

(19)



(11)

EP 2 980 198 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

03.02.2016 Bulletin 2016/05

(51) Int Cl.:

C11D 3/37 (2006.01)

C11D 17/04 (2006.01)

C11D 3/22 (2006.01)

C11D 17/00 (2006.01)

(21) Application number: **14179405.7**

(22) Date of filing: **31.07.2014**

(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

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

(72) Inventors:

- **Bodet, Jean-Francois**
1853 Strombeek-Bever (BE)
- **Matthys, Bruno Jean-Pierre**
1853 Strombeek-Bever (BE)
- **Boutille, Alice Michele**
1853 Strombeek-Bever (BE)
- **de Poortere, Johan Maurice Theo**
1853 Strombeek-Bever (BE)

- **Maes, Jef Annie Alfons**
1853 Strombeek-Bever (BE)
- **Hulskotter, Frank**
65824 Schwalbach am Taunus (DE)
- **Rübenacker, Martin**
67056 Ludwigshafen (DE)
- **Dobrawa, Rainer Anton**
67056 Ludwigshafen (DE)
- **El-Toufaili, Faissal-Ali**
67056 Ludwigshafen (DE)

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

(54) **Composition comprising amphiphilic graft polymer**

(57) A liquid laundry detergent composition comprising an amphiphilic graft polymer.

EP 2 980 198 A1

Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to the field of liquid laundry detergent compositions comprising amphiphilic graft polymers

BACKGROUND OF THE INVENTION

10 **[0002]** Polymers are used as soil detachment-promoting additives for laundry detergents. Of particular interest are amphiphilic graft polymers which are particularly effective at removing hydrophobic soils.

[0003] However, there is a limit to the amount of amphiphilic graft polymers that can be added to laundry detergent compositions. Without wishing to be bound by theory, at higher concentrations there is a tendency for the liquid laundry detergent composition to phase split. Higher levels of polymer are desirable to provide improved cleaning benefit.

15 **[0004]** Therefore, there remains a need in the art for laundry detergent compositions comprising an amphiphilic graft polymer in which higher levels of the polymer can be added than used today.

[0005] It was surprisingly found that a liquid laundry detergent composition comprising an amphiphilic graft polymer according to the present invention allowed higher levels of the polymer to be added than is known today.

20 **[0006]** It was also surprisingly found that the addition of a structurant further reduced the instances of phase splitting and so allowed higher levels of polymer to be added.

SUMMARY OF THE INVENTION

25 **[0007]** A first aspect of the present invention is a liquid laundry detergent composition comprising;
an amphiphilic graft polymer, wherein the polymer is based on water-soluble polyalkylene oxides (A) as a graft base and side chains formed by polymerization of a vinyl ester component (B), and comprising;

30 i. from 15% to 70% by weight of a water-soluble polyalkylene oxide as a graft base and
ii. side chains formed by free-radical polymerization of from 30 to 85% by weight of a vinyl ester component composed of

(B1) from 70 to 100% by weight of vinyl acetate and/or vinyl propionate and
(B2) from 0 to 30% by weight of a further ethylenically unsaturated monomer; and
35 wherein the graft base has a mean molecular weight (M_w) of from 3500 to 5500, or wherein the polymer has a full width at half maximum of the polarity distribution between 0.35 and 1.0, or a mixture thereof.

[0008] A second aspect of the present invention is a water soluble unit dose article comprising a water soluble film and a composition according to the present invention.

40 **[0009]** A third aspect of the present invention is a process of cleaning laundry comprising the step of adding the composition or unit dose article according to the present invention to the drum or dispenser drawer of an automatic washing machine.

DETAILED DESCRIPTION OF THE INVENTION

45 Composition

[0010] The present invention is to a liquid laundry detergent composition. The term 'liquid' encompasses aqueous compositions, non-aqueous compositions, gels, pastes, dispersions and the like. By laundry detergent composition, we
50 herein mean a composition that can be used in a laundry wash and/or rinse operation. A laundry detergent composition can also be a laundry pretreatment composition.

[0011] The liquid laundry detergent composition may be present in a water-soluble unit dose article. In such an embodiment, the water-soluble unit dose article comprises at least one water-soluble film shaped such that the unit-dose article comprises at least one internal compartment surrounded by the water-soluble film. The at least one compartment
55 comprises the liquid laundry detergent composition. The water-soluble film is sealed such that the liquid 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. The water-soluble unit dose article will be described in more detail below.

[0012] The liquid laundry detergent composition comprises an amphiphilic graft polymer. Suitable graft copolymers are described in more detail below.

[0013] The liquid laundry detergent composition may comprise a structurant. Suitable structurants are described in more detail below.

Amphiphilic graft polymer

[0014] The liquid laundry detergent composition comprises an amphiphilic graft polymer. The composition may comprise between 0.1wt% to 10wt%, or even from 1.5wt% to 5.5wt% or even from 2wt% to 5wt% of the amphiphilic graft polymer.

