



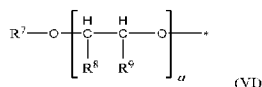
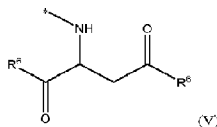
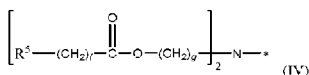
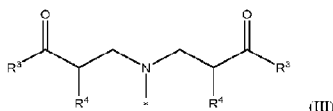
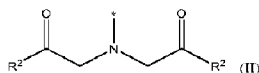
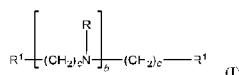
(12) **DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION**

(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 2022/07/13
(87) Date publication PCT/PCT Publication Date: 2023/01/19
(85) Entrée phase nationale/National Entry: 2024/01/03
(86) N° demande PCT/PCT Application No.: US 2022/036888
(87) N° publication PCT/PCT Publication No.: 2023/287837
(30) Priorité/Priority: 2021/07/16 (US63/222,450)

(51) Cl.Int./Int.Cl. *C11D 3/00* (2006.01),
C11D 3/30 (2006.01), *C11D 3/33* (2006.01)
(71) Demandeurs/Applicants:
DOW GLOBAL TECHNOLOGIES LLC, US;
ROHM AND HAAS COMPANY, US
(72) Inventeurs/Inventors:
IZMITLI, ASLIN, US;
MITCHELL, MICHAEL C., US;
PULUKKODY, RANDARA, US;
SATHIOSATHAM, MUHUNTHAN, US;
TULCHINSKY, MICHAEL L., US;
WASSERMAN, ERIC, US
(74) Agent: SMART & BIGGAR LP

(54) Titre : RENFORCATEUR DE NETTOYAGE
(54) Title: CLEANING BOOSTER



(57) **Abrégé/Abstract:**

Cleaning booster for cleaning dirty laundry is provided, wherein the cleaning booster is of formula (I), wherein b is 0-2; wherein c is 2-4; wherein R is selected from hydrogen, C₁₋₂₂ alkyl and -CH₂C(=O)R¹⁴; wherein R¹⁴ is of formula (VI); wherein R¹ is selected from formula (II)-formula (V); (II) wherein R² is of formula (VI); (III) wherein R³ is of formula (VI); and wherein R⁴ is selected from hydrogen and methyl group; (IV) wherein R⁵ is of formula (VI); wherein f is 1-2; and wherein g is 2-10; (V) wherein R⁶ is of formula (VI); (VI) wherein R⁷ is selected from hydrogen and C₁₋₂₂ alkyl group; wherein each R⁸ and R⁹ is independently a hydrogen or a C₁₋₂ alkyl group, with the proviso that at least one of R⁸ and R⁹ is hydrogen in each subunit a; and wherein a is 0-30.



Date Submitted: 2024/01/03

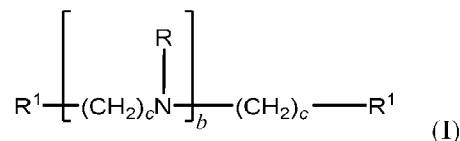
CA App. No.: 3224837

Abstract:

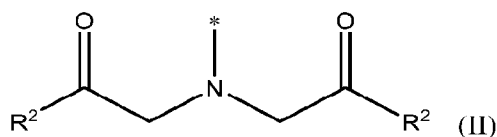
Cleaning booster for cleaning dirty laundry is provided, wherein the cleaning booster is of formula (I), wherein b is 0-2; wherein c is 2-4; wherein R is selected from hydrogen, C1-22 alkyl and -CH₂C(=O)R₁₄; wherein R₁₄ is of formula (VI); wherein R₁ is selected from formula (II)-formula (V); (II) wherein R₂ is of formula (VI); (III) wherein R₃ is of formula (VI); and wherein R₄ is selected from hydrogen and methyl group; (IV) wherein R₅ is of formula (VI); wherein f is 1-2; and wherein g is 2-10; (V) wherein R₆ is of formula (VI); (VI) wherein R₇ is selected from hydrogen and C1-22 alkyl group; wherein each R₈ and R₉ is independently a hydrogen or a C1-2 alkyl group, with the proviso that at least one of R₈ and R₉ is hydrogen in each subunit a; and wherein a is 0-30.

