(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 415 594 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
19.12.2018 Bulletin 2018/51

(51) Int Cl.:
C11D 3/22 *(2006.01)* ***C11D 17/04*** *(2006.01)*
C11D 3/00 *(2006.01)*

(21) Application number: **17176200.8**

(22) Date of filing: **15.06.2017**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

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

(72) Inventors:
- **SOMERVILLE ROBERTS, Nigel Patrick**
  Newcastle-upon-Tyne, NE12 9TS (GB)
- **BROOKER, Alan Thomas**
  Newcastle upon Tyne, NE12 9TS (GB)
- **PICKERING, Carly**
  Newcastle upon Tyne, NE12 9TS (GB)

(74) Representative: **Pickford, James Lawrence**
Procter & Gamble
Technical Centres Limited
Whitley Road
Longbenton
Newcastle upon Tyne NE12 9TS (GB)

(54) **WATER-SOLUBLE UNIT DOSE ARTICLE COMPRISING A SOLID LAUNDRY DETERGENT COMPOSITION**

(57) Water-soluble unit dose article containing solid laundry detergent composition and water-soluble film. The solid detergent composition comprises cationic polysaccharide and it is low alkaline, pH 6,5-8,8 in diluted form.

EP 3 415 594 A1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to water-soluble unit dose articles containing solid laundry detergent compositions and methods of using them.

BACKGROUND OF THE INVENTION

[0002] Water-soluble laundry unit dose articles are known and are liked by consumers due to their ease and efficiency of use in the laundry operation. Water-soluble unit dose articles comprise water-soluble film defining at least one internal compartment. A laundry detergent composition is housed within the internal compartment. Upon exposure to water, the water-soluble film dissolves/disintegrates releasing the laundry detergent composition into the surrounding water.

[0003] The laundry detergent composition may be a solid laundry detergent composition. Such detergent compositions comprise known laundry detergent treatment actives. One preferred active ingredient is a cationically modified polysaccharide.

[0004] Due to their compact form, water-soluble unit dose articles have limited space for formulating the solid laundry detergent compositions. This can result in lower than desired cleaning performance as extra detergent composition cannot simply be added to compensate for any under-performance. Addition of further detergent composition to the water-soluble unit dose article would require making the unit dose article bigger making it less convenient and also could contribute to negatives such as impaired dissolution when additional water soluble film would be required to accommodate the bigger water soluble unit dose article and/or reduced structural stability of the unit dose article especially when further stretching the original water soluble film to accommodate the bigger water soluble unit dose article (the film may not provide sufficient structural stability for the volume of solid detergent composition added).

[0005] Therefore, there is a need in the art to provide improved performance of said water-soluble unit dose articles without addition of increased levels of solid laundry detergent composition to the unit dose articles.

[0006] It was surprisingly found that a water-soluble unit dose article comprising a solid laundry detergent composition having a particular pH (upon dilution of the solid laundry detergent composition) provided improved fabric softness performance of a cationically modified polysaccharide formulated into said solid laundry detergent composition as compared to water-soluble unit dose articles having a solid laundry detergent composition having a higher pH (upon dilution of the solid laundry detergent composition) as known from the art.

SUMMARY OF THE INVENTION

[0007] A first aspect of the present invention is a water-soluble unit dose article comprising a water-soluble film and a solid laundry detergent composition, wherein the water-soluble film defines a first internal compartment and wherein the solid laundry detergent composition is comprised within the first internal compartment, and wherein the water soluble unit dose article composition comprises a cationically modified polysaccharide; and wherein the solid composition at 1wt% dilution in deionized water at 20°C, has an equilibrium pH in the range of from 6.5 to 8.8, preferably between 6.7 and 8.5.

[0008] A second 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 solid laundry detergent composition by a factor of at least 300 fold to create a wash liquor and contacting fabrics to be washed with said wash liquor.

[0009] A third aspect of the present invention is the use of a solid laundry detergent composition comprising a non-soap surfactant and having at 1wt% dilution in deionized water at 20°C an equilibrium pH in the range of from 6.5 to 8.8 in a water-soluble unit dose article to improve the performance of cationically modified polysaccharide.

DETAILED DESCRIPTION OF THE INVENTION

Water-soluble unit dose article

[0010] The present invention is to a water-soluble unit dose article comprising a water-soluble film and a solid laundry detergent composition.

[0011] The water-soluble film is described in more detail below.

[0012] The solid laundry detergent composition is described in more detail below.

[0013] The water-soluble unit dose article comprises the water-soluble film shaped such that the unit-dose article comprises at least a first internal compartment surrounded by the water-soluble film. The compartment should be understood as meaning a closed internal space within the unit dose article, which holds the solid laundry detergent com-

position. 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 solid laundry detergent composition is comprised within the first internal compartment. The water-soluble unit dose article is constructed such that the solid laundry 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.