[0015] The amphiphilic graft polymer is based on water-soluble polyalkylene oxides (A) as a graft base and side chains formed by polymerization of a vinyl ester component (B), and comprising;

- i. from 15% to 70% by weight of a water-soluble polyalkylene oxide as a graft base and
- ii. side chains formed by free-radical polymerization of from 30 to 85% by weight of a vinyl ester component composed of

(B1) from 70 to 100% by weight of vinyl acetate and/or vinyl propionate and

(B2) from 0 to 30% by weight of a further ethylenically unsaturated monomer; and

wherein the graft base has a mean molecular weight (M_w) of from 3500 to 5500, or wherein the polymer has a full width at half maximum of the polarity distribution between 0.35 and 1.0, or a mixture thereof.

[0016] The polyalkylene oxide (A) is preferably water-soluble, wherein water-soluble in the sense of the present invention means a polyalkylene oxide of which at least 50 % by weight is soluble in water. In the sense of the present invention, a polyalkylene oxide can be referred to as polyethylene glycol.

[0017] Water-soluble polyalkylene oxides suitable for forming the graft base (A) are in principle all polymers based on C2-C4-alkylene oxides which comprise at least 30% by weight, preferably 50% by weight, more preferably at least 60% by weight, even more preferably at least 75% by weight of ethylene oxide in copolymerized form. The polyalkylene oxides (A) preferably have a low polydispersity M_w/M_n , preferably ≤ 2.5 , more preferably ≤ 1.5 , even more preferably ≤ 1.3 . The water-soluble polyalkylene oxide (A) in either polymer has a mean molecular weight M_n from 1,000 to 20,000 g/mol, preferably from 2,000 to 15,000 g/mol, more preferably from 3,000 to 13,000 g/mol and more particularly from 5,000 to 10,000 g/mol or from 3,000 to 9,000 g/mol.

[0018] The polyalkylene oxides (A) may be the corresponding polyalkylene glycols in free form, i.e. with OH end groups, but they may also be capped at one or both end groups. Suitable end groups are, for example, C1-C25-alkyl, phenyl, and C1-C14-alkylphenyl groups. Specific examples of particularly suitable polyalkylene oxides (A) include:

(A1) polyethylene glycols which may be capped at one or both end groups, especially by C1-C25-alkyl groups, but are preferably not etherified, and have mean molar masses M_n of preferably from 1500 to 20,000 g/mol, more preferably from 2500 to 15,000 g/mol;

(A2) copolymers of ethylene oxide and propylene oxide and/or butylene oxide with an ethylene oxide content of at least 50% by weight, which may likewise be capped at one or both end groups, especially by C1-C25-alkyl groups, but are preferably not etherified, and have mean molar masses M_n of preferably from 1500 to 20,000 g/mol, more preferably from 2500 to 15,000 g/mol;

(A3) chain-extended products having mean molar masses of, in particular, from 2500 to 20,000, which are obtainable by reacting polyethylene glycols (A1) having mean molar masses M_n of from 200 to 5000 or copolymers (A2) having mean molar masses M_n of from 200 to 5,000 g/mol with C2-C12-dicarboxylic acids or dicarboxylic esters or C6-C18-diisocyanates.

[0019] Preferred graft bases (A) are the polyethylene glycols (A1).

[0020] In accordance with their low degree of branching, the molar ratio of grafted to ungrafted alkylene oxide units in the inventive graft polymers is from 0.002 to 0.05, preferably from 0.002 to 0.035, more preferably from 0.003 to 0.025 and most preferably from 0.004 to 0.02.

[0021] The side chains are formed by polymerization of a vinyl ester component (B) in the presence of the graft base (A).

[0022] The vinyl ester component (B) in either the first or second polymer may consist advantageously of (B1) vinyl acetate or vinyl propionate or of mixtures of vinyl acetate and vinyl propionate, particular preference being given to vinyl acetate as the vinyl ester component (B).

[0023] The side chains may also be formed by copolymerizing vinyl acetate and/or vinyl propionate (B1) and a further

ethylenically unsaturated monomer (B2). The fraction of monomer (B2) in the vinyl ester component (B) may be up to 30% by weight, which corresponds to a content in the polymer of (B2) of 24% by weight.

[0024] Suitable comonomers (B2) are, for example, monoethylenically unsaturated carboxylic acids and dicarboxylic acids and their derivatives, such as esters, amides and anhydrides, and styrene. It is of course also possible to use mixtures of different comonomers. For the purpose of this invention the prefix (meth) written before a compound means the respective unsubstituted compound and/or the compound substituted by the methyl group. For instance, "(meth)acrylic acid" means acrylic acid and/or methacrylic acid, (meth)acrylate means acrylate and/or methacrylate, (meth)acrylamide means acrylamide and/or methacrylamide.

[0025] Specific examples include: (meth)acrylic acid, C1-C12-alkyl and hydroxy-C2-C12-alkyl esters of (meth)acrylic acid, (meth)acrylamide, N-C1-C12-alkyl(meth)acrylamide, where the alkyl moiety can be branched or linear, N,N di(C1-C6-alkyl)(meth)acrylamide, maleic acid, maleic anhydride and mono(C1-C12-alkyl)esters of maleic acid. Preferred monomers (B2) are the C1-C8-alkyl esters of (meth)acrylic acid and hydroxyethyl acrylate, particular preference being given to the C1-C4-alkyl esters of (meth)acrylic acid. Very particularly preferred monomers (B2) are methyl acrylate, ethyl acrylate, and, in particular, n-butyl acrylate.

