with a magnetic stir bar was charged with trans-1,4-diaminocyclohexane (3.945 g, 34.2 mmol, from TCI America >98%) and methanol (38 mL). Gentle mixing was initiated, and the flask was equipped with a short-path distillation head with Vigreux column connected to an oil bubbler and fitted with a 50 mL collection flask. The still head was sealed to the center neck with silicone grease and the flask was further sealed with 1 rubber septum and an adapter to enable a nitrogen sweep. The flask was then cooled by submerging inside an ice water bath to absorb the heat of reaction. A thermocouple was inserted into the septum to track temperature during reaction. While under a nitrogen sweep to the still head, dimethyl maleate (10.110 g, 68.0 mmol, from TCI America 97%) was slowly added to the contents of the flask via syringe injection over 26 minutes. A minor exotherm was observed during the addition of dimethyl maleate. Once the temperature had stopped increasing, the flask was then placed in a heated water bath and stirred and allowed to reflux and distill for 4 hours. The resultant transparent orange solution was removed from the nitrogen and exposed to air and became turbid as precipitation began to occur. The precipitate was collected by partially removing methanol via rotary evaporation until a slightly viscous slurry formed and then this slurry was dried in a crystallization dish in a 50° C. oven for 16 hours. The resultant paste was determined to be the disubstituted adduct via ¹H and ¹³C NMR and was used without further purification. ¹H NMR (500 MHz, CDCl₃) δ 3.54-3.47 (m, 4H), 3.45 (s, 3H), 3.16 (s, 4H), 2.55-2.33 (m, 2H), 2.18 (tt, J=10.4, 3.6 Hz, 1H), 1.79-1.46 (m, 2H), 1.04-0.71 (m, 2H). ¹H NMR (500 MHz, CDCl₃) δ 174.3 (2C), 171.2 (2C), 51.7 (2C), 51.3 (2C), 38.0 (2C), 31.7 (1C), 31.5 (1C), 30.7 (1C), 30.4 (1C).

Synthesis S5: Michael Addition of 1,7-Diaminoheptane to Dimethyl Maleate

[0038] A 100 mL 3-necked, glass, round bottom flask with a magnetic stirrer was charged with 1,7-diaminoheptane (4.5 g, 34 mmol, from Sigma Aldrich 98%) and ethanol (14 mL). Gentle mixing was initiated, and the flask was equipped with a cold-water condenser connected to an oil bubbler and

sealed with silicone grease and 2 rubber septa. The flask was then cooled by submerging in an ice water bath in order to absorb the heat of reaction. A needle style thermocouple was inserted into one septum to track temperature during reaction. To the contents of the flask was slowly added dimethyl maleate (10.1 g, 68 mmol, from TCI America 97%) via a syringe. A great exotherm was observed during the addition of dimethyl maleate. The resulting solution was then placed on a block heater and stirred at 60° C. for five hours. Progress of the reaction was monitored by ¹H and ¹³C NMR spectroscopy. Upon complete conversion of amine to disubstituted adduct, ethanol was distilled off in a rotary evaporator to yield a slightly viscous light yellow adduct. ¹H NMR (500 MHz, CDCl₃) δ 3.62 (s, 6H), 3.57 (s, 6H), 3.52 (t, J=6.5 Hz, 2H), 2.62 (d, J=6.1 Hz, 1H), 2.59 (d, J=6.1 Hz, 1H), 2.56-2.47 (m, 4H), 2.36 (ddd, J=11.1, 7.9, 6.3 Hz, 2H), 1.40-1.25 (m, 4H), 1.24-1.12 (m, 7H); ¹³C NMR (500 MHz, CDCl₃) δ 174.1 (2C), 171.2 (2C), 57.6 (2C), 51.9 (2C), 51.7 (2C), 47.9 (2C), 37.7 (2C), 29.9 (2C), 29.1 (1C), 26.9 (2C).