[0014] During manufacture, a first water-soluble film may be shaped to comprise an open compartment into which the solid laundry 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.

[0015] 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 at least 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, but 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.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] The water-soluble unit dose article may comprise at least a first compartment and a second compartment, preferably at least a first compartment, a second compartment and a third compartment. Preferably, the compartments are arranged in a side-by-side arrangement, a superposed arrangement or a mixture thereof. Preferably, at least the second compartment, more preferably at least the second compartment and the third compartment are superposed onto the first compartment. The second compartment and the third compartment are preferably arranged in a side-by-side arrangement superposed onto the first compartment.

[0020] The first i.e. bottom compartment preferably comprises the free flowing solid detergent composition. The second and subsequent compartments i.e. superposed compartments comprise a liquid, a solid or a mixture thereof, preferably a liquid. All compartments might comprise a gas in addition to the enclosed compositions, preferably will comprise a gas. Without wishing to be bound by theory, such a gas will create an 'air space' in the compartment and will facilitate free flowing of the enclosed compositions, and furthermore can act as an additional barrier against eventual compartment to compartment active migration through the film. Preferably the gas is air.

[0021] The water-soluble unit dose article comprises a cationically modified polysaccharide. Preferably, the solid laundry detergent composition comprises the cationically modified polysaccharide. More preferably, the cationically modified polysaccharide is selected from cationic guar gums, cationic cellulosic polymers, and mixtures thereof, most preferably cationic cellulosic polymers.

[0022] The solid laundry detergent composition preferably comprises between 0.05% and 5%, preferably between 0.1% and 4%, preferably between 0.2% and 3%, more preferably between 0.25% and 2% by weight of the solid laundry detergent composition of the cationically modified polysaccharide.

[0023] Preferably the cationically modified cellulose polymer is selected from cationically modified hydroxyethyl cellulose, cationically modified hydroxypropyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, cationically and hydrophobically modified hydroxypropyl cellulose, or a mixture thereof, more preferably cationically modified hydroxyethyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, or a mixture thereof.

[0024] By "cationically modified" we herein mean that one or more cationically charged groups are bound to the polymer.

[0025] The cationically modified hydroxyethyl cellulose preferably is hydroxyethyl cellulose derivatised with trimethyl ammonium substituted epoxide.

[0026] The cationic guar gum may comprise guar hydroxypropyl trimonium chloride

[0027] The cationically modified polysaccharide can be synthesized in, and are commercially available in, a number of different molecular weights. In order to achieve optimal softening performance from the product, it is desirable that the cationically modified polysaccharide used in this invention be of an appropriate molecular weight. Without wishing to be bound by theory, it is believed that polymers that are too high in mass can entrap soils and prevent them from being removed. The use of cationically modified polysaccharide with an average molecular weight of less than 1,250,000

daltons, or with an average molecular weight of less than 850,000 daltons, and especially those with an average molecular weight of less than 500,000 daltons can help to minimise this effect without significantly reducing the softening performance of properly formulated products. On the other hand, polymers with a molecular weight of about 10,000 daltons or less are believed to be too small to give an effective softening benefit. Therefore the cationic polymer according to the invention preferably has a molecular weight of from about 10,000 daltons to about 1,250,000 daltons, preferably from about 30,000 daltons to about 850,000 daltons, more preferably from about 50,000 daltons to about 750,000 daltons, even more preferably from about 100,000 daltons to about 600,000 daltons, most preferably from about 200,000 daltons to about 500,000 daltons.

[0028] The cationically modified polysaccharide may also have a cationic charge density ranging from about 0.1meq/g to about 5meq/g, preferably from about 0.12meq/g to about 4 meq/g, more preferably from about 0.14meq/g to about 2.5 meq/g, even more preferably from about 0.16meq/g to about 1.5 meq/g, most preferably from about 0.18 meq/g to about 0.7 meq/g, at the pH of intended use of the laundry composition. As used herein the "charge density" of the cationic polymers is defined as the number of cationic sites per polymer gram atomic weight (molecular weight), and can be expressed in terms of meq/gram of cationic charge. In general, adjustments of the proportions of amine or quaternary ammonium moieties in the polymer in function of the pH of the liquid laundry formulation in the case of amines, will affect the charge density. Without intending to be bound by theory, cationic polymers with a too high charge density are thought to be too sensitive to precipitate out with anionic compounds in the formulation, while cationic polymers with a too low charge density are thought to have a too low affinity to fabrics, compromising softness accordingly. Any anionic counterions can be used in association with cationic polymers. Non-limiting examples of such counterions include halides (e.g. chlorine, fluorine, bromine, iodine), sulphate and methylsulfate, preferably halides, more preferably chlorine.

