



- (51) **International Patent Classification:**
C11D 3/37 (2006.01) *C11D 1/83* (2006.01)
- (21) **International Application Number:**
PCT/CN2018/092765
- (22) **International Filing Date:**
26 June 2018 (26.06.2018)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (71) **Applicant: THE PROCTER & GAMBLE COMPANY**
[US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).
- (72) **Inventors; and**
- (71) **Applicants (for US only): LI, Fei** [CN/CN]; No. 35, Yu'an Road, B Zone, Tianzhu Konggang Development Zone, Shunyi District, Beijing 101312 (CN). **TANG, Ming** [CN/CN]; No. 35, Yu'an Road, B Zone, Tianzhu Konggang Development Zone, Shunyi District, Beijing 101312 (CN). **GUO, Yu** [CN/CN]; No. 35, Yu'an Road, B Zone, Tianzhu Konggang Development Zone, Shunyi District, Beijing 101312 (CN). **HUANG, Biyan** [CN/CN]; No. 35, Yu'an Road, B Zone, Tianzhu Konggang Development Zone, Shunyi District, Beijing 101312 (CN).
- (74) **Agent: SHANGHAI PATENT & TRADEMARK LAW OFFICE, LLC**; 435 Guiping Road, Shanghai 200233 (CN).

- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— with international search report (Art. 21(3))

(54) **Title:** LIQUID LAUNDRY DETERGENT COMPOSITION

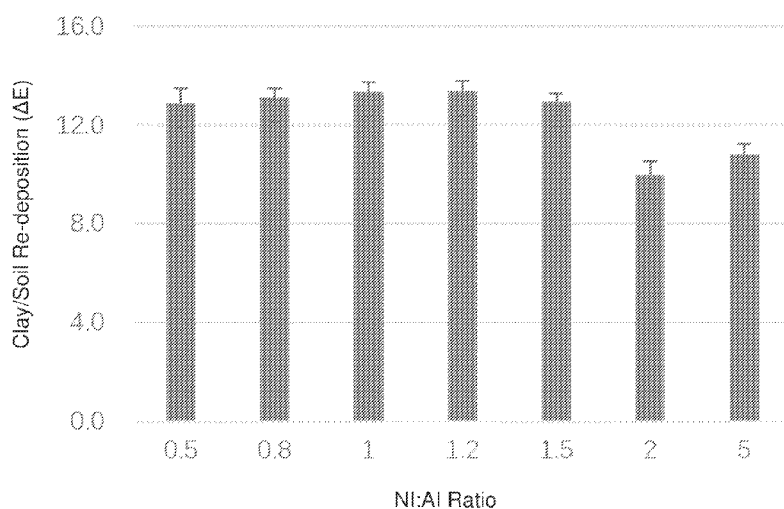


FIG. 1

(57) **Abstract:** A liquid laundry detergent with improved soil suspension benefit is provided, which contains a from about 0.1 wt% to about 5 wt% of an alkoxylated polyethyleneimine and a specific surfactant system including both nonionic (NI) surfactant (s) and anionic (AI) surfactant (s) at an NI-to-AI weight ratio of about 1.7-20.

WO 2020/000167 A1

LIQUID LAUNDRY DETERGENT COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a cleaning composition, and particularly a liquid laundry
5 detergent composition that is useful for treating fabrics.

BACKGROUND OF THE INVENTION

Modern day consumers desire laundry detergents that provide excellent overall cleaning
benefit with minimal environmental impact. The detergent industry has traditionally utilized
10 surfactants to deliver the cleaning benefit. However, due to increasing environmental concerns, as
well as rising costs of raw materials, the conventional way of either solely or heavily relying on
surfactants to achieve the cleaning benefit is gradually losing favor with the modern-day consumers.

Correspondingly, laundry detergent manufacturers are exploring new ways to reduce the
total amount of surfactants used in their products and to minimize the adverse impact of laundering
15 on the environment, while still providing the consumer with excellent overall cleaning results.

Alkoxylated polyalkyleneimines (APEI) are a group of polymers having a
polyalkyleneimine backbone or core that is surrounded by polyalkylene oxide blocks. They have
been used as detergent additives in low-surfactant liquid detergent formulations to assist removal
of soil from the fabric surface, stabilize suspension of soils dispersed in the wash liquor, and to
20 prevent the suspended soil from redepositing back onto the fabric surface. The use of such APEI
polymers enables reduction of the total surfactant level in such liquid laundry detergent products
while still providing the consumer with excellent overall cleaning performance. Correspondingly,
less surfactant is released into the environment after each wash, resulting in reduced environmental
“footprint” of such laundry detergent products.

25 There is a continuing need to further improve the soil removal benefit or cleaning
performance of liquid laundry detergent compositions without increasing the total surfactant
content therein or enlarging the environmental “footprint” thereof.

SUMMARY OF THE INVENTION

30 It is a surprising discovery of the present invention that when the liquid laundry detergent
compositions employ a specific surfactant system, i.e., one that contains both nonionic (NI) and
anionic (AI) surfactants at a specific NI-to-AI weight ratio, in combination with an APEI polymer,
the resulting soil removal benefit or cleaning performance is further improved in comparison with

APEI-containing liquid laundry detergent compositions that employ a different surfactant system (e.g., with an NI-to-AI weight ratio falling outside of the desired range of the present invention).

In one aspect, the present invention relates to a liquid laundry detergent composition comprising:

- 5 a) from 0.1 wt% to 5 wt% of an alkoxyated polyethyleneimine having a polyalkyleneimine core with one or more alkoxy side chains bonded to at least one nitrogen atom in the polyalkyleneimine core; and
- b) from 6 wt% to 50 wt% of one or more nonionic (NI) surfactants and one or more anionic (AI) surfactants,

10 while the NI-to-AI weight ratio ranges from 1.7 to 20.