[0026] When the polymer comprises the monomer (B2) as a constituent of the vinyl ester component (B), the content of graft polymers in (B2) is preferably from 0.5 to 20% by weight, more preferably from 1 to 15% by weight and most preferably from 2 to 10% by weight.

[0027] The polymer also has only a low content of ungrafted polyvinyl ester (B). In general, they comprise $\leq 10\%$ by weight, preferably $\leq 7.5\%$ by weight and more preferably $\leq 5\%$ by weight of ungrafted polyvinyl ester (B).

[0028] Owing to the low content of ungrafted polyvinyl ester and the balanced ratio of components (A) and (B), the polymer is soluble in water or in water/alcohol mixtures (for example a 25% by weight solution of diethylene glycol monobutyl ether in water). They have pronounced, low cloud points which, for the graft polymers soluble in water at up to 50°C, are generally $\leq 95^\circ\text{C}$, preferably $\leq 85^\circ\text{C}$ and more preferably $\leq 75^\circ\text{C}$, and, for the other graft polymers in 25% by weight diethylene glycol monobutyl ether, generally $\leq 90^\circ\text{C}$, preferably from 45 to 85°C.

[0029] In some embodiments, the polymers of the invention comprise from 25 to 60% by weight of the graft base (A) and from 40 to 75% by weight of the polyvinyl ester component (B).

[0030] The polymer features a narrow molar mass distribution and hence a polydispersity M_w/M_n of generally ≤ 3 , preferably ≤ 2.8 , more preferably ≤ 2.5 , and even more preferably ≤ 2.3 . Most preferably, the polydispersity M_w/M_n is in the range from 1.5 to 2.2. The polydispersity of the polymer can be determined, for example, by gel permeation chromatography using narrow-distribution polymethyl methacrylates as the standard.

[0031] The mean molecular weight M_w of the graft base may be from 3500 to 5500, or even from 3500 to 4500, or even from 3750 to 4250.

[0032] The mean molecular weight M_w of the inventive graft polymers is from 4000 to 100,000, preferably from 6000 to 45,000 and more preferably from 8000 to 30,000.

[0033] Without wishing to be bound by theory, it was surprisingly found that the stability of an opacifier formulated into a liquid laundry detergent composition was improved when the liquid laundry detergent composition also comprised a graft polymer according to the present invention, wherein the molecular weight of the polymer was carefully regulated, as compared to a liquid laundry detergent composition comprising a graft polymer outside of the scope of the present invention.

[0034] Graft polymers of polyvinylacetate (PVAc) grafted on polyethyleneglycol (PEG) are amphiphilic polymers with a polarity depending mainly on the ratio of polyethyleneglycol as the hydrophilic part and polyvinylacetate as the hydrophobic part and their amount of individual grafted polymer chains. Higher amounts of vinylacetate in the polymers renders the polymer more apolar, whereas increasing the amount of PEG renders the polymer more polar. This can be controlled by the ratio of PEG and VAc in the polymerization reaction. The distribution of polarity can be assessed by GPEC (gradient polymer elution chromatography). A way to analyze the data of the polarity measurement is to transform the results obtained by the GPEC method into numeric results, in the form of a ratio of broadness and height, meaning the full width at half maximum of the polarity distribution divided by the peak height at the maximum of the polarity distribution.

[0035] Gradient Polymer Elution Chromatography (GPEC) was conducted via the following method: Test solutions were prepared by dissolving polymer samples in tetrahydrofuran (THF) with a concentration of 10g/l. Of the solution, 2 μl were injected in the HPLC measurement device. The separation was done using a Waters XBridge Hilic HPLC column with dimensions of 4.6 X 50 mm and a particle size of 2.5 μm . The eluent starting conditions were 100% acetonitrile (ACN), after 0.3 ml the composition was changed linear to a composition of 60%/40% water/acetonitrile within 5.7 ml. Subsequently, the composition was changed to 95%/5% water/acetonitrile within 0.3 ml. The chromatographic column was rinsed using 1.5 ml of the last mentioned eluent composition and reset within 0.3 ml to initial condition. The volumetric flow was 3 ml/min and the column temperature was 80°C. For detection, an evaporative light scattering detector (ELSD, type PL-ELS 2100 by Polymer Laboratories GmbH, Darmstadt) was used (ELSD conditions: blue LED wavelength = 480nm, evaporation temperature = 85°C, nebulizer temperature = 50°C, gas flow = 1.5 SLM (standard liter per minute)). As reference materials, polyethylene glycol (molecular weight M_n = 6000 g/mol, available as Pluriol® E 6000 from BASF

SE), and polyvinylacetate (molecular weight 50 000 g/mol, available from Alfa Aesar Company (Polyvinyl acetate M.W. ca 50 000, order number A12732, lot-number 10163914) were used. Care is taken that the molecular weight of the polyethylene glycol reference is the same as that of the polyethylene glycol used as the graft base (compound A) for the synthesis of the amphiphilic graft polymer.

