

(19)



(11)

EP 3 754 010 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

23.12.2020 Bulletin 2020/52

(51) Int Cl.:

C11D 11/00 (2006.01)

C11D 1/40 (2006.01)

C11D 17/06 (2006.01)

C11D 3/39 (2006.01)

(21) Application number: **19180707.2**

(22) Date of filing: **17.06.2019**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

(71) Applicant: **The Procter & Gamble Company**
Cincinnati, OH 45202 (US)

(72) Inventors:

- **BROOKER, Alan Thomas**
Newcastle upon Tyne, NE12 9TS (GB)
- **FULLER, Linsey Sarah**
Newcastle upon Tyne, NE12 9TS (GB)
- **STERRY, Robert William John**
Newcastle upon Tyne, NE12 9TS (GB)

(74) Representative: **P&G Patent Belgium UK**

N.V. Procter & Gamble Services Company S.A.
Temselaan 100
1853 Strombeek-Bever (BE)

(54) **A SOLID FREE-FLOWING PARTICULATE LAUNDRY DETERGENT COMPOSITION
COMPRISES A DETERSIVE SURFACTANT AND A LINEAR POLYAMINE SALT**

(57) A solid free-flowing particulate laundry detergent composition comprising a deterative surfactant and a linear polyamine salt.

EP 3 754 010 A1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a solid free-flowing particulate laundry detergent composition comprises a deterative surfactant and a linear polyamine salt. The composition of the present invention has good anti-malodour performance.

BACKGROUND OF THE INVENTION

[0002] Manufacturers of solid free-flowing particulate laundry detergent compositions continue to seek improved freshness profiles, especially anti-malodour performance. The present invention addresses this need and provides a solid free-flowing particulate laundry detergent composition having a good freshness profile, and especially a good anti-malodour performance. The solid free-flowing particulate laundry detergent composition of the present invention comprises a linear polyamine in the form of a salt. The salt form of the linear polyamine provides improved anti-malodour performance compared to the acid form when incorporated into a solid free-flowing particulate laundry detergent composition. Without wishing to be bound by theory, the inventors believe that the active species in the wash solution is the free amine of the linear polyamine salt. However, it is essential for the present invention that the linear polyamine is in a salt form when comprised by the composition of the invention. The inventors believe that upon contact with water, the linear polyamine salt undergoes an exothermic reaction. This leads to the formation of the free amine active form in the wash liquor in a localised area of the wash liquor having an elevated temperature due to the heat generated by the exothermic reaction. The elevated temperature aids the dispersion of the remaining linear polyamine salt.

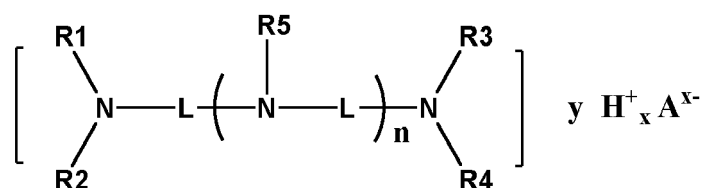
[0003] The composition of the present invention provides a good anti-malodour performance, especially under conditions of reduced rinsing, for example during a single rinse laundering cycle, or during multiple low water rinsing cycles.

SUMMARY OF THE INVENTION

[0004] The present invention provides a solid free-flowing particulate laundry detergent composition comprises a deterative surfactant and a linear polyamine salt.

DETAILED DESCRIPTION OF THE INVENTION

[0005] Solid free-flowing particulate laundry detergent composition: The solid free-flowing particulate laundry detergent composition comprises a deterative surfactant and a linear polyamine salt, wherein the linear polyamine salt has the following general formula:



wherein:

each L is independently $-(\text{C}_m\text{H}_{2m})-$, wherein the index m is an integer from 2 to 6;

n is an integer from 1 to 10;

each of R1 to R5 is independently selected from H and C_1 - C_4 alkyl;

$\text{H}^+_x \text{A}^{x-}$ is an acid to protonate at least one N atoms of the linear polyamine, x is an integer of 1 or above, A^{x-} is a anionic counter ion derived from an acid; and

y is any number not bigger than $n+2$,

wherein at least one nitrogen atom of linear polyamine salt is protonated.

[0006] The composition preferably comprises from 0.01wt% to 3.0wt%, or from 0.05wt% to 2.0wt% linear polyamine salt.

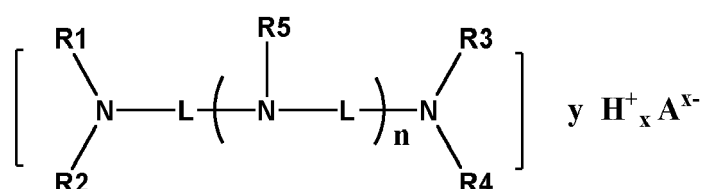
[0007] Typically, the solid free-flowing particulate laundry detergent composition is a fully formulated laundry detergent composition, not a portion thereof such as a spray-dried, extruded or agglomerate particle that only forms part of the laundry detergent composition. Typically, the solid composition comprises a plurality of chemically different particles,