[0029] The cationically modified polysaccharide might be "hydrophobically modified". We herein mean that one or more hydrophobic groups are bound to the polymer. Without intending to be bound by theory we believe that hydrophobic modification can increase the affinity of the polymer towards the fabric. Without intending to be limiting, the one or more hydrophobic groups can be independently selected from C_1-C_{32} preferably C_5-C_{32} alkyl; C_1-C_{32} preferably C_5-C_{32} substituted alkyl, C_5-C_{32} alkylaryl, or C_5-C_{32} substituted alkylaryl, (poly)alkoxy C_1-C_{32} preferably C_5-C_{32} alkyl or (poly)alkoxy substituted C_1-C_{32} preferably C_5-C_{32} alkyl or mixtures thereof. Hydrophobic substitution on the polymer, preferably on the anhydroglucose rings or alternatively on the nitrogen of the cationic substitution of the cationic polymer may range from 0.01% to 5% per glucose unit, more preferably from 0.05% to 2% per glucose unit, of the polymeric material.

[0030] Those skilled in the art will be aware of ways to make the cationically modified polysaccharide using conventional chemical techniques. The cationically modified polysaccharide may be lightly cross-linked with a dialdehyde, such as glyoxal, to prevent forming lumps, nodules or other agglomerations when added to water at ambient temperatures.

[0031] The cationically modified polysaccharide include those which are commercially available and further include materials which can be prepared by conventional chemical modification of commercially available materials. Commercially available cationically modified polysaccharides include those with the INCI name Polyquaternium 10, such as those sold under the trade names: Ucare Polymer JR 30M, JR 400, JR 125, LR 400 and LK 400 polymers; Polyquaternium 67 such as those sold under the trade name Softcat SK ™, all of which are marketed by Amerchol Corporation, Edgewater NJ; and Polyquaternium 4 such as those sold under the trade name: Celquat H200 and Celquat L-200, available from National Starch and Chemical Company, Bridgewater, NJ. Other suitable polysaccharides include hydroxyethyl cellulose or hydoxypropylcellulose quaternized with glycidyl C_{12}-C_{22} alkyl dimethyl ammonium chloride. Examples of such polysaccharides include the polymers with the INCI names Polyquaternium 24 such as those sold under the trade name Quaternium LM 200 by Amerchol Corporation, Edgewater NJ. Commercially available guar gums include the N-HANCE series from the Ashland Corporation.

Water-soluble film

[0032] The 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 micron, even more preferably 50 to 110 micron, most preferably about 76 micron.

[0033] 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 ±0.1 gram of film material is added in a pre-weighed 3L beaker and 2L ± 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 dispersability can be calculated.

[0034] 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.

[0035] Preferred polymers, copolymers or derivatives thereof suitable for use as pouch material are selected from polyvinyl alcohols, polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts, polyaminoacids or peptides, polyamides, polyacrylamide, copolymers of maleic/acrylic acids, polysaccharides including starch and gelatine, natural gums such as xanthum and carragum. More preferred polymers are selected from polyacrylates and water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose sodium, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltodextrin, polymethacrylates, and most preferably selected from polyvinyl alcohols, polyvinyl alcohol copolymers and hydroxypropyl methyl cellulose (HPMC), and combinations thereof. Preferably, the level of polymer in the pouch material, for example a PVA polymer, is at least 60%. The polymer can have any weight average molecular weight, preferably from about 1000 to 1,000,000, more preferably from about 10,000 to 300,000 yet more preferably from about 20,000 to 150,000.

[0036] Mixtures of polymers and/or copolymers can also be used as the pouch material, especially mixtures of polyvinylalcohol polymers and/or copolymers, especially mixtures of polyvinylalcohol homopolymers and/or anionic polyvinylalcohol copolymers preferably 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.

[0037] 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.

[0038] Preferred films are those supplied by Monosol under the trade references M8630, M8900, M8779, M8310.

[0039] The film may be opaque, transparent or translucent. The film may comprise a printed area.

[0040] The area of print may be achieved using standard techniques, such as flexographic printing or inkjet printing.

[0041] 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.

Solid laundry detergent composition

[0042] The first internal compartment comprises a solid laundry detergent composition. The solid laundry detergent composition may comprise solid particulates or may be a single homogenous solid. Preferably, the solid laundry detergent composition comprises particles. This means the solid laundry detergent composition comprises individual solid particles as opposed to the solid being a single homogenous solid. The particles may be free-flowing or may be compacted, preferably free-flowing.

[0043] The particles may be spray-dried particles, agglomerates, extrudates or a mixture thereof. Those skilled in the art will know how to make spray-dried particles, agglomerates or extrudates using techniques commonly known in the art.

[0044] The solid particulate laundry detergent composition preferably has a mean particle size of between 400 microns and 1000 microns, more preferably between 450 microns and 850 microns.

[0045] Preferably, the solid particulate laundry detergent composition has a bulk density of between 400 and 1000g/l, more preferably between 500 and 800g/l, as measured through ISO 697 test method.

