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(54) Title: WATER-SOLUBLE UNIT DOSE ARTICLE COMPRISING LIQUID LAUNDRY DETERGENT COMPOSITION WHICH COMPRISES POLYETHYLENE GLYCOL AND PROTEASE

(57) Abstract: The present invention relates to water-soluble unit dose articles comprising a liquid laundry detergent composition which comprises polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons, and protease.



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WATER-SOLUBLE UNIT DOSE ARTICLE COMPRISING LIQUID LAUNDRY DETERGENT COMPOSITION WHICH COMPRISES POLYETHYLENE GLYCOL AND PROTEASE

FIELD OF THE INVENTION

The present invention relates to water-soluble unit dose articles comprising a liquid laundry detergent composition which comprises polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons and protease.

BACKGROUND OF THE INVENTION

Water-soluble unit dose articles are liked by consumers due their convenience and ease of use. Consumers also like the fact that they do not need to measure a detergent dose and so this eliminates accidental spillage during the dosing operation. Accidental dosage can be messy and inconvenient. The water-soluble unit dose article comprises the water-soluble film shaped such that the unit dose article comprises at least one internal compartment surrounded by the water-soluble film. Preferred film materials are preferably polymeric materials. The film material can, for example, be obtained by casting, blow-moulding, extrusion or blown extrusion of the polymeric material, as known in the art.

There are various aspects of requirements for detergent unit dose articles such as stability, and physical properties for films etc. For example, protease enzymes are widely used in liquid detergent compositions to help aid with removal of stains by breaking down protein-containing stains such as grass, blood, mucus, and the like. However, there is a stability challenge for protease enzymes which may occur self-degradation or deactivation with interaction with other active ingredients. In many cases, protease inhibitor e.g. inorganic inhibitor has to be added in order to prevent degradation of protease. Therefore, there is a continuous need for the unit dose articles comprising protease-containing liquid detergent to be stable during the shelf life.

It is surprisingly found that a water-soluble unit dose article can provide an improvement on active stability (esp. enzyme activities) when such water-soluble unit dose article is formed by using a liquid detergent composition comprising protease and a polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons.

SUMMARY OF THE INVENTION

The present invention in one aspect relates to a water-soluble unit dose article comprising a water-soluble film and a liquid laundry detergent composition wrapped with the water-soluble film, wherein the liquid laundry detergent composition comprises from 1% to 25%, by weight of the composition, of polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons, and from 0.02% to 10% of a protease, by weight of the composition.

It may be an advantage of the present invention to provide unit dose articles comprising protease-containing liquid detergent exhibiting improved protease stability performance.

It may be an advantage of the water-soluble unit dose article according to the present application to provide an improved stability, e.g., during the shelf life, i.e., no phase separation or flocculation.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

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

As used herein, the terms “comprise”, “comprises”, “comprising”, “include”, “includes”, “including”, “contain”, “contains”, and “containing” are meant to be non-limiting, i.e., other steps and other ingredients which do not affect the end of result can be added. The above terms encompass the terms “consisting of” and “consisting essentially of”.

As used herein, when a composition is “substantially free” of a specific ingredient, it is meant that the composition comprises less than a trace amount, alternatively less than 0.1%, alternatively less than 0.01%, alternatively less than 0.001%, by weight of the composition, of the specific ingredient.

As used herein, the term “laundry detergent composition” means a composition for cleaning soiled materials, including fabrics. Such compositions may be used as a pre-laundering treatment, a post-laundering treatment, or may be added during the rinse or wash cycle of the laundering operation. The term of “unit dose laundry detergent composition” herein refers to a water-soluble pouch containing a certain volume of liquid wrapped with a water-soluble film.

As used herein, the terms “non-aqueous solvent” means any non-aqueous solvent except the polyethylene glycol contained in the water-soluble unit dose article according to the present

disclosure (e.g., the polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons).

As used herein, the term "alkyl" means a hydrocarbyl moiety which is branched or unbranched, substituted or unsubstituted. Included in the term "alkyl" is the alkyl portion of acyl groups.

As used herein, the term "washing solution" refers to the typical amount of aqueous solution used for one cycle of laundry washing, preferably from 1 L to 50 L, alternatively from 1 L to 20 L for hand washing and from 10 L to 50 L for machine washing.

As used herein, the term "soiled fabric" is used non-specifically and may refer to any type of natural or artificial fibers, including natural, artificial, and synthetic fibers, such as, but not limited to, cotton, linen, wool, polyester, nylon, silk, acrylic, and the like, as well as various blends and combinations.

Water-Soluble Unit Dose Article

The present invention discloses a water-soluble unit dose article comprising a water-soluble film and a liquid laundry detergent composition. Particularly, the liquid laundry detergent composition is wrapped with the water-soluble film. The water-soluble film and the liquid detergent composition are described in more detail below.

The water-soluble unit dose article comprises the water-soluble film shaped such that the unit-dose article comprises at least one internal compartment surrounded by the water-soluble film. The unit dose article may comprise a first water-soluble film and a second water-soluble film sealed to one another such to define the internal compartment. The water-soluble unit dose article is constructed such that the detergent composition does not leak out of the compartment during storage. However, upon addition of the water-soluble unit dose article to water, the water-soluble film dissolves and releases the contents of the internal compartment into the wash liquor.

The compartment should be understood as meaning a closed internal space within the unit dose article, which holds the detergent composition. During manufacture, a first water-soluble film may be shaped to comprise an open compartment into which the detergent composition is added. A second water-soluble film is then laid over the first film in such an orientation as to close the opening of the compartment. The first and second films are then sealed together along a seal region.

The unit dose article may comprise more than one compartment, even at least two compartments, or even at least three compartments. The compartments may be arranged in

superposed orientation, i.e., one positioned on top of the other. In such an orientation the unit dose article will comprise three films, top, middle and bottom. Alternatively, the compartments may be positioned in a side-by-side orientation, i.e., one orientated next to the other. The compartments may even be orientated in a 'tyre and rim' arrangement, i.e., a first compartment is positioned next to a second compartment, and the first compartment at least partially surrounds the second compartment but does not completely enclose the second compartment. Alternatively, one compartment may be completely enclosed within another compartment.

Wherein the unit dose article comprises at least two compartments, one of the compartments may be smaller than the other compartment. Wherein the unit dose article comprises at least three compartments, two of the compartments may be smaller than the third compartment, and preferably the smaller compartments are superposed on the larger compartment. The superposed compartments preferably are orientated side-by-side.

In a multi-compartment orientation, the detergent composition according to the present invention may be comprised in at least one of the compartments. It may for example be comprised in just one compartment, or may be comprised in two compartments, or even in three compartments.

Each compartment may comprise the same or different compositions. The different compositions could all be in the same form, or they may be in different forms.

The water-soluble unit dose article may comprise at least two internal compartments, wherein the liquid laundry detergent composition is comprised in at least one of the compartments, preferably wherein the unit dose article comprises at least three compartments, wherein the detergent composition is comprised in at least one of the compartments.

