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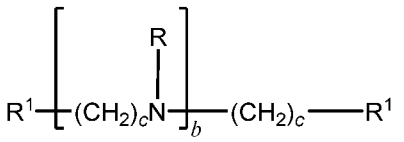
(54) Title: LIQUID LAUNDRY DETERGENT FORMULATION

(57) Abstract: A liquid laundry detergent is provided, comprising: liquid carrier; cleaning surfactant; and cleaning booster of formula (I) (I) wherein b is 0-2; wherein c is 2-4; wherein R is selected from hydrogen, C_{1-22} alkyl and $-CH_2C(=O)R^{14}$; wherein R^{14} is of formula (VI); wherein R^1 is selected from formula (II)-formula (V); (II) wherein R^2 is of formula (VI); (III) wherein R^3 is of formula (VI); and wherein R^4 is selected from hydrogen and methyl group; (IV) wherein R^5 is of formula (VI); wherein f is 1-2; and wherein g is 2-10; (V) wherein R^6 is of formula (VI); (VI) wherein R^7 is selected from hydrogen and C_{1-22} alkyl group; wherein each R^8 and R^9 is independently a hydrogen or C_{1-2} alkyl group, with the proviso that at least one of R^8 and R^9 is hydrogen in each subunit α; and wherein α is 0-30.

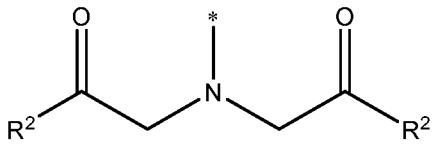
LIQUID LAUNDRY DETERGENT FORMULATION

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



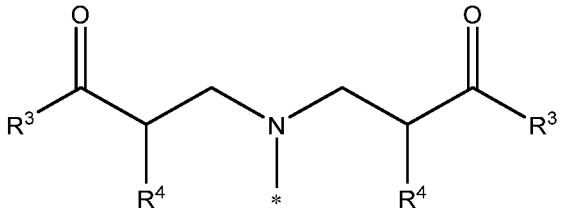
(I)

wherein *b* is 0 to 2; wherein *c* is 2 to 4; wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group, an R^1 and a $-CH_2C(=O)R^{14}$ group; wherein each R^1 is independently selected from the group consisting of formula (II), formula (III), formula (IV) and formula (V); wherein R^{14} is of formula (VI);



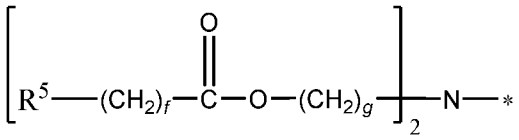
(II)

wherein the * indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI);



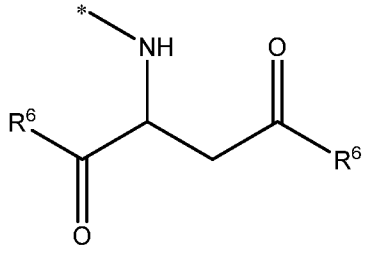
(III)

wherein the * indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



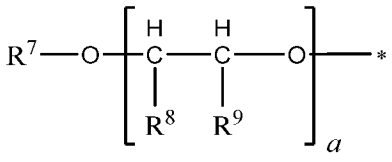
(IV)

wherein the * indicates the point of attachment to formula (I); wherein each R^5 is independently according to formula (VI); wherein *f* is 1 to 2; and wherein *g* is 2 to 10;



(V)

wherein the * indicates the point of attachment to formula (I); and wherein each R^6 is independently according to formula (VI);



(VI)

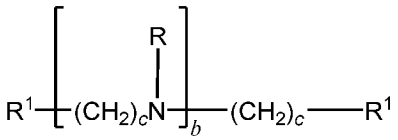
wherein the * indicates the point of attachment to the associated base formula; wherein R^7 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^8 and R^9 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with the proviso that at least one of R^8 and R^9 is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30.

[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.

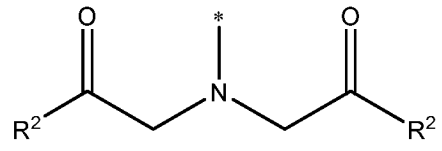
[0004] Notwithstanding, there remains a continuing need for liquid laundry detergent formulations exhibiting maintained primary cleaning performance with a reduced surfactant loading; preferably, while also providing improved anti-redeposition performance. There is also a continuing need for new cleaning boosters with improved biodegradability according to OECD 301F protocol when compared with conventional cleaning boosters.

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



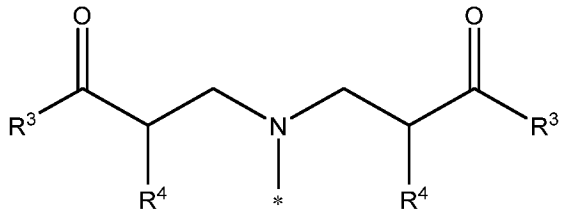
(I)

wherein *b* is 0 to 2; wherein *c* is 2 to 4; wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group, an R^1 and a $-CH_2C(=O)R^{14}$ group; wherein each R^1 is independently selected from the group consisting of formula (II), formula (III), formula (IV) and formula (V); wherein R^{14} is of formula (VI);



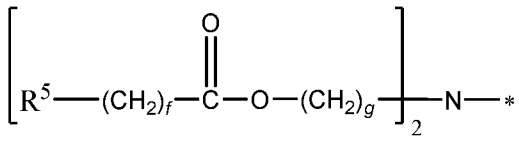
(II)

wherein the * indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI);



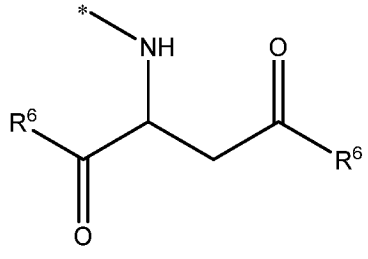
(III)

wherein the * indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



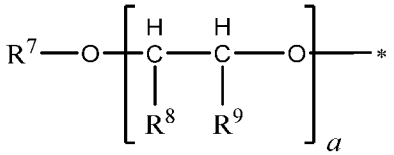
(IV)

wherein the * indicates the point of attachment to formula (I); wherein each R^5 is independently according to formula (VI); wherein *f* is 1 to 2; and wherein *g* is 2 to 10;



(V)

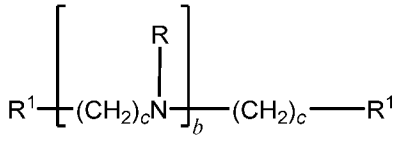
wherein the * indicates the point of attachment to formula (I); and wherein each R^6 is independently according to formula (VI);



(VI)

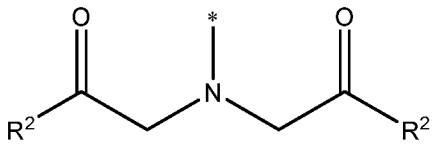
wherein the * indicates the point of attachment to the associated base formula; wherein R^7 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^8 and R^9 is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group, with the proviso that at least one of R^8 and R^9 is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30.