Synthesis S6: Michael Addition of 1,7-Diaminoheptane to Dimethyl Maleate

[0039] A 250 mL 3-necked, glass, round bottom flask with a magnetic stirrer was charged with 1,7-diaminoheptane (20.7 g, 155 mmol, from Sigma Aldrich 98%) and ethanol (50 mL). Gentle mixing was initiated, and the flask was equipped with a cold-water condenser connected to an oil bubbler and sealed with silicone grease and 2 rubber septa. The flask was then cooled by submerging in an ice water bath in order to absorb the heat of reaction. A needle style thermocouple was inserted into one septum to track temperature during reaction. To the contents of the flask was slowly added dimethyl maleate (46.1 g, 310 mmol, from TCI America 97%) via a syringe. A great exotherm was observed during the addition of dimethyl maleate. The resulting solution was then placed on a block heater and stirred at 60° C. for five hours. Progress of the reaction was monitored by ¹H and ¹³C NMR spectroscopy. Upon complete conversion of amine to disubstituted adduct, ethanol was distilled off in a rotary evaporator to yield a slightly viscous light yellow adduct. ¹³C NMR (500 MHz, CDCl₃) δ 174.09, 173.58, 171.22, 165.18, 133.27, 60.87, 57.77, 57.68, 57.59, 52.16 (d, J=4.1 Hz), 51.92, 51.68, 47.93, 37.66, 29.85, 29.12, 26.92, 18.28, 14.15-13.93 (m).

Syntheses S7-S10: Preparation of Alkoxyate Polymers

[0040] In Syntheses S7-S10, alkoxyate polymers according to the formula CH₃O-(EO)_m(PO)_n-H having values of m and n as noted in TABLE 1 were prepared in a Symyx Parallel Pressure Reactor (PPR®) with a glass insert and equipped with removable polyether ether ketone (PEEK) paddle for mechanical stirring. Both the glass insert and the removable PEEK stir paddle was dried in a vacuum oven at 125° C. overnight prior to the reaction. An ethoxylated intermediate of type CH₃O-(EO)_m-H was prepared by ethoxylation of 2-methoxyethanol (from Sigma-Aldrich). A stock solution was prepared by dissolving in 2-methoxyethanol, under nitrogen, an amount of potassium hydride of about 3 wt % based on weight of the 2-methoxyethanol. Then a calculated amount of the stock solution was added to the glass insert under nitrogen. The glass insert was then loaded into a reactor, followed by attachment of the stirring paddle.

[0041] The reactor was then sealed, heated to 120° C., and pressurized with nitrogen to 345 kPa. Ethylene oxide was then delivered to the reactor in several injections via an Isco syringe pump equipped with a robotically controlled needle and compressed gas micro-valve connected to the reactor. The overall amount of ethylene oxide added to the reactor was calculated to provide the desired length of the (EO)_n block assuming complete consumption of the ethylene oxide added to the reactor. After addition of the ethylene oxide, the temperature was maintained at 120° C. and the reaction mixture was stirred for 4 hours. The reactor contents were then cooled. The reactor was vented and purged with nitrogen to remove any residual ethylene oxide.

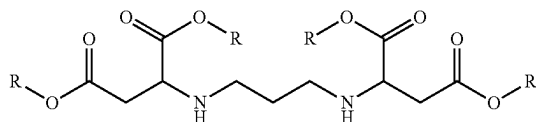
[0042] The reactor was then heated to 50° C. and pressurized with nitrogen to a pressure of 345 kPa. Propylene oxide was then charged to the reactor via an Isco syringe pump. The amount of propylene oxide added to the reactor was calculated to correspond to the desired length of the (PO)_n block of the targeted material assuming complete consumption of the propylene oxide added to the reactor. After addition of the propylene oxide, the temperature was increased to 115° C. and maintained at that temperature while the contents of the reactor were stirred for 20 hours. The reactor contents were then cooled. The reactor was vented and purged with nitrogen to remove any residual ethylene oxide. The product from the reactor was used without further purification. The molecular weight of the product collected was determined by GPC and the composition was determined by quantitative ¹³C NMR as reported in Table 1.

TABLE 1

Ex.	Calculated		¹³ C NMR		GPC		
	m	n	m	n	Mn	Mw	PDI
S7	4.0	4.0	3.59	3.40	661	717	1.08
S8	7.1	15.7	7.2	14.9	1,458	1,624	1.11
S9	8.5	7.7	8.1	7.5	1,000	1,132	1.13
S10	14.9	12.6	13.8	12.4	1,595	1,810	1.13

Comparative Example C1: Preparation of Transesterification Product

[0043] In Comparative Example C1, a transesterification product of the following general formula

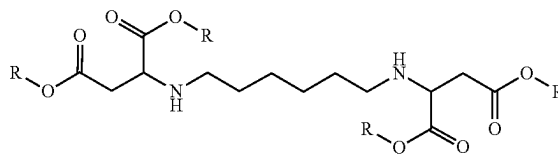


was prepared by charging an alkoxyate polymer (R—OH) (14.2490 g, 27.4 mmol, 4.4 eq., from The Dow Chemical Company as UCON™ 50-HB-100), material prepared according to Synthesis S1 (2.3113 g, 6.2 mmol) and titanium isopropoxide (0.234 g, 0.82 mmol, 13.2 mol %, from Sigma