CLEANING BOOSTER

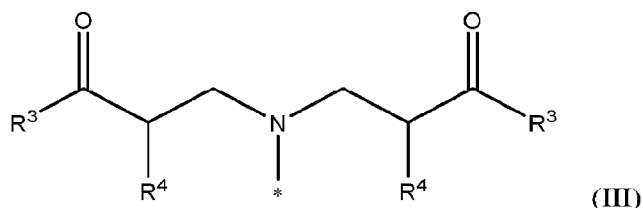
[0001] The present invention relates to a cleaning booster for cleaning dirty laundry. In particular, the present invention relates to a cleaning booster for cleaning dirty laundry, wherein the cleaning booster is of formula (I)



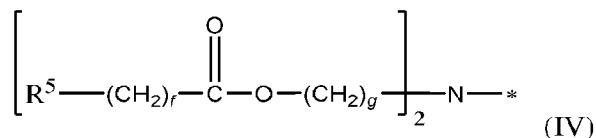
wherein b is 0 to 2; wherein c is 2 to 4; wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group, an R^1 and a $-CH_2C(=O)R^{14}$ group; wherein each R^1 is independently selected from the group consisting of formula (II), formula (III), formula (IV)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



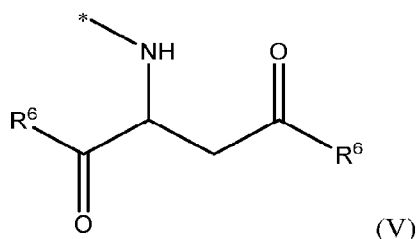
wherein the $*$ indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI);



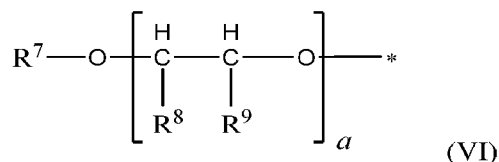
wherein the $*$ indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



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;



wherein the * indicates the point of attachment to formula (I); and wherein each R⁶ is independently according to formula (VI);



wherein the * indicates the point of attachment to the associated base formula; wherein R⁷ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group; wherein each R⁸ and R⁹ is independently selected from the group consisting of a hydrogen and a C₁₋₂ alkyl group, with the proviso that at least one of R⁸ and R⁹ is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30.

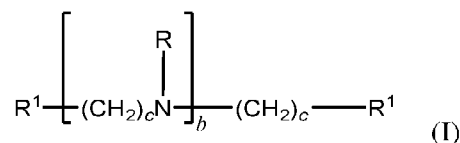
[0002] Laundry detergents, particularly those in liquid and gel forms, providing excellent overall cleaning are desirable to consumers. Such laundry detergents typically include surfactants among other components to deliver the consumer desired cleaning benefits. Nevertheless, increasing sensitivity 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.

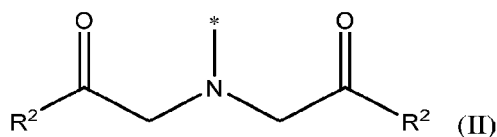
[0004] Notwithstanding, there remains a continuing need for cleaning boosters that facilitate maintained primary cleaning performance with reduced surfactant loading laundry detergent formulations (particularly in liquid or gel laundry detergent formulations); preferably, while also providing improved 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.

