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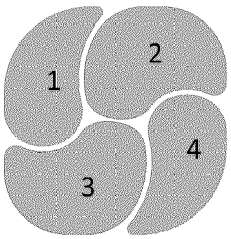
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(54) **UNIT DOSE PRODUCT**

(57) Liquid unit dose product comprising a first, a second, a third and a fourth chamber, said first and third chambers having a volume of from 5 to 10ml, and said first and fourth chambers having a volume of from 3 to 8ml, where the first chamber has a higher volume than the second chamber and wherein at least one of the first or third chamber comprises a solid laundry treatment particle and wherein at least one of the second or fourth chambers contains a laundry liquid treatment composition.



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Description

[0001] The present invention relates to improved unit dosed products comprising solid particles.

[0002] Despite the prior art there remains a need for improved unit dose detergent products with solid particles.

[0003] Accordingly, and in a first aspect there is provided a unit dose product comprising a first, a second, a third and a fourth chamber, said first and third chambers having a volume of from 5 to 10ml, and said first and fourth chambers having a volume of from 3 to 8ml, where the first chamber has a higher volume than the second chamber and wherein at least one of the first or third chamber comprises a solid laundry treatment particle and wherein at least one of the second or fourth chambers contains a laundry liquid treatment composition

[0004] We have surprisingly found that unit dose products comprising a laundry treatment particle are more easily processed with specific design of the chambers. In particular we have found that those containing particles in one chamber and liquids in another need specific arrangement of chambers to avoid adverse consequences, in particular leaking and sticking during packaging when they have asymmetric arrangement of chambers.

[0005] Preferably, at least three chambers contain laundry liquid composition.

[0006] Preferably, the first chamber contains a solid laundry treatment particle and the third chamber contains a laundry treatment liquid.

[0007] Preferably, the first chamber contains from 3 to 6ml laundry treatment particle.

[0008] Preferably, the first chamber contains from 30 to 50% headspace.

[0009] Preferably, the density of the particle is from 0.7 to 1.5 g/ml.

[0010] Preferably, the product comprises a first and second hemisphere, when considered in plan view, comprise a first and second hemisphere, said first hemisphere comprising said first and third chambers and said second hemisphere comprising said second and fourth chambers.

[0011] In a preferred embodiment, said first and second hemispheres are separated by a substantially diametric seal.

[0012] In an alternative preferred embodiment, the first, second, third and fourth chambers are disposed such that they are sequentially arranged in a circumferential direction. Having irregular chamber volumes creates advantages in the context of flow characteristics, and hence dissolution profiles, but also disadvantages when it comes to manufacture. The most desirable capsule is thus one with a regular arrangement of irregular dimensioned chambers. Having a capsule with a repeating arrangement of a small chamber followed by a larger chamber and then followed by a further small chamber and then a bigger one in a circumferential direction is a highly attractive proposition in that it may be manufactured more easily but has a dissolution profile which leads to improved performance.

[0013] Preferably, the capsule comprises a perimeter seal and an inner seal, said inner seal separating the chambers. Preferably, the average width of the seal between the chambers is from 2 to 3.5mm. Preferably, the average width of the perimeter seal is from 2 to 3.5mm.

[0014] Preferably, the first, second, third and fourth chamber comprise a straight edge. Preferably, the straight edge is along the perimetric seal. A straight edge improves the visual impact of the capsule and creates a lower stretch contortion when the capsule is removed from the mould during manufacture. It also improves the perimeter seal integrity and reduces the prospect of leakages.

[0015] Preferably, the difference in volume between the first and third chambers is from 0 to 1ml, more preferably from 0 to 0.5ml, and most preferably from 0 to 0.1 ml. In a most preferred embodiment the first and third chambers have substantially the same volume.

[0016] Preferably, the second chamber has a volume of from 4.5 to 7.0 ml, more preferably from 5.0 to 6.0 ml and most preferably from 5.5 to 5.7 ml.

[0017] Preferably, the fourth chamber has a volume of from 4.5 to 7.0 ml, more preferably from 5.0 to 6.0 ml and most preferably from 5.5 to 5.7 ml.

[0018] Preferably, the difference in volume between the second and fourth chambers is from 0 to 1ml, more preferably from 0 to 0.7ml, and most preferably from 0 to 0.2 ml. In a most preferred embodiment the second and fourth chambers have substantially the same volume.

[0019] Preferably, the capsule comprises a first inner seal separating the first and second chamber, a second inner seal separating the second and third chambers, a third inner seal separating the third and fourth chambers, a fourth seal separating the fourth and first chambers.

[0020] Preferably, the capsule comprises a fifth seal separating the second and fourth chambers.

[0021] Preferably, the capsule comprises a pair of dissolution aid seal trivia, the first seal trivium between the first, second and fourth chamber and the second seal trivium between the second, third and fourth chambers.

[0022] Preferably, the chambers are disposed and dimensioned such that there is 180 degree rotational symmetry. This improves the balance between manufacturability and dissolution profile.

[0023] Preferably the first chamber is a tear drop shape, more preferably a curved tear drop shape.

[0024] By curved tear drop shape is meant that the chamber footprint has a semi-circle part and a first and second side which depend from either side respectively of the semi-circular part and meet at their opposite ends to form a tip part.

Further, the first side is longer than the second side such that the tail of the tear drop curves to one side.

[0025] More preferably, the longer first side of the tear drop shape has a substantially straight part.

[0026] Preferably the third chamber is a tear drop shape, more preferably a curved tear drop shape.

[0027] By curved tear drop shape is meant that the chamber footprint has a semi-circle part and a first and second side which depend from either side respectively of the semi-circular part and meet at their opposite ends to form a tip part. Further, the first side is longer than the second side such that the tail of the tear drop curves to one side.

[0028] More preferably, the longer first side of the tear drop shape has a substantially straight part.

[0029] Preferably, the second chamber is substantially U-shaped. Preferably, the fourth chamber is U-shaped.

[0030] Preferably, the design of the capsule is such that the semi-circle part of the third chamber nestles within the recess formed by the U of the second chamber. The two are separated by the second seal described above. Similarly, it is preferred that the semi-circle part of the first chamber nestles within the recess formed by the U of the fourth chamber. The two are separated by the fourth seal described above.

[0031] Preferably, the design of the capsule is such that the short side of the first chamber forms a recess in which nestles a part of the second chamber. The two chambers are separated by the first seal as described above.

[0032] Preferably, the design of the capsule is such that the short side of the third chamber forms a recess in which nestles a part of the fourth chamber. The two chambers are separated by the third seal as described above.

[0033] Preferably, the second and fourth chambers are disposed such that they abut one another to form a broken 'S'. The broken part in the middle of the 'S' being the fifth seal as described above.

[0034] Preferably, the second, third and fourth chambers contain laundry liquid composition. Preferably, the headspace in the second chamber is from 15 to 25% the volume of the chamber. Preferably, the headspace in the third chamber is from 15 to 25% the volume of the chamber. Preferably, the headspace in the fourth chamber is from 15 to 25% the volume of the chamber.

[0035] Preferably, said water-soluble film comprises maleic acid copolymerised with polyvinyl alcohol.

[0036] Preferably, the solid laundry particle comprises at least 50% wt. of the solid laundry particle a carrier.

[0037] Preferably, the solid laundry particle comprises at least 90% wt. of the solid laundry particle a carrier.

[0038] Preferably, the carrier is selected from the group consisting of: synthetic polymers, proteins, saccharides, polysaccharides, water-soluble or water dispersible fillers, vegetable soap, ethoxylated non-ionic surfactants, urea and combinations thereof.

[0039] Preferably, the solid laundry particle includes a carrier selected from water soluble organic alkali metal salt, water soluble inorganic alkaline earth metal salt, water soluble organic alkaline earth metal salt, water soluble carbohydrate, water soluble silicate, water soluble urea, starch, xanthan gum, dextrose, clay, water insoluble silicate, citric acid carboxymethyl cellulose, fatty acid, fatty alcohol, glyceryl diester of hydrogenated tallow, glycerol, polyvinyl alcohol, non-ionic surfactants and combinations thereof.

[0040] Preferably, the solid laundry particle includes a carrier selected from of synthetic polymers, polysaccharides, saccharides, vegetable soap, urea, ethoxylated non-ionic surfactants having a formula $R_1O(EO)xH$, wherein R_1 comprises 12 to 20 carbon atoms and x is 1 to 12, and combinations thereof.

[0041] Preferably, the solid laundry particle includes a carrier selected from polyethylene glycol, starch, dextrose, coconut soap beads, palm soap, urea and combinations thereof.

Water-Soluble Film Compositions

[0042] The liquid unit dose product comprises at least two chambers, preferably, three chambers and more preferably four chambers. At least one chamber contains a liquid laundry detergent composition and at least one chamber contains a solid particle composition.

[0043] The chambers are defined by water-soluble film in preferably each chamber is formed between two opposing sheets of film which are sealed at the edges to define the chambers.

[0044] Preferably, the product is from 10 to 50g in weight to represent a unit dose.

[0045] Water-soluble film compositions, optional ingredients for use therein, and methods of making the same are well known in the art, whether being used for making relatively thin water-soluble films (e.g., as capsule materials) or otherwise.

[0046] Polyvinyl alcohol (PVA) is a synthetic resin generally prepared by the alcoholysis, usually termed hydrolysis or saponification, of polyvinyl acetate. Fully hydrolyzed PVA, wherein virtually all the acetate groups have been converted to alcohol groups, is a strongly hydrogen-bonded, highly crystalline polymer which dissolves only in hot water- greater than about 140 degrees Fahrenheit (60 degrees C). If a sufficient number of acetate groups are allowed to remain after the hydrolysis of polyvinyl acetate, the PVA polymer then being known as partially hydrolyzed, it is more weakly hydrogen-bonded and less crystalline and is soluble in cold water- less than about 10 degrees C. An intermediate cold or hot water-soluble film can include, for example, intermediate partially- hydrolyzed PVA (e.g., with degrees of hydrolysis of about 94 percent to about 98 percent), and is readily soluble only in warm water- e.g., rapid dissolution at temperatures of about 40 degrees centigrade and greater. Both fully and partially hydrolyzed PVA types are commonly referred to as PVA

homopolymers although the partially hydrolyzed type is technically a vinyl alcohol- vinyl acetate copolymer.

[0047] Other water soluble polymers for use in addition to the PVA polymers and PVA copolymers in the blend can include, but are not limited to modified polyvinyl alcohols, polyacrylates, water-soluble acrylate copolymers, polyvinyl pyrrolidone, polyethyleneimine, pullulan, water-soluble natural polymers including, but not limited to, guar gum, gum Acacia, xanthan gum, carrageenan, and starch, water-soluble polymer derivatives including, but not limited to, modified starches, ethoxylated starch, and hydroxypropylated starch, copolymers of the forgoing and combinations of any of the foregoing. Yet other water-soluble polymers can include polyalkylene oxides, polyacrylamides, polyacrylic acids and salts thereof, celluloses, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts thereof, polyaminoacids, polyamides, gelatines, methylcelluloses, carboxymethylcelluloses and salts thereof, dextrins, ethylcelluloses, hydroxyethyl celluloses, hydroxypropyl methylcelluloses, maltodextrins, and polymethacrylates. Such water-soluble polymers, whether PVOH or otherwise are commercially available from a variety of sources.

[0048] Any of the foregoing water-soluble polymers are generally suitable for use as film-forming polymers. In general, the water- soluble film can include copolymers and/or blends of the foregoing resins.

[0049] The weight ratio of the amount of all water-soluble polymers as compared to the combined amount of all plasticizers, compatibilizing agents, and secondary additives can be in a range of about 0.5 to about 18, about 0.5 to about 15, about 0.5 to about 9, about 0.5 to about 5, about 1 to 3, or about 1 to 2, for example. The specific amounts of plasticizers and other non-polymer component can be selected in a particular embodiment based on an intended application of the water-soluble film to adjust film flexibility and to impart processing benefits in view of desired mechanical film properties. It is well known in the art that the viscosity of a water-soluble polymer (PVA or otherwise) is correlated with the weight-average molecular weight (W) of the same polymer, and often the viscosity is used as a proxy for Mw. Thus, the weight-average molecular weight of the water-soluble polymers, including the first PVA copolymer and second PVA polymer, can be in a range of about 30,000 to about 175,000, or about 30,000 to about 100,000, or about 55,000 to about 80,000, for example.

[0050] The water-soluble film can contain other auxiliary agents and processing agents, such as, but not limited to, plasticizers, plasticizer compatibilizers, surfactants, lubricants, release agents, fillers, extenders, cross-linking agents, antiblocking agents, antioxidants, detackifying agents, antifoams, nanoparticles such as layered silicate-type nanoclays (e.g., sodium montmorillonite), bleaching agents (e.g., sodium metabisulfite, sodium bisulfite or others), aversive agents such as bitterants (e.g., denatonium salts such as denatonium benzoate, denatonium saccharide, and denatonium chloride; sucrose octaacetate; quinine; flavonoids such as quercetin and naringen; and quassinoids such as quassin and brucine) and pungents (e.g., capsaicin, piperine, allyl isothiocyanate, and resinferatoxin), and other functional ingredients, in amounts suitable for their intended purposes. Embodiments including plasticizers are preferred. The amount of such agents can be up to about 50 wt., 20 wt percent, 15 wt percent, 10 wt percent, 5 weight percent, 4 wt percent and/or at least 0.01 weight percent, 0.1 wt percent, 1 wt percent, or 5 wt, individually or collectively.

[0051] The plasticizer can include, but is not limited to, glycerin, diglycerin, sorbitol, ethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, tetraethylene glycol, propylene glycol, polyethylene glycols up to 400 MW, neopentyl glycol, trimethylolpropane, polyether polyols, sorbitol, 2-methyl-l,3-propanediol, ethanolamines, and a mixture thereof. A preferred plasticizer is glycerin, sorbitol, triethyleneglycol, propylene glycol, diproyplene glycol, 2-methyl-l,3-propanediol, trimethylolpropane, or a combination thereof. The total amount of the plasticizer can be in a range of about 10 weight percent to about 40 wt., or about 15 weight percent to about 35 wt., or about 20 weight percent to about 30 wt., for example about 25 wt., based on total film weight. Combinations of glycerin, dipropylene glycol, and sorbitol can be used. Optionally, glycerin can be used in an amount of about 5 wt percent to about 30 wt, or 5 wt percent to about 20 wt, e.g., about 13 wt percent.

[0052] Optionally, dipropylene glycol can be used in an amount of about 1 weight percent to about 20 wt., or about 3 weight percent to about 10 wt., for example 6 weight percent. Optionally, sorbitol can be used in an amount of about 1 wt percent to about 20 wt, or about 2 wt percent to about 10 wt, e.g., about 5 wt percent. The specific amounts of plasticizers can be selected in a particular embodiment based on desired film flexibility and processability features of the water-soluble film. At low plasticizer levels, films may become brittle, difficult to process, or prone to breaking. At elevated plasticizer levels, films may be too soft, weak, or difficult to process for a desired use.

[0053] In a preferred embodiment the composition comprises a taste aversive such as denatonium benzoate and/or a pungent agent such as capsaicin.

[0054] Maleic acid copolymerised with polyvinyl alcohol is well known in the field and is commercially available from a number of water-soluble film manufacturers.

[0055] Preferably, the maleic acid copolymerised PVA comprises from 10 to 70% wt. and more preferably from 30 to 60% wt. of the water-soluble film.

[0056] Preferably, the film comprises a phthalocyanine based pigment.

[0057] Preferably, the film comprises less than 10% wt. acrylic acid copolymerised PVA.

[0058] Preferably, the pH of the laundry liquid composition is from 6.1 to 8.2. More preferably, the pH of the composition is from 6.5 to 7.5.

Solid Laundry Treatment Particle

Carrier material:

[0059] The laundry particles of the present invention comprise carrier materials. By carrier material is meant a solid material which provides the solid structure of the laundry particle. The compositions described herein preferably comprises at least 50 wt.% carrier materials, preferably 65 wt.%, more preferably 80 wt.% and most preferably at least 90 wt.% carrier materials, by weight of the composition.

[0060] Generally, carrier materials may be any material which disperses, dissolves, disintegrates or solubilises in water. The composition may comprise one carrier material or a combination of different carrier materials.