Aldrich 99.999%) to a 250 mL Airfree® Schlenk flask with a magnetic stir bar. The flask was sealed with a septum having a needle probe thermocouple inserted, attached to a Schlenk line, and then heated in an OptiTHERM® Reaction Block attached to an IKA magnetic heating plate with a set point temperature of 120° C. while under a nitrogen blanket. After 35 minutes, the temperature reached 118.3° C. and vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap housed inside a Dewar flask and submerged in a bed of dry ice. The mixing speed was adjusted from a setting of 200 to 300 rpm as the contents of the flask were heated to account for changes in viscosity. The flask contents were held at a temperature of 118.3-125.3° C. for seven hours under vacuum. The flask contents were then cooled and characterized by NMR to confirm completion of the reaction. Based on the ratio of total carbonyl carbon integral (peaks at 173.1, 170.2 ppm) to that of the residual methyl ester carbon peak at 51 ppm of ~28:1, the extent of conversion of methyl ester is estimated to be >95%.

Example 1: Preparation of Cleaning Booster

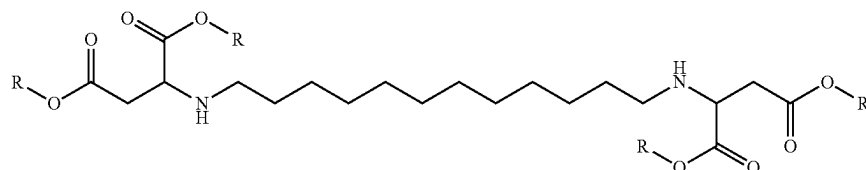
[0044] In Example 1, a transesterification product cleaning booster of the following general formula



was prepared by charging an alkoxyate polymer (R—OH) (9.6139 g, 18.5 mmol, 4.6 eq., from The Dow Chemical Company as UCON™ 50-HB-100), material prepared according to Synthesis S2 (1.6793 g, 4.0 mmol) and titanium isopropoxide (0.142 g, 0.50 mmol, 12.5 mol %, from Sigma Aldrich 99.999%) to a 250 mL Airfree® Schlenk flask with a magnetic stir bar. The flask was sealed with a septum with a needle probe thermocouple inserted, attached to a Schlenk line, and then heated in an OptiTHERM® Reaction Block attached to an IKA magnetic heating plate with a set point temperature of 120° C. while under a nitrogen blanket. After 34 minutes, the temperature reached 112.7° C. and vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap housed inside a dewar flask and submerged in a bed of dry ice. The mixing speed was adjusted to 280 rpm. The flask contents were held at a temperature of 117.9-119.9° C. for nine hours under vacuum. The flask contents were then cooled and characterized by NMR to confirm completion of the reaction. Based on the ratio of total carbonyl carbon integral (peaks at 173.1, 170.2 ppm) to that of the residual methyl ester carbon peak at 51 ppm of >50:1, the extent of conversion of methyl ester is estimated to be >98%.

Example 2: Preparation of Cleaning Booster

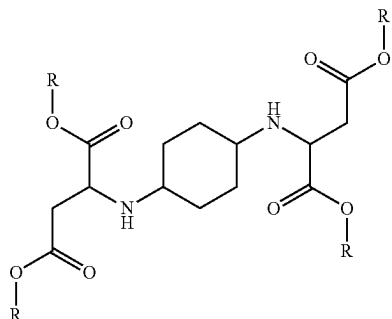
[0045] In Example 2, a transesterification product cleaning booster of the following general formula



was prepared by charging an alkoxyate polymer (R—OH) (7.2037 g, 13.9 mmol, 4.5 eq., from The Dow Chemical Company as UCON™ 50-HB-100), material prepared according to Synthesis S3 (1.5627 g, 3.1 mmol) and titanium isopropoxide (0.191 g, 0.67 mmol, 21.6 mol %, from Sigma Aldrich 99.999%) to a 50 mL Airfree® Schlenk flask with a magnetic stir bar. The flask was sealed with a septum with a needle probe thermocouple inserted, attached to a Schlenk line, and then heated in an OptiTHERM® Reaction Block attached to an IKA magnetic heating plate with a set point temperature of 120° C. while under a nitrogen blanket. After 48 minutes, the temperature reached 90.5° C. and vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap housed inside a dewar flask and submerged in a bed of dry ice. The mixing speed was adjusted to 450 rpm. The flask contents were held at a temperature of 113.8-121.4° C. for five hours under vacuum. The flask contents were then cooled and characterized by NMR to confirm completion of the reaction. Based on the ratio of total carbonyl carbon integral (peaks at 173.0, 170.1 ppm) to that of the residual methyl ester carbon peak at 51 ppm of ~29:1, the extent of conversion of methyl ester is estimated to be >95%.