[0046] Preferably, the solid particulate laundry detergent composition fills between 25% and 95%, preferably between 30% and 90%, more preferably between 40% and 80% of the available volume within the first compartment, the remaining volume preferably filled with a gas. The gas may be any suitable gas. The gas may comprise oxygen, nitrogen, carbon dioxide or a mixture thereof. The gas may be air.

[0047] The first compartment preferably comprises between 1g and 25g, preferably between 5g and 20 g, more preferably between 8g and 18g of the solid particulate laundry composition.

[0048] The solid particulate laundry detergent composition is preferably free flowing within the first internal compartment. That is to say, if the water-soluble unit dose article is moved or repositioned, the solid particulate laundry detergent composition can be seen to freely move, or flow within the first internal compartment. This is opposed to where the solid particulate laundry detergent composition is compressed such as happens when excess air is drawn out of the first internal compartment so that the film contracts and compresses around the solid particulate laundry detergent composition. Such water-soluble unit dose articles comprising compressed solids are commonly known from the art.

[0049] The solid laundry detergent composition comprises a non-soap surfactant. Preferably, the solid laundry detergent composition comprises between 20% and 75%, more preferably between 30% and 70%, most preferably between 40% and 60% by weight of the solid laundry detergent composition of the non-soap surfactant

[0050] The non-soap surfactant may comprise a non-soap anionic surfactant, a non-ionic surfactant or a mixture

thereof, preferably a non-soap anionic surfactant.

[0051] The solid composition may comprise a non-soap anionic surfactant, preferably, the solid laundry detergent composition comprises between 20% and 75%, more preferably between 30% and 70%, most preferably between 40% and 60% by weight of the solid laundry detergent composition of the non-soap anionic surfactant.

[0052] Preferably, the non-soap anionic surfactant comprises linear alkylbenzene sulphonate, alkoxylated alkyl sulphate or a mixture thereof, more preferably a mixture thereof. Preferably, the ratio of linear alkylbenzene sulphonate to alkoxylated alkyl sulphate preferably the ratio of linear alkylbenzene sulphonate to ethoxylated alkyl sulphate is from 1:2 to 20:1, preferably from 1.1:1 to 15:1, more preferably from 1.2:1 to 10:1, even more preferably from 1.3:1 to 5:1, even more preferably from 1.4:1 to 3:1, most preferably from 2:1 to 3:1.

[0053] Preferably, the alkoxylated alkyl sulphate is an ethoxylated alkyl sulphate with an average degree of ethoxylation of between 0.5 and 7, preferably between 0.5 and 5, more preferably between 0.5 and 3, even more preferably from 1 to 2 most preferably about 1, and an average alkyl chain length of between 8 and 18. Preferably the alkoxylated alkyl sulphate has an average alkyl chain length between 10 and 16, more preferably between 12 and 14. Preferably, the linear alkylbenzene sulphonate is a C_{10}-C_{16} linear alkylbenzene sulphonate or a C_{11}-C_{14} linear alkylbenzene sulphonate or a mixture thereof.

[0054] When present, preferably the non-ionic surfactant is selected from an alkoxylated alcohol preferably selected from a natural or olefin derived fatty alcohol alkoxylate, an oxo-synthesised fatty alcohol alkoxylate, Guerbet fatty alcohol alkoxylates, alkyl phenol alcohol alkoxylates or a mixture thereof. The alcohol alkoxylate may have an average degree of alkoxylation of between 0.5 and 10, preferably between 1 and 9, more preferably between 3 and 8, more preferably a degree of ethoxylation of between 0.5 and 10, preferably between 1 and 9, more preferably between 3 and 8, most preferably between 5 and 8 or even from about 7 to about 8. The alcohol alkoxylate may have an average alkyl chain length of between 8 and 18, preferably between 10 and 16, more preferably between 12 and 15.

[0055] The solid composition at 1wt% dilution in deionized water at 20°C has an equilibrium pH in the range of from 6.5 to 8.8, preferably between 6.7 and 8.5, more preferably between 7 and 8. Without wishing to be bound by theory, the specific low pH of the solid laundry detergent composition provides for improved fabric cleaning or treatment performance of the water-soluble unit dose article according to the present invention as compared to water-soluble unit dose articles wherein the solid laundry detergent composition has a higher pH. Such higher pH solid laundry detergent composition formulated into water-soluble unit dose articles are known in the art.

[0056] Those skilled in the art will know how to measure the pH using common known techniques. A preferred method is to obtain a 10g sample accurately weighed to two decimal places, of the solid laundry detergent composition. The sample should preferably be obtained using a Pascall sampler in a dust cabinet. Add the 10g sample to a plastic beaker and add 200 ml of carbon dioxide-free de-ionised water. Agitate using a magnetic stirrer on a stirring plate at 150 rpm until fully dissolved and for at least 15 minutes. Transfer the contents of the beaker to a 1 litre volumetric flask and make up to 1 litre with Cardon dioxide-free de-ionised water. Mix well and take a 100 mls $\pm$ 1 ml aliquot using a 100 mls pipette immediately. Measure and record the pH and temperature of the sample using a pH meter capable of reading to $\pm$0.01pH units, with stirring, ensuring temperature is 20°C +/- 0.5°C.