In a particularly preferred embodiment, the present invention relates to a liquid laundry detergent composition comprising:

- 1) from 0.5 wt% to 1 wt% of an alkoxyated polyethyleneimine an empirical formula of (PEI) a -(EO) b -(PO) c -R₁, wherein a is the weight average molecular weight of the polyalkyleneimine core (MWPEI) of the alkoxyated polyalkyleneimine and is in the range of from 500 to 2,000 Daltons; wherein b is the weight average degree of ethoxylation in said one or more side chains of the alkoxyated polyalkyleneimine and is in the range of from 15 to 25; wherein c is the weight average degree of propoxylation in said one or more side chains of the alkoxyated polyalkyleneimine and is 0; and wherein R₁ is hydrogen;
- 20 2) from 9 wt% to 30 wt% of a nonionic (NI) surfactant that is a C₈-C₁₈ alkyl ethoxylated alcohol having a weight average degree of ethoxylation ranging from 7 to 10; and
- 3) from 2 wt% to 10 wt% of a C₁₀-C₂₀ linear alkyl benzene sulphonate (LAS) and a C₁₀-C₂₀ linear or branched alkylethoxy sulfate (AES) having a weight average degree of ethoxylation ranging from 1 to 3,

25 while the NI-to-AI weight ratio ranges from 2 to 5.

The present invention may also relate to the use of above-described liquid laundry detergent composition for treating fabrics.

These and other features of the present invention will become apparent to one skilled in the art upon review of the following detailed description when taken in conjunction with the appended
30 claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph plotting the color change (ΔE) caused by clay/soil re-deposition as a function of the NI-to-AI weight ratio in different APEI-containing liquid laundry detergent compositions with the same total surfactant level.

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DETAILED DESCRIPTION OF THE INVENTION

As used herein, the articles "a" and "an" when used in a claim, are understood to mean one or more of what is claimed or described.

As used herein, the terms "comprising," "comprises," "include", "includes" and "including" are meant to be non-limiting.

10 As used herein, the term "substantially free of" or "substantially free from" means that the indicated material is present in an amount of no more than about 5 wt%, preferably no more than about 2%, and more preferably no more than about 1 wt%.

As used therein, the term "essentially free of" or "essentially free from" means that the indicated material is at the very minimal not deliberately added to the composition, or preferably
15 not present at an analytically detectible level in such composition. It may include compositions in which the indicated material is present only as an impurity of one or more of the materials deliberately added to such compositions.

As used herein, the term "liquid" refers to a fluid having a liquid having a viscosity of from about 1 to about 2000 mPa*s at 25°C and a shear rate of 20 sec⁻¹. In some embodiments, the
20 viscosity of the liquid may be in the range of from about 200 to about 1000 mPa*s at 25°C at a shear rate of 20 sec⁻¹. In some embodiments, the viscosity of the liquid may be in the range of from about 200 to about 500 mPa*s at 25°C at a shear rate of 20 sec⁻¹.

Unless otherwise specified, the term "molecular weight" as used herein refers to the weight
25 average molecular weight (MW_w) of the polymer chains in a polymer composition, which may be calculated using the equation:

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

wherein N_i is the number of molecules having a molecular weight M_i .

Unless otherwise specified, the term "alkyl" as used herein means a C₁-C₁₀ hydrocarbyl moiety which can be linear or branched, substituted or unsubstituted.

30 As used herein, the term "hydrocarbyl" is defined herein as any organic unit or moiety which is comprised of carbon atoms and hydrogen atoms. Included with the definition of "hydrocarbyl" are the aromatic (aryl) and non-aromatic carbocyclic rings. Further included

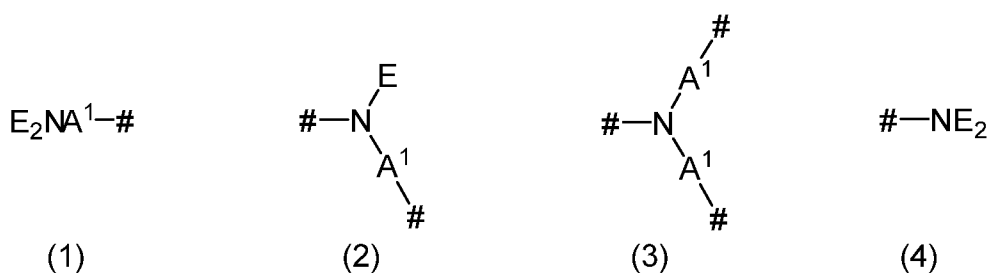
within the term hydrocarbonyl are heterocycles. The term “heterocycle” includes both aromatic (heteroaryl) and non-aromatic heterocyclic rings.

All temperatures herein are in degrees Celsius (°C) unless otherwise indicated. Unless otherwise specified, all measurements herein are conducted at 25°C and under the atmospheric pressure. In all embodiments of the present invention, all percentages are by weight of the total composition, unless specifically stated otherwise. All ratios are weight ratios, unless specifically stated otherwise.

It is understood that the test methods that are disclosed in the Test Methods Section of the present application must be used to determine the respective values of the parameters of Applicants’ inventions are described and claimed herein.