Example 3: Preparation of Cleaning Booster

[0046] In Example 3, a transesterification product cleaning booster of the following general formula



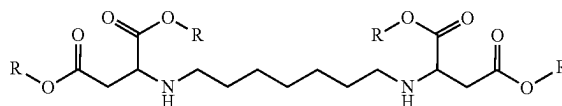
was prepared by charging an alkoxyate polymer (R—OH) (8.5855 g, 16.5 mmol, 4.3 eq., from The Dow Chemical Company as UCON™ 50-HB-100), material prepared according to Synthesis S4 (1.5268 g, 3.8 mmol) and titanium isopropoxide (0.180 g, 0.63 mmol, 16.6 mol %, from Sigma Aldrich 99.999%) to a 250 mL Airfree® Schlenk flask with a magnetic stir bar. The flask was sealed with a septum with a needle probe thermocouple inserted, attached to a Schlenk

line, and then heated in an OptiTHERM® Reaction Block attached to an IKA magnetic heating plate with a set point temperature of 120° C. while under a nitrogen blanket. After

32 minutes, the temperature reached 118.3° C. and the sample turned from a hazy slurry to a clear solution. Vacuum was then applied to the flask contents via a mechanical pump with an intervening solvent trap housed inside a dewar flask and submerged in a bed of dry ice. The mixing speed was held constantly at 320 rpm. The flask contents were held at a temperature of 116.1-120.4° C. for 12.5 hours under vacuum. The flask contents were then cooled and characterized by NMR to confirm completion of the reaction. Based on the ratio of total carbonyl carbon integral (peaks at 173.7, 173.5, 171.1, 170.2, 170.1 ppm) to that of the residual methyl ester carbon peak at 51 ppm of ~12:1, the extent of conversion of methyl ester is estimated to be about 90%.

Example 4: Preparation of Cleaning Booster

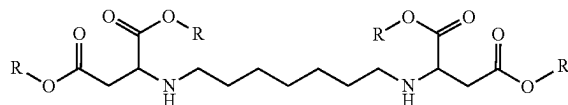
[0047] In Example 4, a transesterification product cleaning booster of the following general formula



was prepared by charging an alkoxyate polymer (R—OH) (10.2631 g, 19.7 mmol, 4.4 eq., from The Dow Chemical Company as UCON™ 50-HB-100), material prepared according to Synthesis S5 (1.9334 g, 4.5 mmol) and titanium isopropoxide (0.1685 g, 0.59 mmol, 13 mol %, from Sigma Aldrich 99.999%) to a 250 mL flask with a magnetic stir bar and needle probe thermometer attached via a septum. The flask was sealed with silicone grease, purged with nitrogen and then heated in an OptiTHERM® Reaction Block attached to an IKA magnetic heating plate with a set point temperature of 120° C. After the contents of the flask reach an internal temperature of 120° C., vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap cooled via dry ice in a dewar flask. The mixing speed setting was constant at 230 rpm as the contents of the flask maintained constant viscosity for duration of heating. The flask contents were held at a temperature of 119-121° C., for eight and a half hours under vacuum. The flask contents were then cooled and characterized. The extent of displacement of methyl ester groups was estimated by the integrated peaks in the quantitative 13C NMR spectra for the methyl groups of the methyl ester (51.5 ppm) and the α-methylene group (38.1 ppm) on the heptanediamine-dimethyl maleate adduct. This ratio was 0.12:1, and since the original unreacted heptanediamine-dimethyl maleate adduct has a methyl ester: α-methylene ratio of 2.18:1, this would suggest that ~94% of the methyl groups had been converted.