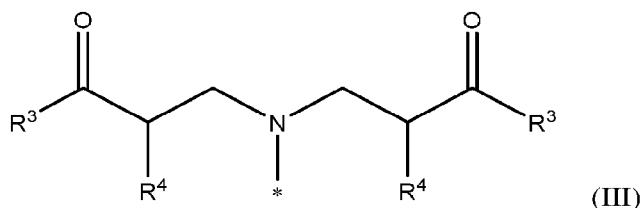
[0005] The present invention provides a cleaning booster for cleaning dirty laundry, wherein the cleaning booster is of formula (I)



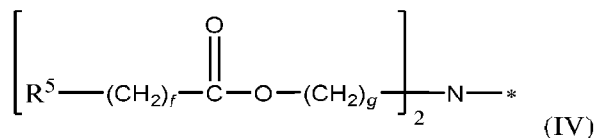
wherein b is 0 to 2; wherein c is 2 to 4; wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group, an R^1 and a $-CH_2C(=O)R^{14}$ group; wherein each R^1 is independently selected from the group consisting of formula (II), formula (III), formula (IV)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



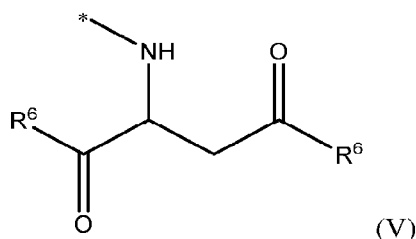
wherein the $*$ indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI);



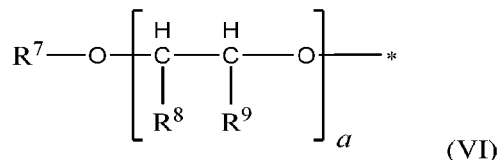
wherein the $*$ indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



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;

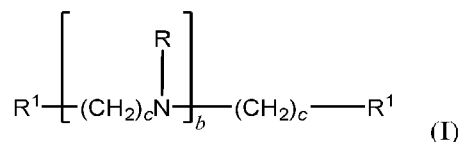


wherein the * indicates the point of attachment to formula (I); and wherein each R⁶ is independently according to formula (VI);

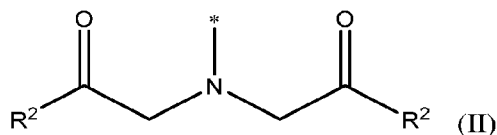


wherein the * indicates the point of attachment to the associated base formula; wherein R⁷ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group; wherein each R⁸ and R⁹ is independently selected from the group consisting of a hydrogen and a C₁₋₂ alkyl group, with the proviso that at least one of R⁸ and R⁹ is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30.

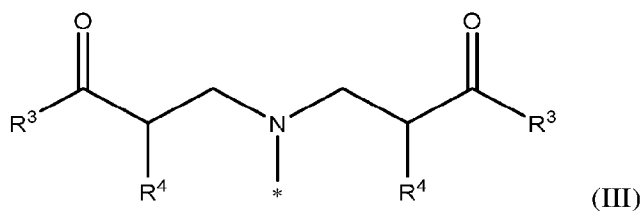
[0006] The present invention provides a cleaning booster for cleaning dirty laundry, wherein the cleaning booster is of formula (I)



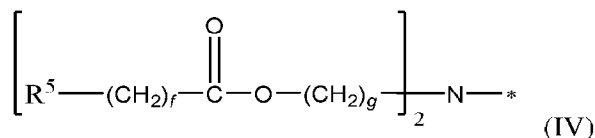
wherein *b* is 0 to 2; wherein *c* is 2 to 4; wherein each R is independently selected from the group consisting of a hydrogen, a C₁₋₂₂ alkyl group, an R¹ and a -CH₂C(=O)R¹⁴ group; wherein each R¹ is independently selected from the group consisting of formula (II), formula (III), formula (IV) and formula (V); wherein R¹⁴ is of formula (VI);



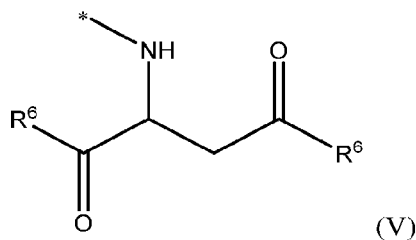
wherein the * indicates the point of attachment to formula (I); wherein each R² is independently of formula (VD);