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



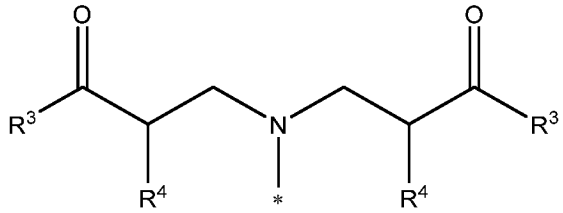
(I)

wherein *b* is 0 to 2; wherein *c* is 2 to 4; wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group, an R^1 and a $-CH_2C(=O)R^{14}$ group; wherein each R^1 is independently selected from the group consisting of formula (II), formula (III), formula (IV) and formula (V); wherein R^{14} is of formula (VI);



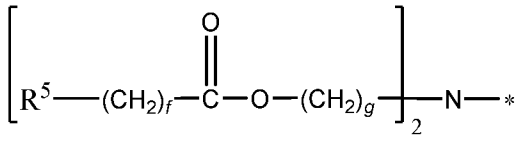
(II)

wherein the * indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI);



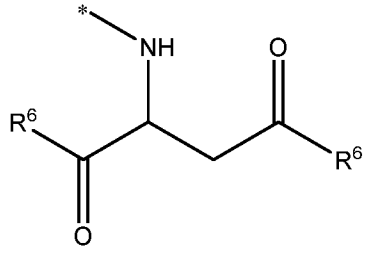
(III)

wherein the * indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



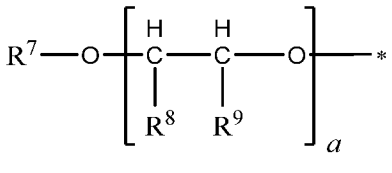
(IV)

wherein the * indicates the point of attachment to formula (I); wherein each R^5 is independently according to formula (VI); wherein *f* is 1 to 2; and wherein *g* is 2 to 10;



(V)

wherein the * indicates the point of attachment to formula (I); and wherein each R^6 is independently according to formula (VI);



(VI)

wherein the * indicates the point of attachment to the associated base formula; wherein R^7 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^8 and R^9 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^8 and R^9 is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30, with the proviso that *a* is 2 to 30 in 70 to 100 mol% of the occurrences of formula (VI) in the cleaning booster.

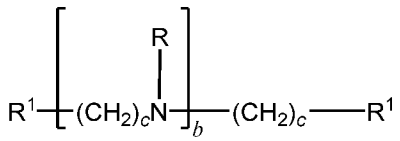
[0007] The present invention provides a method of washing a fabric article, comprising: providing a soiled fabric article; providing a liquid laundry detergent formulation according to claim 1; providing a wash water; and applying the wash water and the liquid laundry detergent formulation to the soiled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

DETAILED DESCRIPTION

[0008] It has been surprisingly found that the liquid laundry detergent formulations with a cleaning booster as described herein facilitate improvement in primary cleaning performance for sebum soil removal, while imparting good anit-redeposition performance for dust sebum and clay; and also exhibiting desirable biodegradability profiles according to OECD 301F protocol.

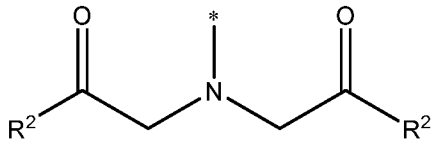
[0009] Unless otherwise indicated, ratios, percentages, parts, and the like are by weight. Weight percentages (or wt%) in the composition are percentages of dry weight, i.e., excluding any water that may be present in the composition.

[0010] Preferably, the liquid laundry detergent formulation of the present invention, comprises a liquid carrier (preferably, 25 to 97.9 wt% (more preferably, 30 to 95.8 wt%; still more preferably, 40 to 93.5 wt%; yet more preferably, 45 to 91.75 wt%; most preferably, 50 to 89 wt%), based on weight of the liquid 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 liquid laundry detergent formulation, of the cleaning surfactant); and a cleaning booster (preferably, 0.1 to 15 wt% (more preferably, 0.2 to 12 wt%; still more preferably, 0.5 to 10 wt%; yet more preferably, 0.75 to 8 wt%; most preferably 1 to 7.5 wt%), based on weight of the liquid laundry detergent formulation, of the cleaning booster), wherein the cleaning booster is of formula (I)



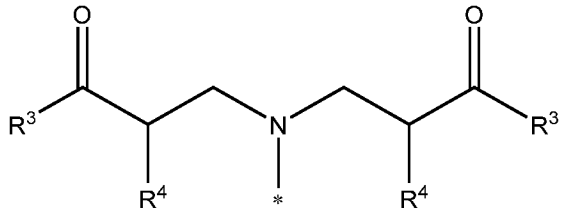
(I)

wherein *b* is 0 to 2 (preferably, 1); wherein *c* is 2 to 4 (preferably, 2); wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group and a $-CH_2C(=O)R^{14}$ group (preferably, a hydrogen, a C_{1-5} alkyl group and a $-CH_2C(=O)R^{14}$ group; more preferably, a hydrogen, a C_{1-2} alkyl group and a $-CH_2C(=O)R^{14}$; still more preferably, a methyl and a $-CH_2C(=O)R^{14}$ group; most preferably, a $-CH_2C(=O)R^{14}$ group); wherein R^{14} is of formula (VI); and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III), formula (IV) and formula (V) (preferably, formula (II) and formula (III); most preferably, formula (II));



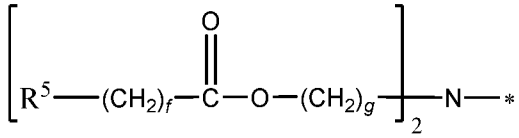
(II)

wherein the * indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI) (i.e., the individual occurrences of R^2 in formula (II) can be the same or different from one another);



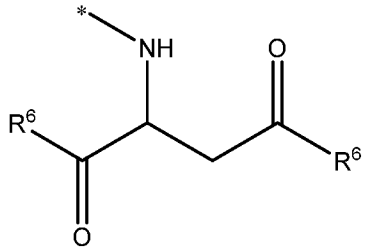
(III)

wherein the * indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



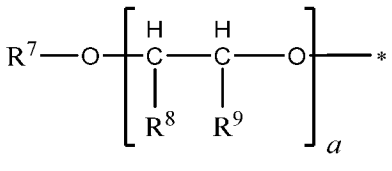
(IV)

wherein the * indicates the point of attachment to formula (I); wherein each R^5 is independently according to formula (VI); wherein *f* is 1 to 2; and wherein *g* is 2 to 10;



(V)

wherein the * indicates the point of attachment to formula (I); and wherein each R^6 is independently according to formula (VI);



(VI)

wherein the * indicates the point of attachment to the associated base formula (i.e., formula (II), formula (III), formula (IV) or formula (V)); wherein R^7 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group (preferably, a hydrogen and a C_{1-12} alkyl group; more preferably, a hydrogen and a C_{1-5} alkyl group; still more preferably, a hydrogen and a C_{1-4} alkyl group; most preferably, a hydrogen and a C_4 alkyl group); wherein each R^8 and R^9 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^8 and R^9 is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30 (preferably, with the proviso that *a* 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 (VI) in the cleaning booster).