Example 5: Preparation of Cleaning Booster

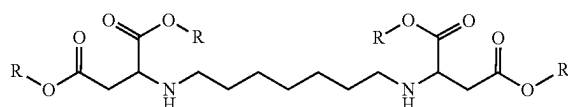
[0048] In Example 5, a transesterification product cleaning booster of the following general formula



was prepared by charging the alkoxyate polymer product of Synthesis S7 (R—OH) (42.6 g, 110 mmol, 5.7 eq.) to a 250 mL Chemglass Airfree® flask with a magnetic stir bar and needle probe thermometer attached via a septum. The flask was sealed with silicone grease, purged with nitrogen and then heated in an OptiTHERM® Reaction Block attached to an IKA magnetic heating plate with a set point of 400 rpm at room temperature. After mixing was initiated, vacuum was applied via mechanical pump with intervening solvent trap cooled by a bed of dry ice. After 1 hour of vacuum stripping, the flask was disconnected from vacuum source and refilled with nitrogen. The product of Synthesis S6 (8.2913 g, 19.4 mmol), and titanium isopropoxide (0.9364 g, 3.29 mmol, 17 mol %, from Sigma Aldrich 99.999%) were added to the flask and the flask was resealed with a septum. The flask was then heated and stirred with a set point temperature of 120° C. and 400 rpm. After 1 hours of heating and mixing, vacuum was applied for 7 hours with a final reduced pressure of 0.1 Torr. The product was cooled and characterized using NMR. ¹³C NMR revealed 100% conversion of methyl ester to the tetrasubstituted product. ¹³C NMR (126 MHz, CDCl₃) δ 75.87-74.12 (m), 73.54-72.30 (m), 72.00-70.98 (m), 70.77-69.23 (m), 58.89, 17.43-15.75 (m).

Examples 6-8: Preparation of Cleaning Boosters

[0049] In Examples 6-8, a transesterification product cleaning booster of the following general formula



was prepared by charging the alkoxyate polymer of the type and in the amount noted in Table 2 to a 250 mL Chemglass Airfree® flask with a magnetic stir bar and needle probe thermometer attached via a septum. The flask was sealed with silicone grease, purged with nitrogen and then heated in an OptiTHERM® Reaction Block attached to an IKA magnetic heating plate with a set point of 400 rpm at room temperature. After mixing was initiated, vacuum was applied via mechanical pump with intervening solvent trap cooled by a bed of dry ice. After 1 hour of vacuum stripping, the flask was disconnected from vacuum source and refilled with nitrogen. The product of Synthesis S6 and titanium isopropoxide (from Sigma Aldrich 99.999%) in the amount noted in Table 2 was added to the flask and the flask was resealed with a septum. The flask was then heated and stirred with a set point temperature of 120° C. and 400 rpm. After 1 hours of heating and mixing, vacuum was applied for 7 hours with a final reduced pressure of 0.1 Torr. The product was collected.

TABLE 2

Reagent		Example		
		6	7	8
alkoxyate	Synthesis S8	4.88	0	0
polymer	Synthesis S9	0	4.49	0
	Synthesis S10	0	0	4.60
	Synthesis S6	0.39	0.58	0.45
Titanium isopropoxide		0.036	0.070	0.044

Comparative Examples CF1-CF3 and Examples F1-F3: Liquid Laundry Detergent

[0050] The liquid laundry detergent formulations used in the cleaning tests in the subsequent Examples were prepared having the generic formulation as described in TABLE 3 with the cleaning booster as noted in TABLE 4 neutralized to a pH of 8.5 were prepared by standard liquid laundry formulation preparation procedures.

TABLE 3

Ingredient	Commercial Name	wt %
Linear alkyl benzene sulfonate	Nacconal 90G*	12.0
Sodium lauryl ethoxysulfate	Steol CS-460*	3.0
Propylene glycol	—	3.0
Ethanol	—	1.2
Sodium citrate	—	1.0
Sodium xylenesulfonate	Stepanate SXS-93	3.3
Fatty acid	Prifac 7908*	1.8
Cleaning Booster	—	5.0
Deionized water	—	QS to 100

*from Stepan Company

^afrom Croda

TABLE 4

Example	Cleaning Booster
Comparative Example CF1	Alcohol ethoxylate ¹
Comparative Example CF2	Ethoxylated poly(ethyleneimine) ²
Comparative Example CF3	Comparative Example C1
Example F1	Example 1
Example F2	Example 2
Example F3	Example 3