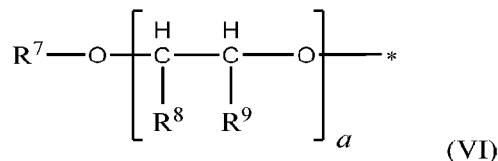
wherein the * indicates the point of attachment to formula (I); wherein each R³ is independently according to formula (VI); and wherein each R⁴ is independently selected from the group consisting of a hydrogen and a methyl group;



wherein the * indicates the point of attachment to formula (I); wherein each R⁵ is independently according to formula (VI); wherein *f* is 1 to 2; and wherein *g* is 2 to 10;

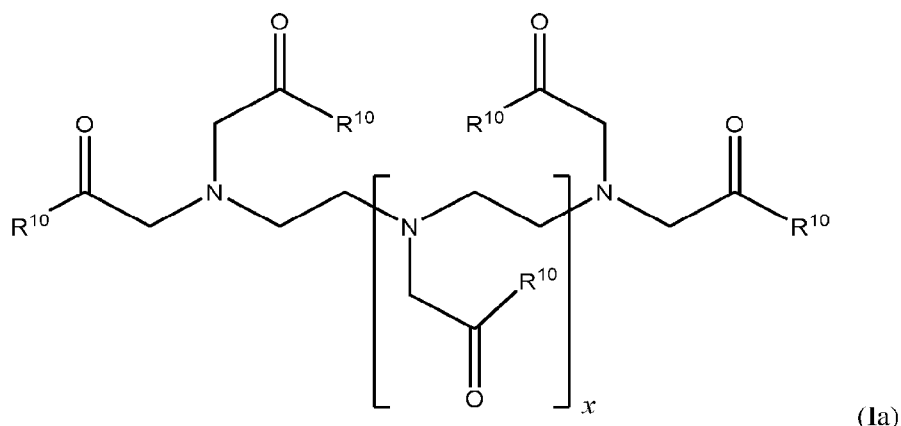


wherein the * indicates the point of attachment to formula (I); and wherein each R⁶ is independently according to formula (VI);



wherein the * indicates the point of attachment to the associated base formula; wherein R⁷ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group; wherein each R⁸ and R⁹ is independently selected from the group consisting of a hydrogen and a C₁₋₂ alkyl group, with the proviso that at least one of R⁸ and R⁹ is a hydrogen in each subunit *a*; 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 cleaning booster for cleaning dirty laundry, wherein the cleaning booster is of formula (Ia)



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

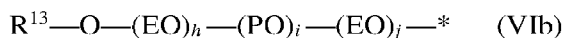
[0008] The present invention provides a cleaning booster for cleaning dirty laundry, wherein the cleaning booster is of formula (Ia); wherein an average of 70 to 100 mol% of the R^{10} groups in the cleaning booster are of formula (VI) wherein a is 2 to 30.

[0009] The present invention provides a cleaning booster for cleaning dirty laundry, wherein the cleaning booster is of formula (Ia); wherein an average of 70 to 100 mol% of the R^{10} groups in the cleaning booster are of formula (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.

[0010] The present invention provides a cleaning booster for cleaning dirty laundry, wherein the cleaning booster is of formula (Ia); wherein an average of 70 to 100 mol% of the R^{10} groups in the cleaning booster are of formula (VIb)



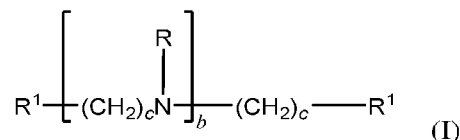
wherein the * indicates the point of attachment to formula (Ia); wherein R^{13} is selected from the group consisting of a hydrogen and a C_{1-12} alkyl group; wherein EO is an ethylene oxide group; wherein PO is a propylene oxide group; wherein h is 0 to 30; wherein i is 0 to 30; wherein j is 0 and 30; and wherein $h + i + j$ is 2 to 30.