such as spray-dried base detergent particles and/or agglomerated base detergent particles and/or extruded base detergent particles, in combination with one or more, typically two or more, or five or more, or even ten or more particles selected from: surfactant particles, including surfactant agglomerates, surfactant extrudates, surfactant needles, surfactant noodles, surfactant flakes; phosphate particles; zeolite particles; silicate salt particles, especially sodium silicate particles; carbonate salt particles, especially sodium carbonate particles; polymer particles such as carboxylate polymer particles, cellulosic polymer particles, starch particles, polyester particles, polyamine particles, terephthalate polymer particles, polyethylene glycol particles; aesthetic particles such as coloured noodles, needles, lamellae particles and ring particles; enzyme particles such as protease granulates, amylase granulates, lipase granulates, cellulase granulates, mannanase granulates, pectate lyase granulates, xyloglucanase granulates, bleaching enzyme granulates and co-granulates of any of these enzymes, preferably these enzyme granulates comprise sodium sulphate; bleach particles, such as percarbonate particles, especially coated percarbonate particles, such as percarbonate coated with carbonate salt, sulphate salt, silicate salt, borosilicate salt, or any combination thereof, perborate particles, bleach activator particles such as tetra acetyl ethylene diamine particles and/or alkyl oxybenzene sulphonate particles, bleach catalyst particles such as transition metal catalyst particles, and/or isoquinolinium bleach catalyst particles, pre-formed peracid particles, especially coated pre-formed peracid particles; filler particles such as sulphate salt particles and chloride particles; clay particles such as montmorillonite particles and particles of clay and silicone; flocculant particles such as polyethylene oxide particles; wax particles such as wax agglomerates; silicone particles, brightener particles; dye transfer inhibition particles; dye fixative particles; perfume particles such as perfume microcapsules and starch encapsulated perfume accord particles, or pro-perfume particles such as Schiff base reaction product particles; hueing dye particles; chelant particles such as chelant agglomerates; and any combination thereof.

[0008] Suitable laundry detergent compositions comprise a detergent ingredient selected from: deterative surfactant, such as anionic deterative surfactants, non-ionic deterative surfactants, cationic deterative surfactants, zwitterionic deterative surfactants and amphoteric deterative surfactants; polymers, such as carboxylate polymers, soil release polymer, anti-redeposition polymers, cellulosic polymers and care polymers; bleach, such as sources of hydrogen peroxide, bleach activators, bleach catalysts and pre-formed peracids; photobleach, such as such as zinc and/or aluminium sulphonated phthalocyanine; enzymes, such as proteases, amylases, cellulases, lipases; zeolite builder; phosphate builder; co-builders, such as citric acid and citrate; carbonate, such as sodium carbonate and sodium bicarbonate; sulphate salt, such as sodium sulphate; silicate salt such as sodium silicate; chloride salt, such as sodium chloride; brighteners; chelants; hueing agents; dye transfer inhibitors; dye fixative agents; perfume; silicone; fabric softening agents, such as clay; flocculants, such as polyethyleneoxide; suds suppressors; and any combination thereof.

[0009] Suitable laundry detergent compositions may have a low buffering capacity. Such laundry detergent compositions typically have a reserve alkalinity to pH 9.5 of less than 5.0gNaOH/100g. These low buffered laundry detergent compositions typically comprise low levels of carbonate salt.

[0010] Linear polyamine salt: The linear polyamine salt has the following general formula:



wherein:

each L is independently $-(C_mH_{2m})-$, wherein the index m is an integer from 2 to 6, or preferably from 2 to 4, or preferably from 2 to 3;

n is an integer from 1 to 10, or preferably from 1 to 5, or preferably from 1 to 3, most preferably 1;

each of R1 to R5 is independently selected from H and C_1 - C_4 alkyl;

$H^+_x A^{x-}$ is an acid to protonate at least one N atoms of the linear polyamine, x is an integer of 1 or above, A^{x-} is an anionic counter ion derived from an acid; and

y is any number not bigger than n+2,

wherein at least one nitrogen atom of linear polyamine salt is protonated

[0011] Suitable acids include inorganic acids and organic acids. Polyacids are also suitable, for example: HCl, H_2SO_4 , citric acid, fatty acid. A suitable acid may also derived from anionic surfactant, such as the acid form of LAS, AES, MCAS and AEC.

y may be an integer, such as 1, 2 or 3, y may also be a fraction, such as 1/2 or 1/3.

[0012] The linear polyamine salt is a chlorine salt of a linear polyamine selected from: ethylenediamine (EDA); 1,2-

or 1,3-propylenediamine (PDA); butylenediamine (BDA); pentamethylenediamine (PMDA); hexamethylenediamine (HMDA); diethylenetriamine (DETA); dipropylenetriamine (DPTA); triethylenetetraamine (TETA); tripropylenetetraamine (TPTA); tetraethylenepentaamine (TEPA); tetrapropylenepentaamine (TPPA); pentaethylenehexaamine (PEHA); pentapropylenehexaamine (PPHA); hexaethyleneheptaamine (HEHA); hexapropyleneheptaamine (HPHA); N,N'-Bis(3-aminopropyl)ethylenediamine; and any mixture thereof.

[0013] Preferably, the linear polyamine salt is a chlorine salt of a linear polyamine selected from: diethylenetriamine (DETA); triethylenetetraamine (TETA); and any mixture thereof.

[0014] Deterative Surfactant: Suitable deterative surfactants include anionic deterative surfactants, non-ionic deterative surfactant, cationic deterative surfactants, zwitterionic deterative surfactants and amphoteric deterative surfactants. Suitable deterative surfactants may be linear or branched, substituted or un-substituted, and may be derived from petrochemical material or biomaterial.

[0015] Anionic deterative surfactant: Suitable anionic deterative surfactants include sulphonate and sulphate deterative surfactants.

[0016] Suitable sulphonate deterative surfactants include methyl ester sulphonates, alpha olefin sulphonates, alkyl benzene sulphonates, especially alkyl benzene sulphonates, preferably C₁₀₋₁₃ alkyl benzene sulphonate. Suitable alkyl benzene sulphonate (LAS) is obtainable, preferably obtained, by sulphonating commercially available linear alkyl benzene (LAB); suitable LAB includes low 2-phenyl LAB, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®.

[0017] Suitable sulphate deterative surfactants include alkyl sulphate, preferably C₈₋₁₈ alkyl sulphate, or predominantly C₁₂ alkyl sulphate.