[0061] Suitable carrier materials may be selected from the group consisting of: synthetic polymers (e g, polyethylene glycol, ethylene oxide/propylene oxide block copolymers, polyvinyl alcohol, polyvinyl acetate, and derivatives thereof), proteins (e.g., gelatin, albumin, casein), saccharides (e.g. dextrose, fructose, galactose, glucose, isoglucose, sucrose), polysaccharides (e.g., starch, xanthan gum, cellulose, or derivatives thereof), water-soluble or water dispersible fillers (e.g. sodium chloride, sodium sulfate, sodium carbonate/bicarbonate, zeolite, silica, clay), vegetable soap (e.g. coconut soap beads or palm soap), ethoxylated non-ionic surfactants (having a formula R1O(R2O)xH, wherein R1 preferably comprises 12 to 20 carbon atoms, R2 is C2H4 or mixture of C2H4 and C3H6 units and x = 8 to 120), urea and combinations thereof. Examples of suitable carrier materials include: water soluble organic alkali metal salt, water soluble inorganic alkaline earth metal salt, water soluble organic alkaline earth metal salt, water soluble carbohydrate, water soluble silicate, water soluble urea, starch, xanthan gum, dextrose, clay, water insoluble silicate, citric acid carboxymethyl cellulose, fatty acid, fatty alcohol, glyceryl diester of hydrogenated tallow, glycerol, polyvinyl alcohol, non-ionic surfactants sold under the trade name Lutensol ex. BASF and combinations thereof.

[0062] Preferred carrier materials may be selected from the group consisting of synthetic polymers (e g, polyethylene glycol, ethylene oxide/propylene oxide block copolymers, polyvinyl alcohol, polyvinyl acetate, and derivatives thereof), polysaccharides (e.g., starch, xanthan gum, cellulose, or derivatives thereof), saccharides (e.g., dextrose, fructose, galactose, glucose, isoglucose, sucrose), vegetable soap (e.g. coconut soap beads or palm soap), urea, ethoxylated non-ionic surfactants (having a formula R1O(R2O)xH, wherein R1 preferably comprises 12 to 20 carbon atoms, R2 is C2H4 or mixture of C2H4 and C3H6 units and x = 8 to 120) and combinations thereof.

[0063] More preferably carriers are selected from polyethylene glycol, starch, dextrose, coconut soap beads, palm soap, urea and combinations thereof.

[0064] Saccharides are molecular compounds comprising carbon, hydrogen and oxygen. For the purposes of this invention a saccharide is defined as comprising one to ten monosaccharide units and mixtures thereof. In other words either a monosaccharide or an oligosaccharide or mixtures thereof. An oligosaccharide is a short saccharide polymer, typically considered in the art to comprise between two and ten monosaccharides units. It is preferred that a saccharide comprises 1 to 5 monosaccharide units, more preferably 1 to 4 monosaccharide units, most preferably the saccharide comprises monosaccharides, disaccharides or mixtures thereof. Disaccharides are the product of a reaction between two monosaccharides. They may be formed from two identical monosaccharides or two different monosaccharides. Examples of disaccharides include: sucrose, maltose, lactose. Monosaccharides are simple sugar units having the general formula (CH2O)n. Commonly n is 3, 5 or 6. According, monosaccharides can be classified by the number n, for example: trioses (e.g. glyceraldehyde), pentoses (e.g. ribose) and hexoses (e.g. fructose, glucose and galactose). Some monosaccharides may be substituted with additional functional groups, e.g. Glucosamine, others may have undergone deoxgenation and lost an oxygen atom e.g. deoxyribose. Therefore, the general chemical formulae can vary slightly depending on the monosaccharide.

[0065] Preferred monosaccharides for the present invention are hexose molecules (n=6). Hexose molecules all have the same molecular formula, however, have a different structural formula, i.e. are structural isomers. It is preferred that the hexose comprises a 6-membered ring, opposed to a 5 membered ring. Glucose and galactose have 6-membered rings. In a preferred embodiment the hexose monosaccharide is glucose. Glucose is a chiral molecule, having a mixture of D and L stereo isomers. Particularly preferably, the glucose of the present invention is the D isomer of glucose, also known as dextrose.

[0066] Preferably a saccharide material used in the present invention is anhydrous, i.e. free of any water. For example, dextrose monohydrate contains one molecule of water whereas anhydrous dextrose contains none.

[0067] Non-limiting examples of suitable saccharides for the present invention are: C*Dex ex Cargill, Treha ex Cargill, Anhydrous Dextrose ex Foodchem.

[0068] In all compositions, particularly those comprising a saccharide, it may be preferable to include bitter material such as Bitrex ex Johnson Matthey Fine Chemicals, due to the sweetness of the saccharide.

[0069] Preferred synthetic polymers for the present invention include polyethylene glycols.

[0070] Preferably the polyethylene glycol has a weight average molecular weight between 3000 and 14000, preferably between 4000 and 12000. Synthetic polymers preferably comprise carbon derived from non-petrochemical sources. Such

sources preferably include carbon capture and biomass.

Manufacture:

[0071] The laundry particles may be in any solid form, for example: powder, pellet, tablet, prill, pastille or extrudate. Preferably the composition in the form of a pastille or extrudate. Pastilles can, for example, be produced using ROTOFORMER Granulation Systems ex. Sandvick Materials.

[0072] The laundry particle compositions of the present invention may be formed from a melt. The solid composition can for example, be formed into particles by: Pastillation e.g. using a ROTOFORMER ex Sandvick Materials, extrusion, prilling, by using moulds, casting the melt and cutting to size or spraying the melt.

[0073] An example manufacturing process may involve melting the carrier material at a temperature above the melting point of that carrier material, preferably at least 2°C above the melting point of the carrier material, more preferably at least 5°C above the melting point of the carrier material. Where more than one carrier materials are used, the melting point is considered to the highest of the melting points of the individual materials. Once melted, microcapsules and other ingredients may be mixed into the compositions. This is followed by a process in which the melt in cooled and shaped, e.g. extrusion or pastillation.

Shape:

[0074] The laundry particle compositions of the present invention are preferably homogeneously structured. By homogeneous, it is meant that there is a continuous phase throughout the solid product. There is not a core and shell type structure. Any particles present such as perfume microcapsules will be distributed within the continuous phase. The continuous phase is provided predominately by the carrier materials.

[0075] The laundry particles may be any shape or size suitable for dissolution in the laundry process. Preferably, each individual particle of the solid composition has a mass of between 0.95mg to 5 grams, more preferably 0.01 to 1 gram and most preferably 0.02 to 0.5 grams. Preferably each individual particle has a maximum linear dimension in any direction of 10 mm, more preferably 0.5-10 mm, more preferably 1-8 mm and most preferably a maximum linear dimension of 4-6 mm. The shape of the particles may be selected for example from spherical, hemispherical, compressed hemispherical, lentil shaped, oblong, or planar shapes such as petals. A preferred shape for the particles is hemispherical, i.e. a dome shape wherein the height of the dome is less than the radius of the base. When the particles are compressed hemispherical, it is preferred that diameter of the substantially flat base provides the maximum linear dimension and the height of the particle is 1-5mm, more preferably 2-3mm. The dimensions of the particles of the present invention can be measured using Calipers.

Laundry Liquid Composition

[0076] The laundry liquid composition is described below.

Surfactant

[0077] The liquid detergent of the invention preferably comprises from 2 to 60 wt. % of total surfactant, most preferably from 4 to 30 wt. %. Anionic and non-ionic surfactant are preferred.

[0078] Anionic surfactants are discussed in the Anionic Surfactants: Organic Chemistry edited by Helmut W. Stache (Marcel Dekker 1995), Surfactant Science Series published by CRC press. Preferred anionic surfactants are sulfonate and sulfate surfactants, preferably alkylbenzene sulphonates, alkyl sulfates and alkyl ether sulfates. The alkyl chain is preferably C10-C18. Alkyl ether sulfates are also called alcohol ether sulfates. Commonly used in laundry liquid compositions are C12-C14 alkyl ether sulfates having a straight or branched chain alkyl group having 12 to 14 carbon atoms (C12-14) and containing an average of 1 to 3EO units per molecule. A preferred example is sodium lauryl ether sulfate (SLES) in which the predominantly C12 lauryl alkyl group has been ethoxylated with an average of 3EO units per molecule.

[0079] The anionic surfactant is preferably added to the detergent composition in the form of a salt. Preferred cations are alkali metal ions, such as sodium and potassium. However, the salt form of the anionic surfactant may be formed in situ by neutralization of the acid form of the surfactant with alkali such as sodium hydroxide or an amine, such as mono-, di-, or tri-ethanolamine. Weight ratios are calculated for the protonated form of the surfactant. Nonionic surfactant are discussed in Non-ionic Surfactants: Organic Chemistry edited by Nico M. van Os (Marcel Dekker 1998), Surfactant Science Series published by CRC press. Preferred non-ionic surfactants are alkoxylate, preferably ethoxylated, Preferred non-ionic surfactant are alcohol ethoxylates and methyl ester ethoxylates, with C10-C18 alkyl chains. Commonly used in laundry liquid compositions are C12-C15 alcohol ethoxylates having a straight or branched chain alkyl group having 12 to 15 carbon atoms and containing an average of 5 to 12EO units per molecule. A preferred example is C12-C15 alcohol

ethoxylates with a mole average of 7 to 9 ethoxylate units.

[0080] Ethoxy units may be partially replaced by propoxy units in anionic and non-ionic surfactants.

[0081] Further examples of suitable anionic surfactants are rhamnolipids, alpha-olefin sulfonates, olefin sulfonates, alkene sulfonates, alkane-2,3-diylbis(sulfates), hydroxyalkanesulfonates and disulfonates, fatty alcohol sulfates (FAS), paraffin sulfonates, ester sulfonates, sulfonated fatty acid glycerol esters, methyl ester sulfonate alkyl- or alkenylsuccinic acid, dodecenyl/tetradecenyl succinic acid (DTSA), fatty acid derivatives of amino acids, DATEM's, CITREM's and diesters and monoesters of sulfosuccinic acid.

[0082] The non-ionic surfactant fraction is preferably greater than 50wt%, more preferably greater than 80wt%, most preferably greater than 95wt% alcohol ethoxylate. More preferably the non-ionic surfactant fraction is preferably greater than 50wt%, more preferably greater than 80wt%, most preferably greater than 95wt% the alcohol ethoxylate as claimed in claim 1.

[0083] Further examples of suitable nonionic surfactants include, alkoxylated fatty acid alkyl esters,, alkylpolyglycosides, alkoxylated amines, ethoxylated glycerol esters, fatty acid monoethanolamides, fatty acid diethanolamides, ethoxylated fatty acid monoethanolamides, propoxylated fatty acid monoethanolamides, polyhydroxyalkyl fatty acid amides, or N-acyl N-alkyl derivatives of glucosamine, polysorbates (TWEENS). The formulation may contain soaps, and zwitterionic or cationic surfactants as minor components, preferably at levels from 0.1 to 3 wt%. Betaines such as CAPB are preferred zwitterionic surfactants.

[0084] Preferred non-ionic surfactant include the narrow range ethoxylates. Preferably, the detergent composition comprises an alcohol ethoxylate of formula R-O-(CH_2CH_2O)q-H where q is the mole average degree of ethoxylation, said alcohol ethoxylate comprising greater than 70 wt.% of the alcohol ethoxylate in the range R-O-$(CH_2CH_2O)_x$-H to R-O-$(CH_2CH_2O)_y$-H and x and y are absolute numbers, where x=q-q/2 and y=q+q/2, R is C12-15 alkyl.

[0085] Preferably, R is a straight or branched alkyl and preferably has from 12 to 14 carbon atoms. In the most preferred embodiments R is C12 and/or C14. Most preferably, greater than 50% of the total alcohol ethoxylate is C12 or C14.

[0086] Preferably q is 7, 8, 9, 10, 11, 12, 13 or 14 and mixtures thereof. More preferably, q is 8, 9, 10 or 11 and mixtures thereof, most preferably 9 and 10.

[0087] Alcohol ethoxylate non-ionic surfactant are discussed in Non-ionic Surfactants: Organic Chemistry edited by Nico M. van Os (Marcel Dekker 1998), Surfactant Science Series published by CRC press. Commonly used in laundry liquid compositions are C12-C15 alcohol ethoxylates having a straight or branched chain alkyl group having 12 to 15 carbon atoms and containing an average of 5 to 12EO units per molecule.

[0088] Preferably, the alcohol ethoxylate is present at from 1 to 35% wt., preferably 5 to 25wt% of the composition.

[0089] Typically, ethoxylation reactions to form alcohol ethoxylates are base catalysed using NaOH, KOH, or NaOCH3. The reaction produces a distribution of ethoxy chain lengths in the alcohol ethoxylate. Narrow range ethoxylation provides a narrower distribution of ethoxy chain lengths than NaOH, KOH, or NaOCH3. Preferably the narrow ethoxy distribution has greater than 70 wt.%, more preferably greater than 80 w.t% of the alcohol ethoxylate R-O-$(CH_2CH_2O)_q$-H in the range R-O-$(CH_2CH_2O)_x$-H to R-O-$(CH_2CH_2O)_y$-H where q is the mole average degree of ethoxylation and x and y are absolute numbers, where x = q-q/2 and y = q+q/2. For example when q=10, then greater than 70 wt.% of the alcohol ethoxylate should consist of ethoxylate with 5, 6, 7, 8, 9 10, 11, 12, 13, 14 and 15 ethoxylate groups.

[0090] Narrow range ethoxylation catalyst are described in EP3289790 (Procter & Gamble), EP1747183(Hacros); Santacesatia et al Ind. Eng. Chem. Res. 1992, 31, 2419-2421; US4239917(Conoco); Li et al ACS Omega. 2021 Nov 9; 6(44): 29774-29780; Hreczuch et al J. Am. Oil Chem. Soc. 1996, 73, 73-78 and WO2022/ 129374 (Unilever). Catalyst based on Ca or Ba are preferred, most preferably in combination with sulfuric acid. Preferred anionic surfactants are further described below.

C16/C18 Alcohol Ethoxylate

[0091] A preferred C16/18 alcohol ethoxylate is of the formula:

$$R_1\text{-}O\text{-}(CH_2CH_2O)_q\text{-}H$$

where R_1 is selected from saturated, monounsaturated and polyunsaturated linear C16 and C18 alkyl chains and where q is from 4 to 20, preferably 5 to 14, more preferably 8 to 12. The mono-unsaturation is preferably in the 9 position of the chain, where the carbons are counted from the ethoxylate bound chain end. The double bond may be in a cis or trans configuration (oleyl or elaidyl), preferably cis. The cis or trans alcohol ethoxylate $CH_3(CH_2)_7$-CH=CH-$(CH_2)_8O$-$(OCH_2CH_2)_n$OH, is described as C18:1(Δ9) alcohol ethoxylate. This follows the nomenclature *CX:Y*(ΔZ) where *X* is the number of carbons in the chain, Y is the number of double bonds and ΔZ the position of the double bond on the chain where the carbons are counted from the OH bound chain end.

[0092] Preferably, R1 is selected from saturated C16, saturated C18 and monounsaturated C18. More preferably, the saturated C16 alcohol ethoxylate is at least 90% wt. of the total C16 linear alcohol ethoxylate. As regards the C18 alcohol

ethoxylate content, it is preferred that the predominant C18 moiety is C18:1, more preferably C18:1(Δ9). The proportion of monounsaturated C18 alcohol ethoxylate constitutes at least 50% wt. of the total C16 and C18 alcohol ethoxylate surfactant. Preferably, the proportion of monounsaturated C18 constitutes at least 60% wt., most preferably at least 75 of the total C16 and C18 alcohol ethoxylate surfactant.

[0093] Preferably, the C16 alcohol ethoxylate surfactant comprises at least 2% wt. and more preferably, from 4% of the total C16 and C18 alcohol ethoxylate surfactant.

[0094] Preferably, the saturated C18 alcohol ethoxylate surfactant comprises up to 20% wt. and more preferably, up to 11% of the total C16 and C18 alcohol ethoxylate surfactant.

[0095] Preferably the saturated C18 content is at least 2% wt. of the total C16 and C18 alcohol ethoxylate content.

[0096] Alcohol ethoxylates are discussed in the Non-ionic Surfactants: Organic Chemistry edited by Nico M. van Os (Marcel Dekker 1998), Surfactant Science Series published by CRC press. Alcohol ethoxylates are commonly referred to as alkyl ethoxylates.