[0011] The present invention provides a laundry additive comprising a mixture of a cleaning booster of the present invention and water.

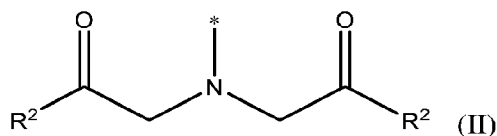
DETAILED DESCRIPTION

[0012] It has been surprisingly found that the cleaning boosters 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.

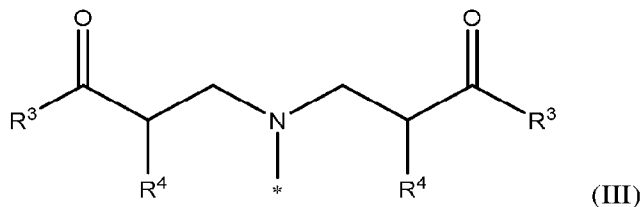
[0013] Preferably, the cleaning booster for cleaning dirty laundry, of the present invention, is of formula (I)



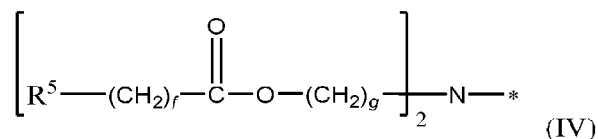
wherein b is 0 to 2 (preferably, 1); wherein c is 2 to 4 (preferably, 2); wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group and a $-CH_2C(=O)R^{14}$ group (preferably, a hydrogen, a C_{1-5} alkyl group and a $-CH_2C(=O)R^{14}$ group; more preferably,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



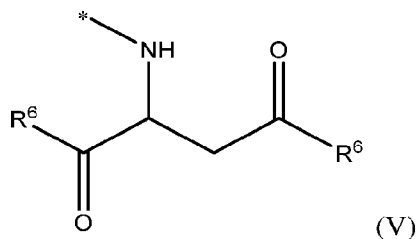
wherein the $*$ indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI) (i.e., the individual occurrences of R^2 in formula (II) can be the same or different from one another);



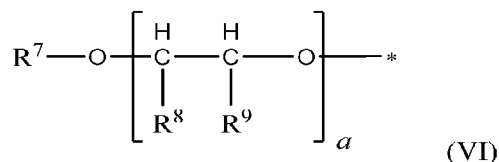
wherein the $*$ indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



wherein the * indicates the point of attachment to formula (I); wherein each R⁵ is independently according to formula (VI); wherein *f* is 1 to 2; and wherein *g* is 2 to 10;

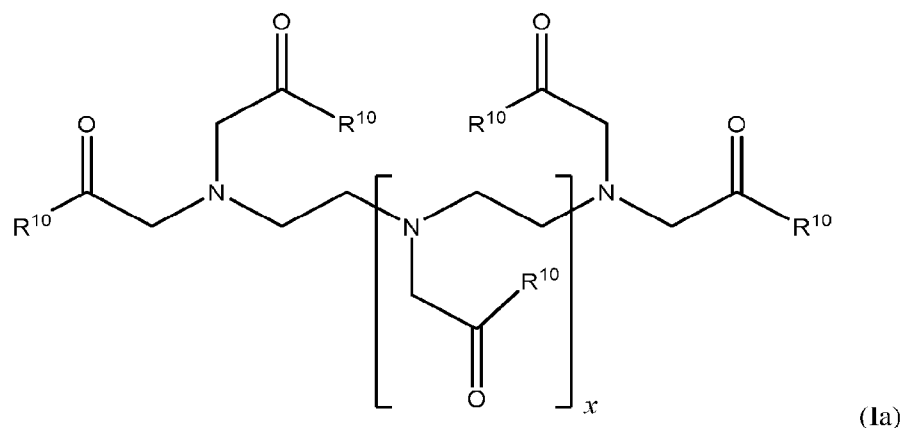


wherein the * indicates the point of attachment to formula (I); and wherein each R⁶ is independently according to formula (VI);