Alkoxylated Polyalkyleneimine (APEI)

The liquid laundry detergent composition of the present invention contains at least one alkoxylated polyalkyleneimine (APEI), which may be represented as containing repeating units of formulae (1), (2), (3) and (4)

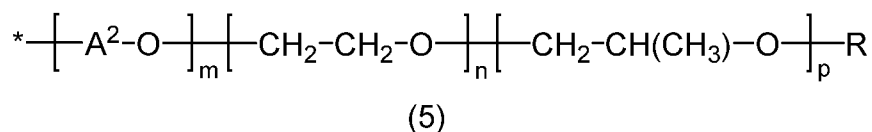


wherein:

in each case denotes one-half of a bond between a nitrogen atom and the free binding position of a group A¹ of two adjacent repeating units of formulae (1), (2), (3) or (4);

A¹ is independently selected from linear or branched C₂-C₆ alkylene;

E is independently selected from alkyleneoxy units of the formula (5):



wherein:

* in each case denotes the bond to the nitrogen atom of the repeating unit of formula (1), (2) or (4);

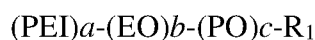
A² is in each case independently selected from 1,2-propylene, 1,2-butylene and 1,2-isobutylene;

R is in each case independently selected from hydrogen and C₁-C₄-alkyl;
 m has a weight average value in the range of from 0 to about 2;
 n has a weight average value in the range of from about 20 to about 50; and
 p is a rational number from about 10 to about 50;

5 the individual APEIs consisting of 1 repeating unit of formula (1), x repeating units of formula (2),
 y repeating units of formula (3) and y+1 repeating units of formula (4), wherein x and y in each
 case have a value in the range of from 0 to about 150; and the polymer has a degree of
 quaternization of from 0 to about 50%.

In a simplified representation, the APEIs of the present invention can be considered as
 10 having a polyalkyleneimine core with one or more alkoxy side chains bonded to at least one
 nitrogen atom in the polyalkyleneimine core. The polyalkyleneimine core is formed by the
 repeating units of formulae (1), (2), (3) and (4) as described hereinabove, but minus the alkylenoxy
 units E. The one or more alkoxy side chain is formed by alkylenoxy units E as described
 hereinabove, preferably has an inner polyethylene oxide block and an outer polypropylene oxide
 15 block.

The APEIs of the present invention may be represented by an empirical formula of:



Specifically, *a* is the weight average molecular weight of the polyalkyleneimine core (MWPEI) of
 the alkoxyated polyalkyleneimine and is in the range of from 100 to 100,000 Daltons, preferably
 20 from 200 to 20,000 Daltons, more preferably from 500 to 2,000 Daltons. Further, *b* is the weight
 average degree of ethoxylation in said one or more side chains of the alkoxyated
 polyalkyleneimine and is in the range of from 5 to 40, preferably from 10 to 30, more preferably
 from 15 to 25. Still further, *c* is the weight average degree of propoxylation in said one or more
 side chains of the alkoxyated polyalkyleneimine which ranges from 0 to 50, preferably from 0 to
 25 30, more preferably from 0 to 20. The terminal group R₁ is independently selected from the group
 consisting of hydrogen, C₁-C₄ alkyl, and combinations thereof.

In a preferred embodiment of the present invention, the liquid laundry detergent
 composition contains at least a first APEI that can be represented by an empirical formula of
 (PEI)₅₀₀₋₂₀₀₀(EO)₁₅₋₂₅.

30 Optionally, the liquid laundry detergent composition of the present invention may further
 contain a second APEI that can be represented by an empirical formula of (PEI)₅₀₀₋₂₀₀₀(EO)<sub>15-
 25</sub>(PO)₁₀₋₂₀. If both are present, the weight ratio between such first and second APEIs may range

from about 1:1 to about 10:1, preferably from about 1:1 to about 5:1, more preferably from about 1:1 to about 2:1.

The above-described APEIs may be present in the liquid laundry detergent composition of the present invention in an amount ranging from about 0.1 wt% to about 5 wt%, preferably from about 0.2 wt% to about 3 wt%, more preferably from about 0.5 wt% to about 1 wt%. In a particularly preferred embodiment, the liquid laundry detergent composition contains from about 0.5 wt% to about 1 wt% of an APEI having an empirical formula of $(PEI)_{500-2000}(EO)_{15-25}$.

Surfactant System

In addition to the APEIs described hereinabove, the liquid laundry detergent composition of the present invention also includes a surfactant system comprising one or more surfactants selected from the group consisting of anionic surfactants, nonionic surfactants, zwitterionic surfactants, amphoteric surfactants, cationic surfactants, and combinations thereof. The total surfactant content of such liquid laundry detergent composition may range from about 10% to about 90%, preferably from about 10% to about 80%, more preferably from about 15% to about 60% by total weight of the composition.

It is an important feature of the present invention that the surfactant system of the liquid laundry detergent composition comprises both nonionic (NI) and anionic (AI) surfactants at a specific NI-to-AI weight ratio ranging from about 1.7 to about 20, preferably from about 1.8 to about 10, more preferably from about 2 to about 5. The total amount of NI and AI surfactants in the liquid laundry detergent composition may range from about 6 wt% to about 50 wt%, preferably from about 10 wt% to about 40 wt%, more preferably from about 12 wt% to about 30 wt%.

Nonionic surfactants that can be included into the liquid laundry detergent composition of the present invention may be any conventional nonionic surfactants, including but not limited to: alkyl alkoxyated alcohols, alkyl alkoxyated phenols, alkyl polysaccharides, polyhydroxy fatty acid amides, and the like. Preferred nonionic surfactants are those of the formula $R^1(OC_2H_4)_nOH$, wherein R^1 is a C_8 - C_{18} alkyl group or alkyl phenyl group, and n is from about 1 to about 80. Particularly preferred are C_8 - C_{18} alkyl ethoxyated alcohols having a weight average degree of ethoxylation from about 1 to about 20, preferably from about 5 to about 15, more preferably from about 7 to about 10, such as NEODOL[®] nonionic surfactants commercially available from Shell.