¹from Stepan Company under the tradename BIO-SOFT ® N25-9

²from BASF under tradename SOKOLAN™ HP-20

Primary Cleaning Performance

[0051] The primary cleaning performance of the liquid laundry detergent formulations of Comparative Examples CF1-CF2 and Examples F1-F3 were assessed in a Launder-Ometer (SDL Atlas, Model M228AA) at a set test temperature of 22° C. using an 18 minute wash cycle. Twenty of the 1.2 liter canisters were filled with 500 mL of hardness adjusted water at 100 ppm by mass with 2:1 Ca²⁺:Mg²⁺ molar ratio were used for each run. The washed fabrics were rinsed in 300 mL of 100 ppm (2/1 Ca²⁺/Mg²⁺) hardness adjusted water at ambient temperature for 5 minutes at 260 osc/min pm on an Eberbach E6000 reciprocal shaker. The stained fabrics and soiled ballasts used in the tests were PCS-S-132 high discriminative sebum BEY pigment and PCS-S-94 sebum/dust ASTM stains from Testfabrics stitched to a pre-shrunk cotton interlock fabric. The size of

the cotton interlock was 5×5 cm. The stained swatches were 2.5×3 cm. One 5×5 cm cut SBL-CFT soil ballast was added to each canister to provide baseline soil to the wash solution. The total surfactant concentration in the wash liquor was 200 ppm.

Reflectance Measurement and Stain Removal Index (SRI)

[0052] The soil removal index (SRI) for each of the Liquid Laundry Detergent formulations evaluated in Primary Cleaning Performance Test were determined using ASTM Method D4265-14. The average SRI taken from 8 swatches per condition (two swatches per pot, 4 pots) is provided in TABLE 5.

[0053] The L*, a* and b* values of the stained fabrics were measured pre and post wash with a Mach 5 spectrophotometer from Colour Consult. The L*, a* and b* values for the unwashed, unstained polycotton fabric was measured in the SRI calculations as follows:

$$SRI = \frac{(\Delta E^*_{(US-UF)} - \Delta E^*_{(WS-UF)})}{\Delta E^*_{(US-UF)}} \times 100$$

wherein US is the unwashed stain area, UF is the unwashed (unstained) fabric area, WS is the washed stain area, $\Delta E^*_{(US-UF)}$ is the ΔE^* color difference between the unwashed stain and the unwashed fabric and $\Delta E^*_{(WS-UF)}$ is the ΔE^* color difference between the washed stain and the unwashed fabric. The value of ΔE^* is calculated as

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

The ΔSRI values provided in TABLE 5 give the difference between the SRI measured for the noted example relative to the SRI measured for Comparative Example CF1. A positive value indicates an increase in soil removal relative to Comparative Example CF1.

TABLE 5

Example	Cleaning Booster	ΔSRI	
		PCS-94	PCS-132
Comparative Example CF2	Ethoxylated poly(ethyleneimine) ¹	-0.6	-3.2
Comparative Example CF3	Comparative Example C1	1.01	4.79
Example F1	Example 1	2.21	3.92
Example F2	Example 2	2.6	2.12
Example F3	Example 3	1.8	4.25

¹from BASF under tradename SOKOLAN™ HP-20

Comparative Examples CF4-CF6 and Examples F4-F6: Liquid Laundry Detergent

[0054] The liquid laundry detergent formulation of Comparative Examples CF4-CF6 and Examples F4-F6 used in the subsequent cleaning tests were prepared by combining 0.5 g of a standard liquid laundry detergent formulation with an adjusted pH of 8.5 as described in TABLE 6 with 1.5 g of a 1 wt % aqueous solution of the cleaning booster noted in TABLE 7.

TABLE 6

Ingredient	Commercial Name	wt %
Linear alkyl benzene sulfonate	Nacconal 90G*	12
Sodium lauryl ethoxysulfate	Steol CS-460*	2
Propylene glycol	—	3.5
Ethanol	—	1.5
Deionized water	—	QS to 100

*from Stepan Company

^a from The Dow Chemical Company

TABLE 7

Example	Cleaning Booster
Comparative Example CF4	None
Comparative Example CF5	Ethoxylated poly(ethyleneimine) ¹
Comparative Example CF6	Comparative Example C1
Example F4	Example 1
Example F5	Example 2
Example F6	Example 3

¹from BASF under tradename SOKOLAN™ HP-20

Anti-Redeposition

[0055] The anti-redeposition performance of the combination of the standard liquid laundry detergent+cleaning booster of Comparative Examples CF4-CF6 and Examples F4-F6 was assessed in a Terg-o-tometer Model 7243ES agitated at 90 cycles per minute with the conditions noted in TABLE 8.