[0011] 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, 30 to 95.8 wt%; more preferably, 40 to 93.5 wt%; yet more preferably, 45 to 91.75 wt%; most preferably, 50 to 89 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, 30 to 95.8 wt%; more preferably, 40 to 93.5 wt%; yet more preferably, 45 to 91.75 wt%; most preferably, 50 to 89 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, 30 to 95.8 wt%; more preferably, 40 to 93.5 wt%; yet more preferably, 45 to 91.75 wt%; most preferably, 50 to 89 wt%), based on weight of the liquid laundry detergent formulation, of a liquid carrier; wherein the liquid carrier is water.

[0012] 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.

[0013] 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% (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 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% (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 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% (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 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% (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 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.

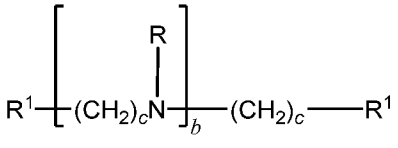
[0014] Anionic surfactants include alkyl sulfates, alkyl benzene sulfates, alkyl benzene sulfonic acids, alkyl benzene sulfonates, alkyl polyethoxy sulfates, alkoxylated alcohols, paraffin sulfonic acids, paraffin sulfonates, olefin sulfonic acids, olefin sulfonates, alpha-sulfocarboxylates, esters of 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 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, alkoxylated 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.

[0015] Non-ionic surfactants include alkoxylates (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 caped ethoxylated 2-ethylhexanol and mixtures thereof. Most preferred non-ionic surfactants include secondary alcohol ethoxylates.

[0016] 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.

[0017] 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 C_{12-14} 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 C_{12-14} alkyldimethylamine oxide.

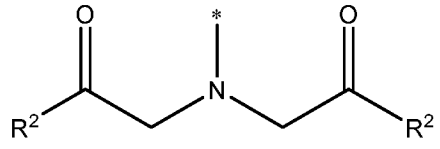
[0018] Preferably, the liquid laundry detergent formulation of the present invention, comprises: 0.1 to 15 wt% (preferably, 0.2 to 12 wt%; more preferably, 0.5 to 10 wt%; yet more preferably, 0.75 to 8 wt%; most preferably 1 to 7.5 wt%), based on weight of the liquid laundry detergent formulation, of the cleaning booster; wherein the cleaning booster is of formula (I)



(I)

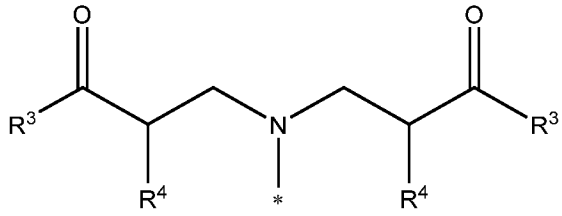
wherein *b* is 0 to 2 (preferably, 1); wherein *c* is 2 to 4 (preferably, 2); wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group and a $-CH_2C(=O)R^{14}$ group (preferably, a hydrogen, a C_{1-5} alkyl group and a $-CH_2C(=O)R^{14}$ group; more preferably, a hydrogen, a C_{1-2} alkyl group and a $-CH_2C(=O)R^{14}$; still more preferably, a methyl and a $-CH_2C(=O)R^{14}$ group; most preferably, a $-CH_2C(=O)R^{14}$ group); wherein R^{14} is of formula (VI); and wherein each R^1 is independently selected from the group

consisting of formula (II), formula (III), formula (IV) and formula (V) (preferably, formula (II) and formula (III); most preferably, formula (II));



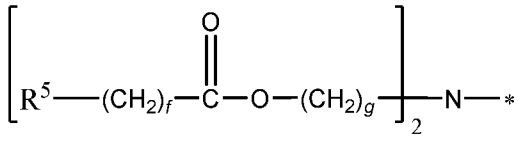
(II)

wherein the * indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI) (i.e., the individual occurrences of R^2 in formula (II) can be the same or different from one another);



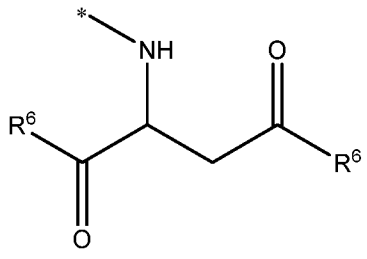
(III)

wherein the * indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



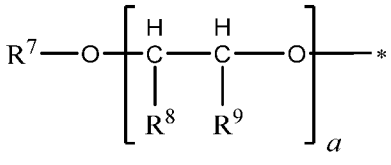
(IV)

wherein the * indicates the point of attachment to formula (I); wherein each R^5 is independently according to formula (VI); wherein *f* is 1 to 2; and wherein *g* is 2 to 10;



(V)

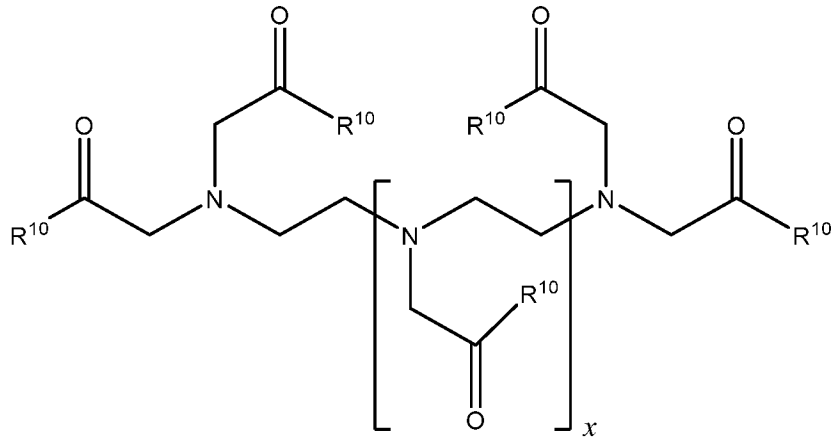
wherein the * indicates the point of attachment to formula (I); and wherein each R^6 is independently according to formula (VI);



(VI)

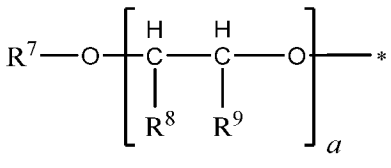
wherein the * indicates the point of attachment to the associated base formula (i.e., formula (II), formula (III), formula (IV) or formula (V)); wherein R^7 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group (preferably, a hydrogen and a C_{1-12} alkyl group; more preferably, a hydrogen and a C_{1-5} alkyl group; still more preferably, a hydrogen and a C_{1-4} alkyl group; most preferably, a hydrogen and a C_4 alkyl group); wherein each R^8 and R^9 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^8 and R^9 is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30 (preferably, wherein *a* 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 (VI) in the cleaning booster).