[0018] A preferred sulphate deterative surfactant is alkyl alkoxyated sulphate, preferably alkyl ethoxyated sulphate, preferably a C₈₋₁₈ alkyl alkoxyated sulphate, preferably a C₈₋₁₈ alkyl ethoxyated sulphate, preferably the alkyl alkoxyated sulphate has an average degree of alkoxylation of from 0.5 to 20, preferably from 0.5 to 10, preferably the alkyl alkoxyated sulphate is a C₈₋₁₈ alkyl ethoxyated sulphate having an average degree of ethoxylation of from 0.5 to 10, preferably from 0.5 to 5, more preferably from 0.5 to 3 and most preferably from 0.5 to 1.5.

[0019] The alkyl sulphate, alkyl alkoxyated sulphate and alkyl benzene sulphonates may be linear or branched, substituted or un-substituted, and may be derived from petrochemical material or biomaterial.

[0020] Other suitable anionic deterative surfactants include alkyl ether carboxylates.

[0021] Suitable anionic deterative surfactants may be in salt form, suitable counter-ions include sodium, calcium, magnesium, amino alcohols, and any combination thereof. A preferred counterion is sodium.

[0022] Non-ionic deterative surfactant: Suitable non-ionic deterative surfactants are selected from the group consisting of: C₈-C₁₈ alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C₆-C₁₂ alkyl phenol alkoxyates wherein preferably the alkoxyate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C₁₂-C₁₈ alcohol and C₆-C₁₂ alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; alkylpolysaccharides, preferably alkylpolyglycosides; methyl ester ethoxylates; polyhydroxy fatty acid amides; ether capped poly(oxyalkylated) alcohol surfactants; and mixtures thereof.

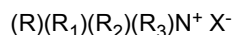
[0023] Suitable non-ionic deterative surfactants are alkylpolyglucoside and/or an alkyl alkoxyated alcohol.

[0024] Suitable non-ionic deterative surfactants include alkyl alkoxyated alcohols, preferably C₈₋₁₈ alkyl alkoxyated alcohol, preferably a C₈₋₁₈ alkyl ethoxyated alcohol, preferably the alkyl alkoxyated alcohol has an average degree of alkoxylation of from 1 to 50, preferably from 1 to 30, or from 1 to 20, or from 1 to 10, preferably the alkyl alkoxyated alcohol is a C₈₋₁₈ alkyl ethoxyated alcohol having an average degree of ethoxylation of from 1 to 10, preferably from 1 to 7, more preferably from 1 to 5 and most preferably from 3 to 7. The alkyl alkoxyated alcohol can be linear or branched, and substituted or un-substituted.

[0025] Suitable nonionic deterative surfactants include secondary alcohol-based deterative surfactants.

[0026] Cationic deterative surfactant: Suitable cationic deterative surfactants include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof.

[0027] Preferred cationic deterative surfactants are quaternary ammonium compounds having the general formula:



wherein, R is a linear or branched, substituted or unsubstituted C₆₋₁₈ alkyl or alkenyl moiety, R₁ and R₂ are independently selected from methyl or ethyl moieties, R₃ is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, preferred anions include: halides, preferably chloride; sulphate; and sulphonate.

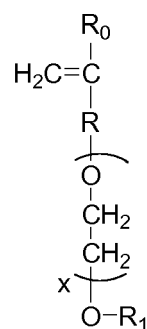
[0028] Zwitterionic deterative surfactant: Suitable zwitterionic deterative surfactants include amine oxides and/or betaines.

[0029] Polymer: Suitable polymers include carboxylate polymers, soil release polymers, anti-redeposition polymers, cellulosic polymers, care polymers and any combination thereof.

[0030] Carboxylate polymer: The composition may comprise a carboxylate polymer, such as a maleate/acrylate random copolymer or polyacrylate homopolymer. Suitable carboxylate polymers include: polyacrylate homopolymers having a molecular weight of from 4,000 Da to 9,000 Da; maleate/acrylate random copolymers having a molecular weight of from 50,000 Da to 100,000 Da, or from 60,000 Da to 80,000 Da.

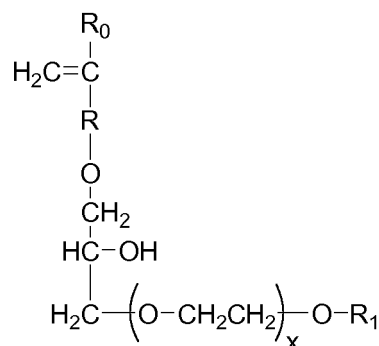
[0031] Another suitable carboxylate polymer is a co-polymer that comprises: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; and (iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

formula (I):



wherein in formula (I), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5 provided X represents a number 1-5 when R is a single bond, and R_1 is a hydrogen atom or C_1 to C_{20} organic group;

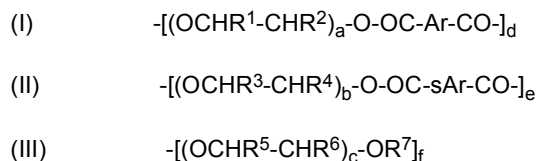
formula (II)



wherein in formula (II), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5, and R_1 is a hydrogen atom or C_1 to C_{20} organic group.

It may be preferred that the polymer has a weight average molecular weight of at least 50kDa, or even at least 70kDa.

[0032] Soil release polymer: The composition may comprise a soil release polymer. A suitable soil release polymer has a structure as defined by one of the following structures (I), (II) or (III):



wherein:

a, b and c are from 1 to 200;

d, e and f are from 1 to 50;

Ar is a 1,4-substituted phenylene;

sAr is 1,3-substituted phenylene substituted in position 5 with SO₃ Me;

Me is Li, K, Mg/2, Ca/2, Al/3, ammonium, mono-, di-, tri-, or tetraalkylammonium wherein the alkyl groups are C₁-C₁₈ alkyl or C₂-C₁₀ hydroxyalkyl, or mixtures thereof;

R¹, R², R³, R⁴, R⁵ and R⁶ are independently selected from H or C₁-C₁₈n- or iso-alkyl; and

R⁷ is a linear or branched C₁-C₁₈ alkyl, or a linear or branched C₂-C₃₀ alkenyl, or a cycloalkyl group with 5 to 9 carbon atoms, or a C₈-C₃₀ aryl group, or a C₆-C₃₀ arylalkyl group. Suitable soil release polymers are sold by Clariant under the TexCare® series of polymers, e.g. TexCare® SRN240 and TexCare® SRA300. Other suitable soil release polymers are sold by Solvay under the Repel-o-Tex® series of polymers, e.g. Repel-o-Tex® SF2 and Repel-o-Tex® Crystal.