Liquid Laundry Detergent Composition

The water-soluble unit dose article comprises a liquid laundry detergent composition. The term 'liquid laundry detergent composition' refers to any laundry detergent composition comprising a liquid capable of wetting and treating a fabric, and includes, but is not limited to, liquids, gels, pastes, dispersions and the like. The liquid composition can include solids or gases in suitably subdivided form, but the liquid composition excludes forms which are non-fluid overall, such as tablets or granules.

The liquid detergent composition can be used in a fabric hand wash operation or may be used in an automatic machine fabric wash operation.

Without wishing to be bound by theory, it is believed that the presence of the polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons in the protease-containing detergent composition provides surprisingly improvement for protease stability in the unit dose articles, compared to otherwise-similar composition that do not contain the specific polyethylene glycol.

It may be an advantage of the water-soluble unit dose article comprising the protease-containing detergent composition containing specific polyethylene glycol to provide an improved physical property, e.g., desired viscosity.

It may be an advantage of the water-soluble unit dose article comprising the protease-containing detergent composition containing specific polyethylene glycol to provide an improvement on “weeping” phenomenon.

It may be an advantage of the water-soluble unit dose article comprising the protease-containing detergent composition containing specific polyethylene glycol to exhibit balanced performance on film properties (e.g., not being too floppy and no premature breakage).

It may be an advantage of the water-soluble unit dose article comprising the protease-containing detergent composition containing specific polyethylene glycol to provide an improved balance among stability, physical property and “weeping” phenomenon.

Polyethylene Glycol

The liquid laundry detergent composition may comprise from 1% to 25%, by weight of the composition, of polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons. Preferably, the polyethylene glycol may be present at a level of from 4% to 23%, preferably from 8% to 21%, more preferably from 10% to 20%, for example 2%, 3%, 5%, 7%, 12%, 15%, 17%, 20%, or any ranges therebetween, by weight of the composition.

The polyethylene glycol may have a weight average molecular weight of from about 150 to about 350 Daltons, preferably from about 150 to about 250 Daltons, e.g., 150 Daltons, 200 Daltons, 250 Daltons and any ranges therebetween.

Proteases

The liquid laundry detergent composition may comprise from 0.02% to 10%, by weight of the composition, of a protease (also known as “protease enzyme” or “proteolytic enzymes”). The protease enzyme(s) should be present as raw material in the composition, such as from about 0.2% to about 9.5%, or from about 0.4% to about 8%, or from about 0.5% to 6%, or from about 0.6% to about 5%, based on the total weight of the wash composition, in various embodiments.

Proteolytic enzymes cleave the peptide bonds that connect two amino acids. They follow a hydrolytic reaction mechanism. Proteolytic enzymes are produced by both prokaryotic and eukaryotic organisms in which they perform key biological functions. Microorganisms are a major source of commercial proteolytic enzymes because of high productivity and the ease of purification of the enzymes. Proteolytic enzymes may include the protease enzymes subtilisin, bromelain, papain, trypsin, metalloprotease, and pepsin.

Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzyme®, Kannase®, Liquease®, Liquease Ultra®, Savinase Ultra®, Ovozime®, Neutrase®, Everlase®, Coronase®, Blaze®, Blaze Ultra® and Esperase® by Novozymes A/S (Denmark); those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Properase®, Purafect®, Purafect Prime®, Purafect Ox®, FN3®, FN4®, Excellase®, Ultimase®, Purafect OXP®, and Preferenz® by Dupont; those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes; and those available from Henkel/Kemira; and KAP from Kao.

Especially preferred for use herein are commercial proteases selected from the group consisting of Properase®, Blaze®, Ultimase®, Everlase®, Savinase®, Excellase®, Preferenz®, Blaze Ultra®, BLAP and BLAP variants.

Free of Inorganic Protease Inhibitors

Preferably, the liquid laundry detergent composition in the water-soluble unit dose article is substantially free of inorganic protease inhibitor. Inorganic protease inhibitor may include inorganic salts e.g., calcium salts, magnesium salts and mixtures thereof; boron containing compound e.g., boric acid or derivatives thereof. Without wishing to be bound by theory, it is believed that the incorporation of the polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons into the protease-containing detergent composition surprisingly and unexpectedly help the protease stability, so that the inorganic protease inhibitor does not have to be added.

Other Enzymes

In some embodiments, the detergent composition of the present invention may comprise further a secondary enzyme, other than protease. For example, the detergent composition may comprise a mixture of a protease enzyme and an amylase enzyme. Possible secondary enzymes that may be in the detergent composition contemplated herein include one or more of a lipase,

cutinase, amylase, carbohydrase, cellulase, pectinase, mannanase, arabinase, galactanase, xylanase, oxidase, (e.g., a laccase), and/or peroxidase, but others are also possible.

In some embodiments, the detergent composition comprises protease and a secondary enzyme selected from amylase, mannanase, lipase or combinations thereof, where the weight ratio of the protease to the secondary enzyme is 10:1 to 1:10, preferably from 5:1 to 1:5, more preferably from 3:1 to 1:3, and even more preferably from 2:1 to 1:2.

The detergent enzyme(s) may be included in the wash composition by adding separate additives containing one or more enzymes, or by adding a combined additive comprising all the enzymes that are added to the wash composition. In an exemplary embodiment, the wash composition includes three or more different enzymes. In one embodiment, the wash composition includes protease, mannanase, and amylase, but other embodiments are also possible.

The liquid laundry detergent composition is characterized by a high shear viscosity ranging from about 100 to about 900 mPa s, preferably from about 150 to about 800 mPa s, more preferably from about 200 to about 600 mPa s measured at a shear rate of about 1000 s^{-1} and at a temperature of about 20°C , measured following the test method described herein. The fluid is preferably a non-Newtonian fluid with shear-thinning properties, hence is further characterized by a low shear viscosity ranging from about 1000 mPa.s to about 10000 mPa.s, preferably from about 1500 mPa.s to about 7500 mPa.s, more preferably from about 2000 mPa.s to about 5000 mPa.s when measured at a shear rate of about 0.5 s^{-1} . Without wishing to be bound by any theory, non-Newtonian fluids with shear thinning properties are believed to have enhanced physical stability properties, especially enhanced phase separation prevention properties, as well as ability to suspend particles. Viscosity is measured using a rotational rheometer. More particularly, the high shear viscosity is measured at about 20°C at a shear rate of about 1000 s^{-1} and the low shear viscosity is measured at about 20°C at a shear rate of about 0.5 s^{-1} using a TA instruments AR-G2 Rheometer (spindle: 40mm 2° steel cone geometry). The measurement method includes a conditioning step (10 s^{-1} for 10 seconds), a peak hold step (0.05 s^{-1} for 180 seconds) and a shear ramp (180 seconds) from 0.1 to 1200 s^{-1} , all at 20°C . Suitable fluids may include, but are not limited to, detergent compositions, such as those sold under the tradenames TIDE, GAIN, ARIEL, TIDE PODS, GAIN FLINGS, FAIRY and CASCADE manufactured by The Procter & Gamble Company, Cincinnati, Ohio, USA.