Other non-limiting examples of nonionic surfactants useful herein include: C_6 - C_{12} alkyl phenol alkoxyates where the alkoxyate units may be ethyleneoxy units, propyleneoxy units, or a mixture thereof; C_{12} - C_{18} alcohol and C_6 - C_{12} alkyl phenol condensates with ethylene

oxide/propylene oxide block polymers such as Pluronic[®] from BASF; C₁₄-C₂₂ mid-chain branched alcohols (BA); C₁₄-C₂₂ mid-chain branched alkyl alkoxyates, BAE_x, wherein *x* is from 1 to 30; alkyl polysaccharides, specifically alkyl polyglycosides; Polyhydroxy fatty acid amides; and ether capped poly(oxyalkylated) alcohol surfactants. Suitable nonionic surfactants also include those
5 sold under the tradename Lutensol[®] from BASF.

The nonionic surfactants can be provided in the liquid laundry detergent compositions of the present invention at levels ranging from about 5 wt% to about 45 wt%, preferably from about 8 wt% to about 40 wt%, more preferably from about 9 wt% to about 30 wt%. In one particularly preferred embodiment, the liquid laundry detergent composition contains from about 9 wt% to
10 about 30 wt% of a C₈-C₁₈ alkyl ethoxylated alcohol having a weight average degree of ethoxylation ranging from 7 to 10.

Anionic surfactants that are used in the liquid laundry detergent compositions of the present invention are preferably non-soap synthetic anionic surfactants, such as the water-soluble salts, preferably the alkali metal salts and/or ammonium salts, of organic sulphonic reaction products
15 having in their molecular structure an alkyl group (included in the term "alkyl" is the alkyl portion of acyl groups) containing from about 10 to about 20 carbon atoms and a sulphonic/phosphonic acid or sulfuric/phosphoric acid ester group. Examples of suitable synthetic anionic surfactants include, but are not limited to: C₁₀-C₂₀ linear alkyl benzene sulphonates, C₁₀-C₂₀ linear or branched
20 alkyl sulfates, C₁₀-C₂₀ linear or branched alkylethoxy sulfates having a weight average degree of ethoxylation ranging from 0.1 to 5.0, C₁₀-C₂₀ linear or branched alkyl ester sulfates, C₁₀-C₂₀ linear or branched alkyl sulphonates, C₁₀-C₂₀ linear or branched alkyl ester sulphonates, C₁₀-C₂₀ linear or branched alkyl phosphates, C₁₀-C₂₀ linear or branched alkyl phosphonates, C₁₀-C₂₀ linear or branched alkyl carboxylates, and combinations thereof (including their sodium, potassium, and/or ammonium salts).

Especially preferred for the practice of the present invention are anionic surfactants containing C₁₀-C₂₀ linear alkyl benzene sulphonates (LAS) and C₁₀-C₂₀ linear or branched
25 alkylethoxy sulfates (AES) having a weight average degree of ethoxylation ranging from about 0.1 to about 5, preferably from about 0.5 to about 4, more preferably from about 1 to about 3. In a particularly preferred embodiment of the present invention, the liquid laundry detergent
30 composition comprises both the LAS and AES.

The anionic surfactants can be provided in the liquid laundry detergent compositions of the present invention at levels ranging from about 0.5 wt% to about 15 wt%, more preferably from about 1 wt% to about 12 wt%, and more preferably from about 2 wt% to about 10 wt%. In one

particularly preferred embodiment, the liquid laundry detergent composition contains from about 2 wt% to about 10 wt% of LAS and AES, while the AES has a weight average degree of ethoxylation ranging from 1 to 3, and the weight ratio between LAS and AES ranges from 1:2 to 5:1, preferably from 1:1 to 4:1, more preferably from 1.5:1 to 3:1. Most preferably, the NI-to-AI (i.e., LAS+AES) weight ratio ranges from about 2 to about 5.

Other surfactants useful herein include amphoteric surfactants, zwitterionic surfactants and cationic surfactants. Such surfactants are well known for use in laundry detergents and are typically present at levels from about 0.2 wt%, 0.5 wt% or 1 wt% to about 10 wt%, 20 wt% or 30 wt%.

In a preferred but not necessary embodiment of the present invention, the liquid laundry detergent composition further contains from about 0.5 wt% to about 20 wt% of one or more amphoteric and/or zwitterionic surfactants.

Preferred amphoteric surfactants are selected from the group consisting of amine oxide surfactants, such as, for example, alkyl dimethyl amine oxide or alkyl amido propyl dimethyl amine oxide, more preferably alkyl dimethyl amine oxide and especially coco dimethyl amino oxide. Amine oxide may have a linear or mid-branched alkyl moiety. Typical linear amine oxides are characterized by a formula $R_1-N(R_2)(R_3)-O$, wherein R_1 is a C_{8-18} alkyl, and wherein R_2 and R_3 are independently selected from the group consisting of C_{1-3} alkyls and C_{1-3} hydroxyalkyls, such as methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl and 3-hydroxypropyl. As used herein "mid-branched" means that the amine oxide has one alkyl moiety having n_1 carbon atoms with one alkyl branch on the alkyl moiety having n_2 carbon atoms. The alkyl branch is located on the α carbon from the nitrogen on the alkyl moiety. This type of branching for the amine oxide is also known in the art as an internal amine oxide. The total sum of n_1 and n_2 is from about 10 to about 24 carbon atoms, preferably from about 12 to about 20, and more preferably from about 10 to about 16. The number of carbon atoms for the one alkyl moiety (n_1) should be approximately the same number of carbon atoms as the one alkyl branch (n_2) such that the one alkyl moiety and the one alkyl branch are symmetric. As used herein "symmetric" means that $|n_1 - n_2|$ is less than or equal to 5, preferably 4, most preferably from 0 to 4 carbon atoms in at least about 50 wt%, more preferably at least about 75 wt% to about 100 wt%, of the mid-branched amine oxides for use herein. Particularly preferred amphoteric surfactants are C_{10} - C_{14} alkyl dimethyl amine oxides.