[0097] Preferably the weight fraction of C18 alcohol ethoxylate / C16 alcohol ethoxylate is greater than 1, more preferably from 2 to 100, most preferably 3 to 30. 'C18 alcohol ethoxylate' is the sum of all the C18 fractions in the alcohol ethoxylate and 'C16 alcohol ethoxylate' is the sum of all the C16 fractions in the alcohol ethoxylate.

[0098] Linear saturated or mono-unsaturated C20 and C22 alcohol ethoxylate may also be present. Preferably the weight fraction of sum of 'C18 alcohol ethoxylate' /'C20 and C22 alcohol ethoxylate' is greater than 10.

[0099] Preferably the C16/18 alcohol ethoxylate contains less than 15wt%, more preferably less than 8wt%, most preferably less than 5wt% of the alcohol ethoxylate polyunsaturated alcohol ethoxylates. A polyunsaturated alcohol ethoxylate contains a hydrocarbon chains with two or more double bonds.

[0100] C16/18 alcohol ethoxylates may be synthesised by ethoxylation of an alkyl alcohol, via the reaction:

$$R_1\text{-OH} + q \text{ ethylene oxide} \rightarrow R_1\text{-O-}(CH_2CH_2O)_q\text{-H}$$

[0101] The alkyl alcohol may be produced by transesterification of the triglyceride to a methyl ester, followed by distillation and hydrogenation to the alcohol. The process is discussed in Journal of the American Oil Chemists' Society. 61 (2): 343-348 by Kreutzer, U. R. Preferred alkyl alcohol for the reaction is oleyl alcohol with in an iodine value of 60 to 80, preferably 70 to 75, such alcohol are available from BASF, Cognis, Ecogreen.

[0102] Production of the fatty alcohol is futher discussed in Sanchez M.A. et al J.Chem.Technol.Biotechnol 2017; 92:27-92 and and Ullmann's Enzyclopaedie der technischen Chemie, Verlag Chemie, Weinheim, 4th Edition, Vol. 11, pages 436 et seq. Preferably the ethoxylation reactions are base catalysed using NaOH, KOH, or $NaOCH_3$. Even more preferred are catalyst which provide narrower ethoxy distribution than NaOH, KOH, or $NaOCH_3$. Preferably these narrower distribution catalysts involve a Group II base such as Ba dodecanoate; Group II metal alkoxides; Group II hyrodrotalcite as described in WO2007/147866. Lanthanides may also be used. Such narrower distribution alcohol ethoxylates are available from Azo Nobel and Sasol.

[0103] Preferably the narrow ethoxy distribution has greater than 70 wt.%, more preferably greater than 80 w.t% of the alcohol ethoxylate R-O-(CH_2CH_2O)q-H in the range R-O-$(CH_zCH_zO)_x$-H to R-O-$(CH_2CH_2O)_y$-H where q is the mole average degree of ethoxylation and x and y are absolute numbers, where x = q-q/2 and y = q+q/2. For example when q=10, then greater than 70 wt.% of the alcohol ethoxylate should consist of ethoxylate with 5, 6, 7, 8, 9 10, 11, 12, 13, 14 and 15 ethoxylate groups.

C16 and/or C18 Alcohol ether sulfates

[0104] A preferred ether sulfate is of the formula:

$$R_2\text{-O-}(CH_2CH_2O)_pSO_3H$$

[0105] Where R_2 is selected from saturated, monounsaturated and polyunsaturated linear C16 and C18 alkyl chains and where p is from 3 to 20, preferably 4 to 12, more preferably 5 to 10. The mono-unsaturation is preferably in the 9 position of the chain, where the carbons are counted from the ethoxylate bound chain end. The double bond may be in a cis or trans configuration (oleyl or elaidyl), but is preferably cis. The cis or trans ether sulfate $CH_3(CH_2)_7$-CH=CH-$(CH_2)_8$O-$(CH_2CH_2O)_nSO_3H$, is described as C18:1(Δ9) ether sulfate. This follows the nomenclature CX:Y(ΔZ) where X is the number of carbons in the chain, *Y* is the number of double bonds and ΔZ the position of the double bond on the chain where the carbons are counted from the OH bound chain end.

[0106] Preferably, R2 is selected from saturated C16, saturated C18 and monounsaturated C18. More preferably, the saturated C16 is at least 90% wt. of the C16 content linear alkyl. As regards the C18 content, it is preferred that the predominant C18 moiety is C18:1, more preferably C18:1(Δ9). Preferably, the proportion of monounsaturated C18 constitutes at least 50% wt. of the total C16 and C18 alkyl ether sulphate surfactant.

[0107] More preferably, the proportion of monounsaturated C18 constitutes at least 60% wt., most preferably at least 75 of the total C16 and C18 alkyl ether sulphate surfactant. Preferably, the C16 alcohol ethoxylate surfactant comprises at least 2% wt. and more preferably, from 4% of the total C16 and C18 alkyl ether sulphate surfactant.

[0108] Preferably, the saturated C18 alkyl ether sulphate surfactant comprises up to 20% wt. and more preferably, up to11% of the total C16 and C18 alkyl ether sulphate surfactant.

[0109] Preferably the saturated C18 content is at least 2% wt. of the total C16 and C18 alkyl ether sulphate content.

[0110] Where the composition comprises a mixture of the C16/18 sourced material for the alkyl ether sulphate as well as the more traditional C12 alkyl chain length materials it is preferred that the total C16/18 alkyl ether sulphate content should comprise at least 10% wt. of the total alkyl ether sulphate, more preferably at least 50%, even more preferably at least 70%, especially preferably at least 90% and most preferably at least 95% of alkyl ether sulphate in the composition.

[0111] Ether sulfates are discussed in the Anionic Surfactants: Organic Chemistry edited by Helmut W. Stache (Marcel Dekker 1995), Surfactant Science Series published by CRC press.

[0112] Linear saturated or mono-unsaturated C20 and C22 ether sulfate may also be present.

[0113] Preferably the weight fraction of sum of 'C18 ether sulfate' / 'C20 and C22 ether sulfate' is greater than 10.

[0114] Preferably the C16 and C18 ether sulfate contains less than 15 wt.%, more preferably less than 8 wt.%, most preferably less than 4wt% and most preferably less than 2% wt. of the ether sulfate polyunsaturated ether sulfate. A polyunsaturated ether sulfate contains a hydrocarbon chains with two or more double bonds.

[0115] Ether sulfate may be synthesised by the sulphonation of the corresponding alcohol ethoxylate. The alcohol ethoxylate may be produced by ethoxylation of an alkyl alcohol. The alkyl alcohol used to produced the alcohol ethoxylate may be produced by transesterification of the triglyceride to a methyl ester, followed by distillation and hydrogenation to the alcohol. The process is discussed in Journal of the American Oil Chemists' Society. 61 (2): 343-348 by Kreutzer, U. R. Preferred alkyl alcohol for the reaction is oleyl alcohol with an iodine value of 60 to 80, preferably 70 to 75, such alcohol are available from BASF, Cognis, Ecogreen.

[0116] The degree of polyunsaturation in the surfactant may be controlled by hydrogenation of the triglyceride as described in: A Practical Guide to Vegetable Oil Processing (Gupta M.K. Academic Press 2017). Distillation and other purification techniques may be used. Ethoxylation reactions are described in Non-ionic Surfactant Organic Chemistry (N. M. van Os ed), Surfactant Science Series Volume 72, CRC Press.

[0117] Preferably the ethoxylation reactions are base catalysed using NaOH, KOH, or $NaOCH_3$. Even more preferred are catalyst which provide narrower ethoxy distribution than NaOH, KOH, or $NaOCH_3$. Preferably these narrower distribution catalysts involve a Group II base such as Ba dodecanoate; Group II metal alkoxides; Group II hyrodrotalcite as described in WO2007/147866. Lanthanides may also be used. Such narrower distribution alcohol ethoxylates are available from Azo Nobel and Sasol.

[0118] Preferably the narrow ethoxy distribution has greater than 70 wt.%, more preferably greater than 80 w.t% of the ether sulfate R_2-O-$(CH_2CH_2O)_pSO_3H$ in the range R_2-O-$(CH_2CH_2O)_zSO_3H$ to R_2-O-$(CH_2CH_2O)_wSO_3H$ where q is the mole average degree of ethoxylation and x and y are absolute numbers, where z = p-p/2 and w = p+p/2. For example when p=6, then greater than 70 wt.% of the ether sulfate should consist of ether sulfate with 3, 4, 5, 6, 7, 8, 9 ethoxylate groups.

[0119] The ether sulfate weight is calculated as the protonated form: R_2-O-$(CH_2CH_2O)_pSO_3H$. In the formulation it will be present as the ionic form R_2-O-$(CH_2CH_2O)_pSO_3^-$ with a corresponding counter ion, preferred counter ions are group I and II metals, amines, most preferably sodium.

Methyl Ester Ethoxylate (MEE)

[0120] A preferred methyl ester ethoxylate surfactant is of the form:

$$R_3(-C=O)-O-(CH_2CH_2-O)_n-CH_3$$

[0121] Where R_3COO is a fatty acid moiety, such as oleic, stearic, palmitic. Fatty acid nomenclature is to describe the fatty acid by 2 numbers A:B where A is the number of carbons in the fatty acid and B is the number of double bonds it contains. For example oleic is 18:1, stearic is 18:0 and palmitic 16:0. The position of the double bond on the chain may be given in brackets, 18:1(9) for oleic, 18:2 (9,12) for linoleic where 9 if the number of carbons from the COOH end.

[0122] The integer n is the mole average number of ethoxylates.

[0123] Methyl Ester Ethoxylates (MEE) are described in chapter 8 of Biobased Surfactants (Second Edition) Synthesis, Properties, and Applications Pages 287-301 (AOCS press 2019) by G.A. Smith; J.Am.Oil. Chem.Soc. vol 74 (1997) page 847-859 by Cox M.E. and Weerasooriva U; Tenside Surf.Det. vol 28 (2001) page by 72-80 by Hreczuch et al; by C. Kolano. Household and Personal Care Today (2012) page 52-55; J.Am.Oil. Chem.Soc. vol 72 (1995) page 781-784 by A.Hama *et al*. MEE may be produced the reaction of methyl ester with ethylene oxide, using catalysts based on calcium or magnesium. The catalyst may be removed or left in the MEE.

[0124] An alternative route to preparation is transesterification reaction of a methyl ester or esterification reaction of a

carboxylic acid with a polyethylene glycol that is methyl terminated at one end of the chain.

[0125] The methyl ester may be produced by transesterification reaction of methanol with a triglyceride, or esterification reaction of methanol with a fatty acid. Transesterification reactions of a triglyceride to fatty acid methyl esters and glycerol are discussed in Fattah et al (Front. Energy Res., June 2020, volume 8 article 101) and references therein.

[0126] Common catalysts for these reactions include sodium hydroxide, potassium hydroxide, and sodium methoxide. Esterase and lipases enzyme may also be used. Triglycerides occur naturally in plant fats or oils, preferred sources are rapeseed oil, castor oil, maize oil, cottonseed oil, olive oil, palm oil, safflower oil, sesame oil, soybean oil, high steric/high oleic sunflower oil, high oleic sunflower oil, non-edible vegetable oils, tall oil and any mixture thereof and any derivative thereof. The oil from trees is called tall oil. Used food cooking oils may be utilised. Triglycerides may also be obtained from algae, fungi, yeast or bacteria. Plant sources are preferred.

[0127] Distillation and fractionation process may be used in the production of the methyl ester or carboxylic acid to produce the desired carbon chain distribution. Preferred sources of triglyceride are those which contain less than 35%wt polyunsaturated fatty acids in the oil before distillation, fractionation, or hydrogenation.

[0128] Fatty acid and methyl ester may be obtained from Oleochemical suppliers such as Wilmar, KLK Oleo, Unilever oleochemical Indonesia. Biodiesel is methyl ester and these sources may be used.

[0129] When ESB is MEE preferably has a mole average of from 8 to 30 ethoxylate groups (EO), more preferably from 10 to 20. The most preferred ethoxylate comprises 12 to 18EO. Preferably, at least 10% wt., more preferably at least 30% wt. of the total C18:1 MEE in the composition has from 9 to 11EO, even more preferably at least 10wt% is exactly 10EO. For example when the MEE has a mole average of 10EO then at least 10 wt.% of the MEE should consist of ethoxylate with 9, 10 and 11 ethoxylate groups.

[0130] The methyl ester ethoxylate preferably has a mole average of from 8 to 13 ethoxylate groups (EO). The most preferred ethoxylate has a mol average of from 9 to 11EO, even more preferably 10EO. When the MEE has a mole average of 10EO then at least 10 wt.% of the MEE should consist of ethoxylate with 9, 10 and 11 ethoxylate groups.

[0131] In the context of the wider MEE contribution, it is preferred that at least 40wt% of the total MEE in the composition is C18:1.

[0132] In addition, it is preferred that the MEE component also comprises some C16 MEE.

[0133] Accordingly, it is preferred that the total MEE component comprises from 5 to 50% wt. total MEE, C16 MEE. Preferably the C16 MEE is greater than 90wt%, more preferably greater than 95wt% C16:0.

[0134] Further, it is preferred that the total MEE component comprises less than 15% wt, more preferably less than 10wt%, most preferably less than 5wt% total MEE of polyunsaturated C18, i.e. C18:2 and C18:3. Preferably C18:3 is present at less than 1 wt%, more preferably less than 0.5wt%, most preferably essentially absent. The levels of polyunsaturation may be controlled by distillation, fractionation or partial hydrogenation of the raw materials (triglyceride or methyl ester) or of the MEE.

[0135] Further, it is preferred that the C18:0 component is less than 10wt% by weight of the total MEE present.

[0136] Further, it is preferred that the components with carbon chains of 15 or shorter comprise less than 4wt% by weight of the total MEE present.

[0137] A particularly preferred MEE has 2 to 26 wt.% of the MEE C16:0 chains, 1 to 10 wt.% C18:0 chains, 50 to 85 wt.% C18:1 chains and 1 to 12 wt.% C18:2 chains.

[0138] Preferred sources for the alkyl groups for the MEE include methyl ester derived from distilled palm oil and distilled high oleic methyl ester derived from palm kernel oil, partially hydrogenated methyl ester of low euric rapeseed oil, methyl ester of high oleic sunflower oil, methyl ester of high oleic safflower oil and methyl ester of high oleic soybean oil. High Oleic oils are available from DuPont (Plenish high oleice soybean oil), Monsanto (Visitive Gold Soybean oil), Dow (Omega-9 Canola oil, Omega-9 sunflower oil), the National Sunflower Association and Oilseeds International.

[0139] Preferably the double bonds in the MEE are greater than 80wt% in the cis configuration. Preferably the 18:1 component is oleic. Preferably the 18:2 component is linoleic.

[0140] The methyl group of the methyl ester may be replace by an ethyl or propyl group. Methyl is most preferred.

[0141] Preferably, the methyl ester ethoxylate comprises from 0.1 to 95% wt. of the composition methyl ester ethoxylate. More preferably the composition comprises from 2 to 40% MEE and most preferably from 4 to 30% wt. MEE.

[0142] Preferably, the composition comprises at least 50% wt. water but this depends on the level of total surfactant and is adjusted accordingly.

[0143] Preferably the methyl ester ethoxylate surfactant is used in combination with anionic surfactant. Preferably the weight fraction of methyl ester ethoxylate surfactant/total anionic surfactant is from 0.1 to 9, more preferably 0.15 to 2, most preferably 0.2 to 1. By total anionic surfactant means the total content of any of the classes of anionic surfactant preferably ether sulfates, linear alkyl benzene sulfonates, alkyl ether carboxylates, alkyl sulfates, rhamnolipids and mixtures thereof.

[0144] Anionic surfactant weights are calculated as the protonated form.

Source of alkyl chains

[0145] The alkyl chain of C16/18 surfactant is preferably obtained from a renewable source, preferably from a triglyceride. A renewable source is one where the material is produced by natural ecological cycle of a living species, preferably by a plant, algae, fungi, yeast or bacteria, more preferably plants, algae or yeasts.

[0146] Preferred plant sources of oils are rapeseed, sunflower, maze, soy, cottonseed, olive oil and trees. The oil from trees is called tall oil. Most preferably Palm and Rapeseed oils are the source.