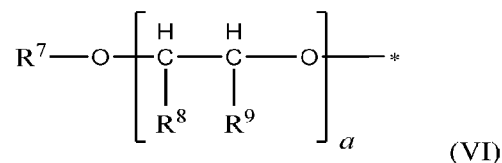


wherein the * indicates the point of attachment to the associated base formula (i.e., formula (II), formula (III), formula (IV) or formula (V)); wherein R⁷ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group (preferably, a hydrogen and a C₁₋₁₂ alkyl group; more preferably, a hydrogen and a C₁₋₅ alkyl group; still more preferably, a hydrogen and a C₁₋₄ alkyl group; most preferably, a hydrogen and a C₄ alkyl group); wherein each R⁸ and R⁹ is independently selected from the group consisting of a hydrogen and a C₁₋₂ alkyl group, with the proviso that at least one of R⁸ and R⁹ 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).

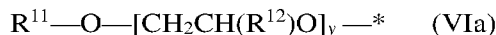
[0014] Preferably, the cleaning booster for cleaning dirty laundry, of the present invention, is of formula (I); wherein formula (I) is of formula (Ia)



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

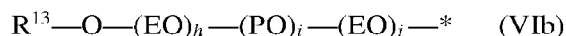


wherein the * indicates the point of attachment to formula (Ia); wherein R^7 is selected from the group consisting of a hydrogen and a C_{1-22} alkyl group (preferably, a hydrogen and a C_{1-12} alkyl group; more preferably, a hydrogen and a C_{1-5} alkyl group; still more preferably, a hydrogen and 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)



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 R¹⁰ groups are of formula (VI); wherein formula (VI) is of formula (VIb)



wherein the * indicates the point of attachment to formula (Ia); wherein R¹³ is selected from the group consisting of a hydrogen and a C₁₋₁₂ alkyl group (preferably, a hydrogen and a C₁₋₁₂ alkyl group; more preferably, a hydrogen and a C₁₋₅ alkyl group; still more preferably, a C₁₋₄ alkyl group; most preferably, a C₄ 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).

[0015] Preferably, the laundry additive of the present invention comprises a mixture of a cleaning booster of the present invention and water. More preferably, the laundry additive of the present invention is a mixture comprising 0.1 to 99 wt% (preferably, 0.2 to 98 wt%; more preferably, 0.5 to 95 wt%; most preferably, 0.75 to 90 wt%), based on weight of the laundry additive, of a cleaning booster of the present invention; and 1 to 99.9 wt% (preferably, 2 to 99.8 wt%; more preferably, 5 to 99.5 wt%; most preferably, 10 to 99.25 wt%), based on weight of the laundry additive, of a water. Most preferably, the laundry additive of the present invention is a mixture comprising 0.1 to 99 wt% (preferably, 0.2 to 98 wt%; more preferably, 0.5 to 95 wt%; most preferably, 0.75 to 90 wt%), based on weight of the laundry additive, of a cleaning booster of the present invention; and 1 to 99.9 wt% (preferably, 2 to 99.8 wt%; more preferably, 5 to 99.5 wt%; most preferably, 10 to 99.25 wt%), based on weight of the laundry additive, of a water; wherein the laundry additive is a liquid (preferably, wherein the laundry additive is a liquid at 21 °C and 1 standard atmosphere of pressure).

[0016] Some embodiments of the present invention will now be described in detail in the following **Examples**.