Preferred zwitterionic surfactants are betaine surfactants, such as, for example, alkyl betaines, alkylamidobetaines, amidazoliniumbetaines, sulfobetaines (also referred to as sultaines) as well as phosphobetaines. A particularly preferred betaine is cocoamidopropylbetaine.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are also useful anionic surfactants in the liquid laundry detergent compositions of the present invention, although such soaps are not counted when calculating the NI-to-AI weight ratio in the present invention. Suitable soaps include alkali metal salts (such as the sodium, potassium, ammonium, and alkyl ammonium salts) of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap. However, the liquid laundry detergent compositions of the present invention preferably contain soaps at a relatively low level, e.g., no more than about 3 wt%, more preferably not more than about 2 wt% or 1 wt%, and most preferably said liquid laundry detergent compositions are substantially or essentially free of soaps.

Liquid Laundry Detergent Compositions

The liquid laundry detergent composition of the present invention is suitable for fabric cleaning application, including automatic machine washing or hand-washing of fabrics, or cleaning auxiliaries, such as for example, bleach, rinse aids, additives or pre-treat types.

The liquid laundry detergent composition can be a fully formulated laundry detergent product. Liquid compositions contained in encapsulated and/or unitized dose products are included, as are compositions which comprise two or more separate but jointly dispensable portions. Preferably, the liquid laundry detergent composition contains water as an aqueous carrier, and it can contain either water alone or mixtures of organic solvent(s) with water as carrier(s). Suitable organic solvents are linear or branched lower C₁-C₈ alcohols, diols, glycerols or glycols; lower amine solvents such as C₁-C₄ alkanolamines, and mixtures thereof. Exemplary organic solvents include 1,2-propanediol, ethanol, glycerol, monoethanolamine and triethanolamine. The carriers are typically present at levels in the range of from about 0.1% to about 98%, preferably from about 10% to about 95%, more preferably from about 25% to about 75% by total weight of the liquid laundry detergent composition. In some embodiments, water is from about 85 to about 100 wt% of the carrier. In other embodiments, water is absent and the composition is anhydrous. Highly preferred compositions afforded by the present invention are clear, isotropic liquids.

The liquid laundry detergent composition of the present invention has a viscosity from about 1 to about 2000 centipoise (1-2000 mPa·s), or from about 200 to about 800 centipoises (200-

800 mPa·s). The viscosity can be determined using a Brookfield viscometer, No. 2 spindle, at 60 RPM/s, measured at 25°C.

In addition to the ingredients described hereinabove, the liquid laundry compositions of the present invention may comprise an external structurant, which may be present in an amount ranging from about 0.001% to about 1.0%, preferably from about 0.05% to about 0.5%, more preferably from about 0.1% to about 0.3% by total weight of the composition. A particularly preferred external structurant for the practice of the present invention is hydrogenated castor oil, which is also referred to as trihydroxylstearin and is commercially available under the tradename Thixin®.

In addition to those ingredients described hereinabove, the balance of the liquid laundry detergent composition of the present invention typically contains from about 5 wt% to about 70 wt%, or about 10 wt% to about 60 wt% of adjunct ingredients. Suitable adjunct ingredients for laundry detergent products include: builders, chelating agents, dye transfer inhibiting agents, dispersants, rheology modifiers, enzymes, and enzyme stabilizers, catalytic materials, bleach activators, hydrogen peroxide, sources of hydrogen peroxide, preformed peracids, polymeric dispersing agents, clay soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, photobleaches, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids, solvents, hueing agents, anti-microbial agents, free perfume oils, and/or pigments. The precise nature of these adjunct ingredients and the levels thereof in the liquid laundry detergent composition will depend on factors like the specific type of the composition and the nature of the cleaning operation for which it is to be used.

Methods of Using the Liquid Laundry Detergent Composition

The present invention in one aspect is directed to a method of using the above-described liquid laundry detergent composition for treating fabrics, the method comprising the steps of: (i) providing a liquid laundry detergent composition as described above; (ii) forming a laundry liquor by diluting the liquid laundry detergent composition with water; (iii) washing fabric in the laundry liquor; and (iv) rinsing the fabric in water.

Machine laundry methods may comprise treating soiled fabrics with an aqueous wash solution in a top-loading or front-loading automatic or semi-automatic washing machine having dissolved or dispensed therein an effective amount of a liquid laundry cleaning composition in accord with the invention. An "effective amount" of the liquid laundry detergent composition means from about 20g to about 300g of product dissolved or dispersed in a wash solution of volume

Citric acids	1.39	1.39	1.39	1.39	1.39	1.39	1.39
Sodium Tetraborates	1.40	1.40	1.40	1.40	1.40	1.40	1.40
sodium Cumene Sulfonate (NaCS)	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Di-propylene glycol	1	1	1	1	1	1	1
NaOH	pH Adjusted to 8						
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.
NI-to-AI Weight Ratio							
0.5 0.8 1 1.2 1.5 2 5							

¹ An ethoxylated polyethyleneimine with an empirical formula of PEI₆₀₀EO₂₀.

² A C₁₂-C₁₅ alkyl ethoxylated alcohol with a weight average degree of ethoxylation of 7.

³ A C₁₁-C₁₂ linear alkylbenzene sulphonate.

5 ⁴ A C₁₂₋₁₄ alkyl ethoxylated sulfate with a weight average degree of ethoxylation of about 3.