[0033] Anti-redeposition polymer: Suitable anti-redeposition polymers include polyethylene glycol polymers and/or polyethyleneimine polymers.

[0034] Suitable polyethylene glycol polymers include random graft co-polymers comprising: (i) hydrophilic backbone comprising polyethylene glycol; and (ii) hydrophobic side chain(s) selected from the group consisting of: C₄-C₂₅ alkyl group, polypropylene, polybutylene, vinyl ester of a saturated C₁-C₆ mono-carboxylic acid, C₁-C₆ alkyl ester of acrylic or methacrylic acid, and mixtures thereof. Suitable polyethylene glycol polymers have a polyethylene glycol backbone with random grafted polyvinyl acetate side chains. The average molecular weight of the polyethylene glycol backbone can be in the range of from 2,000 Da to 20,000 Da, or from 4,000 Da to 8,000 Da. The molecular weight ratio of the polyethylene glycol backbone to the polyvinyl acetate side chains can be in the range of from 1:1 to 1:5, or from 1: 1.2 to 1:2. The average number of graft sites per ethylene oxide unit can be less than 0.02, or less than 0.016, the average number of graft sites per ethylene oxide unit can be in the range of from 0.010 to 0.018, or the average number of graft sites per ethylene oxide unit can be less than 0.010, or in the range of from 0.004 to 0.008.

[0035] Suitable polyethylene glycol polymers are described in WO08/007320.

[0036] A suitable polyethylene glycol polymer is Sokalan HP22.

[0037] Cellulosic polymer: Suitable cellulosic polymers are selected from alkyl cellulose, alkyl alkoxyalkyl cellulose, carboxyalkyl cellulose, alkyl carboxyalkyl cellulose, sulphoalkyl cellulose, more preferably selected from carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, methyl carboxymethyl cellulose, and mixures thereof.

[0038] Suitable carboxymethyl celluloses have a degree of carboxymethyl substitution from 0.5 to 0.9 and a molecular weight from 100,000 Da to 300,000 Da.

Suitable carboxymethyl celluloses have a degree of substitution greater than 0.65 and a degree of blockiness greater than 0.45, e.g. as described in WO09/154933.

[0039] Care polymers: Suitable care polymers include cellulosic polymers that are cationically modified or hydrophobically modified. Such modified cellulosic polymers can provide anti-abrasion benefits and dye lock benefits to fabric during the laundering cycle. Suitable cellulosic polymers include cationically modified hydroxyethyl cellulose.

[0040] Other suitable care polymers include dye lock polymers, for example the condensation oligomer produced by the condensation of imidazole and epichlorhydrin, preferably in ratio of 1:4:1. A suitable commercially available dye lock polymer is Polyquart® FDI (Cognis).

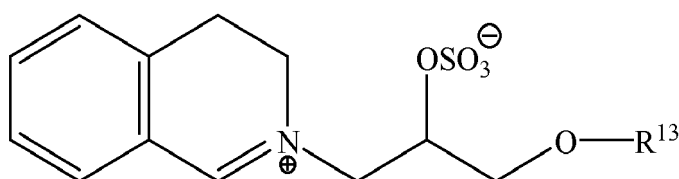
[0041] Other suitable care polymers include amino-silicone, which can provide fabric feel benefits and fabric shape retention benefits.

[0042] Bleach: Suitable bleach includes sources of hydrogen peroxide, bleach activators, bleach catalysts, pre-formed peracids and any combination thereof. A particularly suitable bleach includes a combination of a source of hydrogen peroxide with a bleach activator and/or a bleach catalyst.

[0043] Source of hydrogen peroxide: Suitable sources of hydrogen peroxide include sodium perborate and/or sodium percarbonate.

[0044] Bleach activator: Suitable bleach activators include tetra acetyl ethylene diamine and/or alkyl oxybenzene sulphonate.

[0045] Bleach catalyst: The composition may comprise a bleach catalyst. Suitable bleach catalysts include oxaziridinium bleach catalysts, transition metal bleach catalysts, especially manganese and iron bleach catalysts. A suitable bleach catalyst has a structure corresponding to general formula below:



wherein R¹³ is selected from the group consisting of 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl, 2-pentylnonyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, isodecyl, iso-tridecyl and iso-pentadecyl.

[0046] Pre-formed peracid: Suitable pre-form peracids include phthalimido-peroxycaproic acid.

[0047] Enzymes: Suitable enzymes include lipases, proteases, cellulases, amylases and any combination thereof.

[0048] Protease: Suitable proteases include metalloproteases and/or serine proteases. Examples of suitable neutral or alkaline proteases include: subtilisins (EC 3.4.21.62); trypsin-type or chymotrypsin-type proteases; and metalloproteases. The suitable proteases include chemically or genetically modified mutants of the aforementioned suitable proteases.