[0036] The relative polarity and the polarity distribution of the amphiphilic graft polymer may be determined by analyzing the GPEC signals of the graft polymer sample as well as the GPEC signals of polyethylene glycol and polyvinylacetate, as reference compounds. The quantification of the polarity of the product is performed by analyzing the results from the GPEC chromatograms, either considering them as non-normal distributions (Modern Engineering Statistics, Thomas P. Ryan, Wiley-Interscience, John Wiley & Sons, Inc., Hoboken, New Jersey, 2007) or taking the maximum of the polarity distribution and the full width at half maximum of the polarity distribution. Two homopolymers were used as reference to convert these chromatograms into a polarity distribution expressed in % of polyvinylacetate. That means that μ is 0, when polyvinylacetate is 0 and μ is 1, when polyethyleneglycol is 1.

[0037] The polymer may have a full width at half maximum of the polarity distribution between 0.35 and 1.0, in particular between 0.40 and 0.8, alternatively between 0.50 and 0.75. In certain aspects, the polymer has a full width at half maximum of the polarity distribution between 0.35 and 1.0 and a maximum of the polarity distribution between 0.45 and 1. In some aspects, the maximum of the polarity distribution of the polymer is between 0.5 and 0.8.

[0038] In certain aspects, the polymer has a polarity distribution with a square root σ^2 greater than 18. In some aspects, the first polymer has a polarity distribution expressed in % of polyvinylacetate with a square root σ^2 greater than 20. In particular, the first polymer has a polarity distribution expressed in % of polyvinylacetate with a square root σ^2 greater than 20 and a mean value μ less than 50. In certain aspects, the square root σ^2 of the first polymer is greater than 20 and the mean value μ is less than 45.

[0039] Without wishing to be bound by theory, it was surprisingly found that the stability of an opacifier formulated into a liquid laundry detergent composition was improved when the liquid laundry detergent composition also comprised a graft polymer according to the present invention, wherein the polarity distribution of the polymer was carefully regulated, as compared to a liquid laundry detergent composition comprising a graft polymer outside of the scope of the present invention.

[0040] In some aspects, the polymer may have a full width at half maximum of the polarity distribution between 0.35 and 1.0, in particular between 0.40 and 0.8, alternatively between 0.50 and 0.75. In certain aspects, the second polymer may have a full width at half maximum of the polarity distribution between 0.35 and 1.0 and a maximum of the polarity distribution between 0.45 and 1. In some aspects, the maximum of the polarity distribution of the second polymer is between 0.5 and 0.8.

[0041] Without wishing to be bound by theory, it is believed that the amphiphilic graft polymer exists as droplets in the liquid laundry detergent composition. There is a tendency for the droplets to coalesce and so cause the liquid laundry detergent composition to phase split. This generally occurs at higher levels of polymer concentration since there are more droplets available to coalesce. It was surprisingly found that liquid laundry detergent compositions comprising the polymer of the present invention were less likely to phase split at a given concentration of polymer. Hence a higher level of polymer could be added.

[0042] It was also surprisingly found that compositions comprising the amphiphilic graft polymer of the present invention exhibited improved clarity as to compositions comprising amphiphilic graft polymers in the art, especially wherein the composition comprised an opacifier. Without wishing to be bound by theory it is believed this is due to improved dissolution of the amphiphilic graft polymer of the present invention compared to those known in the art. Therefore, it is a further object of the present invention to provide a composition comprising amphiphilic graft polymer that exhibits improved clarity versus compositions known in the art that comprise amphiphilic graft polymers.

Structurant

[0043] The composition of the present invention may comprise a structurant. If a structurant is present, preferably the composition comprises from 0.05% to 2%, preferably from 0.1% to 1% by weight of a structurant. The structurant may be selected from non-polymeric or polymeric structurants. The structurant may be a non-polymeric structurant, preferably a crystallisable glyceride. The structurant may be a polymeric structurant, preferably a fibre based polymeric structurant, more preferably a cellulose based fibre-based structurant.

[0044] Suitable structurants are preferably ingredients which impart a sufficient yield stress or low shear viscosity to stabilize the liquid laundry detergent composition independently from, or extrinsic from, any structuring effect of the deterative surfactants of the composition. Preferably, they impart to the laundry detergent composition a high shear viscosity at 20 sec⁻¹ at 21°C of from 1 to 1500 cps and a viscosity at low shear (0.05 sec⁻¹ at 21°C) of greater than 5000 cps. The viscosity is measured using an AR 550 rheometer from TA instruments using a plate steel spindle at 40 mm diameter and a gap size of 500 μ m. The high shear viscosity at 20s⁻¹ and low shear viscosity at 0.5s⁻¹ can be obtained from a logarithmic shear rate sweep from 0.1-1 to 25-1 in 3 minutes time at 21°C.

[0045] The composition may comprise a non-polymeric crystalline, hydroxyl functional structurant. Such non-polymeric crystalline, hydroxyl functional structurants generally comprise a crystallizable glyceride which can be pre-emulsified to aid dispersion into the final liquid laundry detergent composition. A non-limiting example of such a pre-emulsified external structuring system comprises: (a) crystallizable glyceride(s); (b) anionic surfactant; and (c) water and optionally, non-aminofunctional organic solvents. Each of these components is discussed in detail below.