[0019] Preferably, the cleaning booster for cleaning dirty laundry, of the present invention, is of formula (I); wherein formula (I) is of formula (Ia)



(Ia)

wherein *x* is 0 to 2 (preferably, 1); wherein each R^{10} is independently of formula (VI)



(VI)

wherein the * indicates the point of attachment to formula (Ia); wherein R^7 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group (preferably, a hydrogen and a C_{1-12} alkyl group; more preferably, a hydrogen and a C_{1-5} alkyl group; still more preferably, a hydrogen and a C_{1-4} alkyl group; most preferably, a hydrogen and a C_4 alkyl group); wherein each R^8 and R^9 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^8 and R^9 is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30. More preferably, the cleaning booster of the present invention is of

formula (I); wherein formula (I) is of formula (Ia); 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 R^{10} groups are of formula (VI) wherein *a* is 2 to 30. Still more preferably, the cleaning booster for cleaning dirty laundry of the present invention is of formula (I); wherein formula (I) is of formula (Ia); 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 R^{10} groups are of formula (VI); wherein formula (VI) is of formula (VIa)

$$R^{11}—O—[CH_2CH(R^{12})O]_y—* \quad \text{(VIa)}$$

wherein the * indicates the point of attachment to formula (Ia); wherein R^{11} is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group (preferably, a hydrogen and a C_{1-12} alkyl group; more preferably, a hydrogen and a C_{1-5} alkyl group; still more preferably, a C_{1-4} alkyl group; most preferably, a C_4 alkyl group); wherein each R^{12} is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group; and wherein *y* is 2 to 30 (preferably, 2 to 25; more preferably, 2 to 17; most preferably, 4 to 12). Most preferably, the cleaning booster for cleaning dirty laundry of the present invention is of formula (I); wherein formula (I) is of formula (Ia); 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 R^{10} groups are of formula (VI); wherein formula (VI) is of formula (VIb)

$$R^{13}—O—(EO)_h—(PO)_i—(EO)_j—* \quad \text{(VIb)}$$

wherein the * indicates the point of attachment to formula (Ia); wherein R^{13} is selected from the group consisting of a hydrogen and a C_{1-12} alkyl group (preferably, a hydrogen and a C_{1-12} alkyl group; more preferably, a hydrogen and a C_{1-5} alkyl group; still more preferably, a C_{1-4} alkyl group; most preferably, a C_4 alkyl group); wherein EO is an ethylene oxide group; wherein PO is a propylene oxide group; wherein *h* is 0 to 30 (preferably, 0 to 5; more preferably, 0 to 2; most preferably, 0 to 1); wherein *i* is 0 to 30 (preferably, 0 to 10; more preferably, 0 to 7; most preferably, 2 to 5); wherein *j* is 0 and 30 (preferably, 2 to 10; more preferably, 2 to 8; most preferably, 2 to 6); and wherein $h + i + j$ is 2 to 30 (preferably, 2 to 25; more preferably, 2 to 17; most preferably, 4 to 12).

[0020] 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.

[0021] 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 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 liquid laundry detergent formulation, of a hydrotrope. More preferably, the liquid 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 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 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 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.

[0022] 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.

[0023] 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; 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; aminotrismethylenephosphonic acid; salts of aminotrismethylenephosphonic acid; hydroxyethanediphosphonic acid; salts of hydroxyethanediphosphonic acid; diethylenetriaminepenta(methylenephosphonic acid); salts of diethylenetriaminepenta(methylenephosphonic acid); ethylenediaminetetraethylene-phosphonic acid; salts of ethylenediaminetetraethylene-phosphonic acid; oligomeric phosphonates; polymeric phosphonates; mixtures thereof.

[0024] 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).

[0025] 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).

[0026] 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.

[0027] Some embodiments of the present invention will now be described in detail in the following **Examples**.

[0028] Reagents used in the **Examples** are described in **TABLE 1**.

TABLE 1

Identifier	Description
DTPA	Diethylenetriaminepentacetic acid (393.35 g/mol) available from TCI
Ethyl Alcohol	200 proof available from Pharmco/Greenfield Global
Ethylene glycol monobutyl ether	available from The Dow Chemical Company under tradename BUTYL CELLOSOLVE™
Sulfuric acid	Certified ACS Plus, available from Fisher Scientific
AE1	C_{12-15} alcohol ethoxylate-9 (600 g/mol) available from Stepan Company under tradename BIO-SOFT® N25-9
AE2	C_{12-15} alcohol ethoxylate-7 (510 g/mol) available from Stepan Company under tradename BIO-SOFT® N25-7
Poly(ethylene glycol)	available from The Dow Chemical Company under tradename CARBOWAX™ PEG 300
Butylstannoic acid	available from OMC Organometallix under tradename FASCAT® 9100
EO	Ethylene oxide
PO	Propylene oxide
BO	Butylene oxide
Capryleth-6 carboxylic acid	available from Kao Chemicals under tradename AKYPO® LF 1
Titanium isopropoxide	available from Sigma Aldrich
Dimethyl maleate	97% available from TCI Chemicals

Synthesis S1: EO-terminated block PO-copolymer

[0029] Potassium hydride (0.5 g) was dissolved with stirring, under nitrogen, in ethylene glycol monobutyl ether (25 g). Of this mixture, 23.6 g was charged by syringe to a nitrogen-purged reactor. The reactor was sealed and then charged with propylene oxide (41.5 g; 50.0 mL) at 120 °C with a pumping rate of 1 mL/min. A reactor pressure increase was noted as the propylene oxide was added. The reactor contents were allowed to react with the addition of the propylene oxide for 9 hours; during which time the reactor pressure was observed to decrease and then leveled off as the propylene oxide was consumed. Then ethylene oxide (33.5 g; 38.0 mL) was charged to the reactor contents at 130 °C with a pumping rate of 1 mL/min. The reactor contents were allowed to react with the addition of the ethylene oxide for 4 hours. The reactor was then vented, purged with nitrogen, and the product was recovered. The yield was quantitative. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.90 t (3H, CH_3), 1.13 m (8.48 H, CH_3 of PO), 1.35 m (2H, CH_2), 1.55 m (2H, CH_2), 3.55 m (35.93 H, $CHCH_2$ of PO + CH_2CH_2 of EO). NMR analysis suggested the following formula for the recovered product: $CH_3CH_2CH_2CH_2OCH_2CH_2O(PO)_{2.83}(EO)_{5.36}H$. GPC (in THF): M_n = 739, M_w = 859, PDI = 1.16. For the purposes of calculating reaction stoichiometries in the referenced

Syntheses to follow, the FW calculated from the established above empirical formula from NMR was used: 519 Daltons.

Synthesis S2: EO-terminated block PO-copolymer

[0030] Potassium hydride (0.4 g) was dissolved with stirring, under nitrogen, in ethylene glycol monobutyl ether (20.75 g). Of this mixture, 21.15 g was charged by syringe to a nitrogen-purged reactor. The reactor was sealed and then charged with propylene oxide (41.5 g; 50.0 mL) at 115 °C with a pumping rate of 1 mL/min. A reactor pressure increase was noted as the propylene oxide was added. The reactor contents were allowed to react with the addition of the propylene oxide for 22 hours; during which time the reactor pressure was observed to decrease and then leveled off as the propylene oxide was consumed. Then ethylene oxide (28.85 g; 33.0 mL) was charged to the reactor contents at 130 °C with a pumping rate of 1 mL/min. The reactor contents were allowed to react with the addition of the ethylene oxide for 4 hours. The reactor was then vented, purged with nitrogen, and the product was recovered. The yield was 85.4 g (93%). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.90 t (3H, CH_3), 1.13 m (11.05 H, CH_3 of PO), 1.35 m (2H, CH_2), 1.55 m (2H, CH_2), 3.55 m (31.02 H, $CHCH_2$ of PO + CH_2CH_2 of EO). NMR analysis suggests the following formula: $CH_3CH_2CH_2CH_2OCH_2CH_2O(PO)_{3.68}(EO)_{3.49}H$. GPC (in THF): M_n = 641, M_w = 761, PDI = 1.19. For the purposes of calculating reaction stoichiometries in the examples to follow, the FW calculated from the established above empirical formula from NMR was used: 486 Daltons.