[0049] Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzyme®, Kannase®, Liquezyme®, Liquezyme Ultra®, Savinase Ultra®, Ovozyme®, Neutrase®, Everlase® and Esperase® by Novozymes A/S (Denmark), those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Preferenz P® series of proteases including Preferenz® P280, Preferenz® P281, Preferenz® P2018-C, Preferenz® P2081-WE, Preferenz® P2082-EE and Preferenz® P2083-A/J, Properase®, Purafect®, Purafect Prime®, Purafect Ox®, FN3®, FN4®, Excellase® and Purafect OXP® by DuPont, those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes, those available from Henkel/ Kemira, namely BLAP (sequence shown in Figure 29 of US 5,352,604 with the following mutations S99D + S101 R + S103A + V104I + G159S, hereinafter referred to as BLAP), BLAP R (BLAP with S3T + V4I + V199M + V205I + L217D), BLAP X (BLAP with S3T + V4I + V205I) and BLAP F49 (BLAP with S3T + V4I + A194P + V199M + V205I + L217D) - all from Henkel/Kemira; and KAP (Bacillus alkalophilus subtilisin with mutations A230V + S256G + S259N) from Kao.

[0050] A suitable protease is described in WO11/140316 and WO11/072117.

[0051] Amylase: Suitable amylases are derived from AA560 alpha amylase endogenous to Bacillus sp. DSM 12649, preferably having the following mutations: R118K, D183*, G184*, N195F, R320K, and/or R458K. Suitable commercially available amylases include Stainzyme®, Stainzyme® Plus, Natalase, Termamyl®, Termamyl® Ultra, Liquezyme® SZ, Duramyl®, Everest® (all Novozymes) and Spezyme® AA, Preferenz S® series of amylases, Purastar® and Purastar® Ox Am, Optimize® HT Plus (all Du Pont).

A suitable amylase is described in WO06/002643.

[0052] Cellulase: Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are also suitable. Suitable cellulases include cellulases from the genera *Bacillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, e.g., the fungal cellulases produced from *Humicola insolens*, *Myceliophthora thermophila* and *Fusarium oxysporum*.

[0053] Commercially available cellulases include Celluzyme®, Carezyme®, and Carezyme® Premium, Celluclean® and Whitezyme® (Novozymes A/S), Revitalenz® series of enzymes (Du Pont), and Biotouch® series of enzymes (AB Enzymes). Suitable commercially available cellulases include Carezyme® Premium, Celluclean® Classic. Suitable cellulases are described in WO07/144857 and WO10/056652.

[0054] Lipase: Suitable lipases include those of bacterial, fungal or synthetic origin, and variants thereof. Chemically modified or protein engineered mutants are also suitable. Examples of suitable lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g., from *H. lanuginosa* (*T. lanuginosus*).

[0055] The lipase may be a "first cycle lipase", e.g. such as those described in WO06/090335 and WO13/116261. In one aspect, the lipase is a first-wash lipase, preferably a variant of the wild-type lipase from *Thermomyces lanuginosus* comprising T231R and/or N233R mutations. Preferred lipases include those sold under the tradenames Lipex®, Lipolex® and Lipoclean® by Novozymes, Bagsvaerd, Denmark.

[0056] Other suitable lipases include: Lip1 139, e.g. as described in WO2013/171241; and TfuLip2, e.g. as described in WO2011/084412 and WO2013/033318.

[0057] Other enzymes: Other suitable enzymes are bleaching enzymes, such as peroxidases/oxidases, which include those of plant, bacterial or fungal origin and variants thereof. Commercially available peroxidases include Guardzyme® (Novozymes A/S). Other suitable enzymes include choline oxidases and perhydrolases such as those used in Gentle Power Bleach™.

[0058] Other suitable enzymes include pectate lyases sold under the tradenames X-Pect®, Pectaway® (from Novozymes A/S, Bagsvaerd, Denmark) and PrimaGreen® (DuPont) and mannanases sold under the tradenames Mannaway® (Novozymes A/S, Bagsvaerd, Denmark), and Mannastar® (Du Pont).

[0059] Zeolite builder: The composition may comprise zeolite builder. The composition may comprise from 0wt% to 5wt% zeolite builder, or 3wt% zeolite builder. The composition may even be substantially free of zeolite builder; substantially free means "no deliberately added". Typical zeolite builders include zeolite A, zeolite P and zeolite MAP.

[0060] Phosphate builder: The composition may comprise phosphate builder. The composition may comprise from 0wt% to 5wt% phosphate builder, or to 3wt%, phosphate builder. The composition may even be substantially free of phosphate builder; substantially free means "no deliberately added". A typical phosphate builder is sodium tri-polyphosphate.

[0061] Carbonate salt: The composition may comprise carbonate salt. The composition may comprise from 0wt%

to 10wt% carbonate salt, or to 5wt% carbonate salt. The composition may even be substantially free of carbonate salt; substantially free means "no deliberately added". Suitable carbonate salts include sodium carbonate and sodium bicarbonate.

[0062] Silicate salt: The composition may comprise silicate salt. The composition may comprise from 0wt% to 10wt% silicate salt, or to 5wt% silicate salt. A preferred silicate salt is sodium silicate, especially preferred are sodium silicates having a $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of from 1.0 to 2.8, preferably from 1.6 to 2.0.

[0063] Sulphate salt: A suitable sulphate salt is sodium sulphate.

[0064] Brightener: Suitable fluorescent brighteners include: di-styryl biphenyl compounds, e.g. Tinopal® CBS-X, di-amino stilbene di-sulfonic acid compounds, e.g. Tinopal® DMS pure Xtra and Blankophor® HRH, and Pyrazoline compounds, e.g. Blankophor® SN, and coumarin compounds, e.g. Tinopal® SWN.

Preferred brighteners are: sodium 2 (4-styryl-3-sulfophenyl)-2H-naphthol[1,2-d]triazole, disodium 4,4'-bis[[4-anilino-6-(N-methyl-N-2-hydroxyethyl)amino 1,3,5-triazin-2-yl]]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis[[4-anilino-6-morpholino-1,3,5-triazin-2-yl]]amino} stilbene-2-2' disulfonate, and disodium 4,4'- bis(2-sulfostyryl)biphenyl. A suitable fluorescent brightener is C.I. Fluorescent Brightener 260, which may be used in its beta or alpha crystalline forms, or a mixture of these forms.