[0017] 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
Butylstannous acid	available from OMC Organometallics 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

[0018] 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. ¹H NMR (CDCl₃, δ, ppm): 0.90 t (3H, CH₃), 1.13 m (8.48 H, CH₃ of PO), 1.35 m (2H, CH₂), 1.55 m (2H, CH₂), 3.55 m (35.93 H, CHCH₂ of PO + CH₂CH₂ of EO). NMR analysis suggested the following formula for the recovered product: CH₃CH₂CH₂CH₂OCH₂CH₂O(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

[0019] 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%). ¹H NMR (CDCl₃, δ, ppm): 0.90 t (3H, CH₃), 1.13 m (11.05 H, CH₃ of PO), 1.35 m (2H, CH₂), 1.55 m (2H, CH₂), 3.55 m (31.02 H, CHCH₂ of PO + CH₂CH₂ of EO). NMR analysis suggests the following formula: CH₃CH₂CH₂CH₂OCH₂CH₂O(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

[0020] 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. ¹H 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

[0021] 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 ¹³C 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

[0022] 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 ¹³C 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

[0023] 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 ¹³C 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

[0024] 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 alkoxyated butanol and acid catalyst

[0025] 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 ¹³C 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

[0026] 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 polvester

[0027] 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 ¹H NMR spectra, and the ¹³C 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

[0028] 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. ¹H 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). ¹³C 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

[0029] 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 ¹H 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 alkoxyated butanol

[0030] 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

[0031] 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 ¹H 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 alkoxyated butanol

[0032] 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

[0033] 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

<u>Ingredient</u>	<u>Commercial Name</u>	<u>wt%</u>
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

<u>Example</u>	<u>Cleaning Booster</u>
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

[0034] 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)

[0035] 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**.

[0036] 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

[0037] 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

[0038] 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

[0039] 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 ΔE^* is according to the equation

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

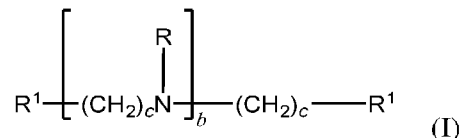
wherein ΔE_{aw} is measured from fabrics after washing, and ΔE_{bw} is measured from fabrics before washing. A higher ΔE^* corresponds with better antiredeposition performance.

TABLE 8

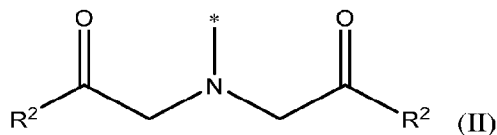
Example	ΔE^*					
	CT	CI	CT	PB	PK	PW
Comp. Ex. C3	9.61	18.80	16.56	12.61	24.62	16.87
Comp. Ex. C4	10.22	19.15	21.06	12.27	23.80	14.99
Example 5	9.55	16.82	13.33	13.17	25.05	15.39
Example 6	7.48	15.68	15.27	13.28	24.03	17.17
Example 7	8.18	16.67	14.19	14.03	28.66	18.64

We claim:

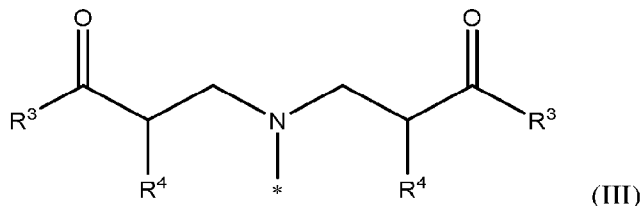
1. A cleaning booster for cleaning dirty laundry, wherein the cleaning booster is of formula (I)



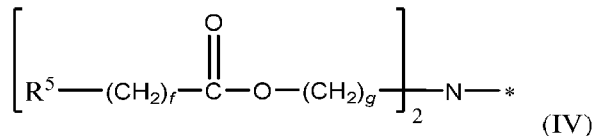
wherein b is 0 to 2; wherein c is 2 to 4; wherein each R is independently selected from the group consisting of a hydrogen, a C_{1-22} alkyl group and a $-CH_2C(=O)R^{14}$ group; wherein R^{14} is of formula (VI); and wherein each R^1 is independently selected from the group consisting of formula (II),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