TABLE 8

Parameter	Setting
Temperature	50° C.
Water hardness	300 ppm, Ca ²⁺ /Mg ²⁺ = 2/1
Fabric Types	Cotton (C) Cotton interlock (CI) Cotton Terry (CT) Polyester: cotton blend (PB) Polyester knit (PK) Polyester woven (PW) two cloths of each type in each pot
Wash time	60 minutes
Rinse time	3 minutes
Liquid laundry detergent dosage	0.5 g
Cleaning booster	1.5 g of 1 wt % aqueous solution
Anti-redeposition soils	2.5 g/L dust sebum 0.63 g/L Redart clay
Drying	After final rinse, fabrics were dried in a food dehydrator at 50° C. for 2 hours

[0056] The antiredeposition performance was determined by calculating the ΔE measured with a MACH 5+ instrument (L, a & b). The results are noted in TABLE 9, wherein ΔE^* is according to the equation

$$\Delta E^* = \Delta E_{aw} - \Delta E_{bw}$$

wherein ΔE_{aw} is measured from fabrics after washing, and ΔE_{bw} is measured from fabrics before washing. A higher ΔE^* corresponds with better antiredeposition performance.

TABLE 9

Example	ΔE^*					
	C	CI	CT	PB	PK	PW
Comp. Ex. CF4	13.16	20.79	21.38	13.61	25.31	17.20
Comp. Ex. CF5	9.49	13.48	12.86	8.46	19.67	12.33
Comp. Ex. CF6	7.63	13.23	13.85	11.83	24.93	16.06
Example F5	7.33	11.90	14.43	12.81	25.66	15.42
Example F6	8.05	12.03	13.04	13.28	27.67	17.43
Example F7	8.99	14.25	14.47	12.63	25.82	15.83

Comparative Examples CF7-CF8 and Examples F8-F11: Unit Dose Laundry Detergent

[0057] Unit dose laundry detergent formulations of Comparative Examples CF7-CF8 and Examples F8-F11 used in the subsequent cleaning tests were prepared having the generic formulation as described in TABLE 10 with the cleaning booster as noted in TABLE 11 neutralized to a pH of 8.5 were prepared by standard laundry formulation preparation procedures.

TABLE 10

Ingredient	Commercial Name	wt %
4-Dodecylbenzenesulfonic acid	Product No. 44198 ^a	30
Sodium lauryl ethoxysulfate	Steol CS-460 ^b	10
Propylene glycol	—	19
Monoethanolamine	Monoethanolamine (MEA) ^c	8
Glycerin	—	19
Oleic acid	—	3
Cleaning booster	—	5
Deionized water	—	QS to 100

^afrom Sigma Aldrich

^bfrom Stepan Company

^cfrom The Dow Chemical Company

TABLE 11

Example	Cleaning Booster
Comparative Example CF7	Alcohol ethoxylate ¹
Comparative Example CF8	Ethoxylated poly(ethyleneimine) ²
Example F8	Example 5
Example F9	Example 6
Example F10	Example 7
Example F11	Example 8

¹from Stepan Company under the tradename BIO-SOFT® N25-9

²from BASF under tradename SOKOLAN™ HP-20

Primary Cleaning Performance

[0058] The primary cleaning performance of the unit dose formulations of Comparative Examples CF7-CF8 and Examples F8-F11 was assessed in a Terg-O-Tometer Model 7243ES with canisters (2 L) agitated at 85 cycles per minute with the conditions noted in TABLE 12.

TABLE 12

Parameter	Setting
Temperature	30° C.
Water hardness	120 ppm, Ca ²⁺ /Mg ²⁺ = 3/1
Water volume	1 L per canister
Fabric/Soil	2 inch × 2 inch square cut PC-S-94 dust sebum swatches from Testfabrics

TABLE 12-continued

Parameter	Setting
Wash time	30 minutes
Rinse time	3 minutes
detergent dosage	0.3 g/L
Drying	After final rinse, fabrics were dried in a food dehydrator at 50° C. for 2 hours

Reflectance Measurement and Stain Removal Index (SRI)

[0059] The soil removal index (SRI) for each of the Liquid Laundry Detergent formulations evaluated in Primary Cleaning Performance Test were determined using ASTM Method D4265-14. The average SRI taken from 8 swatches per condition (two swatches per pot, 4 pots) is provided in TABLE 13.

[0060] The L*, a* and b* values of the stained fabrics were measured pre and post wash with a Mach 5 spectrophotometer from Colour Consult. The L*, a* and b* values for the unwashed, unstained fabric was measured in the SRI calculations as follows:

$$SRI = \frac{(\Delta E^*_{(US-UF)} - \Delta E^*_{(WS-UF)})}{\Delta E^*_{(US-UF)}} \times 100$$

wherein US is the unwashed stain area, UF is the unwashed (unstained) fabric area, WS is the washed stain area, $\Delta E^*_{(US-UF)}$ is the ΔE^* color difference between the unwashed stain and the unwashed fabric and $\Delta E^*_{(WS-UF)}$ is the ΔE^* color difference between the washed stain and the unwashed fabric. The value of ΔE^* is calculated as