Synthesis S3: DTPA-ethyl ester using ethanol and sulfuric acid catalyst

[0031] DTPA (8.5449 g), ethanol (168.54 g), and sulfuric acid (1.2000 g) were charged in an open atmosphere to a 500-mL flask containing a magnetic stir bar for stirring. Temperature of the flask contents was controlled by using a heating mantle connected to a variable transformer which was connected to a J-KEM temperature controller unit. The flask was fitted with an adapter connected to a three-way mineral oil bubbler that was connected to a nitrogen source in one neck. A condenser that circulates cold tap water was fitted to another neck of the flask. An alcohol thermometer was placed in another neck of the flask and configured to measure the headspace temperature. All necks of the flask were sealed with hydrocarbon grease. The charged and sealed apparatus was placed on top of a heating mantle which was placed on top of a magnetic stirrer. The flask was purged for the duration of the reaction with nitrogen at 2-3 bubbles per second as indicated by an inlet mineral oil bubbler. Seal quality was verified by an exit mineral oil bubbler connected to the condenser. The flask contents were heated to reflux (~ 78 °C headspace vapor temperature) and held with

adequate mixing for a total of 19 hours over a period of several days (with heating and agitation stopped during overnight periods, which periods were not counted as part of the 19 hours). The flask contents were then filtered through paper using a Buchner funnel with vacuum assistance. Calcium carbonate (5.0 g) was added to the filtrate and allowed to stir for 30 minutes before filtering again using vacuum filtration. The filtrate was separated into 2 aliquots that were distilled sequentially. Approximately 100-150 mL of sample was placed in a 250-mL round bottom flask equipped with a magnetic stir bar and a vacuum distillation head and placed under nitrogen atmosphere with a steady nitrogen flow maintained with a bubbler. Distillation with solvent recovery was continued until the rate of solvent recovery slowed markedly. After the first half of the filtrate was subjected to distillation, the remainder of the filtrate was added and the distillation repeated. The product, DTPA-ethyl ester, was obtained as a dark orange-brown viscous liquid. ^{1}H NMR (acetone-d_6, δ, ppm): 4.91-4.46 (1.87 H), 4.37-4.24 (0.81 H), 4.24-4.10 (5.83 H), 4.01-3.91 (1.69 H), 3.85-3.62 (10.68 H), 3.64-3.54 (0.52 H), 3.46-3.25 (3.55 H), 2.14-1.92 (1.10 H), 1.41-1.16 (13.15 H), 1.16-1.06 (0.58 H). DTPA:ethyl ester groups = 1:4.13. DTPA-ethyl ester active: 98 wt %.

Synthesis S4: DTPA polyester using ethoxylated alcohol and acid catalyst

[0032] DTPA-ethyl ester prepared according to **Synthesis S3** (1.0172 g, 2.0 mmol), AE1 (7.0486 g, 11.8 mmol, 6.0 eq.) and butylstannoic acid (0.0721 g, 0.35 mmol, 18 mol%) were charged to a 250 mL flask with a magnetic stir bar. The flask was sealed with hydrocarbon 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 150 °C. After reaching 135 °C, vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap cooled with a dry ice/acetone bath. The mixing speed was adjusted from a setting of 50 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 145-158 °C for six hours under vacuum. The flask contents were then cooled and characterized. The extent of displacement of ethyl groups was estimated by integrated peaks in the quantitative ^{13}C NMR spectra for the methyl groups of AE1 (14.4 ppm) and ethyl ester (14.6 ppm). This ratio was 6.7:1, and since the original ethyl:DTPA ratio was 4.13:1 and the AE1:DTPA ratio was 6.0, the ethyl:DTPA ratio in the product was 0.9:1 suggesting that ~ 80 % of the ethyl groups had been eliminated.

Synthesis S5: DTPA polyester using ethoxylated alcohol, diol and acid catalyst

[0033] DTPA-ethyl ester prepared according to **Synthesis S3** (0.9676 g, 1.9 mmol), AE1 (5.3243 g, 8.9 mmol, 4.8 eq.), PEG-300 (0.3712 g, 1.24 mmol, 0.65 eq.) and butylstannoic acid (0.0555 g, 0.27 mmol, 14 mol%) were charged to a 250 mL flask with a magnetic stir

bar. The flask was sealed with hydrocarbon 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 150 °C. After reaching 133.5 °C, vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap cooled with a dry ice/acetone bath. The mixing speed was adjusted from a setting of 50 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 142-149 °C for six hours under vacuum. The flask contents were then cooled and characterized. The extent of displacement of ethyl groups was estimated by integrated peaks in the quantitative ^{13}C NMR spectra for the methyl groups of AE1 (14.4 ppm) and ethyl ester (14.6 ppm). This ratio was 4.6:1, and since the original ethyl:DTPA ratio was 4.13:1 and the AE1:DTPA ratio was 4.8:1, the ethyl:DTPA ratio in the product was 1:1 suggesting that ~ 75 % of the ethyl groups had been eliminated.

Synthesis S6: DTPA polyester using ethoxylated alcohol and acid catalyst

[0034] DTPA-ethyl ester prepared according to **Synthesis S3** (1.1378 g, 2.2 mmol), AE1 (6.9510 g, 13.7 mmol, 6.2 eq.) and butylstannoic acid (0.0798 g, 0.38 mmol, 17 mol%) were charged to a 250 mL flask with a magnetic stir bar. The flask was sealed with hydrocarbon 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 150 °C. After reaching 120 °C, vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap cooled with a dry ice/acetone bath. The mixing speed was adjusted from a setting of 50 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 121-149 °C for seven hours under vacuum. The flask contents were then cooled and characterized. The extent of displacement of ethyl groups was estimated by integrated peaks in the quantitative ^{13}C NMR spectra for the methyl groups of AE1 (14.4 ppm) and ethyl ester (14.6 ppm). This ratio was 6.5:1, and since the original ethyl:DTPA ratio was 4.13:1 and the AE1:DTPA ratio was 6.2:1, the ethyl:DTPA ratio in the product was 0.94:1 suggesting that ~ 75 % of the ethyl groups had been eliminated.