Each of the above-described exemplary liquid laundry detergent composition is used to treat fabrics, and then its soil/clay removal performance is measured as follows:

- 10 i) Prepare 3 fabric pieces, each of which has a size of about 5cm×5cm and contains a 50%/50% polyester-cotton blend;
- ii) Measure the L/a/b value of each fabric piece using a Spectro-Guide 45/0 Gloss 6801 color spectrophotometer (commercially available from BYK-Gardner GmbH in Geretsried, Germany), and calculate an average L/a/b value for all 3 pieces of fabric before wash;
- 15 iii) Dissolve about 1.6 grams of the sample liquid laundry detergent composition in 800 ml reverse osmosis (RO) water that has a water hardness level of about 200 gpg (with a Ca²⁺-to-Mg²⁺ weight ratio of about 4:1), to form a wash liquor with a detergent dosage of about 2000 ppm;
- 20 iv) Add about 1 gram of Arizona Test Dust (ISO12103-1, A2 fine test dust with a nominal particle size of 0-3 micron, commercially available from Powder Technology Inc) into the 800-ml wash liquor from step (iii) to form an even mixture;
- v) Add the 3 fabric pieces into the mixture from step (iv) and wash in Tergotometer (Copley Scientific) for about 20 minutes;
- 25 vi) Rinse the washed fabric pieces with RO water for about 1 minute and then dry them out;
- vii) Measure the L/a/b value of each dried fabric pieces using the same Spectro-Guide 45/0 Gloss 6801 color spectrophotometer and calculate an average L/a/b value for all 3 pieces of fabric after wash; and
- 30 viii) Calculate ΔE between the average L/a/b values before and after wash as an indicator of the clay/soil removal performance of the sample liquid laundry detergent

composition. The higher the ΔE value, the more clay/soil is redeposited back to the fabric during the wash, and hence the poorer the clay/soil removal performance of the sample liquid laundry detergent composition.

FIG. 1 plots the respective ΔE values of the above-described 7 exemplary liquid detergent compositions as a function of the NI-to-AI weight ratios in these compositions. It is clear from FIG. 1 that when the NI-to-AI weight ratio is at about 1.5 or below, the clay/soil removal performance of the liquid laundry detergent compositions is relatively poor (as indicated by the higher ΔE values of above 12.0). However, when the NI-to-AI weight ratio is above 1.5, the clay/soil removal performance of the liquid laundry detergent compositions significantly improves (as indicated by the lower ΔE values at the NI-to-AI ratio of 2 and 5). The best clay/soil removal performance is observed when the NI-to-AI ratio of the liquid laundry detergent composition is about 2.

Example 2: Exemplary Liquid Laundry Detergent Compositions

Liquid laundry detergent compositions 1-6 are made by mixing together the ingredients listed in the proportions shown:

TABLE 2

Ingredients (wt%)	1	2	3	4	5	6
Alkoxylated Polyalkyleneimine I ¹	0.1-5	0.1	0.4	0.5	1	2
Alkoxylated Polyalkyleneimine II ²	0-2	--	0.1	1	--	0.5
Neodol®25-7 ³ or Neodol®24-7 ⁴	5-45	8	20	15	11	35
LAS ⁵	0-15	2	3	4	3.5	4
AE3S ⁶	0-15	1	8	1.5	2	2
Fatty acids	0-2	1.5	0	0.5	1.2	1
Sodium Tetraborate	0-2	0	1	1.5	0.8	1.3
Citric acids	0-2	0.5	1.5	0	0.2	0.8
Hydrogenated castor oil	0-0.2	0.1	0.2	0.2	0.1	0.2
Di-propylene glycol	0-1	0	0.5	1	0.2	0
Sodium formate	0-2	1.5	0.6	0.8	0.7	0.5
NaCS	0-0.5	0.25	0.5	0.2	0.3	0.5
NaOH	pH adjusted to 7.8-8.9					
Misc. (enzymes, dyes, perfumes, brighteners, chelants, etc.)	0.5-2	0.5-2	0.5-2	0.5-2	0.5-2	0.5-2
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.

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¹ An ethoxylated polyethyleneimine with an empirical formula of PEI₆₀₀EO₂₀.

² An ethoxylated polyethyleneimine with an empirical formula of PEI₆₀₀EO₂₄PO₁₆.

³ A C₁₂-C₁₅ alkyl ethoxylated alcohol with a weight average degree of ethoxylation of 7.

⁴ A C₁₂-C₁₄ alkyl ethoxylated alcohol with a weight average degree of ethoxylation of 7.

⁵ A C₁₁-C₁₂ linear alkylbenzene sulphonate.

⁶ A C₁₂₋₁₄ alkyl ethoxylated sulfate with a weight average degree of ethoxylation of about 3.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm.”

Every document cited herein, including any cross referenced or related patent or application and any patent application or patent to which this application claims priority or benefit thereof, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

CLAIMS

What is claimed is:

1. A liquid laundry detergent composition comprising:

- a) from 0.1 wt% to 5 wt% of an alkoxyated polyethyleneimine having a polyalkyleneimine core with one or more alkoxy side chains bonded to at least one nitrogen atom in the polyalkyleneimine core; and
- b) from 6 wt% to 50 wt% of one or more nonionic (NI) surfactants and one or more anionic (AI) surfactants,

wherein the NI-to-AI weight ratio ranges from 1.7 to 20.

2. The liquid laundry detergent composition of claim 1, wherein the NI-to-AI weight ratio ranges from 1.8 to 10, preferably from 2 to 5.

3. The liquid laundry detergent composition of claim 1 or 2, wherein said one or more NI surfactants are selected from the group consisting of alkyl alkoxyated alcohols, alkyl alkoxyated phenols, alkyl polysaccharides, polyhydroxy fatty acid amides, and combinations thereof, and preferably said one or more NI surfactants comprise a C₈-C₁₈ alkyl ethoxyated alcohol having a weight average degree of ethoxylation ranging from 1 to 20, preferably from 5 to 15, more preferably from 7 to 10.