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

TABLE 13

Example	Cleaning Booster	ΔSRI PCS-94
Comparative Example CF7	Alcohol ethoxylate ¹	36.4
Comparative Example CF8	Ethoxylated poly(ethyleneimine) ²	31.0
Example F8	Example 5	45.9
Example F9	Example 6	47.2
Example F10	Example 7	43.9
Example F11	Example 8	41.4

¹from Stepan Company under tradename BIO-SOFT® N25-9

²from BASF under tradename SOKOLAN™ HP-20

We claim:

1. A laundry detergent formulation, comprising:

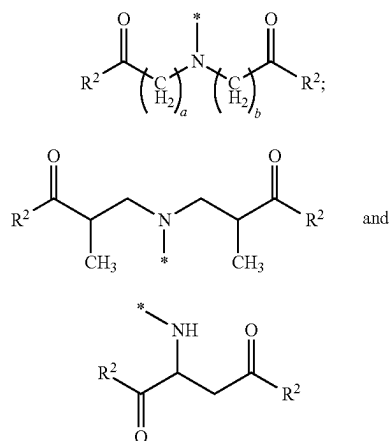
a carrier;

a cleaning surfactant; and

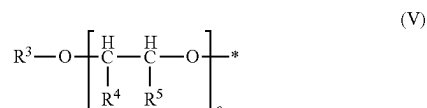
a cleaning booster, wherein the cleaning booster is of formula (I)



wherein A¹ is a divalent linking group having 4 to 24 carbon atoms; and wherein each R¹ is independently selected from the group consisting of formula (II), formula (III) and formula (IV)



wherein the * in formula (II), formula (III) and formula (IV) is the point of attachment to formula (I); wherein a is 1 or 2; wherein b is 1 or 2; and wherein each R² is independently of formula (V)



wherein the * in formula (V) is the point of attachment to the associated base formula;

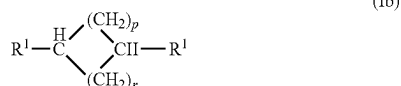
wherein R³ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group; wherein each R⁴ and R⁵ is independently selected from the group consisting of a hydrogen and a C₁₋₂ alkyl group, with the proviso that at least one of R⁴ and R⁵ is a hydrogen in each subunit c; and wherein c is 0 to 30; and with the proviso that when the divalent linking group, A¹, has 4 carbon atoms, the divalent linking group, A¹, includes a cycle.

2. The laundry detergent formulation of claim 1, wherein the cleaning booster of formula (I) is of formula (Ia)



wherein n is 5 to 24.

3. The laundry detergent formulation of claim 1, wherein the cleaning booster of formula (I) is of formula (Ib)



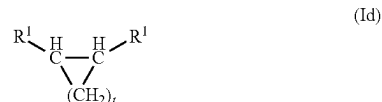
wherein p and r are independently 1 to 4.

4. The laundry detergent formulation of claim 1, wherein the cleaning booster of formula (I) is of formula (Ic)



wherein A² is a divalent linking group having 2 to 22 carbon atoms.

5. The laundry detergent formulation of claim 1, wherein the cleaning booster of formula (I) is of formula (Id)



wherein t is 2 to 10.

6. The laundry detergent formulation of claim 1, wherein c is 2 to 30 in 70 to 100 mol % of the occurrences of R² in the cleaning booster.

7. The laundry detergent formulation of claim 1, wherein 70 to 100 mol % of the R² groups in the cleaning booster are of formula (Va)



wherein the * in formula (Va) is the point of attachment to the associated base formula;

wherein R⁶ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group;

wherein each R⁷ is independently selected from the group consisting of a hydrogen and a C₁₂ alkyl group; and wherein y is 2 to 30.

8. The laundry detergent formulation of claim 1, wherein 70 to 100 mol % of the R² groups in the cleaning booster are of formula (Vb)



wherein the * in formula (Vb) is the point of attachment to the associated base formula;

wherein R⁸ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group;

wherein EO is an ethylene oxide group; wherein PO is a propylene oxide group; wherein h is 0 to 30; wherein i is 0 to 30; wherein j is 0 to 30; and wherein h+i+j is 2 to 30.

9. The laundry detergent formulation of claim 1, wherein the laundry detergent formulation is a liquid laundry detergent formulation comprising

25 to 97.9 wt %, based on weight of the laundry detergent formulation, of the carrier, wherein the carrier is a liquid carrier comprising water;

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

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

10. A method of washing a fabric article, 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.

* * * * *