[0147] Algal oils are discussed in Energies 2019, 12, 1920 *Algal Biofuels: Current Status and Key Challenges* by Saad M.G. et al. A process for the production of triglycerides from biomass using yeasts is described in Energy Environ. Sci., 2019,12, 2717 *A sustainable, high-performance process for the economic production of waste-free microbial oils that can replace plant-based equivalents* by Masri M.A. et al.

[0148] Non edible plant oils may be used and are preferably selected from the fruit and seeds of Jatropha curcas, Calophyllum inophyllum, Sterculia feotida, Madhuca indica (mahua), Pongamia glabra (koroch seed), Linseed, Pongamia pinnata (karanja), Hevea brasiliensis (Rubber seed), Azadirachta indica (neem), Camelina sativa, Lesquerella fendleri, Nicotiana tabacum (tobacco), Deccan hemp, Ricinus communis L.(castor), Simmondsia chinensis (Jojoba), Eruca sativa. L., Cerbera odollam (Sea mango), Coriander (Coriandrum sativum L.), Croton megalocarpus, Pilu, Crambe, syringa, Scheleichera triguga (kusum), Stillingia, Shorea robusta (sal), Terminalia belerica roxb, Cuphea, Camellia, Champaca, Simarouba glauca, Garcinia indica, Rice bran, Hingan (balanites), Desert date, Cardoon, Asclepias syriaca (Milkweed), Guizotia abyssinica, Radish Ethiopian mustard, Syagrus, Tung, Idesia polycarpa var. vestita, Alagae, Argemone mexicana L. (Mexican prickly poppy, Putranjiva roxburghii (Lucky bean tree), Sapindus mukorossi (Soapnut), M. azedarach (syringe),Thevettia peruviana (yellow oleander), Copaiba, Milk bush, Laurel, Cumaru, Andiroba, Piqui, B. napus, Zanthoxylum bungeanum.

SLES and PAS

[0149] SLES and other such alkali metal alkyl ether sulphate anionic surfactants are typically obtainable by sulphating alcohol ethoxylates. These alcohol ethoxylates are typically obtainable by ethoxylating linear alcohols. Similarly, primary alkyl sulphate surfactants (PAS) can be obtained from linear alcohols directly by sulphating the linear alcohol. Accordingly, forming the linear alcohol is a central step in obtaining both PAS and alkalimetal alkyl ether sulphate surfactants.

[0150] The linear alcohols which are suitable as an intermediate step in the manufacture of alcohol ethoxylates and therefore anionic surfactants such as sodium lauryl ether sulphate ca be obtained from many different sustainable sources. These include:

Primary sugars

[0151] Primary sugars are obtained from cane sugar or sugar beet, etc., and may be fermented to form bioethanol. The bioethanol is then dehydrated to form bio-ethylene which then undergoes olefin methathesis to form alkenes. These alkenes are then processed into linear alcohols either by hydroformylation or oxidation.

[0152] An alternative process also using primary sugars to form linear alcohols can be used and where the primary sugar undergoes microbial conversion by algae to form triglycerides. These triglycerides are then hydrolysed to linear fatty acids and which are then reduced to form the linear alcohols.

Biomass

[0153] Biomass, for example forestry products, rice husks and straw to name a few may be processed into syngas by gasification. Through a *Fischer Tropsch* reaction these are processed into alkanes, which in turn are dehydrogenated to form olefins. These olefins may be processed in the same manner as the alkenes described above [primary sugars]. An alternative process turns the same biomass into polysaccharides by steam explosion which may be enzymatically degraded into secondary sugars. These secondary sugars are then fermented to form bioethanol which in turn is dehydrated to form bio-ethylene. This bio-ethylene is then processed into linear alcohols as described above [primary sugars].

Waste Plastics

[0154] Waste plastic is pyrolyzed to form pyrolysed oils. This is then fractioned to form linear alkanes which are dehydrogenated to form alkenes. These alkenes are processed as described above [primary sugars].

[0155] Alternatively, the pyrolyzed oils are cracked to form ethylene which is then processed to form the required alkenes by olefin metathesis. These are then processed into linear alcohols as described above [primary sugars].

Municipal Solid Waste

[0156] MSW is turned into syngas by gasification. From syngas it may be processed as described above [primary sugars] or it may be turned into ethanol by enzymatic processes before being dehydrogenated into ethylene. The ethylene may then be turned into linear alcohols by the *Ziegler Process.*

[0157] The MSW may also be turned into pyrolysis oil by gasification and then fractioned to form alkanes. These alkanes are then dehydrogenated to form olefins and then linear alcohols.

Marine Carbon

[0158] There are various carbon sources from marine flora such as seaweed and kelp. From such marine flora the triglycerides can be separated from the source and which is then hydrolysed to form the fatty acids which are reduced to linear alcohols in the usual manner.

[0159] Alternatively, the raw material can be separated into polysaccharides which are enzymatically degraded to form secondary sugars. These may be fermented to form bioethanol and then processed as described above [Primary Sugars].

Waste Oils

[0160] Waste oils such as used cooking oil can be physically separated into the triglycerides which are split to form linear fatty acids and then linear alcohols as described above. Alternatively, the used cooking oil may be subjected to the Neste Process whereby the oil is catalytically cracked to form bio-ethylene. This is then processed as described above.

Methane Capture

[0161] Methane capture methods capture methane from landfill sites or from fossil fuel production. The methane may be formed into syngas by gasification. The syngas may be processed as described above whereby the syngas is turned into methanol (*Fischer Tropsch* reaction) and then olefins before being turned into linear alcohols by hydroformylation oxidation.

[0162] Alternatively, the syngas may be turned into alkanes and then olefins by *Fischer Tropsch* and then dehydrogenation.

Carbon Capture

[0163] Carbon dioxide may be captured by any of a variety of processes which are all well known. The carbon dioxide may be turned into carbon monoxide by a reverse water gas shift reaction and which in turn may be turned into syngas using hydrogen gas in an electrolytic reaction. The syngas is then processed as described above and is either turned into methanol and/or alkanes before being reacted to form olefins.

[0164] Alternatively, the captured carbon dioxide is mixed with hydrogen gas before being enzymatically processed to form ethanol. This is a process which has been developed by Lanzatech. From here the ethanol is turned into ethylene and then processed into olefins and then linear alcohols as described above.

[0165] The above processes may also be used to obtain the C16/18 chains of the C16/18 alcohol ethoxylate and/or the C16/18 ether sulfates.

Linear Alkyl Benzene Sulfonate

[0166] LAS (linear alkyl benzene sulphonate) is a preferred anionic surfactant.

[0167] The key intermediate compound in the manufacture of LAS is the relevant alkene. These alkenes (olefins) may be produced by any of the methods described above and may be formed from primary sugars, biomass, waste plastic, MSW, carbon capture, methane capture, marine carbon to name a few.

[0168] Whereas in the processed described above the olefin is processed to form linear alcohols by hydroformylation and oxidation instead, the olefin is reacted with benzene and then sulphonate to form the LAS.

[0169] Linear alkylbenzene sulfonates with an alkyl chain length of from 10 to 18 carbon atoms. Commercial LAS is a mixture of closely related isomers and homologues alkyl chain homologues, each containing an aromatic ring sulfonated at the *"para"* position and attached to a linear alkyl chain at any position except the terminal carbons. The linear alkyl chain preferably has a chain length of from 11 to 15 carbon atoms, with the predominant materials having a chain length of about C12. Each alkyl chain homologue consists of a mixture of all the possible sulfophenyl isomers except for the 1-phenyl isomer. LAS is normally formulated into compositions in acid (i.e. HLAS) form and then at least partially neutralized in-situ. Preferably, linear alkyl benzene sulphonate surfactant is present at from 1 to 20% wt., more preferably from 2 to 15% wt. of

the composition, most preferably 8 to 12 wt.%.

AMINOCARBOXYLATE

[0170] Preferably, the liquid composition comprises an aminocarboxylate sequestrant. Preferably the aminocarboxylate sequestrant is selected from GLDA and MGDA.

[0171] Preferably the aminocarboxylate is present in the composition at from 0.1 to 15%wt., more preferably 0.1 to 10% wt., even more preferably 0.3 to 5 % wt., still more preferably 0.8 to 3% wt., and most preferably 1 to 2.5 % wt. (by weight of the composition).

Glutamic Acid Diacetic acid (GLDA)

[0172] GLDA may be present as a salt or a mixture of GDLA and a GDLA salt. Preferred salt forms include mono-, di-, tri- or tetraalkali metal and mono-, di-, tri- or tetraammonium salts of GLDA. Alkali metal salts of glutamic acid diacetic acid GDLA are preferably selected from lithium salts, potassium salts and more preferably sodium salts of GLDA.

[0173] Glutamic acid diacetic acid can be partially or preferably fully neutralized with the respective alkali. Preferably, an average of from 3.5 to 4 COOH groups of GLDA is neutralized with alkali metal, preferably with sodium. Most preferably the composition comprises a tetrasodium salt of GLDA.

[0174] GLDA is at least partially neutralized with alkali metal, more preferably with sodium or potassium, most preferred with sodium.

[0175] The GLDA salt may be an alkali metal salt of L-GLDA, an alkali metal salt of D-GLDA, or enantiomerically enriched mixtures of isomers.

[0176] Preferably the composition comprises a mixture of L- and D- enantiomers of glutamic acid diacetic acid (GLDA) or its respective mono-, di-, tri-, or tetraalkali metal or mono-, di-, tri- or tetraammonium salt or mixtures thereof, said mixtures containing predominantly the respective L-isomer with an enantiomeric excess in the range of from 10 to 95%. Preferably the GLDA salt is essentially L-glutamic acid diacetic acid that is at least partially neutralized with alkali metal.

[0177] Sodium salts of GLDA are preferred.

[0178] A suitable commercial source of GLDA in the form of the tetrasodium salt is DISSOLVINE® GL available from Nouryon.

[0179] Preferably the GLDA is present in the composition at from 0.1 to 15% wt., more preferably 0.1 to 10% wt., even more preferably 0.3 to 5 % wt., still more preferably 0.8 to 3% wt., and most preferably 1 to 2.5 % wt. (by weight of the composition).

Methyl glycine diacetic acid (MGDA)

[0180] Preferred salt forms include mono-, di-, tri- or tetraalkali metal and mono-, di-, tri- or tetraammonium salts of MGDA. Alkali metal salts are preferably selected from lithium salts, potassium salts and more preferably sodium salts of MGDA.

[0181] The sodium salt of methyl glycine diacetic acid is preferred. Especially preferred is the trisodium salt of MGDA.

[0182] MGDA can be partially or preferably fully neutralized with the respective alkali metal. Preferably, an average of from 2.7 to 3 COOH groups per molecule of MGDA is neutralized with alkali metal, preferably with sodium.

[0183] MGDA can be selected from racemic mixtures of alkali metal salts of MGDA and of the pure enantiomers such as alkali metal salts of L-MGDA, alkali metal salts of D-MGDA and of mixtures of enantiomerically enriched isomers.

[0184] Suitable commercial sources of MGDA in the form of the trisodium salt are TRILONO M available from BASF and Dissolvine® M-40 from Nouryon.

[0185] Preferably the MGDA is present in the composition at from 0.1 to 15%wt., more preferably 0.1 to 10% wt., even more preferably 0.3 to 5 % wt., still more preferably 0.8 to 3% wt., and most preferably 1 to 2.5 % wt. (by weight of the composition).

[0186] Minor amounts of the aminocarboxylate may bear a cation other than alkali metal. It is thus possible that minor amounts, such as 0.01 to 5 mol-% bear alkali earth metal cations such as Mg^{2+} or Ca^{2+}, or an Fe(II) or Fe(III) cation. GLDA may contain minor amounts of impurities stemming from its synthesis, such as lactic acid, alanine, propionic acid or the like. "Minor amounts" in this context refer to a total of 0.1 to l% by weight, referring to sequestering agent aminocarboxylate.

ORGANIC ACID

[0187] The liquid composition preferably comprises an organic acid. Preferably, the organic acid has the general structure R-CH(OH)-COOH where R is a linear C1-C5, more preferably C2-C4, most preferably C4 alky group.

[0188] Preferably at least two, more preferably all carbon atoms in the linear C1-4 are substituted with an OH group.

Preferably R comprises a terminal COOH group. Preferred examples are lactic acid, tartaric acid, gluconic acid, mucic acid, glucoheptonic acid. Most preferably the organic acid is gluconic acid.

[0189] The organic acid may be in their D or L form.

[0190] Gluconic acid can be selected from racemic mixtures of salts of gluconic acid (gluconates) and of the pure enantiomers such as alkali metal salts of L-gluconic acid, alkali metal salts of D-gluconic acid and of mixtures of enantiomerically enriched isomers. D-isomeric forms are preferred.

[0191] Preferably the organic acid is present in the range of from 0.1 to 15%wt, more preferably 0.1 to 10wt%, even more preferably 0.2 to 4%wt, still more preferably 0.5 to 3 %wt., and most preferably 0.8 to 2%wt (by weight of the composition). Measured with regard to its protonated form.

[0192] In a most preferred embodiment, the composition comprises GLDA and/or MGDA and gluconic acid, more preferably GLDA and gluconic acid.

CRYSTALLIZABLE GLYCERIDE

[0193] The liquid composition preferably comprises a crystallizable glyceride.

[0194] The crystallizable glyceride is useful in forming an external structuring system as described in WO2011/031940, the contents of which, in particular as regards manufacture of the ESS are incorporated by reference. Where an ESS is present it is preferred that the ESS of the present invention preferably comprises: (a) crystallizable glyceride(s); (b) alkanolamine; (c) anionic surfactant; (d) additional components; and (e) optional components. Each of these components is discussed in detail below.

[0195] Crystallizable glyceride(s) of use herein preferably include "Hydrogenated castor oil" or "HCO". HCO as used herein most generally can be any hydrogenated castor oil, provided that it is capable of crystallizing in the ESS premix. Castor oils may include glycerides, especially triglycerides, comprising C10 to C22 alkyl or alkenyl moieties which incorporate a hydroxyl group. Hydrogenation of castor oil to make HCO converts double bonds, which may be present in the starting oil as ricinoleyl moieties, to convert ricinoleyl moieties to saturated hydroxyalkyl moieties, e.g., hydroxystearyl. The HCO herein may, in some embodiments, be selected from: trihydroxystearin; dihydroxystearin; and mixtures thereof. The HCO may be processed in any suitable starting form, including, but not limited those selected from solid, molten and mixtures thereof. HCO is typically present in the ESS of the present invention at a level of from about 2 percent to about 10 percent, from about 3 percent to about 8 percent, or from about 4 percent to about 6 percent by weight of the structuring system. In some embodiments, the corresponding percentage of hydrogenated castor oil delivered into a finished laundry detergent product is below about 1.0 percent, typically from 0.1 percent to 0.8 percent.

[0196] Useful HCO may have the following characteristics: a melting point of from about 40 degrees centigrade to about 100 degrees centigrade, or from about 65 degrees centigrade to about 95 degrees C; and/or Iodine value ranges of from 0 to about 5, from 0 to about 4, or from 0 to about 2.6. The melting point of HCO can measured using either ASTM D3418 or ISO 11357; both tests utilize DSC: Differential Scanning Calorimetry. HCO of use in the present invention includes those that are commercially available. Non-limiting examples of commercially available HCO of use in the present invention include: THIXCIN(R) from Rheox, Inc. Further examples of useful HCO may be found in U.S. Patent 5,340,390. The source of the castor oil for hydrogenation to form HCO can be of any suitable origin, such as from Brazil or India. In one suitable embodiment, castor oil is hydrogenated using a precious metal, e.g., palladium catalyst, and the hydrogenation temperature and pressure are controlled to optimize hydrogenation of the double bonds of the native castor oil while avoiding unacceptable levels of dehydroxylation.