It has been a surprising and unexpected discovery of the present invention that a sufficient amount of protease enzyme, e.g., from about 0.02 wt% to about 10 wt%, together with the

polyethylene glycol having a weight average molecular weight of from 150 to 350 Daltons can be used in a liquid laundry detergent composition with a high shear viscosity of about 100-900 mPa s (measured at a shear rate of about 1000 s^{-1} and at a temperature of about 20°C) to not only provide stain removal/cleaning benefit, but also to reduce liquid stringing, which in turn helps to prevent or minimize film sealing failure when such liquid laundry detergent composition is enclosed into a pouch formed by a water-soluble film for making a unit dose article.

Preferably, but not necessarily, the liquid laundry detergent composition further comprises from about 0.1% to about 30%, for example 1%, 2%, 3%, 5%, 7%, 12%, 15%, 17%, 20%, 25% or any ranges therebetween, preferably from about 1% to about 25%, more preferably from about 2% to about 20%, still more preferably from about 3% to 15%, by weight of the composition, of a non-aqueous solvent. “Non-aqueous solvent” hereinwith means any non-aqueous solvent except the polyethylene glycol contained in the water-soluble unit dose article according to the present disclosure (e.g., the polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons). Preferably, the non-aqueous solvent may be selected from the group consisting of monoalcohols, diols, polyols, glycol ethers and any combinations thereof. More preferably, the non-aqueous solvent may be selected from the group consisting of ethanol, propanol, isopropanol, terpineol, ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol; 1,3-butanediol; 1,4-butanediol; 2,3-butanediol, glycerin, butanetriol, pentaerythritol, dipropylene glycol (DPG), tripropylene glycol (TPG), polypropylene glycol (PPG), polyethylene glycol having a weight average molecular weight of from 400 to 13000 Daltons, n-butoxy propoxy propanol (nBPP), diethylene glycol, 2-ethoxyethanol, 2-butoxyethanol, and any combinations thereof.

The term of “diol solvent” as used herein means alcohol compounds having two hydroxyl groups. The term of “polyol solvent” as used herein means alcohol compounds having three or more hydroxyl groups. The term of “hydroxyl ether solvent” as used herein means ether compounds having at least one hydroxyl group.

In some embodiments, 1,2-propanediol may be present in an amount ranging from 0.1% to 25%, preferably from 1% to 18%, more preferably from 3% to 15%, by weight of the composition.

In some embodiments, glycerin may be present in an amount ranging from 0.1% to 15%, preferably from 1% to 12%, more preferably from 2% to 10%, by weight of the composition.

In some embodiments, liquid laundry detergent composition may comprise 1,2-propanediol, glycerin and polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons in which the total amount of 1,2-propanediol, glycerin and polyethylene glycol may range from 5% to 50%, preferably from 10% to 45%, more preferably from 15% to 40%, by weight of the composition.

In some embodiments, liquid laundry detergent composition may comprise 1,2-propanediol and polyethylene glycol having a weight average molecular weight of from about 150 to about 350 Daltons in which the weight ratio of 1,2-propanediol and the polyethylene glycol is from 0.1 to 10, preferably from 0.15 to 8, and more preferably from 0.2 to 6.

In some embodiments, liquid laundry detergent composition may comprise glycerin and polyethylene glycol having a weight average molecular weight of from about 150 to about 300 Daltons in which the weight ratio of glycerin and the polyethylene glycol is from 0.1 to 0.7, preferably from 0.2 to 0.6 and more preferably from 0.3 to 0.5.

In some embodiments, liquid laundry detergent composition may comprise 1,2-propanediol and glycerin in which the weight ratio of 1,2-propanediol and glycerin is from 0.2 to 10, preferably from 0.4 to 6, and more preferably from 0.5 to 4.

The liquid laundry detergent composition comprises between about 0.5% and about 20%, more preferably between about 1% and about 15%, most preferably between about 5% and about 12% by weight of the liquid laundry detergent composition of water.

The liquid laundry detergent composition may comprise an alkanolamine, preferably the alkanolamine comprises monoethanolamine, triethanolamine or a mixture thereof, most preferably the alkanolamine comprises monoethanolamine. Preferably, the liquid laundry detergent composition comprises between about 5% and about 15%, more preferably between about 6% and about 10% by weight of the liquid laundry detergent composition of the alkanolamine, preferably of monoethanolamine, triethanolamine or a mixture thereof, most preferably of monoethanolamine.

The water-soluble unit dose article may comprise an adjunct ingredient selected from hueing dyes, polymers, builders, dye transfer inhibiting agents, dispersants, enzymes, enzyme stabilizers, catalytic materials, bleach, bleach activators, polymeric dispersing agents, anti-redeposition agents, suds suppressors, aesthetic dyes, opacifiers, perfumes, perfume delivery systems, structurants, hydrotropes, processing aids, pigments and mixtures thereof.

Preferably, the liquid laundry detergent composition in the unite dose article has a pH between 6 and 10, between 6.5 and 8.9, or between 7 and 8, wherein the pH of the laundry

detergent composition is measured as a 10% product concentration in demineralized water at 20°C.

Surfactant

The liquid detergent composition of the present invention may further comprise from 0.1% to 70%, preferably from 1% to 60%, more preferably from 5% to 50%, most preferably from 10% to 45%, by weight of the composition, of a surfactant. Preferably, the surfactant may be selected from the group consisting of C₆-C₂₀ alkyl dimethyl amine oxides, C₆-C₂₀ amido alkyl dimethyl amine oxides, C₆-C₂₀ linear alkylbenzene sulfonates (LAS), C₆-C₂₀ alkyl sulfates (AS), C₆-C₂₀ alkyl alkoxy sulfates (AAS), C₆-C₂₀ methyl ester sulfonates (MES), C₆-C₂₀ alkyl ether carboxylates (AEC), fatty acids, alkyl alkoxyated alcohols, alkyl alkoxyated phenols, alkyl polysaccharides, alkyl polyglycosides, methyl ester ethoxylates, polyhydroxy fatty acid amides, alkoxyated fatty acid esters, sucrose esters, sorbitan esters and alkoxyated derivatives of sorbitan esters, and any combinations thereof. More preferably, the surfactant may comprise one or more surfactants selected from the group consisting of a C₆-C₂₀ alkyl dimethyl amine oxide, a C₆-C₂₀ LAS, a C₆-C₂₀ alkoxyated alcohol having a weight average degree of alkoxylation ranging from 1 to 20, preferably a C₆-C₂₀ ethoxylated alcohol having a weight average degree of ethoxylation ranging from 1 to 20 and the combination thereof.

Preferably, the anionic surfactant may be selected from the group consisting of C₆-C₂₀ linear alkylbenzene sulfonates (LAS), C₆-C₂₀ alkyl sulfates (AS), C₆-C₂₀ alkyl alkoxy sulfates (AAS), C₆-C₂₀ methyl ester sulfonates (MES), C₆-C₂₀ alkyl ether carboxylates (AEC), fatty acids and any combinations thereof. More preferably, the anionic surfactant system may comprise a C₆-C₂₀ LAS and optionally an additional anionic surfactant such as a C₆-C₂₀ AS and/or a C₆-C₂₀ AAS preferably a C₆-C₂₀ alkyl ethoxylated sulfate having a weight average degree of ethoxylation ranging from 1 to 7. In one embodiment, LAS is C₁₀-C₁₆ LAS, preferably C₁₂-C₁₄ LAS.