[0046] In some embodiments of the invention, the polymeric crystalline, hydroxy-functional structurant comprises a crystallizable glyceride, preferably hydrogenated castor oil or "HCO". HCO as used herein most generally can be any hydrogenated castor oil or derivative thereof, provided that it is capable of crystallizing in the non-polymeric crystalline, hydroxy-functional structurant premix. Castor oils may include glycerides, especially triglycerides, comprising C₁₀ to C₂₂ alkyl or alkenyl moieties which incorporate a hydroxyl group. Hydrogenation of castor oil, to make HCO, converts the double bonds which may be present in the starting oil as ricinoleyl moieties. As such, the ricinoleyl moieties are converted into saturated hydroxyalkyl moieties, e.g., hydroxystearyl. The HCO herein may, in some embodiments, be selected from: trihydroxystearin; dihydroxystearin; and mixtures thereof. The HCO may be processed in any suitable starting form, including, but not limited to those selected from solid, molten and mixtures thereof. HCO is typically present at a level of from 2% to 10%, from 3% to 8%, or from 4% to 6% by weight in the external structuring system. In some embodiments, the corresponding percentage of hydrogenated castor oil delivered into a finished laundry detergent product is below 1.0%, typically from 0.1% to 0.8%.

[0047] Useful HCO may have the following characteristics: a melting point of from 40 °C to 100 °C, or from 65 °C to 95 °C; and/or iodine value ranges of from 0 to 5, from 0 to 4, or from 0 to 2.6. The melting point of HCO can be measured using either ASTM D3418 or ISO 11357; both tests utilize DSC: Differential Scanning Calorimetry.

[0048] HCO of use in the present invention includes those that are commercially available. Non-limiting examples of commercially available HCO of use in the present invention include: THIXCIN® from Rheox, Inc. Further examples of useful HCO may be found in U.S. Patent 5,340,390.

[0049] While the use of hydrogenated castor oil is preferred, any crystallisable glyceride can be used within the scope of the invention. Preferred crystallisable glyceride(s) have a melting point of from 40 °C to 100 °C.

[0050] Anionic surfactant may be present in the non-polymeric crystalline, hydroxy-functional structurant system of use in the present invention and can be present at any suitable weight percentage of the total system. Without wishing to be bound by theory, it is believed that the anionic surfactant acts as an emulsifier of melts of HCO and other crystallizable glycerides. Any suitable anionic surfactant is of use in the non-polymeric crystalline, hydroxy-functional structurant. Non-limiting examples of suitable anionic surfactants of use herein include: Linear Alkyl Benzene Sulphonate (LAS), Alkyl Sulphates (AS), Alkyl Ethoxylated Sulphonates (AES), Laureth Sulfates and mixtures thereof. In some embodiments, the anionic surfactant may be present in the external structuring system at a level of from 5% to 50% by weight of the external structuring system. Note however, that when using more than 25% by weight of the structurant system, of an anionic surfactant, it is typically required to thin the surfactant using a non-aminofunctional organic solvent in addition to water.

[0051] The anionic surfactants are typically present in the form of their salts with alkanolamines or alkali metals such as sodium and potassium. Preferably, the anionic emulsifiers are neutralized with alkanolamines such as monoethanolamine or triethanolamine, and are fully soluble in the liquid phase of the external structuring system.

[0052] The non-polymeric crystalline, hydroxy-functional structurant generally comprises water, at levels of from 5% to 90%, preferably from 10% to 80%, more preferably from 30% to 70% by weight water. However organic non-amino functional organic solvents, typically consisting essentially of C, H and O (i.e., non-silicones and heteroatom-free) may also be present in the non-polymeric crystalline, hydroxy-functional structurant as solvents to help control or reduce viscosity, especially during processing.

[0053] Liquid laundry detergent compositions of the present invention may comprise naturally derived and/or synthetic polymeric structurants.

[0054] Examples of naturally derived polymeric structurants of use in the present invention include: microfibrillated cellulose, hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, carboxymethyl cellulose, polysaccharide derivatives and mixtures thereof. Non-limiting examples of microfibrillated cellulose are described in WO 2009/101545 A1. Suitable polysaccharide derivatives include: pectine, alginate, arabinogalactan (gum Arabic), carrageenan, gellan gum, xanthan gum, guar gum and mixtures thereof.

[0055] The composition may comprise from about 0.005 % to about 1 % by weight of a bacterial cellulose network. The term "bacterial cellulose" encompasses any type of cellulose produced via fermentation of a bacteria of the genus *Acetobacter* such as CELLULON® by CPKelco U.S. and includes materials referred to popularly as microfibrillated cellulose, reticulated bacterial cellulose, and the like. Some examples of suitable bacterial cellulose can be found in US 6,967,027; US 5,207,826; US 4,487,634; US 4,373,702; US 4,863,565 and US 2007/0027108. In one aspect, said fibres have cross sectional dimensions of 1.6 nm to 3.2 nm by 5.8 nm to 133 nm. Additionally, the bacterial cellulose fibres have an average micro fibre length of at least about 100 nm, or from about 100 to about 1,500 nm. In one aspect, the bacterial cellulose microfibrils have an aspect ratio, meaning the average microfibre length divided by the widest cross

sectional microfibre width, of from about 100:1 to about 400:1, or even from about 200:1 to about 300:1.