[0197] The invention is not intended to be directed only to the use of hydrogenated castor oil. Any other suitable crystallizable glyceride(s) may be used. In one example, the structurant is substantially pure triglyceride of 12-hydroxystearic acid. This molecule represents the pure form of a fully hydrogenated triglyceride of 12-hydrox-9-cis-octadecenoic acid. In nature, the composition of castor oil is rather constant, but may vary somewhat. Likewise hydrogenation procedures may vary. Any other suitable equivalent materials, such as mixtures of triglycerides wherein at least 80 percent wt. is from castor oil, may be used. Exemplary equivalent materials comprise primarily, or consist essentially of, triglycerides; or comprise primarily, or consist essentially of, mixtures of diglycerides and triglycerides; or comprise primarily, or consist essentially of, mixtures of triglyerides with diglycerides and limited amounts, e.g., less than about 20 percent wt. of the glyceride mixtures, of monoglyerides; or comprise primarily, or consist essentially of, any of the foregoing glycerides with limited amounts, e.g., less than about 20 percent wt., of the corresponding acid hydrolysis product of any of said glycerides. A proviso in the above is that the major proportion, typically at least 80 percent wt, of any of said glycerides is chemically identical to glyceride of fully hydrogenated ricinoleic acid, i.e., glyceride of 12- hydroxystearic acid. It is for example well known in the art to modify hydrogenated castor oil such that in a given triglyceride, there will be two 12-hydroxystearic- moieties and one stearic moiety. Likewise it is envisioned that the hydrogenated castor oil may not be fully hydrogenated. In contrast, the invention excludes poly(oxyalkylated) castor oils when these fail the melting criteria.

[0198] Crystallizable glyceride(s) of use in the present invention may have a melting point of from about 40 degrees centigrade to about 100 degrees centigrade.

Fatty Acid

[0199] Preferably, fatty acid is present at from 4 to 20% wt. of the composition (as measured with reference to the acid added to the composition), more preferably from 5 to 12% wt. and most preferably 6 to 8% wt.

[0200] Suitable fatty acids in the context of this invention include aliphatic carboxylic acids of formula RCOOH, where R is a linear or branched alkyl or alkenyl chain containing from 6 to 24, more preferably 10 to 22, most preferably from 12 to 18 carbon atoms and 0 or 1 double bond. Preferred examples of such materials include saturated C12-18 fatty acids such as lauric acid, myristic acid, palmitic acid or stearic acid; and fatty acid mixtures in which 50 to 100% (by weight based on the total weight of the mixture) consists of saturated C12-18 fatty acids. Such mixtures may typically be derived from natural fats and/or optionally hydrogenated natural oils (such as coconut oil, palm kernel oil or tallow).

[0201] The fatty acids may be present in the form of their sodium, potassium or ammonium salts and/or in the form of soluble salts of organic bases, such as mono-, di- or triethanolamine.

[0202] Mixtures of any of the above described materials may also be used.

[0203] For formula accounting purposes, in the formulation, fatty acids and/or their salts (as defined above) are not included in the level of surfactant or in the level of builder.

SEQUESTRANT

[0204] The liquid detergent compositions may also preferably comprise a sequestrant material. Examples include the alkali metal citrates, succinates, malonates, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other examples are DEQUEST™, organic phosphonate type sequestering agents sold by Monsanto and alkanehydroxy phosphonates.

[0205] A preferred sequestrant is Dequest(R) 2066 (Diethylenetriamine penta(methylene phosphonic acid or Hepta-sodium DTPMP). HEDP (1 -Hydroxyethylidene -1,1,-diphosphonic acid), is preferably not present.

[0206] In a preferred embodiment the composition comprises fatty acid and sequestrant.

[0207] The composition according to the invention is a low aqueous composition. Preferably, the composition comprises less than 15% wt. water, more preferably less than 10% wt. water.

ALKOXYLATED CATIONIC OR ZWITTERIONIC POLYAMINE POLYMER

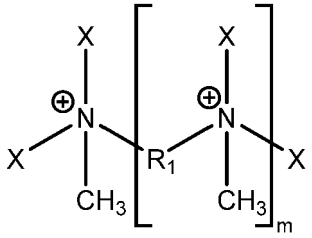
[0208] Preferably, the composition comprises an alkoxylated cationic or zwitterionic di or polyamine polymer, wherein the positive charge is provided by quaternisation of the nitrogen atoms of the amines, and the anionic groups (where present) by sulphation or sulphonation of the alkoxylated group.

[0209] Preferably the alkoxylate is selected from propoxy and ethoxy, most preferably ethoxy.

[0210] Preferably greater than or equal to 50 mol% of nitrogen amines are quaternised, preferably with a methyl group. Preferably the polymer contains 3 to 10, more preferably 3 to 6, most preferably 3 to 5 quaternised nitrogen amines. Preferably the alkoxylate groups are selected from ethoxy and propoxy groups, most preferably ethoxy.

[0211] Preferably the polymer contains ester (COO) or acid amide (CONH) groups within the structure, preferably these groups are placed, so that when all the ester or acid amide groups are hydrolysed, at least one, preferably all of the hydrolysed fragments has a molecular weight of less than 4000, preferably less than 2000, most preferably less than 1000.

[0212] Preferably the polymer is of the form:

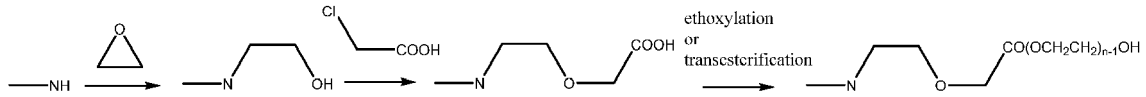


[0213] Where R_1 is a C3 to C8 alkyl group, X is an a (C2H4O)nY group where n is from 15 to 30, where m is from 2 to 10, preferably 2, 3, 4 or 5 and where Y is selected from OH and SO_3^- and preferably the number of SO_3^- groups is greater than the number of OH groups. Preferably there are from 0, 1 or 2 OH groups. X and R_1 may contain ester groups within them. X may contain a carbonyl group, preferably an ester group. There is preferably 1 C_2H_4O unit separating the ester group from the N, such that the structural unit N- C_2H_4O-ester- $(C_2H_4O)_{n-1}Y$ is preferred.

[0214] Such polymers are described in WO2021239547 (Unilever), An example polymer is sulphated ethoxylated

hexamethylene diamine and examples P1, P2, P3, P4, P5 and P6 of WO2021239547. Ester groups may be included using lactones or sodium chloroacetate (Modified Williamson synthesis), addition to an OH or NH group, then subsequent ethoxylation.

[0215] An example reaction scheme for inclusion of an ester group is



[0216] Addition of lactones is discussed in WO2021/165468.

SOIL RELEASE POLYMERS

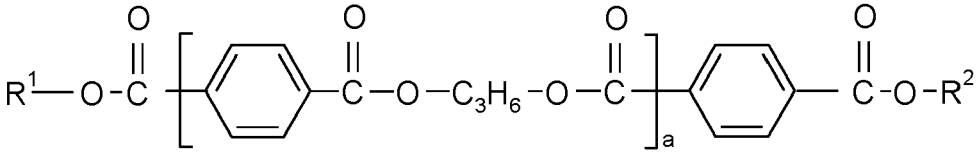
[0217] Soil release polymers help to improve the detachment of soils from fabric by modifying the fabric surface during washing. The adsorption of a SRP over the fabric surface is promoted by an affinity between the chemical structure of the SRP and the target fibre.

[0218] SRPs for use in the invention may include a variety of charged (e.g. anionic) as well as non-charged monomer units and structures may be linear, branched or star-shaped. The SRP structure may also include capping groups to control molecular weight or to alter polymer properties such as surface activity. The weight average molecular weight (M_w) of the SRP may suitably range from about 1000 to about 20,000 and preferably ranges from about 1500 to about 10,000.

[0219] SRPs for use in the invention may suitably be selected from copolyesters of dicarboxylic acids (for example adipic acid, phthalic acid or terephthalic acid), diols (for example ethylene glycol or propylene glycol) and polydiols (for example polyethylene glycol or polypropylene glycol). The copolyester may also include monomeric units substituted with anionic groups, such as for example sulfonated isophthaloyl units. Examples of such materials include oligomeric esters produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, dimethyl terephthalate ("DMT"), propylene glycol ("PG") and poly(ethyleneglycol) ("PEG"); partly- and fully-anionic-endcapped oligomeric esters such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; non-ionic-capped block polyester oligomeric compounds such as those produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate, and copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate.

[0220] Other types of SRP for use in the invention include cellulosic derivatives such as hydroxyether cellulosic polymers, C_1-C_4 alkylcelluloses and C_4 hydroxyalkyl celluloses; polymers with poly(vinyl ester) hydrophobic segments such as graft copolymers of poly(vinyl ester), for example C_1-C_6 vinyl esters (such as poly(vinyl acetate)) grafted onto polyalkylene oxide backbones; poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate; and polyester-polyamide polymers prepared by condensing adipic acid, caprolactam, and polyethylene glycol.

[0221] Preferred SRPs for use in the invention include copolyesters formed by condensation of terephthalic acid ester and diol, preferably 1,2 propanediol, and further comprising an end cap formed from repeat units of alkylene oxide capped with an alkyl group. Examples of such materials have a structure corresponding to general formula (I):



(I)

in which R^1 and R^2 independently of one another are X-$(OC_2H_4)_n$-$(OC_3H_6)_m$;

in which X is C_{1-4} alkyl and preferably methyl;

n is a number from 12 to 120, preferably from 40 to 50;

m is a number from 1 to 10, preferably from 1 to 7; and

a is a number from 4 to 9.

[0222] Because they are averages, m, n and a are not necessarily whole numbers for the polymer in bulk.

[0223] Mixtures of any of the above described materials may also be used.

[0224] The overall level of SRP, when included, may range from 0.1 to 10%, depending on the level of polymer intended for use in the final diluted composition and which is desirably from 0.3 to 7%, more preferably from 0.5 to 5% (by weight based on the total weight of the diluted composition).

[0225] Suitable soil release polymers are described in greater detail in U. S. Patent Nos. 5,574,179; 4,956,447; 4,861,512; 4,702,857, WO 2007/079850 and WO2016/005271. If employed, soil release polymers will typically be incorporated into the liquid laundry detergent compositions herein in concentrations ranging from 0.01 percent to 10 percent, more preferably from 0.1 percent to 5 percent, by weight of the composition.

HYDROTROPES

[0226] A composition of the invention may incorporate non-aqueous carriers such as hydrotropes, cosolvents and phase stabilizers. Such materials are typically low molecular weight, water-soluble or water-miscible organic liquids such as C1 to C5 monohydric alcohols (such as ethanol and n- or i-propanol); C2 to C6 diols (such as monopropylene glycol and dipropylene glycol); C3 to C9 triols (such as glycerol); polyethylene glycols having a weight average molecular weight (M_w) ranging from about 200 to 600; C1 to C3 alkanolamines such as mono-, di- and triethanolamines; and alkyl aryl sulfonates having up to 3 carbon atoms in the lower alkyl group (such as the sodium and potassium xylene, toluene, ethylbenzene and isopropyl benzene (cumene) sulfonates).

[0227] Mixtures of any of the above described materials may also be used.

[0228] Non-aqueous carriers, are preferably included, may be present in an amount ranging from 1 to 50%, preferably from 10 to 30%, and more preferably from 15 to 25% (by weight based on the total weight of the composition). The level of hydrotrope used is linked to the level of surfactant and it is desirable to use hydrotrope level to manage the viscosity in such compositions. The preferred hydrotropes are monopropylene glycol and glycerol.

COSURFACTANTS

[0229] A liquid composition of the invention may contain one or more cosurfactants (such as amphoteric (zwitterionic) and/or cationic surfactants) in addition to the non-soap anionic and/or nonionic detersive surfactants described above.

[0230] Specific cationic surfactants include C8 to C18 alkyl dimethyl ammonium halides and derivatives thereof in which one or two hydroxyethyl groups replace one or two of the methyl groups, and mixtures thereof. Cationic surfactant, when included, may be present in an amount ranging from 0.1 to 5% (by weight based on the total weight of the composition).

[0231] Specific amphoteric (zwitterionic) surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulfobetaines (sultaines), alkyl glycinates, alkyl carboxyglycinates, alkyl amphoacetates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, having alkyl radicals containing from about 8 to about 22 carbon atoms preferably selected from C12, C14, C16 ,C18 and C18:1, the term "alkyl" being used to include the alkyl portion of higher acyl radicals. Amphoteric (zwitterionic) surfactant, when included, may be present in an amount ranging from 0.1 to 5% (by weight based on the total weight of the composition).

[0232] Mixtures of any of the above described materials may also be used.

FLUORESCENT AGENTS

[0233] It may be advantageous to include fluorescer in the liquid compositions. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.5 wt % the composition.

[0234] Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal ® CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra, Tinopal 5BMGX, and Blankophor® HRH, and Pyrazoline compounds, e.g. Blankophor SN.

[0235] Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[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-sulfoslyryl)biphenyl.

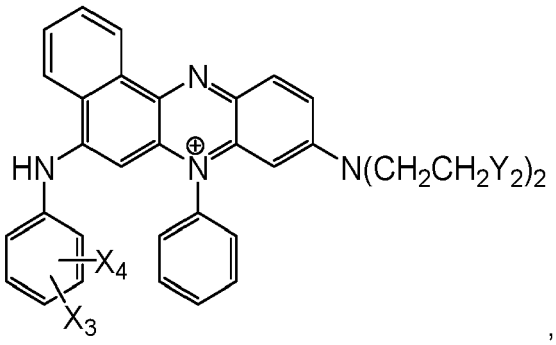
[0236] Most preferably the fluoescer is a di-styryl biphenyl compound, preferably sodium 2,2'-([1,1'-biphenyl]-4,4'-diylbis(ethene-2,1-diyl))dibenzenesulfonate (CAS-No 27344-41-8).

SHADING DYES

[0237] Shading dye can be used to improve the performance of the liquid compositions. Preferred dyes are violet or blue. It is believed that the deposition on fabrics of a low level of a dye of these shades, masks yellowing of fabrics. A further advantage of shading dyes is that they can be used to mask any yellow tint in the composition itself.

[0238] Shading dyes are well known in the art of laundry liquid formulation.

[0239] Suitable and preferred classes of dyes include direct dyes, acid dyes, hydrophobic dyes, basic dyes, reactive dyes and dye conjugates. Preferred examples are Disperse Violet 28, Acid Violet 50, anthraquinone dyes covalently bound to ethoxylate or propoxylated polyethylene imine as described in WO2011/047987 and WO 2012/119859 alkoxylated mono-azo thiophenes, dye with CAS-No 72749-80-5, acid blue 59, and the phenazine dye selected from:



,

wherein:

X_3 is selected from: -H; -F; $-CH_3$; $-C_2H_5$; $-OCH_3$; and, $-OC_2H_5$;

X_4 is selected from: -H; $-CH_3$; $-C_2H_5$; $-OCH_3$; and, $-OC_2H_5$;

Y_2 is selected from: -OH; $-OCH_2CH_2OH$; $-CH(OH)CH_2OH$; $-OC(O)CH_3$; and, $C(O)OCH_3$.

[0240] Alkoxylated thiophene dyes are discussed in WO2013/142495 and WO2008/087497.

[0241] The shading dye is preferably present is present in the composition in range from 0.0001 to 0.1wt %. Depending upon the nature of the shading dye there are preferred ranges depending upon the efficacy of the shading dye which is dependent on class and particular efficacy within any particular class.

EXTERNAL STRUCTURANTS

[0242] Liquid compositions of the invention may have their rheology further modified by use of one or more external structurants which form a structuring network within the composition. Examples of such materials include crystallizable glycerides such as hydrogenated castor oil; microfibrous cellulose and citrus pulp fibre. The presence of an external structurant may provide shear thinning rheology and may also enable materials such as encapsulates and visual cues to be suspended stably in the liquid.

[0243] The composition preferably comprises a crystallizable glyceride.

[0244] The crystallizable glyceride is useful in forming an external structuring system as described in WO2011/031940, the contents of which, in particular as regards manufacture of the ESS are incorporated by reference. Where an ESS is present it is preferred that the ESS of the present invention preferably comprises: (a) crystallizable glyceride(s); (b) alkanolamine; (c) anionic surfactant; (d) additional components; and (e) optional components. Each of these components is discussed in detail below. Crystallizable glyceride(s) of use herein preferably include "Hydrogenated castor oil" or "HCO". HCO as used herein most generally can be any hydrogenated castor oil, provided that it is capable of crystallizing in the ESS premix. Castor oils may include glycerides, especially triglycerides, comprising C10 to C22 alkyl or alkenyl moieties which incorporate a hydroxyl group. Hydrogenation of castor oil to make HCO converts double bonds, which may be present in the starting oil as ricinoleyl moieties, to convert ricinoleyl moieties to saturated hydroxyalkyl moieties, e.g., hydroxystearyl. The HCO herein may, in some embodiments, be selected from: trihydroxystearin; dihydroxystearin; and mixtures thereof. The HCO may be processed in any suitable starting form, including, but not limited those selected from solid, molten and mixtures thereof. HCO is typically present in the ESS of the present invention at a level of from about 2 percent to about 10 percent, from about 3 percent to about 8 percent, or from about 4 percent to about 6 percent by weight of the structuring system. In some embodiments, the corresponding percentage of hydrogenated castor oil delivered into a finished laundry detergent product is below about 1.0 percent, typically from 0.1 percent to 0.8 percent.