Preferably, the non-ionic surfactant may be selected from the group consisting of alkyl alkoxyated alcohols, alkyl alkoxyated phenols, alkyl polysaccharides, alkyl polyglycosides, methyl ester ethoxylates, polyhydroxy fatty acid amides, alkoxyated fatty acid esters, sucrose esters, sorbitan esters and alkoxyated derivatives of sorbitan esters, and any combinations thereof. More preferably, the nonionic surfactant may comprise a C₈-C₁₈ ethoxylated alcohol having a weight average degree of ethoxylation ranging from 1 to 20, preferably from 5 to 15, more preferably from 5 to 10.

In some embodiments, the surfactant may comprise an anionic surfactant and a non-ionic surfactant in which the anionic surfactant comprises a C₆-C₂₀ LAS and optionally a C₆-C₂₀ AS and/or a C₆-C₂₀ AAS and the non-ionic surfactant comprises a C₆-C₂₀ alkoxyated alcohol having a weight average degree of alkoxylation ranging from 1 to 20, preferably from 5 to 15, more preferably from 5 to 10.

In some embodiments, the weight ratio of LAS to AA_xS is at least 0.6, preferably at least 0.8, more preferably at least 0.9, most preferably at least 1, for example 0.6, 0.7, 0.8, 0.9, 1, 1.2, 1.5, 2, 2.5, 3, 4, 5, 8, 10 or any ranges therebetween.

In some embodiments, the C₆-C₂₀ LAS is present in an amount ranging from 1% to 30%, preferably from 2% to 25%, more preferably from 3% to 20%, by weight of the composition.

In some embodiments, the C₆-C₂₀ AAS is present in an amount ranging from 1% to 20%, preferably from 2% to 15%, more preferably from 3% to 10%, by weight of the composition.

In some embodiments, the C₆-C₂₀ alkoxyated alcohol is present in an amount ranging from 1% to 60%, preferably from 2% to 45%, more preferably from 3% to 30%, most preferably from 3% to 20%, by weight of the composition.

In some embodiments, the liquid laundry detergent composition may further comprise from 1% to 30%, preferably from 2% to 25%, more preferably from 3% to 20%, by weight of the composition, of an amine oxide.

In some embodiments, the liquid laundry detergent composition may further comprise from 0.1% to 10%, preferably from 0.5% to 8%, more preferably from 0.7% to 6%, most preferably from 1% to 3, by weight of the composition, of a fatty acid.

In an embodiment, the liquid laundry detergent composition may comprise:

- a) from 2% to 20%, by weight of the composition, of polyethylene glycol having a weight average molecular weight of from 150 to 350 Daltons,
- b) from 0.02% to 10%, by weight of the composition, of a protease,
- c) optionally, from 0.1% to 10%, by weight of the composition, of a second enzyme selected from the group consisting of amylase, mannanase, lipase or combinations thereof,
- d) from 5% to 20%, by weight of the composition, of a non-aqueous solvent which comprises 1,2-propanediol, and
- e) from 30% to 45%, by weight of the composition, of a surfactant selected from the group consisting of a C₆-C₂₀ LAS, a C₆-C₂₀ AAS, a C₆-C₂₀ alkoxyated alcohol having

a weight average degree of ethoxylation ranging from 5 to 10, and the combinations thereof.

Water-Soluble Film

The water-soluble film of the present invention is soluble or dispersible in water. The water-soluble film preferably has a thickness of from 20 to 150 micron, preferably 35 to 125 microns, even more preferably 50 to 110 microns, most preferably about 76 microns.

Preferably, the film has a water-solubility of at least 50%, preferably at least 75% or even at least 95%, as measured by the method set out here after using a glass-filter with a maximum pore size of 20 microns: 5 grams $\pm$ 0.1 gram of film material is added in a pre-weighed 3L beaker and 2L $\pm$ 5ml of distilled water is added. This is stirred vigorously on a magnetic stirrer, Labline model No. 1250 or equivalent and 5 cm magnetic stirrer, set at 600 rpm, for 30 minutes at 30°C. Then, the mixture is filtered through a folded qualitative sintered-glass filter with a pore size as defined above (max. 20 micron). The water is dried off from the collected filtrate by any conventional method, and the weight of the remaining material is determined (which is the dissolved or dispersed fraction). Then, the percentage solubility or dispersibility can be calculated.

The water-soluble film material may be obtained by casting, blow-moulding, extrusion or blown extrusion of the polymeric material, as known in the art.

The water-soluble film comprises polyvinylalcohol. The polyvinylalcohol may be present between 50% and 95%, preferably between 55% and 90%, more preferably between 60% and 80% by weight of the water-soluble film. The polyvinylalcohol preferably comprises polyvinyl alcohol homopolymer, polyvinylalcohol copolymer, or a mixture thereof. Preferably, the water-soluble film comprises a blend of polyvinylalcohol homopolymers and/or anionic polyvinylalcohol copolymers, preferably wherein the polyvinylalcohol copolymers are selected from sulphonated and carboxylated anionic polyvinylalcohol copolymers especially carboxylated anionic polyvinylalcohol copolymers, most preferably the water-soluble film comprises a blend of a polyvinylalcohol homopolymer and a carboxylated anionic polyvinylalcohol copolymer, or a blend of polyvinylalcohol homopolymers. Alternatively, the polyvinylalcohol comprises an anionic polyvinyl alcohol copolymer, most preferably a carboxylated anionic polyvinylalcohol copolymer. When the polyvinylalcohol in the water-soluble film is a blend of a polyvinylalcohol homopolymer and a carboxylated anionic polyvinylalcohol copolymer, the homopolymer and the anionic copolymer are present in a relative weight ratio of 90/10 to 10/90, preferably 80/20 to