[0065] Chelant: The composition may also comprise a chelant selected from: diethylene triamine pentaacetate, diethylene triamine penta(methyl phosphonic acid), ethylene diamine-N'-N'-disuccinic acid, ethylene diamine tetraacetate, ethylene diamine tetra(methylene phosphonic acid) and hydroxyethane di(methylene phosphonic acid). A preferred chelant is ethylene diamine-N'-N'-disuccinic acid (EDDS) and/or hydroxyethane diphosphonic acid (HEDP). The composition preferably comprises ethylene diamine-N'-N'- disuccinic acid or salt thereof. Preferably the ethylene diamine-N'-N'-disuccinic acid is in S,S enantiomeric form. Preferably the composition comprises 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt. Preferred chelants may also function as calcium carbonate crystal growth inhibitors such as: 1-hydroxyethanediphosphonic acid (HEDP) and salt thereof; N,N-dicarboxymethyl-2-aminopentane-1,5-dioic acid and salt thereof; 2-phosphonobutane-1,2,4-tricarboxylic acid and salt thereof; and combination thereof.

[0066] Hueing agent: Suitable hueing agents include small molecule dyes, typically falling into the Colour Index (C.I.) classifications of Acid, Direct, Basic, Reactive (including hydrolysed forms thereof) or Solvent or Disperse dyes, for example classified as Blue, Violet, Red, Green or Black, and provide the desired shade either alone or in combination. Preferred such hueing agents include Acid Violet 50, Direct Violet 9, 66 and 99, Solvent Violet 13 and any combination thereof.

[0067] Many hueing agents are known and described in the art which may be suitable for the present invention, such as hueing agents described in WO2014/089386.

[0068] Suitable hueing agents include phthalocyanine and azo dye conjugates, such as described in WO2009/069077.

[0069] Suitable hueing agents may be alkoxylated. Such alkoxylated compounds may be produced by organic synthesis that may produce a mixture of molecules having different degrees of alkoxylation. Such mixtures may be used directly to provide the hueing agent, or may undergo a purification step to increase the proportion of the target molecule. Suitable hueing agents include alkoxylated bis-azo dyes, such as described in WO2012/054835, and/or alkoxylated thiophene azo dyes, such as described in WO2008/087497 and WO2012/166768.

[0070] The hueing agent may be incorporated into the detergent composition as part of a reaction mixture which is the result of the organic synthesis for a dye molecule, with optional purification step(s). Such reaction mixtures generally comprise the dye molecule itself and in addition may comprise un-reacted starting materials and/or by-products of the organic synthesis route. Suitable hueing agents can be incorporated into hueing dye particles, such as described in WO 2009/069077.

[0071] Dye transfer inhibitors: Suitable dye transfer inhibitors include polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone, polyvinylloxazolidone, polyvinylimidazole and mixtures thereof. Preferred are poly(vinyl pyrrolidone), poly(vinylpyridine betaine), poly(vinylpyridine N-oxide), poly(vinyl pyrrolidone-vinyl imidazole) and mixtures thereof. Suitable commercially available dye transfer inhibitors include PVP-K15 and K30 (Ashland), Sokalan® HP165, HP50, HP53, HP59, HP56K, HP56, HP66 (BASF), Chromabond® S-400, S403E and S-100 (Ashland).

[0072] Perfume: Suitable perfumes comprise perfume materials selected from the group: (a) perfume materials having a ClogP of less than 3.0 and a boiling point of less than 250°C (quadrant 1 perfume materials); (b) perfume materials having a ClogP of less than 3.0 and a boiling point of 250°C or greater (quadrant 2 perfume materials); (c) perfume materials having a ClogP of 3.0 or greater and a boiling point of less than 250°C (quadrant 3 perfume materials); (d) perfume materials having a ClogP of 3.0 or greater and a boiling point of 250°C or greater (quadrant 4 perfume materials); and (e) mixtures thereof.

[0073] It may be preferred for the perfume to be in the form of a perfume delivery technology. Such delivery technologies further stabilize and enhance the deposition and release of perfume materials from the laundered fabric. Such perfume delivery technologies can also be used to further increase the longevity of perfume release from the laundered fabric. Suitable perfume delivery technologies include: perfume microcapsules, pro-perfumes, polymer assisted deliveries,

molecule assisted deliveries, fiber assisted deliveries, amine assisted deliveries, cyclodextrin, starch encapsulated accord, zeolite and other inorganic carriers, and any mixture thereof. A suitable perfume microcapsule is described in WO2009/101593.

[0074] Silicone: Suitable silicones include polydimethylsiloxane and amino-silicones. Suitable silicones are described in WO05075616.

[0075] Process for making the solid composition: Typically, the particles of the composition can be prepared by any suitable method. For example: spray-drying, agglomeration, extrusion and any combination thereof.

[0076] Typically, a suitable spray-drying process comprises the step of forming an aqueous slurry mixture, transferring it through at least one pump, preferably two pumps, to a pressure nozzle. Atomizing the aqueous slurry mixture into a spray-drying tower and drying the aqueous slurry mixture to form spray-dried particles. Preferably, the spray-drying tower is a counter-current spray-drying tower, although a co-current spray-drying tower may also be suitable.

[0077] Typically, the spray-dried powder is subjected to cooling, for example an air lift. Typically, the spray-drying powder is subjected to particle size classification, for example a sieve, to obtain the desired particle size distribution. Preferably, the spray-dried powder has a particle size distribution such that weight average particle size is in the range of from 300 micrometers to 500 micrometers, and less than 10wt% of the spray-dried particles have a particle size greater than 2360 micrometers.

[0078] It may be preferred to heat the aqueous slurry mixture to elevated temperatures prior to atomization into the spray-drying tower, such as described in WO2009/158162.