Synthesis S7: DTPA-penta ethyl ester using ethanol and sulfuric acid catalyst

[0035] DTPA (5.0008 g), ethanol (177.59 g), and sulfuric acid (1.2118 g) were charged in an open atmosphere to a 500-mL flask containing a magnetic stir bar for stirring. Temperature of the flask contents was controlled by using a heating mantle connected to a variable transformer which was connected to a J-KEM temperature controller unit. The flask was fitted with an adapter connected to a three-way mineral oil bubbler that was connected to a

nitrogen source in one neck. A condenser that circulates cold tap water was fitted to another neck of the flask. An alcohol thermometer was placed in another neck of the flask and configured to measure the headspace temperature. All necks of the flask were sealed with hydrocarbon grease. The charged and sealed apparatus was placed on top of a heating mantle which was placed on top of a magnetic stirrer. The flask was purged for the duration of the reaction with nitrogen at 2-3 bubbles per second as indicated by an inlet mineral oil bubbler. Seal quality was verified by an exit mineral oil bubbler connected to the condenser. The flask contents were heated to reflux (~ 78 °C headspace vapor temperature) and held with adequate mixing for a total of 32 hours over a period of several days (with heating and agitation stopped during overnight periods, which periods were not counted as part of the 32 hours). The flask contents were then filtered through paper using a Buchner funnel with vacuum assistance. Calcium carbonate (5.0 g) was added to the filtrate and allowed to stir for 30 minutes before filtering again using vacuum filtration. The filtrate was separated into 2 aliquots that were distilled sequentially. Approximately 100-150 mL of sample was placed in a 250-mL round bottom flask equipped with a magnetic stir bar and a vacuum distillation head and placed under nitrogen atmosphere with a steady nitrogen flow maintained with a bubbler. Distillation with solvent recovery was continued until the rate of solvent recovery slowed markedly. After the first half of the filtrate was subjected to distillation, the remainder of the filtrate was added and the distillation repeated. The product, DTPA-ethyl ester, was obtained as a faint yellow translucent liquid. DTPA:ethyl ester groups = 1:4.17. DTPA-ethyl ester active: 87 wt %.

Synthesis S8: DTPA polyester using alkoxylated butanol and acid catalyst

[0036] DTPA-ethyl ester prepared according to **Synthesis S7** (1.0966 g, 1.86 mmol), EO-terminated block copolymer prepared according to **Synthesis S1** (5.6161 g, 10.8 mmol, 5.8 eq.) and butylstannoic acid (0.0718 g, 0.34 mmol, 18 mol%) were charged to a 250 mL flask with a magnetic stir bar. The flask was sealed with hydrocarbon 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 150 °C. After reaching 133.5 °C, vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap cooled with a dry ice/acetone bath. The mixing speed was adjusted from a setting of 50 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 133-148 °C for five hours under vacuum. The flask contents were then cooled and characterized. The extent of displacement of ethyl groups was estimated by integrated peaks in the quantitative ^{13}C NMR spectra for the methyl groups of

the product of **Synthesis S1** (14.3 ppm) and ethyl ester (14.6 ppm). This ratio was 5.3:1, and since the original ethyl:DTPA ratio was 4.17:1 and the alkoxylate:DTPA ratio was 4.1:1, the ethyl:DTPA ratio in the product was 0.8:1 suggesting that ~ 80 % of the ethyl groups had been eliminated.

Synthesis S9: DTPA-penta ethyl ester using ethanol and sulfuric acid catalyst

[0037] DTPA (8.0224 g), ethanol (304.80 g), and sulfuric acid (2.2318 g) were charged in an open atmosphere to a 500-mL flask containing a magnetic stir bar for stirring. Temperature of the flask contents was controlled by using a heating mantle connected to a variable transformer which was connected to a J-KEM temperature controller unit set at 85 °C. The flask was fitted with an adapter connected to a three-way mineral oil bubbler that was connected to a nitrogen source in one neck. A condenser that circulates cold tap water was fitted to another neck of the flask. An alcohol thermometer was placed in another neck of the flask and configured to measure the headspace temperature. All necks of the flask were sealed with hydrocarbon grease. The charged and sealed apparatus was placed on top of a heating mantle which was placed on top of a magnetic stirrer. The flask was purged for the duration of the reaction with nitrogen at 2-3 bubbles per second as indicated by an inlet mineral oil bubbler. Seal quality was verified by an exit mineral oil bubbler connected to the condenser. The flask contents were heated to reflux (~ 79 °C headspace vapor temperature) and held with adequate mixing for a total of 20 hours over a period of several days (with heating and agitation stopped during overnight periods, which periods were not counted as part of the 20 hours). The flask contents were then filtered through paper using a Buchner funnel with vacuum assistance. Calcium carbonate (5.0 g) was added to the filtrate and allowed to stir for 30 minutes before filtering again using vacuum filtration. The filtrate was placed in a 500-mL round bottom flask equipped with a magnetic stir bar and a vacuum distillation head and placed under nitrogen atmosphere with a steady nitrogen flow maintained with a bubbler. Distillation with solvent recovery was continued until the rate of solvent recovery slowed markedly. The product, DTPA-ethyl ester, was obtained as a faint yellow translucent liquid. DTPA:ethyl ester groups = 1:5. DTPA-ethyl ester active: 82 wt %.

Synthesis S10: DTPA polyester using alkoxylated butanol and acid catalyst

[0038] DTPA-ethyl ester prepared according to **Synthesis S9** (4.1987 g, 6.48 mmol), EO-terminated block copolymer prepared according to **Synthesis S1** (20.0 g, 38.5 mmol, 5.9 eq.) and titanium isopropoxide (0.3371 g, 1.19 mmol, 18 mol%) were charged to a 250 mL flask with a magnetic stir bar. The flask was sealed with hydrocarbon 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 150 °C. After reaching 129 °C, vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap cooled with a dry ice/acetone bath. The mixing speed was adjusted from a setting of 50 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 150-152 °C for five hours under vacuum. The flask contents were then cooled and characterized. According to NMR, no ethyl groups remained in the ^{1}H NMR spectra, and the ^{13}C NMR showed that the carbonyl region is very simple with two peaks for the two types of esters at 168 ppm and 173 ppm.

Synthesis S11: Ester synthesis

[0039] Capryleth-6 carboxylic acid (20.8032 g, 46.91 mmol based on nominal purity of 92 %, 4.1 eq.), *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine (2.6629 g, 11.4 mmol) and titanium isopropoxide (0.5429 g, 1.9102 mmol, 17 mol%) were charged to a 250 mL flask with a magnetic stir bar. The flask was sealed with hydrocarbon 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 150 °C. After reaching 120 °C, vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap cooled with a dry ice/acetone bath. The mixing speed was adjusted from a setting of 50 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 148.3-154.9 °C for 6.5 hours under vacuum. The flask contents were then cooled and characterized via NMR to confirm completion of reaction. ^{1}H NMR (acetone-d_6, δ, ppm): 4.47-3.87 (15.2 H), 3.87-3.25 (97.8 H), 2.99-2.79 (4.3 H), 2.79-2.35 (4.8 H), 1.74-1.44 (8.1 H), 1.44-1.14 (40.3 H), 1.00-0.78 (12.0 H). ^{13}C NMR (126 MHz, acetone-d_6, δ, ppm): 171.06 (2.2 C), 73.36-70.07 (35.5 C), 69.02 (2.7 C), 63.49 (2.8 C), 54.26 (2.8 C), 32.66 (3.6 C), 27.01 (3.3 C), 23.39 (4.0 C), 14.46 (4.0 C).