20/80, more preferably 70/30 to 50/50. Without wishing to be bound by theory, the term “homopolymer” generally includes polymers having a single type of monomeric repeating unit (e.g., a polymeric chain comprising or consisting of a single monomeric repeating unit). For the particular case of polyvinylalcohol, the term “homopolymer” further includes copolymers having a distribution of vinyl alcohol monomer units and optionally vinyl acetate monomer units, depending on the degree of hydrolysis (e.g., a polymeric chain comprising or consisting of vinyl alcohol and vinyl acetate monomer units). In the case of 100% hydrolysis, a polyvinylalcohol homopolymer can include only vinyl alcohol units. Without wishing to be bound by theory, the term “copolymer” generally includes polymers having two or more types of monomeric repeating units (e.g., a polymeric chain comprising or consisting of two or more different monomeric repeating units, whether as random copolymers, block copolymers, etc.). For the particular case of polyvinylalcohol, the term “copolymer” (or “polyvinylalcohol copolymer”) further includes copolymers having a distribution of vinyl alcohol monomer units and vinyl acetate monomer units, depending on the degree of hydrolysis, as well as at least one other type of monomeric repeating unit (e.g., a ter- (or higher) polymeric chain comprising or consisting of vinyl alcohol monomer units, vinyl acetate monomer units, and one or more other monomer units, for example anionic monomer units). In the case of 100% hydrolysis, a polyvinylalcohol copolymer can include a copolymer having vinyl alcohol units and one or more other monomer units, but no vinyl acetate units. Without wishing to be bound by theory, the term “anionic copolymer” includes copolymers having an anionic monomer unit comprising an anionic moiety. General classes of anionic monomer units which can be used for the anionic polyvinyl alcohol copolymer include the vinyl polymerization units corresponding to monocarboxylic acid vinyl monomers, their esters and anhydrides, dicarboxylic monomers having a polymerizable double bond, their esters and anhydrides, vinyl sulfonic acid monomers, and alkali metal salts of any of the foregoing. Examples of suitable anionic monomer units include the vinyl polymerization units corresponding to vinyl anionic monomers including vinyl acetic acid, maleic acid, monoalkyl maleate, dialkyl maleate, monomethyl maleate, dimethyl maleate, maleic anhydride, fumaric acid, monoalkyl fumarate, dialkyl fumarate, monomethyl fumarate, dimethyl fumarate, fumaric anhydride, itaconic acid, monomethyl itaconate, dimethyl itaconate, itaconic anhydride, vinyl sulfonic acid, allyl sulfonic acid, ethylene sulfonic acid, 2-acrylamido-1-methylpropanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-methylacrylamido-2-methylpropanesulfonic acid, 2-sulfoethyl acrylate, alkali metal salts of the foregoing (e.g., sodium, potassium, or other alkali metal salts), esters of the foregoing (e.g., methyl, ethyl, or

other C1-C4 or C6 alkyl esters), and combinations thereof (e.g., multiple types of anionic monomers or equivalent forms of the same anionic monomer). The anionic monomer may be one or more acrylamido methylpropanesulfonic acids (e.g., 2-acrylamido-1-methylpropanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-methylacrylamido-2-methylpropanesulfonic acid), alkali metal salts thereof (e.g., sodium salts), and combinations thereof. Preferably, the anionic moiety of the first anionic monomer unit is selected from a sulphonate, a carboxylate, or a mixture thereof, more preferably a carboxylate, most preferably an acrylate, a methacrylate, a maleate, or a mixture thereof. Preferably, the anionic monomer unit is present in the anionic polyvinyl alcohol copolymer in an average amount in a range of between 1 mol.% and 10 mol.%, preferably between 2 mol.% and 5 mol.%. Preferably, the polyvinyl alcohol, and/or in case of polyvinylalcohol blends the individual polyvinylalcohol polymers, have an average viscosity (μl) in a range of between 4 mPa.s and 30 mPa.s, preferably between 10mPa.s and 25 mPa.s, measured as a 4% polyvinyl alcohol copolymer solution in demineralized water at 20 degrees C. The viscosity of a polyvinyl alcohol polymer is determined by measuring a freshly made solution using a Brookfield LV type viscometer with UL adapter as described in British Standard EN ISO 15023-2:2006 Annex E Brookfield Test method. It is international practice to state the viscosity of 4% aqueous polyvinyl alcohol solutions at 20 °C. It is well known in the art that the viscosity of an aqueous water-soluble polymer solution (polyvinylalcohol or otherwise) is correlated with the weight-average molecular weight of the same polymer, and often the viscosity is used as a proxy for weight-average molecular weight. Thus, the weight-average molecular weight of the polyvinylalcohol can be in a range of 30,000 to 175,000, or 30,000 to 100,000, or 55,000 to 80,000. Preferably, the polyvinyl alcohol, and/or in case of polyvinylalcohol blends the individual polyvinylalcohol polymers, have an average degree of hydrolysis in a range of between 75% and 99%, preferably between 80% and 95%, most preferably between 85% and 95%. A suitable test method to measure the degree of hydrolysis is as according to standard method JIS K6726.

Preferably, the water-soluble film comprises a non-aqueous plasticizer. Preferably, the non-aqueous plasticizer is selected from polyols, sugar alcohols, and mixtures thereof. Suitable polyols include polyols selected from the group consisting of glycerol, diglycerin, ethylene glycol, diethylene glycol, triethyleneglycol, tetraethylene glycol, polyethylene glycols up to 400 molecular weight, neopentyl glycol, 1,2-propylene glycol, 1,3-propanediol, dipropylene glycol, polypropylene glycol, 2-methyl-1,3-propanediol, trimethylolpropane and polyether polyols, or a mixture thereof. Suitable sugar alcohols include sugar alcohols selected from the group

consisting of isomalt, maltitol, sorbitol, xylitol, erythritol, adonitol, dulcitol, pentaerythritol and mannitol, or a mixture thereof. More preferably the non-aqueous plasticizer is selected from glycerol, 1,2-propanediol, dipropylene glycol, 2-methyl-1,3-propanediol, trimethylolpropane, triethyleneglycol, polyethyleneglycol, sorbitol, or a mixture thereof, most preferably selected from glycerol, sorbitol, trimethylolpropane, dipropylene glycol, and mixtures thereof. One particularly suitable plasticizer system includes a blend of glycerol, sorbitol and trimethylolpropane. Another particularly suitable plasticizer system includes a blend of glycerin, dipropylene glycol, and sorbitol. Preferably, the film comprises between 5% and 50%, preferably between 10% and 40%, more preferably between 20% and 30% by weight of the film of the non-aqueous plasticizer.

Preferably, the water-soluble film comprises a surfactant. Preferably, the water-soluble film comprises a surfactant in an amount between 0.1% and 2.5%, preferably between 1% and 2% by weight of the water-soluble film. Suitable surfactants can include the nonionic, cationic, anionic and zwitterionic classes. Suitable surfactants include, but are not limited to, polyoxyethylenated polyoxypropylene glycols, alcohol ethoxylates, alkylphenol ethoxylates, tertiary acetylenic glycols and alkanolamides (nonionics), polyoxyethylenated amines, quaternary ammonium salts and quaternized polyoxyethylenated amines (cationics), and amine oxides, N-alkylbetaines and sulfobetaines (zwitterionics). Other suitable surfactants include dioctyl sodium sulfosuccinate, lactylated fatty acid esters of glycerol and propylene glycol, lactic esters of fatty acids, sodium alkyl sulfates, polysorbate 20, polysorbate 60, polysorbate 65, polysorbate 80, lecithin, acetylated fatty acid esters of glycerol and propylene glycol, and acetylated esters of fatty acids, and combinations thereof.

Preferably the water-soluble film according to the invention comprises lubricants / release agents. Suitable lubricants/release agents can include, but are not limited to, fatty acids and their salts, fatty alcohols, fatty esters, fatty amines, fatty amine acetates and fatty amides. Preferred lubricants/release agents are fatty acids, fatty acid salts, and fatty amine acetates. The amount of lubricant/release agent in the water-soluble film is in a range of from 0.02% to 1.5%, preferably from 0.1% to 1% by weight of the water-soluble film.