[0245] Useful HCO may have the following characteristics: a melting point of from about 40 degrees centigrade to about 100 degrees centigrade, or from about 65 degrees centigrade to about 95 degrees C; and/or Iodine value ranges of from 0 to about 5, from 0 to about 4, or from 0 to about 2.6. The melting point of HCO can measured using either ASTM D3418 or ISO 11357; both tests utilize DSC: Differential Scanning Calorimetry.

[0246] HCO of use in the present invention includes those that are commercially available. Non-limiting examples of commercially available HCO of use in the present invention include: THIXCIN(R) from Rheox, Inc. Further examples of useful HCO may be found in U.S. Patent 5,340,390. The source of the castor oil for hydrogenation to form HCO can be of any suitable origin, such as from Brazil or India. In one suitable embodiment, castor oil is hydrogenated using a precious metal, e.g., palladium catalyst, and the hydrogenation temperature and pressure are controlled to optimize hydrogenation of the double bonds of the native castor oil while avoiding unacceptable levels of dehydroxylation.

[0247] The invention is not intended to be directed only to the use of hydrogenated castor oil. Any other suitable crystallizable glyceride(s) may be used. In one example, the structurant is substantially pure triglyceride of 12-hydroxystearic acid. This molecule represents the pure form of a fully hydrogenated triglyceride of 12-hydrox-9-cis-octadecenoic acid. In nature, the composition of castor oil is rather constant, but may vary somewhat. Likewise hydrogenation procedures may vary. Any other suitable equivalent materials, such as mixtures of triglycerides wherein at least 80 percent wt. is from castor oil, may be used. Exemplary equivalent materials comprise primarily, or consist essentially of, triglycerides; or comprise primarily, or consist essentially of, mixtures of diglycerides and triglycerides; or comprise primarily, or consist essentially of, mixtures of triglyerides with diglycerides and limited amounts, e.g., less than about 20 percent wt. of the glyceride mixtures, of monoglyerides; or comprise primarily, or consist essentially of, any of the foregoing glycerides with limited amounts, e.g., less than about 20 percent wt., of the corresponding acid hydrolysis product of any of said glycerides. A proviso in the above is that the major proportion, typically at least 80 percent wt, of any of said glycerides is chemically identical to glyceride of fully hydrogenated ricinoleic acid, i.e., glyceride of 12- hydroxystearic acid. It is for example well known in the art to modify hydrogenated castor oil such that in a given triglyceride, there will be two 12-hydroxystearic- moieties and one stearic moiety. Likewise it is envisioned that the hydrogenated castor oil may not be fully hydrogenated. In contrast, the invention excludes poly(oxyalkylated) castor oils when these fail the melting criteria.

[0248] Crystallizable glyceride(s) of use in the present invention may have a melting point of from about 40 degrees centigrade to about 100 degrees centigrade.

ENZYMES

[0249] The composition preferably comprises an enzyme selected from cellulase, a protease and an amylase/mannase mixture.

[0250] In addition, further enzymes may be present such as those described below.

[0251] Preferably, the composition may comprise an effective amount of one or more enzyme preferably selected from the group comprising lipases, hemicellulases, peroxidases, hemicellulases, xylanases, xantanase, lipases, phospholipases, esterases, cutinases, pectinases, carrageenases, pectate lyases, keratinases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, tannases, nucleases (such as deoxyribonuclease and/or ribonuclease), phosphodiesterases, or mixtures thereof.

[0252] Preferably the level of an enzyme is from 0.1 to 100, more preferably from 0.5 to 50, most preferably from 5 to 30 mg active enzyme protein per 100g finished laundry liquid composition.

[0253] Examples of preferred enzymes are sold under the following trade names Purafect Prime®, Purafect®, Preferenz® (DuPont), Savinase®, Pectawash®, Mannaway®, Lipex ®, Lipoclean ®, Whitzyme ® Stainzyme®, Stainzyme Plus®, Natalase ®, Mannaway ®, Amplify ® Xpect ®, Celluclean ® (Novozymes), Biotouch (AB Enzymes), Lavergy ® (BASF).

[0254] Detergent enzymes are discussed in WO2020/186028(Procter and Gamble), WO2020/200600 (Henkel), WO2020/070249 (Novozymes), WO2021/001244 (BASF) and WO2020/259949 (Unilever).

[0255] A nuclease enzyme is an enzyme capable of cleaving the phosphodiester bonds between the nucleotide subunits of nucleic acids and is preferably a deoxyribonuclease or ribonuclease enzyme. Preferably the nuclease enzyme is a deoxyribonuclease, preferably selected from any of the classes E.C. 3.1.21.x, where x=l, 2, 3, 4, 5, 6, 7, 8 or 9, E.C. 3.1.22.y where y=l, 2, 4 or 5, E.C. 3.1.30.Z where z= 1 or 2, E.C. 3.1.31.1 and mixtures thereof.

[0256] Protease enzymes hydrolyse bonds within peptides and proteins, in the laundry context this leads to enhanced removal of protein or peptide containing stains. Examples of suitable proteases families include aspartic proteases; cysteine proteases; glutamic proteases; aspargine peptide lyase; serine proteases and threonine proteases. Such protease families are described in the MEROPS peptidase database (http://merops.sanger.ac.uk/). Serine proteases are preferred. Subtilase type serine proteases are more preferred. The term "subtilases" refers to a sub-group of serine protease according to Siezen et al. , Protein Engng. 4 (1991) 719-737 and Siezen et al. Protein Science 6 (1997) 501 -523. Serine proteases are a subgroup of proteases characterized by having a serine in the active site, which forms a covalent adduct with the substrate. The subtilases may be divided into 6 sub divisions, i.e. the Subtilisin family, the Thermitase family, the Proteinase K family, the Lantibiotic peptidase family, the Kexin family and the Pyrolysin family.

[0257] Examples of subtilases are those derived from Bacillus such as Bacillus lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii described in; US7262042 and WO09/021867, and subtilisin

lentus, subtilisin Novo, subtilisin Carlsberg, Bacillus licheniformis, subtilisin BPN', subtilisin 309, subtilisin 147 and subtilisin 168 described in WO 89/06279 and protease PD138 described in (WO 93/18140). Other useful proteases may be those described in WO 92/175177, WO 01/016285, WO 02/026024 and WO 02/016547. Examples of trypsin-like proteases are trypsin (e.g. of porcine or bovine origin) and the Fusarium protease described in WO 89/06270, WO 94/25583 and WO 05/040372, and the chymotrypsin proteases derived from Cellumonas described in WO 05/052161 and WO 05/052146.

[0258] Most preferably the protease is a subtilisins (EC 3.4.21.62).

[0259] Examples of subtilases are those derived from Bacillus such as Bacillus lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii described in; US7262042 and WO09/021867, and subtilisin lentus, subtilisin Novo, subtilisin Carlsberg, Bacillus licheniformis, subtilisin BPN', subtilisin 309, subtilisin 147 and subtilisin 168 described in WO89/06279 and protease PD138 described in (WO93/18140). Preferably the subsilisin is derived from Bacillus, preferably Bacillus lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii as described in US 6,312,936 B1, US 5,679,630, US 4,760,025, US7,262,042 and WO 09/021867. Most preferably the subtilisin is derived from Bacillus gibsonii or Bacillus Lentus.

[0260] Suitable commercially available protease enzymes include those sold under the trade names names Alcalase®, Blaze®; DuralaseTm, DurazymTm, Relase®, Relase® Ultra, Savinase®, Savinase® Ultra, Primase®, Polarzyme®, Kannase®, Liquanase®, Liquanase® Ultra, Ovozyme®, Coronase®, Coronase® Ultra, Neutrase®, Everlase® and Esperase® all could be sold as Ultra® or Evity® (Novozymes A/S).

[0261] Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from Bacillus, e.g. a special strain of B. licheniformis, described in more detail in GB 1 ,296,839, or the Bacillus sp. strains disclosed in WO 95/026397 or WO00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

[0262] Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium, e.g. the fungal cellulases produced from Humicola insolens, Thielavia terrestris, Myceliophthora thermophila, and Fusarium oxysporum disclosed in US 4,435,307, US 5,648,263, US 5,691 ,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Celluclean™, Endolase™,Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation). Celluclean™ is preferred.

LIPASE

[0263] Lipases are lipid esterase enzymes and the terms lipid esterase and lipase are used herein synonymously.

[0264] The composition preferably comprises from 0.0005 to 0.5 wt.%, preferably from 0.005 to 0.2 wt.% of a lipase.

[0265] Cleaning lipid esterases are discussed in Enzymes in Detergency edited by Jan H. Van Ee, Onno Misset and Erik J. Baas (1997 Marcel Dekker, New York).

[0266] The lipid esterase may be selected from lipase enzymes in E.C. class 3.1 or 3.2 or a combination thereof.

[0267] Preferably the cleaning lipid esterases is selected from:

(1) Triacylglycerol lipases (E.C. 3.1.1.3)
(2) Carboxylic ester hydrolase (E.C. 3.1.1.1)
(3) Cutinase (E.C. 3.1.1.74)
(4) Sterol esterase (E.C. 3.1.1.13)
(5) Wax-ester hydrolase (E.C. 3.1.1.50)

[0268] Triacylglycerol lipases (E.C. 3.1.1.3) are most preferred.

[0269] Suitable triacylglycerol lipases can be selected from variants of the Humicola lanuginosa (Thermomyces lanuginosus) lipase. Other suitable triacylglycerol lipases can be selected from variants of Pseudomonas lipases, e.g., from P. alcaligenes or P. pseudoalcaligenes (EP 218 272), P. cepacia (EP 331 376), P. stutzeri (GB 1,372,034), P. fluorescens, Pseudomonas sp. strain SD 705 (WO 95/06720 and WO 96/27002), P. wisconsinensis (WO 96/12012), Bacillus lipases, e.g., from B. subtilis (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), B. stearothermophilus (JP 64/744992) or B. pumilus (WO 91/16422).

[0270] Suitable carboxylic ester hydrolases can be selected from wild-types or variants of carboxylic ester hydrolases endogenous to B. gladioli, P. fluorescens, P. putida, B. acidocaldarius, B. subtilis, B. stearothermophilus, Streptomyces chrysomallus, S. diastatochromogenes and Saccaromyces cerevisiae.

[0271] Suitable cutinases can be selected from wild-types or variants of cutinases endogenous to strains of Aspergillus, in particular Aspergillus oryzae, a strain of Alternaria, in particular Alternaria brassiciola, a strain of Fusarium, in particular

Fusarium solani, Fusarium solani pisi, Fusarium oxysporum, Fusarium oxysporum cepa, Fusarium roseum culmorum, or Fusarium roseum sambucium, a strain of Helminthosporum, in particular Helminthosporum sativum, a strain of Humicola, in particular Humicola insolens, a strain of Pseudomonas, in particular Pseudomonas mendocina, or Pseudomonas putida, a strain of Rhizoctonia, in particular Rhizoctonia solani, a strain of Streptomyces, in particular Streptomyces scabies, a strain of Coprinopsis, in particular Coprinopsis cinerea, a strain of Thermobifida, in particular Thermobifida fusca, a strain of Magnaporthe, in particular Magnaporthe grisea, or a strain of Ulocladium, in particular Ulocladium consortiale.

[0272] In a preferred embodiment, the cutinase is selected from variants of the Pseudomonas mendocina cutinase described in WO 2003/076580 (Genencor), such as the variant with three substitutions at I178M, F180V, and S205G.

[0273] In another preferred embodiment, the cutinase is a wild-type or variant of the six cutinases endogenous to Coprinopsis cinerea described in H. Kontkanen et al, App. Environ. Microbiology, 2009, p2148-2157.

[0274] In another preferred embodiment, the cutinase is a wild-type or variant of the two cutinases endogenous to Trichoderma reesei described in WO2009007510 (VTT). In a most preferred embodiment the cutinase is derived from a strain of Humicola insolens, in particular the strain Humicola insolens DSM 1800. Humicola insolens cutinase is described in WO 96/13580 which is hereby incorporated by reference. The cutinase may be a variant, such as one of the variants disclosed in WO 00/34450 and WO 01/92502. Preferred cutinase variants include variants listed in Example 2 of WO 01/92502. Preferred commercial cutinases include Novozym 51032 (available from Novozymes, Bagsvaerd, Denmark).

[0275] Suitable sterol esterases may be derived from a strain of Ophiostoma, for example Ophiostoma piceae, a strain of Pseudomonas, for example Pseudomonas aeruginosa, or a strain of Melanocarpus, for example Melanocarpus albomyces.

[0276] In a most preferred embodiment the sterol esterase is the Melanocarpus albomyces sterol esterase described in H. Kontkanen et al, Enzyme Microb Technol., 39, (2006), 265-273.

[0277] Suitable wax-ester hydrolases may be derived from Simmondsia chinensis.

[0278] The lipid esterase is preferably selected from lipase enzyme in E.C. class 3.1.1.1 or 3.1.1.3 or a combination thereof, most preferably E.C.3.1.1.3.

[0279] Examples of EC 3.1.1.3 lipases include those described in WIPO publications WO 00/60063, WO 99/42566, WO 02/062973, WO 97/04078, WO 97/04079 and US 5,869,438. Preferred lipases are produced by Absidia reflexa, Absidia corymbefera, Rhizmucor miehei, Rhizopus deleman Aspergillus niger, Aspergillus tubigensis, Fusáηum oxysporum, Fusarium heterosporum, Aspergillus oryzea, Penicilium camembertii, Aspergillus foetidus, Aspergillus niger, Thermomyces lanoginosus (synonym: Humicola lanuginosa) and Landerina penisapora, particularly Thermomyces lanoginosus. Certain preferred lipases are supplied by Novozymes under the tradenames. Lipolase®, Lipolase Ultra®, Lipoprime®, Lipoclean® and Lipex® (registered tradenames of Novozymes) and LIPASE P "AMANO®" available from Areario Pharmaceutical Co. Ltd., Nagoya, Japan, AMANO-CES®, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from Amersham Pharmacia Biotech., Piscataway, New Jersey, U.S.A. and Diosynth Co., Netherlands, and other lipases such as Pseudomonas gladioli. Additional useful lipases are described in WIPO publications WO 02062973, WO 2004/101759, WO 2004/101760 and WO 2004/101763. In one embodiment, suitable lipases include the "first cycle lipases" described in WO 00/60063 and U.S. Patent 6,939,702 B1, preferably a variant of SEQ ID No. 2, more preferably a variant of SEQ ID No. 2 having at least 90% homology to SEQ ID No. 2 comprising a substitution of an electrically neutral or negatively charged amino acid with R or K at any of positions 3, 224, 229, 231 and 233, with a most preferred variant comprising T23 IR and N233R mutations, such most preferred variant being sold under the tradename Lipex® (Novozymes).

[0280] The aforementioned lipases can be used in combination (any mixture of lipases can be used). Suitable lipases can be purchased from Novozymes, Bagsvaerd, Denmark; Areario Pharmaceutical Co. Ltd., Nagoya, Japan; Toyo Jozo Co., Tagata, Japan; Amersham Pharmacia Biotech., Piscataway, New Jersey, U.S.A; Diosynth Co., Oss, Netherlands and/or made in accordance with the examples contained herein.

[0281] Lipid esterase with reduced potential for odour generation and a good relative performance, are particularly preferred, as described in WO 2007/087243. These include lipoclean ® (Novozyme).

[0282] Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ and Lipoclean TM (Novozymes A/S).

FRAGRANCES

[0283] The liquid composition comprises a fragrance and preferably, the fragrance is present at from 0.01 to 5% wt., more preferably 0.1 to 1wt% of the composition.