[0079] It may be preferred for anionic surfactant, such as linear alkyl benzene sulphonate, to be introduced into the spray-drying process after the step of forming the aqueous slurry mixture: for example, introducing an acid precursor to the aqueous slurry mixture after the pump, such as described in WO 09/158449.

[0080] It may be preferred for a gas, such as air, to be introduced into the spray-drying process after the step of forming the aqueous slurry, such as described in WO2013/181205.

[0081] It may be preferred for any inorganic ingredients, such as sodium sulphate and sodium carbonate, if present in the aqueous slurry mixture, to be micronized to a small particle size such as described in WO2012/134969.

[0082] Typically, a suitable agglomeration process comprises the step of contacting a detergent ingredient, such as a detergent surfactant, e.g. linear alkyl benzene sulphonate (LAS) and/or alkyl alkoxyated sulphate, with an inorganic material, such as sodium carbonate and/or silica, in a mixer. The agglomeration process may also be an in-situ neutralization agglomeration process wherein an acid precursor of a detergent surfactant, such as LAS, is contacted with an alkaline material, such as carbonate and/or sodium hydroxide, in a mixer, and wherein the acid precursor of a detergent surfactant is neutralized by the alkaline material to form a detergent surfactant during the agglomeration process.

[0083] Other suitable detergent ingredients that may be agglomerated include polymers, chelants, bleach activators, silicones and any combination thereof.

[0084] The agglomeration process may be a high, medium or low shear agglomeration process, wherein a high shear, medium shear or low shear mixer is used accordingly. The agglomeration process may be a multi-step agglomeration process wherein two or more mixers are used, such as a high shear mixer in combination with a medium or low shear mixer. The agglomeration process can be a continuous process or a batch process.

[0085] It may be preferred for the agglomerates to be subjected to a drying step, for example to a fluid bed drying step. It may also be preferred for the agglomerates to be subjected to a cooling step, for example a fluid bed cooling step.

[0086] Typically, the agglomerates are subjected to particle size classification, for example a fluid bed elutriation and/or a sieve, to obtain the desired particle size distribution. Preferably, the agglomerates have a particle size distribution such that weight average particle size is in the range of from 300 micrometers to 800 micrometers, and less than 10wt% of the agglomerates have a particle size less than 150 micrometers and less than 10wt% of the agglomerates have a particle size greater than 1200 micrometers.

[0087] It may be preferred for fines and over-sized agglomerates to be recycled back into the agglomeration process. Typically, over-sized particles are subjected to a size reduction step, such as grinding, and recycled back into an appropriate place in the agglomeration process, such as the mixer. Typically, fines are recycled back into an appropriate place in the agglomeration process, such as the mixer.

[0088] It may be preferred for ingredients such as polymer and/or non-ionic detergent surfactant and/or perfume to be sprayed onto base detergent particles, such as spray-dried base detergent particles and/or agglomerated base detergent particles. Typically, this spray-on step is carried out in a tumbling drum mixer.

[0089] Method of laundering fabric: The method of laundering fabric comprises the step of contacting the solid composition to water to form a wash liquor, and laundering fabric in said wash liquor. Typically, the wash liquor has a temperature of above 0°C to 90°C, or to 60°C, or to 40°C, or to 30°C, or to 20°C. The fabric may be contacted to the water prior to, or after, or simultaneous with, contacting the solid composition with water. Typically, the wash liquor is formed by contacting the laundry detergent to water in such an amount so that the concentration of laundry detergent composition in the wash liquor is from 0.2g/l to 20g/l, or from 0.5g/l to 10g/l, or to 5.0g/l. The method of laundering fabric can be carried out in a front-loading automatic washing machine, top loading automatic washing machines, including

EP 3 754 010 A1

high efficiency automatic washing machines, or suitable hand-wash vessels. Typically, the wash liquor comprises 90 litres or less, or 60 litres or less, or 15 litres or less, or 10 litres or less of water. Typically, 200g or less, or 150g or less, or 100g or less, or 50g or less of laundry detergent composition is contacted to water to form the wash liquor.

5 EXAMPLES

Example 1: Inventive Example

[0090]

10

15

20

25

30

35

40

45

Ingredient	Example 1 (%)
Propylene Glycol	0.0100
Zeolite	0.7900
NaOH	0.0025
LAB	0.1718
Starch	0.0510
NaCl	0.2714
Dyes	0.0384
Brighteners	0.1286
Polymer	1.9948
Perfume	0.4050
NaSulphate	61.8463
Na ₂ CO ₃	8.7124
Enzymes	0.1903
Sodium Silcate	8.1255
Water	2.0454
LAS	12.9385
AE7 NI	0.5135
AEIS	0.3600
Bentonite	0.8737
Misc	0.4252
Citric Acid	0.0057
TETA 4HCl*	0.10
Total	100
TETA 4HCl: HCl salt of triethylenetetraamine, available from Sigma Aldrich	

Example 2: Comparative Example

50

[0091]

55

Ingredient	Example 1 (%)
Propylene Glycol	0.0100
Zeolite	0.7900
NaOH	0.0025

EP 3 754 010 A1

(continued)

Ingredient	Example 1 (%)
LAB	0.1718
Starch	0.0510
NaCl	0.2714
Dyes	0.0384
Brighteners	0.1286
Polymer	1.9948
Perfume	0.4050
NaSulphate	61.8463
Na ₂ CO ₃	8.7124
Enzymes	0.1903
Sodium Silcate	8.1255
Water	2.0454
LAS	12.9385
AE7 NI	0.5135
AE1S	0.3600
Bentonite	0.8737
Misc	0.4252
Citric Acid	0.0057
TETA*	0.10
Total	100
*TETA: Triethylenetetraamine, available from Sigma Aldrich	

Example 3: Prepare fabric swatches for malodor testing

[0092] PCN-01 polycotton and PN-01 polyester CFT clean tracers were soiled following the "soil step" below, and then washed following the "wash step" using either Example 1 or Example 2 detergent respectively.