Preferably, the water-soluble film comprises fillers, extenders, antiblocking agents, detackifying agents or a mixture thereof. Suitable fillers, extenders, antiblocking agents, detackifying agents or a mixture thereof include, but are not limited to, starches, modified starches, crosslinked polyvinylpyrrolidone, crosslinked cellulose, microcrystalline cellulose, silica, metallic oxides, calcium carbonate, talc and mica. Preferred materials are starches,

modified starches and silica. Preferably, the amount of filler, extender, antiblocking agent, detackifying agent or mixture thereof in the water-soluble film is in a range of from 0.1% to 25%, preferably from 1% to 10%, more preferably from 2% to 8%, most preferably from 3% to 5% by weight of the water-soluble film. In the absence of starch, one preferred range for a suitable filler, extender, antiblocking agent, detackifying agent or mixture thereof is from 0.1% to 1%, preferably 4%, more preferably 6%, even more preferably from 1% to 4%, most preferably from 1% to 2.5%, by weight of the water-soluble film.

Preferably the water-soluble film according to the invention has a residual moisture content of at least 4%, more preferably in a range of from 4% to 15%, even more preferably of from 5% to 10% by weight of the water-soluble film as measured by Karl Fischer titration.

Preferred films exhibit good dissolution in cold water, meaning unheated distilled water. Preferably such films exhibit good dissolution at temperatures of 24°C, even more preferably at 10°C. By good dissolution it is meant that the film exhibits water-solubility of at least 50%, preferably at least 75% or even at least 95%, as measured by the method set out here after using a glass-filter with a maximum pore size of 20 microns, described above.

Preferred films include those supplied by Monosol under the trade references M8630, M8900, M8779, M8310.

The film may be opaque, transparent or translucent. The film may comprise a printed area. The area of print may be achieved using standard techniques, such as flexographic printing or inkjet printing. Preferably, the ink used in the printed area comprises between 0ppm and 20ppm, preferably between 0ppm and 15ppm, more preferably between 0ppm and 10ppm, even more preferably between 0ppm and 5ppm, even more preferably between 0ppm and 1ppm, even more preferably between 0ppb and 100ppb, most preferably 0ppb dioxane. Those skilled in the art will be aware of known methods and techniques to determine the dioxane level within the ink formulations.

The film may comprise an aversive agent, for example a bittering agent. Suitable bittering agents include, but are not limited to, naringin, sucrose octaacetate, quinine hydrochloride, denatonium benzoate, or mixtures thereof. Any suitable level of aversive agent may be used in the film. Suitable levels include, but are not limited to, 1 to 5000ppm, or even 100 to 2500ppm, or even 250 to 2000rpm.

Preferably, the water-soluble film or water-soluble unit dose article or both are coated in a lubricating agent, preferably, wherein the lubricating agent is selected from talc, zinc oxide, silicas, siloxanes, zeolites, silicic acid, alumina, sodium sulphate, potassium sulphate, calcium

carbonate, magnesium carbonate, sodium citrate, sodium tripolyphosphate, potassium citrate, potassium tripolyphosphate, calcium stearate, zinc stearate, magnesium stearate, starch, modified starches, clay, kaolin, gypsum, cyclodextrins or mixtures thereof.

Preferably, the water-soluble film, and each individual component thereof, independently comprises between 0ppm and 20ppm, preferably between 0ppm and 15ppm, more preferably between 0ppm and 10ppm, even more preferably between 0ppm and 5ppm, even more preferably between 0ppm and 1ppm, even more preferably between 0ppb and 100ppb, most preferably 0ppb dioxane. Those skilled in the art will be aware of known methods and techniques to determine the dioxane level within water-soluble films and ingredients thereof.

Method of washing

A further aspect of the present invention is a method of washing comprising the steps of adding the water-soluble unit dose article according to the present invention to sufficient water to dilute the liquid detergent composition by a factor of at least 300 fold to create a wash liquor and contacting items to be washed with said wash liquor.

Packaged product

A further aspect of the present invention is a packaged product comprising a recloseable container and at least one water-soluble unit dose article according to the present invention comprised therein.

Those skilled in the art will be aware of relevant storage receptacles. Preferably, the storage receptacle is a flexible, preferably resealable, bag, a rigid, preferably recloseable, tub or a mixture thereof, preferably, wherein the storage receptacle comprises a child resistant closure. Those skilled in the art will be aware of suitable child resistant closures.

The package may be made from any suitable material. The container may be made from metallic materials, Aluminium, plastic materials, cardboard materials, laminates, cellulose pulp materials or a mixture thereof. The package may be made from a plastic material, preferably a polyolefin material. The package may be made from polypropylene, polystyrene, polyethylene, polyethylene terephthalate, PVC or a mixture thereof or more durable engineering plastics like Acrylonitrile Butadiene Styrene (ABS), Polycarbonates, Polyamides and the like. The material used to make the container may comprise other ingredients, such as colorants, preservatives, plasticisers, UV stabilizers, Oxygen, perfume and moisture barriers recycled materials and the like.

Test Method

Test 1: Protease Activity Test Method

P-nitroaniline assay for determination of protease activity:

The substrate used to measure the protease activity is a four amino acid peptide containing a terminal p-nitroanilide group as a chromophore. This material is called N-Succinyl-ALA-ALA-PRO-PHE p-nitroanilide (PNA). The mechanism for this chemistry is as follows: A solution of detergent/protease is introduced to the PNA substrate in solution. The enzyme cleaves bonds between amino acids and most importantly the amide bond between the phenylalanine and the p-nitroanilide group liberating p-nitroaniline, thus producing a yellow color. The intensity of the color (405nm) is proportional to the amount of enzyme in the solution.

Reagents:

1. TRIS assay buffer (pH=8.3) solution: 12.1 ± 0.05 g of Trizma base, 1.1 ± 0.05 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 5.0 ± 0.1 g of sodium thiosulphate dissolve into purified water and make up to 1L solution.
2. PNA solution: 500mg of PNA dissolve into 5mL DMSO.
3. PNA substrate working solution (1% volume/volume): prepare 1% volume PNA solution + 99% volume TRIS assay buffer solution mixture. E.g. 0.25ml PNA solution mixes with 24.75ml TRIS assay buffer solution.
4. Calcium chloride and sodium thiosulfate solution: use 10.00 ± 0.50 g sodium thiosulfate, 0.50 ± 0.05 g of calcium chloride, and purified water to prepare solution.

Procedure:

1. Weigh 0.5 ± 0.0002 g SUD juice liquid sample into a 100ml volumetric flask.
2. Dilute SUD juice with sodium thiosulfate/calcium chloride solution to 100ml. Shake to homogenize.
3. Allow solution to equilibrate for 15mins or more before use. Place in instrument sample cups.
4. Place PNA reagent in instrument.
5. Set Gallery instrument kinetic at 405nm wavelength and start Gallery instrument.
6. Test needs 10 minutes to obtain results.

Data Calculation:

1. Measure fresh liquid sample protease active level and set this value as 100%.
2. Place SUD samples into 40 °C ovens for 2 and 4 weeks separately.