[0057] The solid laundry detergent composition may comprise between 0% and 10% by weight of the solid laundry detergent composition of carbonate salts. The carbonate salts may be selected from sodium carbonate, potassium carbonate, sodium bicarbonate, sodium bicarbonate, burkeite, sequicarbonate, habit modified carbonate, crystal growth modified burkeite or a mixture thereof, preferably sodium carbonate.

[0058] The solid laundry detergent composition may comprise a material selected from zeolite, sodium sulphate, silica, organic acid or a mixture thereof, preferably wherein the solid laundry detergent composition comprises between 10% and 35%, more preferably between 12% and 25% by weight of the solid laundry detergent composition of the material.

[0059] The solid laundry detergent composition may comprise an organic acid, preferably between 1% and 10% by weight of the solid laundry detergent composition of an organic acid and/or a salt thereof. Preferably, the organic acid is a carboxylic acid, preferably a polycarboxylic acid, more preferably the organic acid is selected from citric acid, malic acid, lactic acid, propionic acid, valeric acid, caproic acid, carbonic acid, adipic acid, gluconic acid, methylglycinediacetic acid or a mixture thereof, most preferably citric acid. Without wishing to be bound by theory such materials may be used to control the pH of the laundry detergent composition.

[0060] The solid laundry detergent composition may comprise an adjunct ingredient, wherein the adjunct ingredient is preferably selected from brighteners, enzymes, dye transfer inhibitors, chelants including aminocarboxylate and aminophosphonate chelants such as HEDP, acrylate-based polymers, perfumes and perfume capsules, polyester terephthalate polymers, PEG-based polymers, ethoxylated polyethyleneimines, polysaccharides, amine oxide, aesthetic dyes, hueing dyes, antifoams, bleaching actives, or a mixture thereof.

[0061] Preferred acrylate-based polymers are acrylate/maleate random copolymers.

[0062] Preferred cationic polysaccharides are cationically-modified polysaccharides. Preferably, the cationically modified polysaccharide is selected from cationic guar gums, cationic cellulosic polymers, and mixtures thereof, most preferably cationic cellulosic polymers even more preferably cationically modified hydroxyethyl cellulose, most preferably,

hydroxyethyl cellulose derivatised with trimethyl ammonium substituted epoxide.

[0063] Preferably, the particulate laundry detergent composition comprises agglomerates. Preferably, the agglomerates comprise non-soap surfactant, sodium sulphate and silica.

[0064] Another aspect of the present invention is the use of a solid laundry detergent composition comprising a non-soap surfactant and having at 1wt% dilution in deionized water at 20°C an equilibrium pH in the range of from 6.5 to 8.8 in a water-soluble unit dose article as according to the present invention to improve the performance of the cationically modified polysaccharide.

Method of washing

[0065] An 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 solid particulate laundry detergent composition by a factor of at least 300 fold to create a wash liquor and contacting fabrics to be washed with said wash liquor.

[0066] The method may be performed in a hand wash operation, an automatic laundry washing machine or a mixture thereof.

Process of making

[0067] Those skilled in the art will know how to make the unit dose article and particulate laundry detergent composition of the present invention using known techniques in the art:

Water soluble pouch making :

[0068] 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 using known sealing means such as solvent, heat or a mixture thereof.

Preparation of free-flowing detergent powders :

[0069] Highly preferred are free-flowing detergent powders. Without wishing to be bound by theory, free-flowing detergent powders are found to have improved dissolution when formulated in a water soluble pouch compared to compressed powders, leaving less detergent residues behind accordingly. Highly free-flowing detergent powders can be prepared by the following process.

[0070] Surfactant-containing particles can be prepared by spray-drying, agglomeration or other processes such as drum drying etc. Such agglomerates are preferred due to the high surfactant loading that can be achieved. However other processes can be used. The surfactant agglomerates preferably contain anionic surfactant, including LAS. An especially preferred feature is that the surfactant agglomerates contain a mixture of anionic surfactants, especially LAS and AES surfactant.

[0071] To improve the flowability and stability of the detergent powder(s), smaller particles are usually removed by sieving. It is especially preferred to sieve the surfactant agglomerates plus other detergent ingredients prior to any subsequent coating step. The surfactant agglomerates, plus other granular detergent ingredients such as HEDP, are sieved to remove particles smaller than 600 microns. The surfactant particles, plus any other detergent ingredients that are optionally added, are then put into a mixer where they are dusted or coated with a fine powder to provide a protective layer on the surface. An example of such a process is where blown powders are coated with non-ionic surfactant as a binder and then zeolite. It has been found, though, that dusting or coating the surfactant agglomerates (and other optional detergent ingredients) in this instance with a blend of micronized sodium sulphate and zeolite gives good results for flowability as well as appearance etc. Inclusion of a liquid binder to help the adhesion of the fine powder(s) to the surface of the larger surfactant agglomerates is also an option.