SOIL STEP

[0093] Full scale Real Item set split between 2 baskets putting A1-4 and B1-4 in the same basket and A5-8 and B5-8 in the other basket (equal to 8 x 1/2 T-shirt, 1/2 Sock, 1/2 Tea Towel, 1/2 Terry Towel and 1/2 cotton pillowcase in each basket).

[0094] 4 x PCN-01 polycotton and PN-01 polyester CFT clean tracers labelled A1-4 and B1-4 and split between ELSA loads (A1-2 & B1-2 in machine 1 and A3-4 & B3-4 in machine 2).

[0095] 12 x 5x10cm polycotton swatches dosed with 1ml of Equest Technical Body Soil and left to cool and solidify for 1 hour. Once solidified 6 swatches are added to each basket.

[0096] WFK SBL2004 sheets mixed into each load along with 2 x 45cm² CS33 Sebum from CFT. Items placed in 2 x Meile 1724 dedicated malodour machines

Both machines run on 30C Delicate Wash 600rpm spin cycle in soft water (<0.2 gpg) nil detergent with 13ml of HMI and 13ml Bicarbonate spike in both the main wash and rinse (make up shown Attachment 1).

[0097] Loads left for 3 days in the machines with the machine drawer slightly open to allow air in.

WASH STEP

[0098] Soiled loads removed from machines and soiling up machines boiled out for use.

EP 3 754 010 A1

[0099] Each soiled load was split in two separating all A items from B to cover 4 x Kenmore 600 Series TL washing machines.

[0100] 1.2Kg clean global ballast (4 x 50:50 polycotton (blue trim) and 6 x cotton (white trim)) is mixed into each load.

[0101] The loads were washed with either the inventive detergent from example 1 or the comparative example from example 2 using conditions specified below switching from Normal cycle to Delicate cycle for rinsing and spinning when machine begins to drain.

[0102] 30ml of 12gpg Hardness spike with Copper addition in both Main wash and rinse (make up shown Attachment 2).

[0103] Any solid additions added to the product before dissolution and any solution additions added during product addition.

Machines	Kenmore 600 Series
Temperature	25oC
Wash Volume	60L
Wash Time	12 mins Normal
Number of Rinses	1
Rinse and spin cycle	Delicate
Water Hardness	Soft <0.2 gpg
Hardness Spike used	Yes (make up specified below)

Example 4: Malodor Sensory Assessment

[0104] Polyester and polycotton tracers prepared according to Example 3 were assessed wet in 800ml glass jars by 3-4 panelists via the 0-10 monadic grading scale (0 = *no malodor*, 10 = *very strong malodor*).

[0105] The results are summarized as below:

Fabric type	Detergent used	Overall Average Grade (0-10 malodour scale)	Standard Deviation
Polyester	Comparative Example (Example 2)	4.00	0.00
	Inventive Example (Example 1)	2.00	0.71
Polycotton	Comparative Example (Example 2)	3.17	0.85
	Inventive Example (Example 1)	2.50	0.00

[0106] This shows significant increase in malodour reduction for inventive example vs comparative.

[0107] 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".

Claims

1. A solid free-flowing particulate laundry detergent composition comprising a deterative surfactant and a linear polyamine salt, wherein the linear polyamine salt has the following general formula:



15

H⁺_xA⁻ is an acid to protonate at least one N atoms of the linear polyamine, x is an integer of 1 or above, A⁻ is a anionic counter ion derived from an acid; and

wherein at least one nitrogen atom of linear polyamine salt is protonated.

- 30

35

40

45

50

55



EUROPEAN SEARCH REPORT

 Application Number
 EP 19 18 0707

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2005/197275 A1 (HSU GREGORY [US] ET AL) 8 September 2005 (2005-09-08)	1-3	INV. C11D11/00 C11D17/06 C11D1/40 C11D3/39
Y	* example 4 * * paragraphs [0004], [0008] * * paragraphs [0003], [0115] * * the whole document *	3	
Y	----- EP 3 330 350 A1 (PROCTER & GAMBLE [US]) 6 June 2018 (2018-06-06) * paragraph [0121] * * paragraphs [0008], [0028] * -----	3	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
			C11D
Place of search		Date of completion of the search	Examiner
The Hague		22 November 2019	Yildirim, Zeynep
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 1
 EPO FORM 1503 03.02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 19 18 0707

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-11-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005197275 A1	08-09-2005	AR 047984 A1	15-03-2006
		AT 393207 T	15-05-2008
		BR PI0507264 A	26-06-2007
		CN 101076583 A	21-11-2007
		DE 602005006244 T2	25-06-2009
		EP 1720968 A1	15-11-2006
		ES 2306092 T3	01-11-2008
		US 2005197275 A1	08-09-2005
		WO 2005095572 A1	13-10-2005

EP 3330350 A1	06-06-2018	NONE	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 08007320 A [0035]
- WO 09154933 A [0038]
- US 5352604 A [0049]
- WO 11140316 A [0050]
- WO 11072117 A [0050]
- WO 06002643 A [0051]
- WO 07144857 A [0053]
- WO 10056652 A [0053]
- WO 06090335 A [0055]
- WO 13116261 A [0055]
- WO 2013171241 A [0056]
- WO 2011084412 A [0056]
- WO 2013033318 A [0056]
- WO 2014089386 A [0067]
- WO 2009069077 A [0068] [0070]
- WO 2012054835 A [0069]
- WO 2008087497 A [0069]
- WO 2012166768 A [0069]
- WO 2009101593 A [0073]
- WO 05075616 A [0074]
- WO 2009158162 A [0078]
- WO 09158449 A [0079]
- WO 2013181205 A [0080]
- WO 2012134969 A [0081]