4. The liquid laundry detergent composition according to any one of the preceding claims, wherein said one or more NI surfactants are present in said liquid laundry detergent composition at an amount ranging from 5 wt% to 45 wt%, preferably from 8 wt% to 40 wt%, more preferably from 9 wt% to 30 wt%.

5. The liquid laundry detergent composition according to any one of the preceding claims, wherein said one or more AI surfactants are selected from the group consisting of C₁₀-C₂₀ linear alkyl benzene sulphonates, C₁₀-C₂₀ linear or branched alkyl sulfates, C₁₀-C₂₀ linear or branched alkylethoxy sulfates having a weight average degree of ethoxylation ranging from 0.1 to 5.0, C₁₀-C₂₀ linear or branched alkyl ester sulfates, C₁₀-C₂₀ linear or branched alkyl sulphonates, C₁₀-C₂₀ linear or branched alkyl ester sulphonates, C₁₀-C₂₀ linear or branched alkyl phosphates, C₁₀-C₂₀ linear or branched alkyl phosphonates, C₁₀-C₂₀ linear or branched alkyl carboxylates, and

combinations thereof; wherein said one or more AI surfactants preferably comprise a C₁₀-C₂₀ linear alkyl benzene sulphonate and a C₁₀-C₂₀ linear or branched alkylethoxy sulfate having a weight average degree of ethoxylation ranging from 0.1 to 5, preferably from 0.5 to 4, more preferably from 1 to 3.

6. The liquid laundry detergent composition according to any one of the preceding claims, wherein said one or more AI surfactants are present in said liquid laundry detergent composition at an amount ranging from 0.5 wt% to 15 wt%, preferably from 1 wt% to 12 wt%, more preferably from 2 wt% to 10 wt%.

7. The liquid laundry detergent composition according to any one of the preceding claims, comprising from 0.2 wt% to 3 wt%, preferably from 0.5 wt% to 1 wt%, of said alkoxyated polyethyleneimine.

8. The liquid laundry detergent composition according to any one of the preceding claims, wherein said alkoxyated polyethyleneimine has an empirical formula of (PEI)*a*-(EO)*b*-(PO)*c*-R₁, wherein *a* is the weight average molecular weight of the polyalkyleneimine core (MWPEI) of the alkoxyated polyalkyleneimine and is in the range of from 100 to 100,000 Daltons, preferably from 200 to 20,000 Daltons, more preferably from 500 to 2,000 Daltons; wherein *b* is the weight average degree of ethoxylation in said one or more side chains of the alkoxyated polyalkyleneimine and is in the range of from 5 to 40, preferably from 10 to 30, more preferably from 15 to 25; wherein *c* is the weight average degree of propoxylation in said one or more side chains of the alkoxyated polyalkyleneimine which ranges from 0 to 50, preferably from 0 to 30, more preferably from 0 to 20; and wherein R₁ is independently selected from the group consisting of hydrogen, C₁-C₄ alkyl, and combinations thereof.

9. A liquid laundry detergent composition comprising:

- 1) from 0.5 wt% to 1 wt% of an alkoxyated polyethyleneimine an empirical formula of (PEI)*a*-(EO)*b*-(PO)*c*-R₁, wherein *a* is the weight average molecular weight of the polyalkyleneimine core (MWPEI) of the alkoxyated polyalkyleneimine and is in the range of from 500 to 2,000 Daltons; wherein *b* is the weight average degree of ethoxylation in said one or more side chains of the alkoxyated polyalkyleneimine and is in the range of

- from 15 to 25; wherein c is the weight average degree of propoxylation in said one or more side chains of the alkoxyated polyalkyleneimine and is 0; and wherein R_1 is hydrogen;
- 2) from 9 wt% to 30 wt% of a nonionic (NI) surfactant that is a C_8 - C_{18} alkyl ethoxylated alcohol having a weight average degree of ethoxylation ranging from 7 to 10; and
 - 3) from 2 wt% to 10 wt% of a C_{10} - C_{20} linear alkyl benzene sulphonate (LAS) and a C_{10} - C_{20} linear or branched alkylethoxy sulfate (AES) having a weight average degree of ethoxylation ranging from 1 to 3,
- wherein the NI-to-AI weight ratio ranges from 2 to 5.

10. The liquid laundry detergent composition of claim 9, wherein the LAS-to-AES weight ratio ranges from 1:2 to 5:1, preferably from 1:1 to 4:1, more preferably from 1.5:1 to 3:1.