[0072] A suitable detergent mix can be prepared as follows. Surfactant agglomerates containing a blend of LAS and AExS anionic surfactants are prepared and dried to give particles with a total surfactant activity of 60% comprising a 2:1 blend of LAS to AExS surfactants. The particles contain 20% of hydrophilic silica. A suitable silica is 22S from Evonik. The balance consists of ground sodium sulphate, water and miscellaneous. The fine particles are then removed by sieving the agglomerates on a 600 micron mesh sieve. Oversize particles are removed by sieving the agglomerates through a 1400 micron mesh size sieve.

[0073] 3kg of the sieved surfactant agglomerates are then put into a 6-litre internal volume paddle mixer from Forberg. 300g of ground sodium sulphate (d90 < 100 microns) and 100g of sodium aluminosilicate type 4A are then added to the mixer and the mixer is run at maximum speed for 2 minutes, thus coating the surface of the agglomerates with sulphate

and zeolite. The coated agglomerates are then removed and blended with other detergent materials to give a free-flowing detergent mixture suitable for use.

[0074] 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."

EXAMPLES

[0075] The below test shows a consistently improved fabric feel performance profile for low versus high pH cationically modified polysaccharide comprising powder compositions within a water soluble pouch.

Test Method:

[0076] In order to show the impact in providing improved fabric feel benefits of formulating with a low pH powder vs high pH powder contained within a water soluble pouch in presence & absence of modified hydroxyethyl cellulose, a softness full scale test has been conducted. Black cotton bath towels (sourced from The Range retail shop, North Tyne Industrial Estate, Whitley Rd, Benton NE12 9EZ, United Kingdom) were desized using a Miele machine (model 1714), cotton short cycle, 60°C, city water (7.8gpg), total wash time 1hour 25mins x 3 wash cycles, the first cycle containing 38g of ECE standard detergent (sourced from wfk Testgewebe GmbH, Christenfeld 10, D-41379 Brüggen, Germany) the remaining two cycles were run with no product. Fabrics were dried using a gas dryer set at medium heat for 30minutes and consequently cut into 15cm x 15cm swatches x 8 ready to be used in full scale test the following day. For the softness test a short cotton cycle at 40°C and 6gpg hardness has been selected on a Miele washing machine (model 3622). Total run time was 1hour and 25minutes, 2.5kg cotton ballast loads (sourced from Calderon Textiles) were added to each machine and washed in either reference A/B or test product A/B. Four wash cycles were carried out. Black towel tracers were removed and left overnight to dry in drying room (20°C /55% RH) and were then paneled by 3 panelists the following day to assess the softness grading, using pairwise comparison Ref A vs Test A, Ref B vs Test B, following standard grading scale :

Grading Scale

[0077]

4 - This product on the left is a whole lot better.
3 - This product on the left is a lot better.
2 - I know this product on the left is a little better.
1 - I think this product on the left is better.
0 - There is no difference between the two products.

Test products:

[0078]

LAS/AE1S Agglomerate

Constituent	%w/w Base Powder
LAS Linear alkyl benzene sulfonate	50
C12-14 Alky Ethoxylate (1) Sulphate	20
Sodium Sulphate	7.5
Silica	18.75
Free water	3.75
Total	100

Liquid Additive Mix

Constituent	%w/w
Ethoxylated Polyethyleneimine (PEI600EO20 - 80%)	28
PEG-Vinyl Acetate co-polymer (72.5%)	38.4
Nonionic surfactant (C24AE7)	33.6
Total	100

Test Base - Low pH

Constituent	%w/w Base Powder
LAS/AE1S Agglomerate	66.27
Carboxymethyl cellulose (98%) (Finnfix GDA ex CP Kelco)	1.75
Brightener 49 Tinopal® CBS-X	1.15
Texcare SRA300 Soil release polymer	0.53
Na HEDP Etidronic Acid (86.8%)	14.09
Zeolite	2.17
Acusol 4445N Polymer (92.6%)	4.03
Dow Corning GP-4314 Powdered Antifoam (12% active)	2.31
Lipase (18.5mg/g)	1.97
Stainzyme Plus (14.4mg/g)	1.14
Protease	1.72
Cellulase (15.6mg/g)	1.39
Mannanase (4mg/g)	1.50