[0056] In one aspect, the bacterial cellulose is at least partially coated with a polymeric thickener. The at least partially coated bacterial cellulose can be prepared in accordance with the methods disclosed in US 2007/0027108 paragraphs 8 to 19. In one aspect the at least partially coated bacterial cellulose comprises from about 0.1 % to about 5 %, or even from about 0.5 % to about 3 %, by weight of bacterial cellulose; and from about 10 % to about 90 % by weight of the polymeric thickener. Suitable bacterial cellulose may include the bacterial cellulose described above and suitable polymeric thickeners include: carboxymethylcellulose, cationic hydroxymethylcellulose, and mixtures thereof.

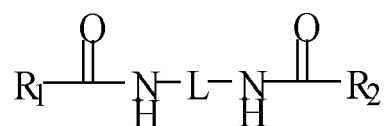
[0057] In one aspect, the composition may comprise from about 0.01 to about 5% by weight of the composition of a cellulosic fiber. Said cellulosic fiber may be extracted from vegetables, fruits or wood. Commercially available examples are Avicel® from FMC, Citri-Fi from Fiberstar or Betafib from Cosun.

[0058] Examples of synthetic polymeric structurants of use in the present invention include: polycarboxylates, polyacrylates, hydrophobically modified ethoxylated urethanes, hydrophobically modified non-ionic polyols and mixtures thereof.

[0059] Preferably the polycarboxylate polymer is a polyacrylate, polymethacrylate or mixtures thereof. In another preferred embodiment, the polyacrylate is a copolymer of unsaturated mono- or di-carbonic acid and 1-30C alkyl ester of the (meth) acrylic acid. Such copolymers are available from Noveon inc under the tradename Carbopol Aqua 30.

[0060] The composition may comprise a dibenzylidene polyol acetal derivative (DBPA) structurant. Non-limiting examples of suitable DBPA molecules are disclosed in US 61/167604. In one aspect, the DBPA derivative may comprise a dibenzylidene sorbitol acetal derivative (DBS). Said DBS derivative may be selected from the group consisting of: 1,3:2,4-dibenzylidene sorbitol; 1,3:2,4-di(p-methylbenzylidene) sorbitol; 1,3:2,4-di(p-chlorobenzylidene) sorbitol; 1,3:2,4-di(2,4-dimethyldibenzylidene) sorbitol; 1,3:2,4-di(p-ethylbenzylidene) sorbitol; and 1,3:2,4-di(3,4-dimethyldibenzylidene) sorbitol or mixtures thereof. These and other suitable DBS derivatives are disclosed in US 6,102,999, column 2 line 43 to column 3 line 65.

[0061] In one aspect, the structurant may comprise a di-amido gellant having a molecular weight from about 150 g/mol to about 1,500 g/mol, or even from about 500 g/mol to about 900 g/mol. Such di-amido gellants may comprise at least two nitrogen atoms, wherein at least two of said nitrogen atoms form amido functional substitution groups. In one aspect, the amido groups are different. In another aspect, the amido functional groups are the same. The di-amido gellant has the following formula:



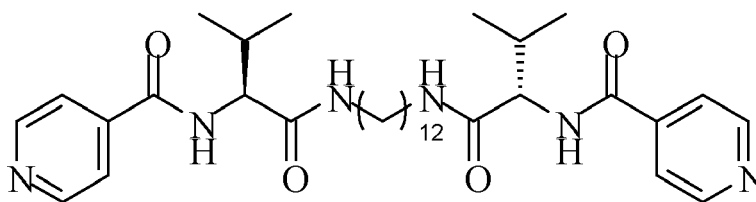
wherein:

R_1 and R_2 is an amino functional end-group, or even amido functional end-group, in one aspect

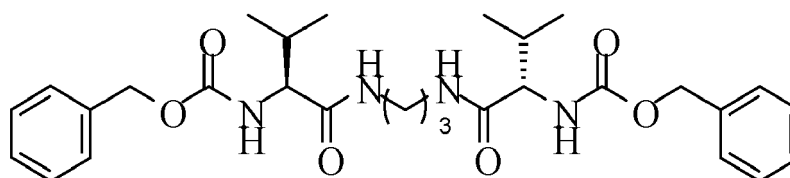
R_1 and R_2 may comprise a pH-tuneable group, wherein the pH tuneable amido-gellant may have a pKa of from about 1 to about 30, or even from about 2 to about 10. In one aspect, the pH tuneable group may comprise a pyridine. In one aspect, R_1 and R_2 may be different. In another aspect, may be the same.