3. Measure aged samples protease active level and calculate leftover protease ratio versus fresh sample value.

Example:

Fresh SUD liquid sample contains 50mg/100g protease active level. After 2 weeks 40°C aging, protease active level is 40mg/100g. The leftover protease ratio is 80%.

Test 2: Amylase Test Method

Amylase test method can refer to the description disclosed in WO2018/144399A1.

Test 3: Stability Test

Stability test is conducted through visual inspection as below:

- 1) Prepare liquid composition samples to be tested by mixing ingredients in 30ml transparent glass bottles;
- 2) Store the samples prepared in Step 1) under 25°C for 4 weeks;
- 3) Visually inspect the samples to determine if they are still homogeneous systems after Step 2). If there is any phase separation such as the formation of separated layers or flocculation, it is determined as “fail”. If there is no phase separation, it is determined as “pass”.

Test 4: Weeping Test for Unit Dose Articles

In this test, Corneometer (available from BMM&DI Clinical Sciences company) is used to measure weeping level of unit dose articles. The Measurement Principle is based on capacitance measurement of a dielectric medium. For Liquitabs it measures the dielectric constant of water and other substances which penetrate the PVA-Film.

The unit dose articles need to be pre-conditioned in room condition 25°C or 32°C, 80%RH CTCH for 48hrs.

To measure the weeping level, put the sensor of the Corneometer on the surface of unit dose articles and press it down slowly until a measurement is registered. For a multi compartment unit dose article, the bottom layer is measured 5 times and each top layer 2 times.

Weeping level can then be defined by correlating average, lower and upper limit of the range with the Weeping Scale being reflected below.

Weeping Category	% Weeping
Light	<50
Light/Medium	50-65
Medium	65-80
Heavy	>80

Test 5: Physical Property Test for Film in Unit Dose Articles

A 76 μm thick polyvinylalcohol based water-soluble film, as provided by the Monosol company, is used to assess film physical properties. Film physical properties is defined through measuring film thickness increase%, area increase%, volume increase%, maximum tensile stress, and tensile strain% after having subjected the water-soluble film to an ageing experiment through immersing in liquid detergent composition samples as above. A film sample of 12.5 cm by 2.5 cm is immersed within 150 ml of test liquid by 1) selecting a flat clean inert glass recipient, 2) covering the bottom of the recipient with a thin layer of the example formulation to be tested, 3) carefully spreading the film to be tested on the liquid, 4) gently pushing air bubbles trapped under the film towards the sides, 5) gently pouring the remaining example formulation on top of the film, in such a way that the film is fully immersed into the liquid, ensuring that the film is free of wrinkles and that no air bubbles are in contact with the film, and 6) closing the glass container and 7) storing the closed container for 5 days at 50°C, 80%RH CTCH. After ageing, the film is removed from the formulation example and gently wiped dry with a soft dry liquid absorbing paper, followed immediately by measuring the post film immersion and stress-strain profile. The film thickness increase%, area increase%, volume increase% are measured by a ruler; maximum tensile stress, and tensile strain% are measured using an Instron instrument which is commercially available from the Instron company.

EXAMPLES

Example 1: Improved Protease Activity for Unit Dose Articles Containing polyethylene glycol having a weight average molecular weight of from 150 to 350 Daltons and Protease

The liquid detergent formulations of Comparative Examples 1-2 and Inventive Examples 1-2 are prepared using standard mixing techniques and equipment known to those skilled in the art, shown in Table 1. Then, the liquid detergent compositions (~10ml) are encapsulated into compartment(s) of the unit dose by using a polyvinyl-alcohol-based film in which the PVA film and the shape of the unit dose are the same with CN Tides Laundry three-chamber side-by-side pouches available in market. Comparative Examples contain protease but without polyethylene glycol having a weight average molecular weight of from 150 to 350 Daltons, while the Inventive Examples contain both protease and polyethylene glycol having a weight average molecular weight of 200 Daltons (PEG200).

Table 1

	Comparative	Comparative	Inventive	Inventive
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	Example 1	Example 2	Example 1	Example 2
Water	6.3	5.3	6.3	5.3
Citric acid (50%)	1.6	1.6	1.6	1.6
PEG200	--	--	12	12
MEA	6.2	6.2	6.2	6.2
Glycerin	5.4	5.4	5.4	5.4
K ₂ SO ₃ solution (39%)	1.7	1.7	1.7	1.7
NI ¹	2.3	2.3	2.3	2.3
HLAS	24	24	24	24
DTPK fatty acid	1.8	1.8	1.8	1.8
AE3S (67.6%)	24	24	24	24
SRP polymer ²	4.4	4.4	4.4	4.4
Perfume	3.7	3.7	3.7	3.7
Amylase ³	--	1.0	--	1.0
Protease ⁴	1.0	1.0	1.0	1.0
1,2-Pdiol	Balance	Balance	Balance	Balance
Total	100	100	100	100

¹ NI: nonionic surfactant: C₁₂₋₁₄ alcohol ethoxylate AE7

² SRP polymer: ethoxylated polyethyleneimine commercially available from BASF

³ Amylase: from Fuji

⁴ Protease: from Preferenz® P283 from DuPont

Protease activity test according to Test 1 as described hereinabove has been conducted and the results are shown in Table 2 below. The protease level (%) contained in the formulation is measured at week 0, week 2 and week 4 respectively, and the ratio of protease activity leftover is calculated per percentage.

Table 2

Aging Time (weeks)	Protease level% in formula	Comparative Example 1	Comparative Example 2	Inventive Example 1	Inventive Example 2
0	Measured	1.01	1.00	0.99	1.00
	Leftover ratio	100%	100%	100%	100%
2	Measured	0.81	0.92	0.96	0.97
	Leftover ratio	81%	92%	97%	98%
4	Measured	0.53	0.81	0.90	0.96
	Leftover ratio	52%	81%	91%	97%

As shown in Table 2, it is found that the combination of PEG having a molecular weight of 200 to 350 Daltons and the protease enzyme (Inventive Examples 1 or 2) provides an improved protease activity/stability than the Comparative Examples where contain no PEG.

Further, the combination of amylase and protease as enzymes helps improvement of the enzyme stability in the Inventive Example 2 containing PEG200.

Example 2: Exemplary Formulations of Unit Dose Laundry Detergent Compositions Containing PEG

The exemplary formulations shown in Table 3 are made for unit dose laundry detergent. These compositions are encapsulated into compartment(s) of the unit dose by using a polyvinyl-alcohol-based film. The unit dose article comprises one single chamber or multiple compartments. The compartments may be arranged in superposed orientation, i.e., one positioned on top of the other, alternatively, the compartments may be positioned in a side-by-side orientation. The composition can be part of a single chamber water soluble unit dose article or can be split over multiple compartments resulting in below “averaged across compartments” full article composition.