Reference Base - High pH

Constituent	%w/w Base Powder
LAS/AE1S Agglomerate	51.25
Carboxymethyl cellulose (98%) (Finnfix GDA ex CP Kelco)	1.35
Brightener 49 Tinopal® CBS-X	0.89
Texcare SRA300 Soil release polymer	0.41
Na HEDP Etidronic Acid (86.8%)	10.89
Zeolite	1.68
Acusol 4445N Polymer (92.6%)	3.11
Dow Corning GP-4314 Powdered Antifoam (12% active)	1.79
Lipase (18.5mg/g)	1.53
Stainzyme Plus (14.4mg/g)	0.88
Protease	1.33
Cellulase (15.6mg/g)	1.07
Mannanase (4mg/g)	1.16
Sodium Carbonate	22.67

Products Tested :

[0079]

- High pH Ref A (nil cationically modified polysaccharide) : 13.9g of High pH reference base formulation contained in a PVA film* pouch & 1.25ml of Liquid additive mix formulation.
- High pH Ref B (with cationically modified polysaccharide) : 13.9g of High p H reference base formulation & 0.2g of modified hydroxyethyl cellulose (Polymer PK ex Dow company) contained in a PVA film* pouch & 1.25ml of liquid additive mix formulation.
- Low pH Test leg A (nil cationically modified polysaccharide) : 10.75g of Low pH reference formulation contained in a PVA film* pouch & 1.25ml Liquid additive mix formulation.
- Low pH Test leg B (with cationically modified polysaccharide) : 10.75g of Low pH reference formulation & 0.2g of modified hydroxyethyl cellulose (Polymer PK ex Dow company) contained in a PVA film* & 1.25ml of liquid additive mix formulation.

* PVA Film : M9400 provided by Monosol LLC, 707 East 80th Place, Suite 301, Merrillville, IN 4641

Results

[0080] The results tabulated below show an improved fabric feel benefit for a low versus high pH powder formulation, a benefit that is further enhanced in presence versus in absence of CatHEC technology.

	Low pH (Preference)	High pH (Preference)	Low pH vs High pH grading
Nil cationically modified polysaccharide	62%	38%	+0.67
With cationically modified polysaccharide	88%	12%	+1.47

Claims

1. A water-soluble unit dose article comprising a water-soluble film and a solid laundry detergent composition, wherein the water-soluble film defines a first internal compartment and wherein the solid laundry detergent composition is comprised within the first internal compartment, and wherein the water soluble unit dose article composition comprises a cationically modified polysaccharide; and
wherein the solid composition at 1wt% dilution in deionized water at 20°C, has an equilibrium pH in the range of from 6.5 to 8.8, preferably between 6.7 and 8.5.

2. The water-soluble unit dose article according to claim 1, wherein the solid laundry detergent composition comprises from 0wt% to 10wt% of carbonate salt, preferably wherein the carbonate salts are selected from sodium carbonate, potassium carbonate, sodium bicarbonate, sodium bicarbonate, burkeite, sequicarbonate, habit modified carbonate, crystal growth modified burkeite or a mixture thereof, preferably sodium carbonate.

3. The water-soluble unit dose article according to any preceding claims wherein the solid laundry detergent composition comprises the cationically modified polysaccharide and preferably wherein the solid laundry detergent composition comprise between 0.05% and 5%, preferably between 0.1% and 4%, preferably between 0.2% and 3%, more preferably between 0.25% and 2% by weight of the solid laundry detergent composition of the cationically modified polysaccharide.

4. The water-soluble unit dose article according to any preceding claims, wherein the cationically modified polysaccharide is selected from cationic guar gums, cationic cellulosic polymers, and mixtures thereof, most preferably cationic cellulosic polymers.

5. The water-soluble unit dose article according to claim 4, wherein the cationically modified polysaccharide is selected from cationically modified hydroxyethyl cellulose, cationically modified hydroxypropyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, cationically and hydrophobically modified hydroxypropyl cellulose,

or a mixture thereof, more preferably cationically modified hydroxyethyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, or a mixture thereof.

6. The water-soluble unit dose article according to any preceding claims wherein the solid laundry detergent composition comprises a non-soap anionic surfactant and wherein preferably the non-soap anionic surfactant comprises linear alkylbenzene sulphonate, alkoxylated alkyl sulphate or a mixture thereof, more preferably a mixture thereof wherein the ratio of linear alkylbenzene sulphonate to alkoxylated alkyl sulphate preferably the ratio of linear alkylbenzene sulphonate to ethoxylated alkyl sulphate is from 1:2 to 20:1, preferably from 1.1:1 to 15:1, more preferably from 1.2:1 to 10:1, even more preferably from 1.3:1 to 5:1, even more preferably from 1.4:1 to 3:1, most preferably from 2:1 to 3:1.

7. The water-soluble unit dose article according to claim 6 wherein the solid laundry detergent composition comprises between 20% and 75%, preferably between 30% and 70%, more preferably between 40% and 60% by weight of the solid laundry detergent composition of the non-soap anionic surfactant.