L is a linking moiety of molecular weight from 14 to 500 g/mol. In one aspect, L may comprise a carbon chain comprising between 2 and 20 carbon atoms. In another aspect, L may comprise a pH-tuneable group. In one aspect, the pH tuneable group is a secondary amine. In one aspect, at least one of R_1 , R_2 or L may comprise a pH-tuneable group. Non-limiting examples of di-amido gellants are:

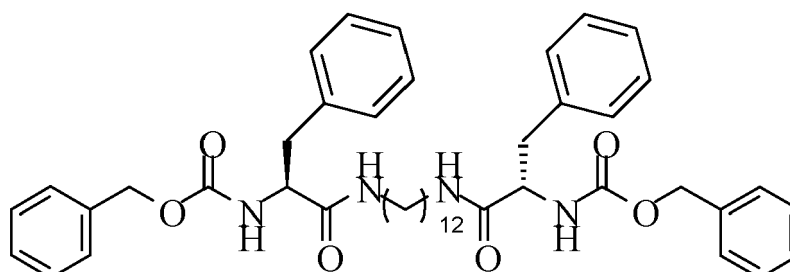
N,N'-(2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide



dibenzyl (2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)dicarbamate



dibenzyl (2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)dicarbamate



[0062] As detailed above, it is believed that the amphiphilic graft polymer exists as droplets in the liquid laundry detergent composition. There is a tendency for the droplets to coalesce and so cause the liquid laundry detergent composition to phase split. This generally occurs at higher levels of polymer concentration since there are more droplets available to coalesce. It was surprisingly found that liquid laundry detergent compositions comprising the polymer of the present invention were less likely to phase split at a given concentration of polymer. Hence a higher level of polymer could be added. Surprisingly, it was also found that the presence of a structurant further reduced the instances of phase split. Without wishing to be bound by theory, it is believed the structurant hinders the ability of the polymer droplets to come into contact with one another since the structurant promotes dispersion of the polymer throughout the liquid composition. Therefore, in the presence of a structurant, even higher levels of the polymer of the present invention could be added.

Solvent

[0063] The liquid laundry detergent composition may comprise a solvent. It was surprisingly found that the stability of the opacifier was further improved when a solvent was also formulated into the laundry detergent composition.

[0064] The solvent may be selected from the group comprising, glycerol, p-diol, dipropylene glycol, polypropylene glycol, diethylene glycol, ethanol, isopropanol, butanol and mixtures thereof.

Adjunct Ingredients

[0065] The liquid laundry detergent composition of the present invention may comprise one or more adjunct ingredients. Suitable adjunct ingredients include, but are not limited to bleach, bleach catalyst, dye, hueing agents, cleaning polymers, alkoxylated polyamines, polyethyleneimines, alkoxylated polyethyleneimines, soil release polymers, surfactants, solvents, dye transfer inhibitors, chelants, enzymes, perfumes, encapsulated perfumes, perfume delivery agents, suds suppressor, brighteners, polycarboxylates, opacifiers, deposition aids and mixtures thereof.

[0066] The liquid laundry detergent composition may comprise less than 50%, or even less than 40% or even less than 30% by weight of water. The liquid laundry detergent composition may comprise from 1% to 30%, or even from 2% to 20% or even from 3% to 15% by weight of the composition of water.

Process of Making Amphiphilic Graft Polymers

[0067] The inventive graft polymers are obtained by a continuous process wherein a vinyl ester component (B) composed of vinyl acetate and/or vinyl propionate (B1) and, if desired, a further ethylenically unsaturated monomer (B2), is polymerized in the presence of a polyalkylene oxide (A), a free radical-forming initiator (C) and, if desired, an additive (D), at a mean polymerization temperature at which the initiator (C) has a decomposition half-time of from 1 to 500 min, in at least one tubular reactor segment with a feed side and an outlet side, through which the reaction mixture comprising at least a part of component (A) to (C), and if desired (D), streams. In a preferred embodiment of the continuous process, the polymerization time is up to 2 hours.

[0068] Preferably, in the process according to the invention the local steady-state concentration of radicals present at

the mean polymerization temperature is substantially constant over time and the graft monomer (B) is present in the reaction mixture or the stream constantly in low concentration (for example of not more than 5% by weight). This allows the reaction to be controlled, and graft polymers can be prepared in a controlled manner with the desired low degree of grafting and the desired low polydispersity. The term "mean polymerization temperature" is intended to mean here that, although the process is substantially isothermal, there may, owing to the exothermicity of the reaction, be temperature variations which are preferably kept within the range of $\pm 10^{\circ}\text{C}$, more preferably in the range of $\pm 5^{\circ}\text{C}$. In another form, the process can be run adiabatically where the heat of polymerization is used to heat the reaction mixture to a desired reaction temperature.

[0069] According to the invention, the free radical-forming initiator (C) at the mean polymerization temperature should have a decomposition half-life of from 2 to 500 min, preferably from 6 to 300 min and more preferably from 8 to 150 min. Preferably the mean polymerization temperature is appropriately in the range from 50 to 160°C , in particular from 60 to 140°C and especially from 65 to 110°C .

[0070] The initiators can be used as such or dissolved in a solvent. Preference is given to using the initiators dissolved in a suitable solvent.

[0071] Preferred initiators (C) are O-C4-C12-acylated derivatives of tert-C4-C5-alkyl hydroperoxides, tert-Butyl hydroperoxide or di-tert-Butyl hydroperoxides, particular preference being given to tert-butyl peroxy-pivalate and tert-butyl peroxy-2-ethylhexanoate. Further preferred initiators that are especially suited for temperatures above 120°C are tert-butyl peroxybenzoate, di-cumylperoxide, di-tert-butyl peroxide, especially preferred di-tert-butyl peroxide.