Synthesis S12: Ethylenediamine-methyl acrylate adduct

[0040] A 40 mL glass vial with a pressure relief cap and a magnetic stirrer was charged with methyl acrylate (8.6 g, 100 mmol) and methanol (4 mL). To the contents of the vial was slowly added ethylenediamine (1.5 g, 25 mmol). A slight exotherm was observed during the addition of amine. The resulting solution was then placed on a block heater and stirred at 50 °C for seven hours. Progress of the reaction was monitored by ^{1}H NMR spectroscopy. Upon complete conversion of amine to tetrasubstituted adduct, methanol was distilled off in a rotary evaporator to yield 9.3 g, 92 % molar yield, of slightly viscous light yellow adduct.

Synthesis S13: Transesterification of methyl acrylate adduct with alkoxylated butanol

[0041] EO-terminated block copolymer prepared according to **Synthesis S1** (10.3419 g, 13.99 mmol, 3.1 eq.), material prepared according to **Synthesis S12** (1.8526 g, 4.58 mmol) and titanium isopropoxide (0.1733 g, 0.61 mmol, 13 mol%) were charged to a 250 mL flask with a magnetic stir bar. The flask was sealed with hydrocarbon 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 reaching 44.4 °C, vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap cooled with a dry ice/acetone bath. The mixing speed was adjusted from a setting of 50 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 118.9-122.3 °C for six hours under vacuum. The flask contents were then cooled and characterized by NMR to confirm completion of the reaction.

Synthesis S14: Adduct from methyl acrylate and 3,3'-diamino-*n*-methyldipropylamine

[0042] Methyl acrylate (8.6 g, 100 mmol) and methanol (4 mL) was charged to a glass vial with a magnetic stir bar and a pressure relief cap. *N,N*-bis(3-aminopropyl)methylamine (3.5 g, 24 mmol) was then slowly added to the contents of the vial. A slight exotherm was observed during the addition of amine. The resulting solution was then placed on a block heater and stirred at 50°C for 4.5 hours. Progress of the reaction was monitored by ^{1}H NMR spectroscopy. Upon complete conversion of amine to tetrasubstituted adduct, methanol was distilled off in a rotary evaporator to yield 11 g, 93.6 % molar yield, of slightly viscous light yellow adduct.

Synthesis S15: Transesterification of methyl acrylate adduct with alkoxylated butanol

[0043] EO-terminated block copolymer prepared according to **Synthesis S1** (10.0539 g, 19.3866 mmol, 4.4 eq.), material prepared according to **Synthesis S14** (2.1746 g, 4.4 mmol) and titanium isopropoxide (0.1694 g, 0.5960 mmol, 13.6 mol%) were charged to a 250 mL flask with a magnetic stir bar. The flask was sealed with hydrocarbon 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 reaching 86.4 °C, vacuum was applied to the flask contents via a mechanical pump with an intervening solvent trap cooled with a dry ice/acetone bath. The mixing speed was adjusted from a setting of 50 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 117.5-124.7 °C for nine hours under vacuum. The flask contents were then cooled and characterized by NMR to confirm completion of the reaction.

Comparative Examples C1-C2 and Examples 1-4: Liquid Laundry Detergent

[0044] The liquid laundry detergent formulations used in the cleaning tests in the subsequent Examples were prepared having the generic formulation as described in **TABLE 2** with the cleaning booster as noted in **TABLE 3** neutralized to a pH of 8.5 were prepared by standard liquid laundry formulation preparation procedures.

TABLE 2

Ingredient	Commercial Name	wt%
Linear alkyl benzene sulfonate	Nacconal 90G*	16.0
Sodium lauryl ethoxysulfate	Steol CS-460*	4.0
Propylene glycol	--	5.0
Ethanol	--	2.0
Sodium citrate	--	5.0
Non-ionic surfactant	Biosoft N25-7*	5.0
Sodium xylenesulfonate	Stepanate SXS-93	5.5
Fatty acid	Prifac 7908[a]	3.0
Cleaning Booster	--	5.0
Deionized water	--	QS to 100
* available from Stepan Company [a] available from Croda		

TABLE 3

Example	Cleaning Booster
Comparative Example C1	none
Comparative Example C2	Alcohol ethoxylate[1]
Example 1	**Synthesis S5**
Example 2	**Synthesis S11**
Example 3	**Synthesis S10**
Example 4	**Synthesis S15**
[1] available from Stepan Company under the tradename BIO-SOFT® N25-9	

Primary Cleaning Performance

[0045] The primary cleaning performance of the liquid laundry detergent formulations of **Comparative Examples C1-C2** and **Examples 1-4** 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 Ca:Mg molar ratio were used for each run. The washed fabrics were rinsed in 300 mL of 100 ppm (2/1 Ca/Mg) 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 5x5 cm. The stained swatches were 2.5 x 3 cm. One 5 x 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)

[0046] 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 4.**

[0047] 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 4** give the difference between the SRI measured for the noted example relative to the SRI measured for **Comparative Example C1**. A positive value indicates an increase in soil removal relative to **Comparative Example C1**.

TABLE 4

Example	Cleaning Booster	ΔSRI	
		PCS-94	PCS-132
Comparative Example C2	Alcohol ethoxylate[1]	4.37	2.65
Example 1	**Synthesis S5**	4.46	--
Example 2	**Synthesis S11**	2.24	2.09
Example 3	**Synthesis S10**	2.58	1.76
Example 4	**Synthesis S15**	5.69	3.99

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

Comparative Examples C3-C4 and Examples 5-7: Liquid Laundry Detergent

[0048] The liquid laundry detergent formulation used in the cleaning tests in the subsequent Examples was prepared by combining 0.5 g of a standard liquid laundry detergent formulation with an adjusted pH of 8.5 as described in **TABLE 5** with 1.5 g of a 1 w% aqueous solution of the cleaning booster noted in **TABLE 6**.

TABLE 5

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
* available from Stepan Company [a] available from The Dow Chemical Company		

TABLE 6

Example	Cleaning Booster
Comparative Example C3	None
Comparative Example C4	Alcohol ethoxylate[1]
Example 5	**Synthesis S8**
Example 6	**Synthesis S11**
Example 7	**Synthesis S10**
[1] available from Stepan Company under the tradename BIO-SOFT® N25-9	

Anti-redeposition

[0049] The anti-redeposition performance of the combination of the standard liquid laundry detergent + cleaning booster of **Comparative Examples C3-C4** and **Examples 5-7** was assessed in a Terg-o-tometer Model 7243ES agitated at 90 cycles per minute with the conditions noted in **TABLE 7**.

TABLE 7

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 minutes

[0050] The antiredeposition performance was determined by calculating the ΔE measured with a MACH 5+ instrument (L, a & b). The results are noted in **TABLE 8**, wherein $\mathbf{\Delta E^*}$ is according to the equation

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

wherein $\mathbf{\Delta E_{aw}}$ is measured from fabrics after washing, and $\mathbf{\Delta E_{bw}}$ is measured from fabrics before washing. A higher $\mathbf{\Delta E^*}$ corresponds with better antiredeposition performance.