11. Use of the liquid laundry detergent composition according to any one of the preceding claims for treating fabrics.

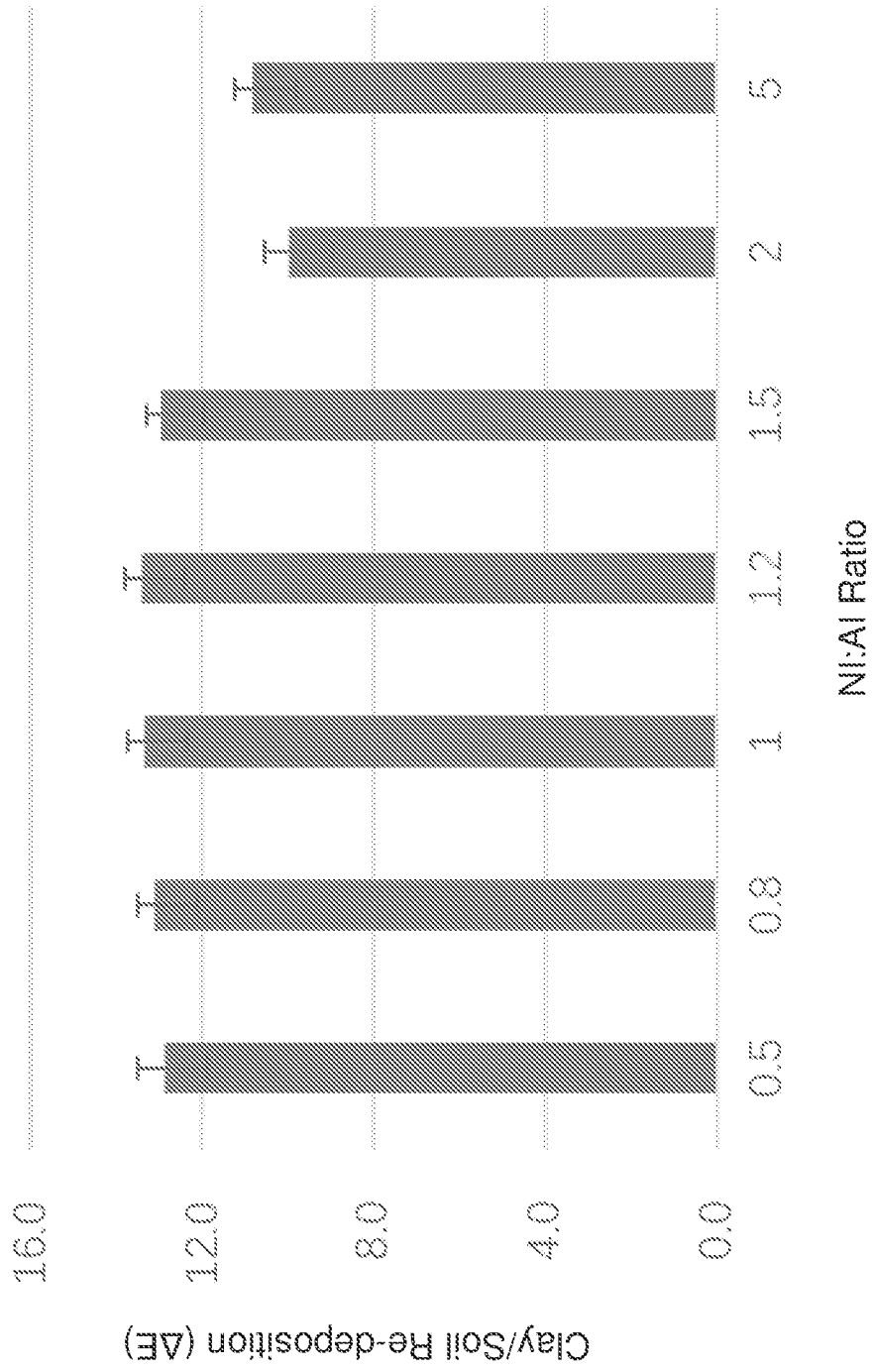


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/092765

A. CLASSIFICATION OF SUBJECT MATTER

C11D 3/37(2006.01)i; C11D 1/83(2006.01)i

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)

CNTXT,USTXT,WOTXT,EPTXT,CNABS,CPRSABS,MOABS,HKABS,TWABS,DWPI,SIPOABS,CPEA,JPABS,CNKI:
polyethyleneimine, PEI, EO, PO, nonionic, anionic, liquid, laundry, linear alkyl benzene sulphonate, LAS,
alkylethoxy sulfate, AES**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006113315 A2 (THE PROCTER & GAMBLE COMPANY ET AL.) 26 October 2006 (2006-10-26) see description, pages 10-11, 15, Example 2-5; claims 1-4	1-11
A	WO 2008007320 A2 (THE PROCTER & GAMBLE COMPANY ET AL.) 17 January 2008 (2008-01-17) see the whole document	1-11
A	WO 2017011230 A1 (THE PROCTER & GAMBLE COMPANY) 19 January 2017 (2017-01-19) see the whole document	1-11

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

22 March 2019

Date of mailing of the international search report

02 April 2019

Name and mailing address of the ISA/CN

National Intellectual Property Administration, PRC
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088
China

Authorized officer

LI,Wei

Facsimile No. (86-10)62019451

Telephone No. 86-(010)-62412172

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2018/092765

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
WO	2006113315	A2	26 October 2006	EP	1869151	A2	26 December 2007
				WO	2006113315	A3	18 May 2007
				AR	053054	A1	18 April 2007
				CA	2602142	A1	26 October 2006
				US	2011036374	A1	17 February 2011
				US	7928050	B2	19 April 2011
				US	2011214696	A1	08 September 2011
				US	2010305920	A1	02 December 2010
				MX	2007012840	A	09 November 2007
				US	2011152162	A1	23 June 2011
				BR	PI0608192	A2	01 December 2009
				JP	2008537974	A	02 October 2008
				US	2006234898	A1	19 October 2006
				WO	2008007320	A2	17 January 2008
AR	061857	A1	24 September 2008				
RU	2432389	C2	27 October 2011				
JP	5474537	B2	16 April 2014				
WO	2008007320	A3	13 March 2008				
EP	1876227	A1	09 January 2008				
CN	101490231	B	07 September 2011				
US	2009105109	A1	23 April 2009				
CN	101490231	A	22 July 2009				
JP	2009542837	A	03 December 2009				
ZA	200900059	B	31 March 2010				
DE	602006020853	D1	05 May 2011				
ZA	200900059	A	31 March 2010				
BR	PI0713558	A2	13 March 2012				
MX	2009000143	A	23 January 2009				
CA	2655347	A1	17 January 2008				
EP	1876227	B1	23 March 2011				
MX	288854	B	28 July 2011				
RU	2008152144	A	20 August 2010				
WO	2017011230	A1	19 January 2017	EP	3118292	B1	14 February 2018
				ES	2666583	T3	07 May 2018
				EP	3118292	A1	18 January 2017
				US	2017015942	A1	19 January 2017
				JP	2018522119	A	09 August 2018