[0284] Preferably, the fragrance comprises a component selected from the group consisting of ethyl-2-methyl valerate (manzanate), limonene, (4Z)-cyclopentadec-4-en-1-one, dihyro myrcenol, dimethyl benzyl carbonate acetate, benzyl acetate, spiro[1,3-dioxolane-2,5'-(4',4',8',8'-tetramethyl-hexahydro-3',9'-methanonaphthalene)], benzyl acetate, Rose Oxide, geraniol, methyl nonyl acetaldehyde, decanal, octanal, undecanal, verdyl acetate, tert-butylcyclohexyl acetate,

cyclamal, beta ionone, hexyl salicylate, tonalid, phenafleur, octahydrotetramethyl acetophenone (OTNE), the benzene, toluene, xylene (BTX) feedstock class such as 2-phenyl ethanol, phenoxanol and mixtures thereof, the cyclododecanone feedstock class, such as habolonolide, the phenolics feedstock class such as hexyl salicylate, the C5 blocks or oxygen containing heterocycle moiety feedstock class such as gamma decalactone, methyl dihydrojasmonate and mixtures thereof, the terpenes feedstock class such as dihydromycernol, linalool, terpinolene, camphor, citronellol and mixtures thereof, the alkyl alcohols feedstock class such as ethyl-2-methylbutyrate, the diacids feedstock class such as ethylene brassylate, and mixtures of these components.

[0285] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15wt.% and especially preferably from 6 to 10% wt. of the fragrance component ethyl-2-methyl valerate (manzanate).

[0286] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15 wt.% and especially preferably from 6 to 10% wt. of the fragrance component limonene.

[0287] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component (4Z)-cyclopentadec-4-en-1-one.

[0288] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component dimethyl benzyl carbonate acetate.

[0289] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component dihyromyrcenol.

[0290] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component rose oxide.

[0291] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component tert-butylcyclohexyl acetate.

[0292] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component verdyl acetate.

[0293] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component benzyl acetate.

[0294] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component spiro[1 ,3-dioxolane-2,5'-(4',4',8',8'-tetramethyl-hexahydro-3',9'-methanonaphthalene)].

[0295] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component geraniol.

[0296] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component methyl nonyl acetaldehyde.

[0297] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15% and especially preferably from 6 to 10% wt. of the fragrance component cyclamal.

[0298] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15wt.% and especially preferably from 6 to 10% wt. of the fragrance component beta ionone.

[0299] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15wt.% and especially preferably from 6 to 10% wt. of the fragrance component hexyl salicylate.

[0300] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15wt.% and especially preferably from 6 to 10% wt. of the fragrance component tonalid.

[0301] Preferably, the fragrance comprises from 0.5 to 30% wt., more preferably from 2 to 15wt.% and especially preferably from 6 to 10% wt. of the fragrance component phenafleur.

[0302] Preferably, the fragrance comprises a component selected from the benzene, toluene, xylene (BTX) feedstock class. More preferably, the fragrance component is selected from 2-phenyl ethanol, phenoxanol and mixtures thereof.

[0303] Preferably, the fragrance comprises a component selected from the cyclododecanone feedstock class. More preferably, the fragrance component is habolonolide.

[0304] Preferably, the fragrance comprises a component selected from the phenolics feedstock class. More preferably, the fragrance component is hexyl salicylate.

[0305] Preferably, the fragrance comprises a component selected from the C5 blocks or oxygen containing heterocycle moiety feedstock class. More preferably, the fragrance component is selected from gamma decalactone, methyl dihydrojasmonate and mixtures thereof.

[0306] Preferably, the fragrance comprises a component selected from the terpenes feedstock class. More preferably, the fragrance component is selected from, linalool, terpinolene, camphor, citronellol and mixtures thereof.

[0307] Preferably, the fragrance comprises a component selected from the alkyl alcohols feedstock class. More preferably, the fragrance component is ethyl-2-methylbutyrate.

[0308] Preferably, the fragrance comprises a component selected from the diacids feedstock class. More preferably, the fragrance component is ethylene brassylate.

[0309] Preferably, the fragrance component listed above is present in the final detergent composition at from 0.0001 to

1% by wt. of the composition.

MICROCAPSULES

[0310] One type of microparticle suitable for use in the invention is a microcapsule. Microencapsulation may be defined as the process of surrounding or enveloping one substance within another substance on a very small scale, yielding capsules ranging from less than one micron to several hundred microns in size. The material that is encapsulated may be called the core, the active ingredient or agent, fill, payload, nucleus, or internal phase. The material encapsulating the core may be referred to as the coating, membrane, shell, or wall material.

[0311] Microcapsules typically have at least one generally spherical continuous shell surrounding the core. The shell may contain pores, vacancies or interstitial openings depending on the materials and encapsulation techniques employed. Multiple shells may be made of the same or different encapsulating materials, and may be arranged in strata of varying thicknesses around the core. Alternatively, the microcapsules may be asymmetrically and variably shaped with a quantity of smaller droplets of core material embedded throughout the microcapsule.

[0312] The shell may have a barrier function protecting the core material from the environment extemal to the microcapsule, but it may also act as a means of modulating the release of core materials such as fragrance. Thus, a shell may be water soluble or water swellable and fragrance release may be actuated in response to exposure of the microcapsules to a moist environment. Similarly, if a shell is temperature sensitive, a microcapsule might release fragrance in response to elevated temperatures. Microcapsules may also release fragrance in response to shear forces applied to the surface of the microcapsules.

[0313] A preferred type of polymeric microparticle suitable for use in the invention is a polymeric core-shell microcapsule in which at least one generally spherical continuous shell of polymeric material surrounds a core containing the fragrance formulation (f2). The shell will typically comprise at most 20% by weight based on the total weight of the microcapsule. The fragrance formulation (f2) will typically comprise from about 10 to about 60% and preferably from about 20 to about 40% by weight based on the total weight of the microcapsule. The amount of fragrance (f2) may be measured by taking a slurry of the microcapsules, extracting into ethanol and measuring by liquid chromatography.

[0314] Polymeric core-shell microcapsules for use in the invention may be prepared using methods known to those skilled in the art such as coacervation, interfacial polymerization, and polycondensation.

[0315] The process of coacervation typically involves encapsulation of a generally water-insoluble core material by the precipitation of colloidal material(s) onto the surface of droplets of the material. Coacervation may be simple e.g. using one colloid such as gelatin, or complex where two or possibly more colloids of opposite charge, such as gelatin and gum arabic or gelatin and carboxymethyl cellulose, are used under carefully controlled conditions of pH, temperature and concentration.

[0316] Interfacial polymerisation typically proceeds with the formation of a fine dispersion of oil droplets (the oil droplets containing the core material) in an aqueous continuous phase. The dispersed droplets form the core of the future microcapsule and the dimensions of the dispersed droplets directly determine the size of the subsequent microcapsules. Microcapsule shell-forming materials (monomers or oligomers) are contained in both the dispersed phase (oil droplets) and the aqueous continuous phase and they react together at the phase interface to build a polymeric wall around the oil droplets thereby to encapsulate the droplets and form core-shell microcapsules. An example of a core-shell microcapsule produced by this method is a polyurea microcapsule with a shell formed by reaction of diisocyanates or polyisocyanates with diamines or polyamines.

[0317] Polycondensation involves forming a dispersion or emulsion of the core material in an aqueous solution of precondensate of polymeric materials under appropriate conditions of agitation to produce capsules of a desired size, and adjusting the reaction conditions to cause condensation of the precondensate by acid catalysis, resulting in the condensate separating from solution and surrounding the dispersed core material to produce a coherent film and the desired microcapsules. An example of a core-shell microcapsule produced by this method is an aminoplast microcapsule with a shell formed from the polycondensation product of melamine (2,4,6-triamino-1,3,5-triazine) or urea with formaldehyde. Suitable cross-linking agents (e.g. toluene diisocyanate, divinyl benzene, butanediol diacrylate) may also be used and secondary wall polymers may also be used as appropriate, e.g. anhydrides and their derivatives, particularly polymers and co-polymers of maleic anhydride.

[0318] One example of a preferred polymeric core-shell microcapsule for use in the invention is an aminoplast microcapsule with an aminoplast shell surrounding a core containing the fragrance formulation (f2). More preferably such an aminoplast shell is formed from the polycondensation product of melamine with formaldehyde.

[0319] Polymeric microparticles suitable for use in the invention will generally have an average particle size between 100 nanometers and 50 microns. Particles larger than this are entering the visible range. Examples of particles in the sub-micron range include latexes and mini-emulsions with a typical size range of 100 to 600 nanometers. The preferred particle size range is in the micron range. Examples of particles in the micron range include polymeric core-shell microcapsules (such as those further described above) with a typical size range of 1 to 50 microns, preferably 5 to 30 microns. The

average particle size can be determined by light scattering using a Malvem Mastersizer with the average particle size being taken as the median particle size D (0.5) value. The particle size distribution can be narrow, broad or multimodal. If necessary, the microcapsules as initially produced may be filtered or screened to produce a product of greater size uniformity.

[0320] Polymeric microparticles suitable for use in the invention may be provided with a deposition aid at the outer surface of the microparticle. Deposition aids serve to modify the properties of the exterior of the microparticle, for example to make the microparticle more substantive to a desired substrate. Desired substrates include cellulosics (including cotton) and polyesters (including those employed in the manufacture of polyester fabrics).

[0321] The deposition aid may suitably be provided at the outer surface of the microparticle by means of covalent bonding, entanglement or strong adsorption. Examples include polymeric core-shell microcapsules (such as those further described above) in which a deposition aid is attached to the outside of the shell, preferably by means of covalent bonding. While it is preferred that the deposition aid is attached directly to the outside of the shell, it may also be attached via a linking species.

[0322] Deposition aids for use in the invention may suitably be selected from polysaccharides having an affinity for cellulose. Such polysaccharides may be naturally occurring or synthetic and may have an intrinsic affinity for cellulose or may have been derivatised or otherwise modified to have an affinity for cellulose. Suitable polysaccharides have a 1-4 linked β glycan (generalised sugar) backbone structure with at least 4, and preferably at least 10 backbone residues which are β1-4 linked, such as a glucan backbone (consisting of β1-4 linked glucose residues), a mannan backbone (consisting of β1-4 linked mannose residues) or a xylan backbone (consisting of β1-4 linked xylose residues). Examples of such β1-4 linked polysaccharides include xyloglucans, glucomannans, mannans, galactomannans, β(1-3),(1-4) glucan and the xylan family incorporating glucurono-, arabino- and glucuronoarabinoxylans. Preferred β1-4 linked polysaccharides for use in the invention may be selected from xyloglucans of plant origin, such as pea xyloglucan and tamarind seed xyloglucan (TXG) (which has a β1-4 linked glucan backbone with side chains of α-D xylopyranose and β-D-galactopyranosyl-(1-2)-α-D-xylo-pyranose, both 1-6 linked to the backbone); and galactomannans of plant origin such as loc ust bean gum (LBG) (which has a mannan backbone of β1-4 linked mannose residues, with single unit galactose side chains linked α1-6 to the backbone).

[0323] Also suitable are polysaccharides which may gain an affinity for cellulose upon hydrolysis, such as cellulose mono-acetate; or modified polysaccharides with an affinity for cellulose such as hydroxypropyl cellulose, hydroxypropyl methylcellulose, hydroxyethyl methylcellulose, hydroxypropyl guar, hydroxyethyl ethylcellulose and methylcellulose.

[0324] Deposition aids for use in the invention may also be selected from phthalate containing polymers having an affinity for polyester. Such phthalate containing polymers may have one or more nonionic hydrophilic segments comprising oxyalkylene groups (such as oxyethylene, polyoxyethylene, oxypropylene or polyoxypropylene groups), and one or more hydrophobic segments comprising terephthalate groups. Typically, the oxyalkylene groups will have a degree of polymerization of from 1 to about 400, preferably from 100 to about 350, more preferably from 200 to about 300. A suitable example of a phthalate containing polymer of this type is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide terephthalate.

[0325] Mixtures of any of the above described materials may also be suitable.

[0326] Deposition aids for use in the invention will generally have a weight average molecular weight (M_w) in the range of from about 5 kDa to about 500 kDa, preferably from about 10 kDa to about 500 kDa and more preferably from about 20 kDa to about 300 kDa.

[0327] One example of a particularly preferred polymeric core-shell microcapsule for use in the invention is an aminoplast microcapsule with a shell formed by the polycondensation of melamine with formaldehyde; surrounding a core containing the fragrance formulation (f2); in which a deposition aid is attached to the outside of the shell by means of covalent bonding. The preferred deposition aid is selected from β1-4 linked polysaccharides, and in particular the xyloglucans of plant origin, as are further described above.

[0328] The present inventors have surprisingly observed that it is possible to reduce the total level of fragrance included in the composition of the invention without sacrificing the overall fragrance experience delivered to the consumer at key stages in the laundry process. A reduction in the total level of fragrance is advantageous for cost and environmental reasons.

[0329] Accordingly, the total amount of fragrance formulation (f1) and fragrance formulation (f2) in the composition of the invention suitably ranges from 0.5 to 1.4%, preferably from 0.5 to 1.2%, more preferably from 0.5 to 1% and most preferably from 0.6 to 0.9% (by weight based on the total weight of the composition).

[0330] The weight ratio of fragrance formulation (f1) to fragrance formulation (f2) in the composition of the invention preferably ranges from 60:40 to 45:55. Particularly good results have been obtained at a weight ratio of fragrance formulation (f1) to fragrance formulation (f2) of around 50:50.

[0331] The fragrance (f1) and fragrance (f2) are typically incorporated at different stages of formation of the composition of the invention. Typically, the discrete polymeric microparticles (e.g. microcapsules) entrapping fragrance formulation (f2) are added in the form of a slurry to a warmed base formulation comprising other components of the composition (such as

surfactants and solvents). Fragrance (f1) is typically post-dosed later after the base formulation has cooled.

FURTHER OPTIONAL INGREDIENTS

[0332] A product of the invention may contain further optional ingredients to enhance performance and/or consumer acceptability. Examples of such ingredients include foam boosting agents, preservatives (e.g. bactericides), polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, ironing aids, colorants, pearlisers and/or opacifiers, and shading dye. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally, these optional ingredients are included individually at an amount of up to 5% (by weight based on the total weight of the diluted composition) and so adjusted depending on the dilution ratio with water.

[0333] Many of the ingredients used in embodiments of the invention may be obtained from so called black carbon sources or a more sustainable green source. The following provides a list of alternative sources for several of these ingredients and how they can be made into raw materials described herein.

[0334] Preferably, the unit dose detergent is packaged in a container such as a plastic tub. Such plastic tubs are typically hermetically sealable and comprise child resistant closures.

[0335] More preferably, the liquid unit dose detergent is packaged within a container comprising at least 80% wt. biodegradable material. Suitable biodegradable materials include cardboard and other pulp based materials. Such biodegradable material may be virgin or recycled but it is preferred if it is recycled.

[0336] Preferably, the container comprises at least 90% wt biodegradable material.

[0337] Preferred pulps include cardboard, in particular corrugated cardboard.

FIGURES

[0338] Embodiments of the invention will now be described with reference to the following non-limiting drawing in which Figure 1 is a plan view of a laundry capsule.

[0339] In detail Figure 1 shows a laundry capsule with four chambers arranged in a planar configuration. The first (1) and third (3) chambers are of equal size and the second (2) and fourth (4) chambers are of equal size.

[0340] Chambers 1 and 4 are separated from chambers 2 and 3 by a seal (5) which runs along the diameter of the capsule. The perimetric seal (6) is also shown.

[0341] In detail, figure 2 shows a mould for a capsule in plan view showing the mould for four chambers (11, 12, 13 and 14), seal areas (15, 16, 17, 18, 21) between the chambers and a pair of dissolution aid seal areas (19 and 20).

[0342] Figure 3 shows the same mould but in side view. Shown are the chambers (2, 3 and 4).

[0343] Figure 4 shows a capsule formed by a mould shown I figures 2 and 3. Shown are four chambers (11, 12, 13, and 14), seals (15, 16, 17, 18, 21) formed by water-soluble film and in particular the perimeter seal (46) providing the leading edge of the capsule.

[0344] Dissolution aid parts to the seals are shown at (39 and 40) and internal seal (41) between chambers 2 and 4.

[0345] The figure also shows flattened portions to the exterior of the chambers at 42, 43, 44 and 45 where the exterior of the chamber has a flattened portion to aid in manufacture.