TABLE 8

	$\mathbf{\Delta E^*}$					
Example	**CT**	**CI**	**CT**	**PB**	**PK**	**PW**
Comp. Ex. C3	9.61	18.80	16.56	12.61	24.62	16.87
Comp. Ex. C4	10.22	19.15	21.06	12.27	23.80	14.99
Example 5	9.55	16.82	13.33	13.17	25.05	15.39
Example 6	7.48	15.68	15.27	13.28	24.03	17.17
Example 7	8.18	16.67	14.19	14.03	28.66	18.64

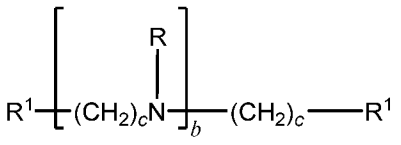
We claim:

1. A liquid laundry detergent formulation, comprising:

a liquid carrier;

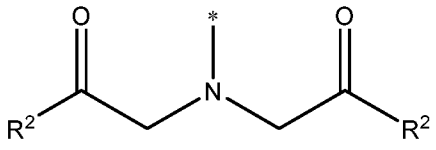
a cleaning surfactant; and

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



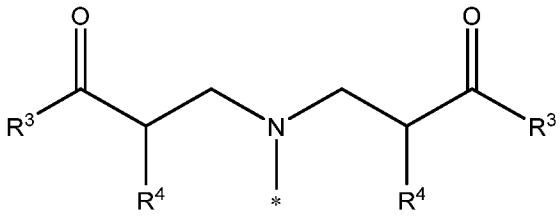
(I)

wherein *b* is 0 to 2; wherein *c* is 2 to 4; wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group and a $-CH_2C(=O)R^{14}$ group; wherein R^{14} is of formula (VI); and wherein each R^1 is independently selected from the group consisting of formula (II), formula (III), formula (IV) and formula (V);



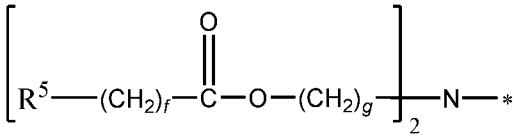
(II)

wherein the * indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI);



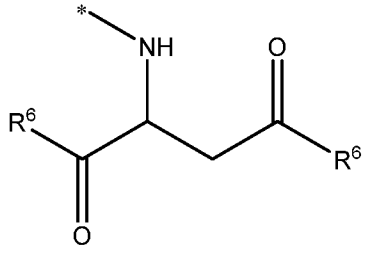
(III)

wherein the * indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



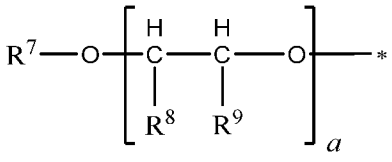
(IV)

wherein the * indicates the point of attachment to formula (I); wherein each R^5 is independently according to formula (VI); wherein *f* is 1 to 2; and wherein *g* is 2 to 10;



(V)

wherein the * indicates the point of attachment to formula (I); and wherein each R^6 is independently according to formula (VI);



(VI)

wherein the * indicates the point of attachment to the associated base formula; wherein R^7 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^8 and R^9 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^8 and R^9 is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30.

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;

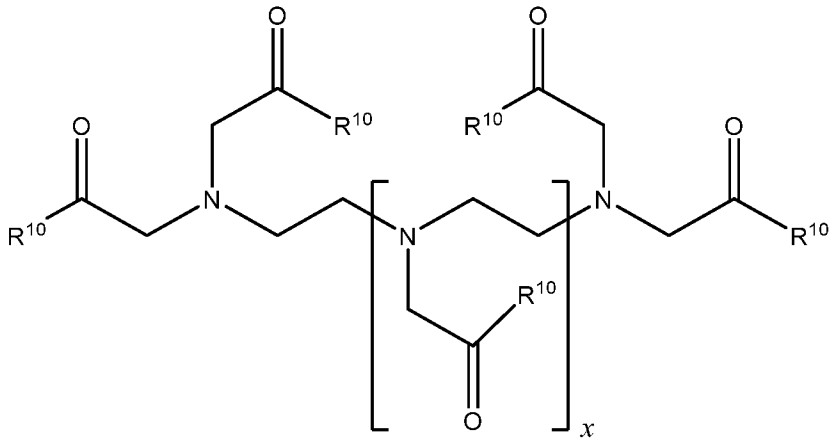
2 to 60 wt%, based on weight of the liquid laundry detergent formulation, of the cleaning surfactant; and

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

3. The liquid laundry detergent formulation of claim 2, wherein the liquid carrier comprises water.

4. The liquid laundry detergent formulation of claim 3, wherein *a* is 2 to 30 in an average of 70 to 100 mol% of the occurrences of formula (VI) in the cleaning booster.

5. The liquid laundry detergent formulation of claim 3, wherein the cleaning booster of formula (I) is of formula (Ia)



(Ia)

wherein x is 0 to 2; wherein each R^{10} is independently of formula (VI).

6. The liquid laundry detergent formulation of claim 5, wherein an average of 70 to 100 mol% of the R^{10} groups in the cleaning booster are of formula (VIa)

$$R^{11}—O—[CH_2CH(R^{12})O]_y—* \quad \text{(VIa)}$$

wherein the * indicates the point of attachment to formula (Ia); wherein R^{11} is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group; wherein each R^{12} is independently selected from the group consisting of a hydrogen and a C_{1-2} alkyl group; and wherein y is 2 to 30.

7. The liquid laundry detergent formulation of claim 5, wherein an average of 70 to 100 mol% of the R^{10} groups in the cleaning booster are of formula (VIb)

$$R^{13}—O—(EO)_h—(PO)_i—(EO)_j—* \quad \text{(VIb)}$$

wherein the * indicates the point of attachment to formula (Ia); wherein R^{13} is selected from the group consisting of a hydrogen and a C_{1-12} 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 and 30; and wherein $h + i + j$ is 2 to 30.

8. The liquid laundry detergent formulation of claim 7, wherein x is 1.

9. The liquid laundry detergent formulation of claim 8, wherein R^{13} is a C_{1-4} alkyl group; wherein h is 0 to 1; wherein i is 2 to 5; and j is 2 to 6.

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.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/036887

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/00 C11D3/30 C11D3/33
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/271458 A1 (ENSELBERG HILLARY [US]) 10 November 2011 (2011-11-10) paragraph [0002]; claim 1; examples	1-3,10
X	WO 03/040281 A1 (GREEN & CLEAN INC [KR]; CHOI KWANG-HWA [KR]) 15 May 2003 (2003-05-15) claim 1	1-3,10
A	WO 2020/123240 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; ROHM & HAAS [US]) 18 June 2020 (2020-06-18) claims	1-10
A	WO 2020/251763 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; ROHM & HAAS [US]) 17 December 2020 (2020-12-17) paragraph [0004]; claims	1-10

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 October 2022	28/10/2022

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2022/036887

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP 4133823 B2	13-08-2008
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