Table 3

Ingredients (weight%)	Sample a	Sample b	Sample c	Sample d	Sample e	Sample f	Sample g	Sample h
Nonionic Surfactant ¹	-	30	5	10	10	30	20	10
Anionic surfactant A ²	15	5	5	25	5	10	10	5
Anionic surfactant B ³	25	10	30	9	20	10	5	9
Amylase	2	1	3	4	1.5	0.5	-	3
Protease	0.2	0.5	1.0	1.5	3	7	5	2
C12-14 Dimethyl Amine Oxide	-	-	3	-	5	-	-	10
DTPK Fatty Acid	8	10	2	8	10	5	5	2
MEA	10	-	9	-	8	7	6	1
NaOH	-	2	-	4	-	-	-	1
Citric Acid	1	-	2	0.5	2	3	3	-
Perfume	0.5	0.5	1	3	5	0.5	9	3
Soil suspension polymer ⁴	-	5	10	3	-	-	5	-
1,2-propanediol	0	18	2	11	15	8	5	20
Glycerin	15	-	5	10	5	8	15	8
(di)ethylene glycol monobutyl ether	5	-	-	4	-	-	-	5
Dipropylene glycol	5	-	-	5	-	-	5	10
Polyethylene glycol (PEG)	2	10	20	2	10	8	5	10

Water	balance	balance	balance	balance	balance	balance	balance	balance
Molecular weight of PEG	200 Daltons	250 Daltons	150 Daltons	200 Daltons	300 Daltons	200 Daltons	300 Daltons	200 Daltons

1: Nonionic surfactant: C₁₂-C₁₄ ethoxylated alcohol

2: Anionic surfactant A: C₁₂-C₁₄ alkyl ethoxylated sulfate

3: Anionic surfactant B: C₁₁-C₁₃ linear alkylbenzene sulfonates

4: SRP polymer: ethoxylated polyethyleneimine (PEI600EO20) commercially available from BASF.

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

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

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

CLAIMS

What is claimed is:

1. A water-soluble unit dose article, comprising:
 - i) a water-soluble film, and
 - ii) a liquid laundry detergent composition wrapped with the water-soluble film, wherein the liquid laundry detergent composition comprises:
 - a) from 1% to 25%, by weight of the composition, of polyethylene glycol having a weight average molecular weight of from 150 to 350 Daltons, and
 - b) from 0.02% to 10%, by weight of the composition, of a protease.
2. The water-soluble unit dose article according to claim 1, wherein the polyethylene glycol is present at a level of from 4% to 23%, preferably from 8% to 21%, more preferably from 10% to 20%, by weight of the composition.
3. The water-soluble unit dose article according to claim 1 or 2, wherein the polyethylene glycol has a weight average molecular weight of from 150 to 250 Daltons.
4. The water-soluble unit dose article according to any preceding claims, wherein the liquid laundry detergent composition from 0.2% to 9%, preferably from 0.4% to 8%, by weight of a protease.
5. The water-soluble unit dose article according to any preceding claims, wherein the protease is selected from the group consisting of subtilisin, bromelain, papain, trypsin, metalloprotease, pepsin and combinations thereof.
6. The water-soluble unit dose article according to any preceding claims, wherein the liquid laundry detergent composition further comprises from a secondary enzyme selected from amylase, mannanase, lipase or combinations thereof, wherein preferably the weight ratio of the protease to the secondary enzyme is from 10:1 to 1:10, preferably from 5:1 to 1:5, more preferably from 3:1 to 1:3, and even more preferably from 2:1 to 1:2.

7. The water-soluble unit dose article according to any preceding claims, wherein the liquid laundry detergent composition has a viscosity of from 100 to 900 mPa s, measured at a shear rate of about 1000 s^{-1} and at a temperature of about 20°C .
8. The water-soluble unit dose article according to any preceding claims, wherein the liquid laundry detergent composition is substantially free of inorganic protease inhibitor selected from calcium salts, magnesium salts, or boron containing compound.
9. The water-soluble unit dose article according to any preceding claims, further comprising from 0.1% to 30%, by weight of the composition, of a non-aqueous solvent, selected from the group consisting of monoalcohols, diols, polyols, glycol ethers, and any combinations thereof; preferably the non-aqueous solvent is selected from the group consisting of ethanol, propanol, isopropanol, terpineol, ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-Butanediol, 1,4-Butanediol, 1,3-Butanediol, 2,3-Butanediol, glycerin, butanetriol, pentaerythritol, dipropylene glycol (DPG), tripropylene glycol (TPG), polypropylene glycol (PPG), polyethylene glycol having a weight average molecular weight of from 400 to 13000 Daltons, n-butoxy propoxy propanol (nBPP), diethylene glycol, 2-ethoxyethanol, 2-butoxyethanol, and any combinations thereof; and most preferably selected from the group consisting of 1,2-propanediol, glycerin, dipropylene glycol, and any combinations thereof.
10. The water-soluble unit dose article according to any preceding claims, wherein the liquid laundry detergent composition comprises less than 15%, preferably less than 12%, by weight of the composition, of water.
11. The water-soluble unit dose article according to any preceding claims, wherein the liquid laundry detergent composition comprises:
 - a) from 2% to 20%, by weight of the composition, of polyethylene glycol having a weight average molecular weight of from 150 to 350 Daltons,
 - b) from 0.02% to 10%, by weight of the composition, of a protease,
 - c) optionally, from 0.1% to 10%, by weight of the composition, of a second enzyme selected from the group consisting of amylase, mannanase, lipase or combinations thereof,

d) optionally, from 5% to 20%, by weight of the composition, of 1,2-propanediol, and

e) from 30% to 45%, by weight of the composition, of a surfactant selected from the group consisting of a C₆-C₂₀ LAS, a C₆-C₂₀ AAS, a C₆-C₂₀ alkoxyated alcohol having a weight average degree of ethoxylation ranging from 5 to 10, and combinations thereof.

12. The water-soluble unit dose article according to any preceding claims, wherein the water-soluble film is a polymeric water-soluble film, preferably wherein the polymeric film comprises polyvinyl alcohol.
13. The water-soluble unit dose article according to any preceding claims comprising an adjunct ingredient selected from hueing dyes, polymers, builders, dye transfer inhibiting agents, dispersants, catalytic materials, bleach, bleach activators, polymeric dispersing agents, anti-redeposition agents, suds suppressors, aesthetic dyes, opacifiers, perfumes, perfume delivery systems, structurants, hydrotropes, processing aids, pigments, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER INV. C11D1/72 C11D3/37 C11D3/386 C11D17/04 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/319311 A1 (LABEQUE REGINE [BE] ET AL) 29 December 2011 (2011-12-29) paragraph [11;54;64]; claim 1; examples 5,7 -----	1, 3, 4, 8-13
X	US 2004/209793 A1 (FREGONESE DANIELE [DE]) 21 October 2004 (2004-10-21) paragraphs [83;108;115] - [0118]; claims 1,4; examples 2-9 -----	1-8, 10-13
A	US 2005/187137 A1 (PEGELOW ULRICH [DE] ET AL) 25 August 2005 (2005-08-25) paragraph [275;276] -----	1-13
A	EP 3 786 272 A1 (BLUESUN CONSUMER BRANDS S L [ES]) 3 March 2021 (2021-03-03) paragraphs [0073] - [0083]; table 1 -----	1-13
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
26 October 2023		03/11/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Douelle, Frédéric

INTERNATIONAL SEARCH REPORT

Information on patent family members

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