[0346] Figure 5 shows the same capsule in side view. Shown are chambers (54), (52) and (53) along with perimeter seal (46).

Claims

1. Liquid unit dose product comprising a first, a second, a third and a fourth chamber, said first and third chambers having a volume of from 5 to 10ml, and said first and fourth chambers having a volume of from 3 to 8ml, where the first chamber has a higher volume than the second chamber and wherein at least one of the first or third chamber comprises a solid laundry treatment particle and wherein at least one of the second or fourth chambers contains a laundry liquid treatment composition.

2. Product according to claim 1 wherein at least three chambers contain laundry liquid composition.

3. Product according to claim 1 or 2 wherein the first chamber contains a solid laundry treatment particle and the third chamber contains a laundry treatment liquid.

4. Product according to claim 3 wherein the first chamber contains from 3 to 6ml laundry treatment particle.

5. Product according to claim 2 or 3 wherein the first chamber contains from 30 to 50% headspace.

6. Product according to any preceding claim wherein the density of the particle is from 0.7 to 1.5 g/ml.

7. Product according to any preceding claim comprising a first and second hemisphere, when considered in plan view, comprise a first and second hemisphere, said first hemisphere comprising said first and third chambers and said second hemisphere comprising said second and fourth chambers.

8. Product according to claim 7 wherein said first and second hemispheres are separated by a substantially diametric seal.

9. Product according to claim 7 or 8 wherein the first and second hemisphere exhibit rotational symmetry about 180 degrees.

10. Product according to any preceding claim wherein said water-soluble film comprises maleic acid copolymerised with polyvinyl alcohol.

11. Product according to any preceding claim wherein the solid particle comprises at least 50% wt. of the solid laundry particle a carrier.

12. Product according to claim 11 wherein the carrier is selected from the group consisting of: synthetic polymers, proteins, saccharides, polysaccharides, water-soluble or water dispersible fillers, vegetable soap, ethoxylated non-ionic surfactants, urea and combinations thereof.

13. Product according to any preceding claim wherein the solid laundry particle includes a carrier selected from water soluble organic alkali metal salt, water soluble inorganic alkaline earth metal salt, water soluble organic alkaline earth metal salt, water soluble carbohydrate, water soluble silicate, water soluble urea, starch, xanthan gum, dextrose, clay, water insoluble silicate, citric acid carboxymethyl cellulose, fatty acid, fatty alcohol, glyceryl diester of hydrogenated tallow, glycerol, polyvinyl alcohol, non-ionic surfactants and combinations thereof.

14. Product according to any preceding claim wherein the solid laundry particle includes a carrier selected from of synthetic polymers, polysaccharides, saccharides, vegetable soap, urea, ethoxylated non-ionic surfactants having a formula R1O(EO)xH, wherein R1 comprises 12 to 20 carbon atoms and x is 1 to 12, and combinations thereof.

15. Product according to any preceding claim wherein the solid laundry particle includes a carrier selected from polyethylene glycol, starch, dextrose, coconut soap beads, palm soap, urea and combinations thereof.

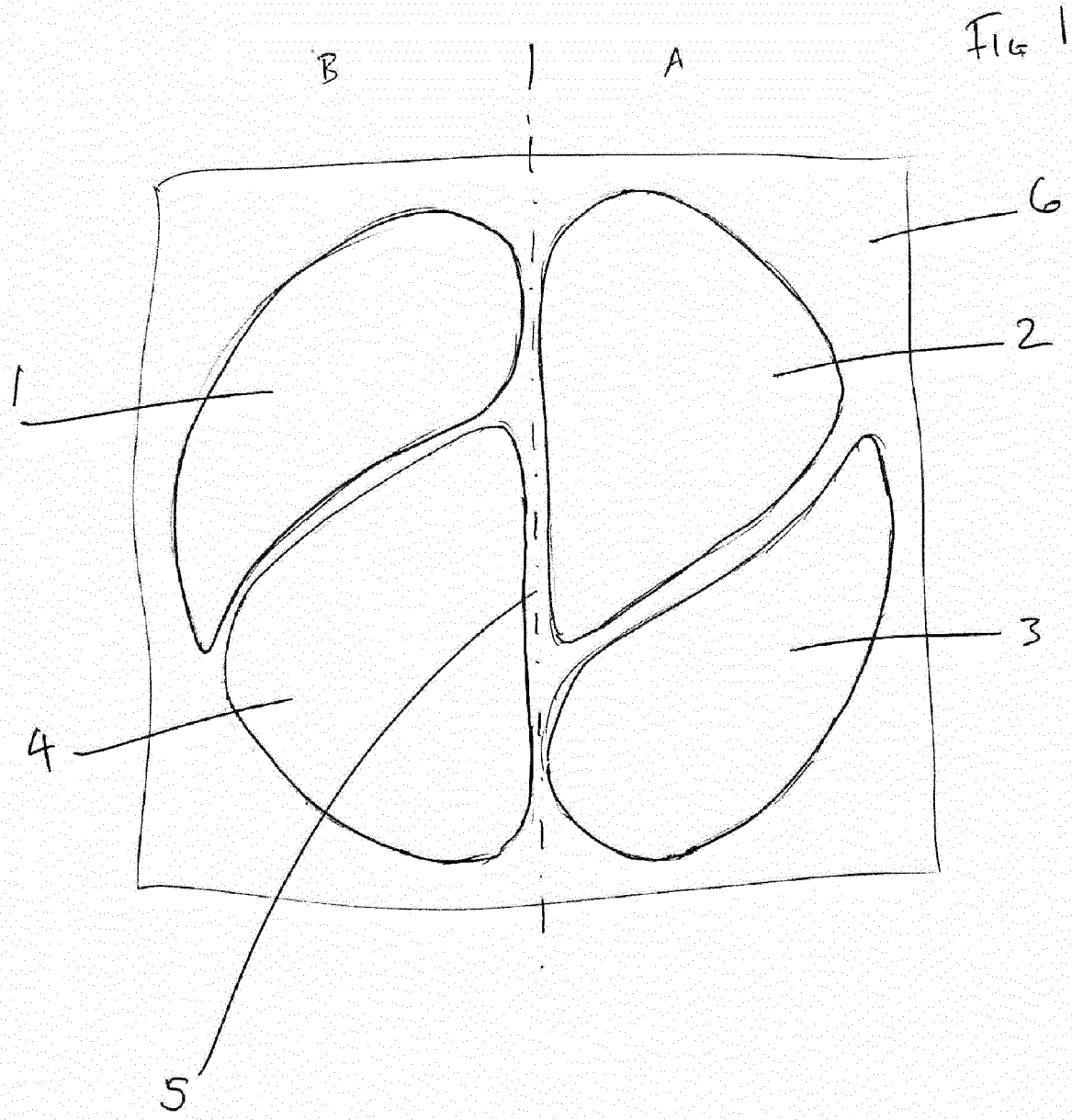


FIG 1.

Fig 2

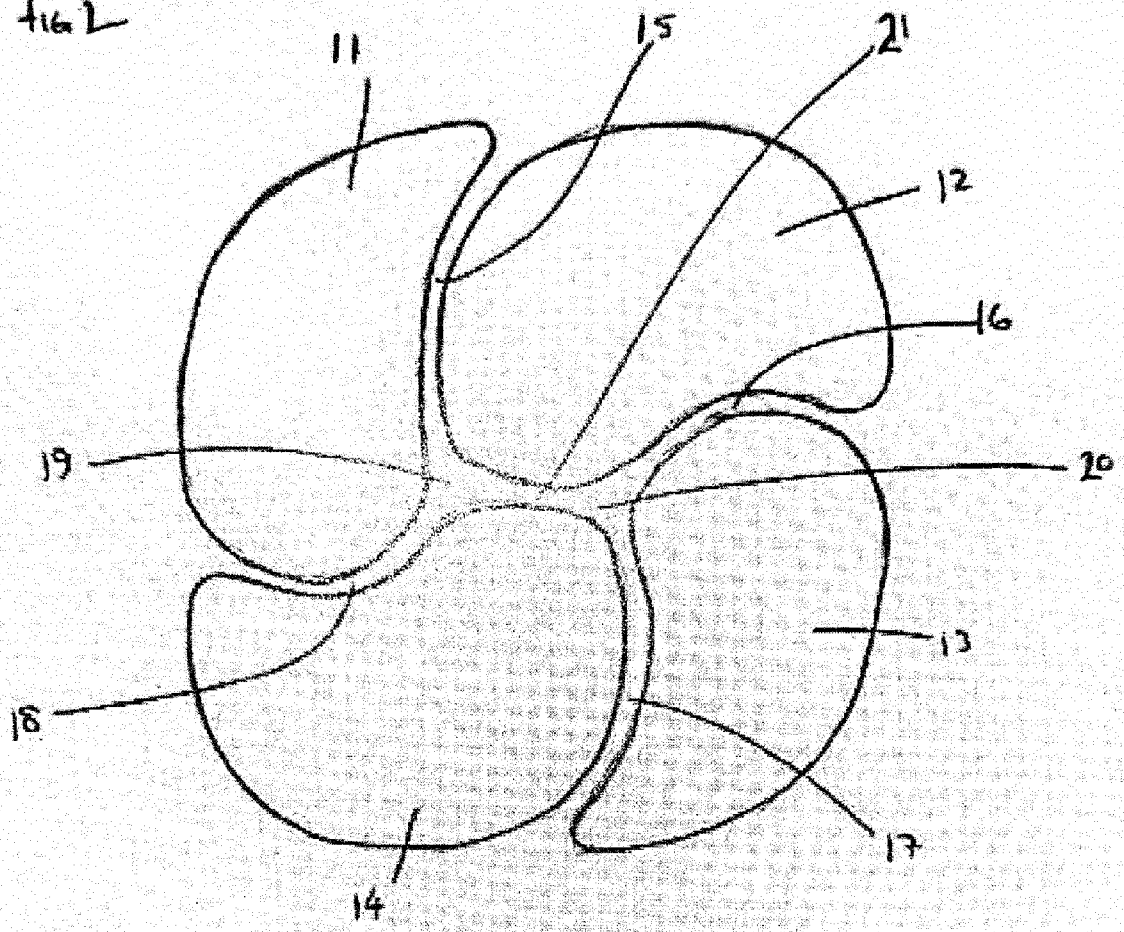


Fig 3.

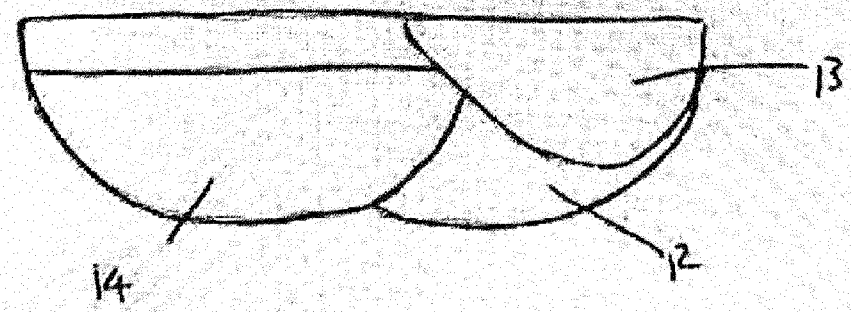


Fig. 4

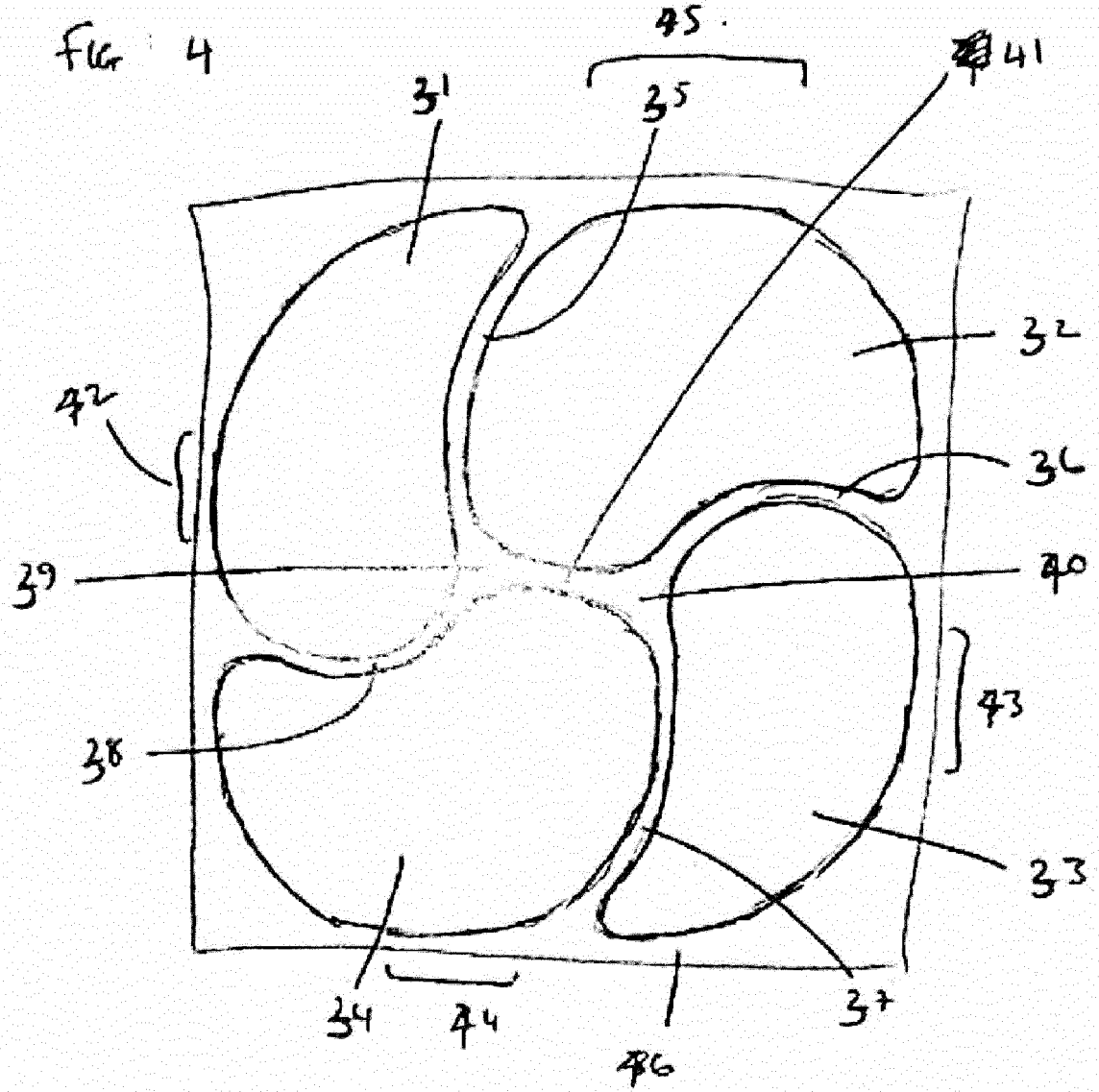
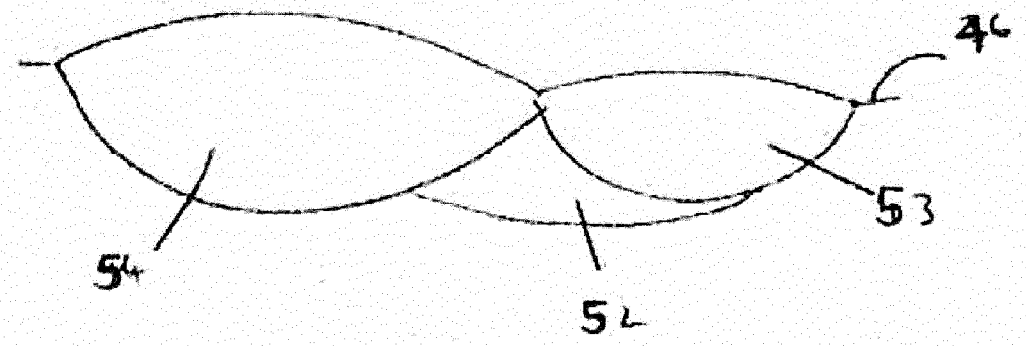


Fig. 5



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EUROPEAN SEARCH REPORT

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The Hague	26 April 2024	Engelskirchen, S

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