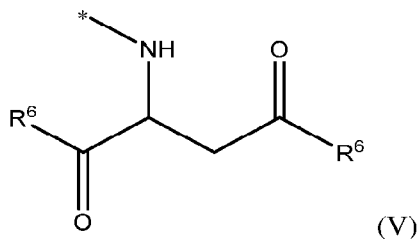
wherein the $*$ indicates the point of attachment to formula (I); wherein each R^2 is independently of formula (VI);



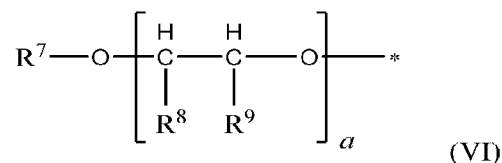
wherein the $*$ indicates the point of attachment to formula (I); wherein each R^3 is independently according to formula (VI); and wherein each R^4 is independently selected from the group consisting of a hydrogen and a methyl group;



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;

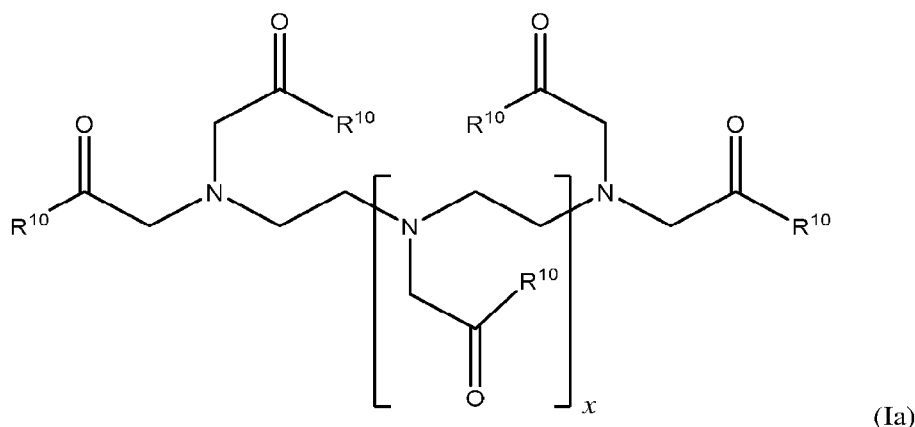


wherein the * indicates the point of attachment to formula (I); and wherein each R⁶ is independently according to formula (VI);



wherein the * indicates the point of attachment to the associated base formula; wherein R⁷ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group; wherein each R⁸ and R⁹ is independently selected from the group consisting of a hydrogen and a C₁₋₂ alkyl group, with the proviso that at least one of R⁸ and R⁹ is a hydrogen in each subunit *a*; and wherein *a* is 0 to 30.

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



wherein *x* is 0 to 2; wherein each R¹⁰ is independently of formula (VI).

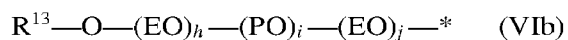
3. The cleaning booster of claim 2, wherein 70 to 100 mol% of the R¹⁰ groups in the cleaning booster are of formula (VI) wherein *a* is 2 to 30.

4. The cleaning booster of claim 2, wherein 70 to 100 mol% of the R¹⁰ groups in the cleaning booster are of formula (VIa)



wherein the * indicates the point of attachment to formula (Ia); wherein R¹¹ is selected from the group consisting of a hydrogen and a C₁₋₂₂ alkyl group; wherein each R¹² is independently selected from the group consisting of a hydrogen and a C₁₋₂ alkyl group; and wherein *y* is 2 to 30.

5. The cleaning booster of claim 2, wherein 70 to 100 mol% of the R¹⁰ groups in the cleaning booster are of formula (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.

6. The cleaning booster of claim 5, wherein x is 1.
7. The cleaning booster of claim 6, wherein R^{13} is a C_{1-4} alkyl group.
8. The cleaning booster of claim 7, wherein h is 0 to 1; wherein i is 2 to 5; and wherein j is 2 to 6.
9. A laundry additive comprising a mixture of a cleaning booster of claim 1 and water.
10. The laundry additive of claim 8, wherein the laundry additive is a liquid.