8. The water-soluble unit dose article according to any preceding claims wherein the solid laundry detergent composition comprises between 1% and 10% by weight of the solid laundry detergent composition of an organic acid and wherein preferably the organic acid is a carboxylic acid, preferably a polycarboxylic acid, more preferably the organic acid is selected from citric acid, malic acid, lactic acid, propionic acid, valeric acid, caproic acid, carbonic acid, adipic acid, gluconic acid, methylglycinediacetic acid or a mixture thereof, most preferably citric acid.

9. The water-soluble unit dose article according to any preceding claims wherein the solid laundry detergent composition is a free flowing particulate solid, a compressed particulate solid or a mixture thereof and has a mean particle size between 400 microns and 1000 microns, preferably between 450 microns and 850 microns.

10. The water-soluble unit dose article according to any preceding claims wherein the solid laundry detergent composition has a bulk density of between 400 and 1000g/l, preferably between 500 and 800g/l.

11. The water-soluble unit dose article according to any preceding claims wherein the first compartment comprises between 1g and 25g, preferably between 5g and 20 g, preferably between 8g and 18g of the solid laundry composition.

12. The water-soluble unit dose article according to any preceding claims wherein the water-soluble film comprises polyvinyl alcohol, preferably wherein the water-soluble film comprises polyvinyl alcohol polymer or copolymer, preferably a blend of polyvinylalcohol polymers and/or polyvinylalcohol copolymers, more preferably selected from sulphonated and carboxylated anionic polyvinylalcohol copolymers especially carboxylated anionic polyvinylalcohol copolymers, most preferably a blend of a polyvinylalcohol homopolymer and a carboxylated anionic polyvinylalcohol copolymer.

13. The water-soluble unit dose article according to any preceding claims wherein the water-soluble unit dose article comprises at least a first compartment and a second compartment, preferably at least a first compartment, a second compartment and a third compartment.

14. The water-soluble unit dose article according to claim 13 wherein the compartments are arranged in a side-by-side arrangement, a superposed arrangement or a mixture thereof, preferably wherein at least one compartment, preferably wherein at least two compartments are superposed onto a third compartment, even more preferably wherein at least one of the superposed compartments comprises a liquid, preferably wherein the both superposed compartments comprise a liquid.

15. A method of washing comprising the steps of adding the water-soluble unit dose article according to any preceding claims to sufficient water to dilute the solid laundry detergent composition by a factor of at least 300 fold to create a wash liquor and contacting fabrics to be washed with said wash liquor.

16. Use of a solid laundry detergent composition comprising a non-soap surfactant and having at 1wt% dilution in deionized water at 20°C an equilibrium pH in the range of from 6.5 to 8.8 in a water-soluble unit dose article to improve the performance of cationically modified polysaccharide.

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 17 17 6200

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2016/160157 A1 (VANBLARCOM DAVID [US] ET AL) 9 June 2016 (2016-06-09) * paragraphs [0377] - [0378], [0423], [0275] - [0281]; claims *	1-5,9-15	INV. C11D3/22 C11D17/04 C11D3/00
X	US 2015/057210 A1 (LABEQUE REGINE [BE] ET AL) 26 February 2015 (2015-02-26) * paragraph [0035]; claims; examples *	1-16	
E	EP 3 181 673 A1 (PROCTER & GAMBLE [US]) 21 June 2017 (2017-06-21) * examples *	1,2,4,5, 10,12-14	

TECHNICAL FIELDS SEARCHED (IPC)

C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	15 December 2017	Pfannenstein, Heide

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 17 17 6200

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

15-12-2017

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2016160157 A1	09-06-2016	CA 2847546 A1	14-03-2013
		CN 103946360 A	23-07-2014
		EP 2751248 A1	09-07-2014
		JP 2014529693 A	13-11-2014
		KR 20140068141 A	05-06-2014
		US 2013095717 A1	18-04-2013
		US 2016160156 A1	09-06-2016
		US 2016160157 A1	09-06-2016
		WO 2013036662 A1	14-03-2013
US 2015057210 A1	26-02-2015	AR 081983 A1	31-10-2012
		BR 112012032888 A2	29-11-2016
		CA 2800008 A1	29-12-2011
		CN 102959070 A	06-03-2013
		CN 105820885 A	03-08-2016
		EP 2399979 A1	28-12-2011
		ES 2527679 T3	28-01-2015
		JP 5675971 B2	25-02-2015
		JP 2013534554 A	05-09-2013
		RU 2012148752 A	27-07-2014
		US 2011319311 A1	29-12-2011
		US 2015057210 A1	26-02-2015
		WO 2011163428 A1	29-12-2011
		ZA 201208667 B	30-04-2014
EP 3181673 A1	21-06-2017	EP 3181673 A1	21-06-2017
		US 2017175059 A1	22-06-2017
		WO 2017106004 A1	22-06-2017

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82