[0072] The inventive polymerization reaction can be carried out in the presence of an additive (D). The additive is selected from the group consisting of surfactants, e.g., nonionic surfactant, solvents, diluents, fillers, colorants, rheology modifiers, crosslinkers or emulsifiers or mixtures thereof. In particular, additives are solvents, which are also used to formulate the inventive graft polymers for use and can therefore remain in the polymerization product. Preference is given to using water-soluble or water-miscible solvents. Preferred examples of solvents are polyethylene glycols having 2-15 ethylene glycol units, polypropylene glycols having 2-6 propylene glycol units and in particular alkoxylation products of C6-C16-alcohols (alkylene glycol monoalkyl ethers and polyalkylene glycol monoalkyl ethers).

[0073] The polymerization is preferably effected under pressure so that all the components are in liquid form, especially component B, whereby the pressure ranges from 2 to 200 bar, preferably from 3 to 100 bar or can be effected under standard pressure or at reduced or elevated pressure. When the boiling point of the monomers (B) or of any additive (D) used, is exceeded at the selected pressure, the polymerization is carried out with cooling.

[0074] In certain aspects of the invention, 15 to 85% by weight of a vinyl ester component (B), composed of 70 to 100% by weight of vinyl acetate and/or vinyl propionate (B1) and 0 to 30% by weight of the further ethylenically unsaturated monomer (B2), 15 to 70% by weight of the polyalkylene oxide (A) of mean molecular mass M_n of from 1000 to 20,000 g/mol, 0.1 to 3% by weight, based on compound (B), of the free radical-forming initiator (C) and 0 to 40% by weight, based on the sum of the components (A), (B) and (C), of an additive (D), are used, whereby the sum of which is in total 100%.

[0075] In particular aspects, 20 to 70 %, by weight of the vinyl ester component (B), 25 to 60 % by weight of a water-soluble polyalkylene oxide (A) of mean molecular mass M_n of from 1000 to 20,000 g/mol, 0.2 to 2.5 % by weight based on component (B), of the free-radical forming initiator (C) and 0 to 30 % by weight, based on the sum of the components (A), (B) and (C) of an additive, are used, whereby the sum of which is in total 100 %.

Water-soluble unit dose article

[0076] The liquid laundry detergent composition may be present in a water-soluble unit dose article. In such an embodiment, the water-soluble unit dose article comprises at least one water-soluble film shaped such that the unit-dose article comprises at least one internal compartment surrounded by the water-soluble film. The at least one compartment comprises the liquid laundry detergent composition. The water-soluble film is sealed such that the liquid 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.

[0077] The compartment should be understood as meaning a closed internal space within the unit dose article, which holds the composition. Preferably, the unit dose article comprises a water-soluble film. The unit dose article is manufactured such that the water-soluble film completely surrounds the composition and in doing so defines the compartment in which the composition resides. The unit dose article may comprise two films. A first film may be shaped to comprise an open compartment into which the composition is added. A second 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 film is described in more detail below.

[0078] 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. 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.

[0079] 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.

[0080] In a multi-compartment orientation, the 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.

[0081] 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.

[0082] 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:

50 grams $\pm$ 0.1 gram of film material is added in a pre-weighed 400 ml beaker and 245ml $\pm$ 1ml 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 24°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.

[0083] 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.

[0084] 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.

[0085] Mixtures of polymers can also be used as the pouch material. This can be beneficial to control the mechanical and/or dissolution properties of the compartments or pouch, depending on the application thereof and the required needs. Suitable mixtures include for example mixtures wherein one polymer has a higher water-solubility than another polymer, and/or one polymer has a higher mechanical strength than another polymer. Also suitable are mixtures of polymers having different weight average molecular weights, for example a mixture of PVA or a copolymer thereof of a weight average molecular weight of about 10,000- 40,000, preferably around 20,000, and of PVA or copolymer thereof, with a weight average molecular weight of about 100,000 to 300,000, preferably around 150,000. Also suitable herein are polymer blend compositions, for example comprising hydrolytically degradable and water-soluble polymer blends such as polylactide and polyvinyl alcohol, obtained by mixing polylactide and polyvinyl alcohol, typically comprising about 1-35% by weight polylactide and about 65% to 99% by weight polyvinyl alcohol. Preferred for use herein are polymers which are from about 60% to about 98% hydrolysed, preferably about 80% to about 90% hydrolysed, to improve the dissolution characteristics of the material.

[0086] 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.

[0087] Preferred films are those supplied by Monosol under the trade references M8630, M8900, M8779, M8310, films described in US 6 166 117 and US 6 787 512 and PVA films of corresponding solubility and deformability characteristics. Further preferred films are those described in US2006/0213801, WO 2010/119022 and US6787512.

[0088] Of the total PVA resin content in the film described herein, the PVA resin can comprise about 30 to about 85 wt% of the first PVA polymer, or about 45 to about 55 wt% of the first PVA polymer. For example, the PVA resin can

contain about 50 w.% of each PVA polymer, wherein the viscosity of the first PVA polymer is about 13 cP and the viscosity of the second PVA polymer is about 23 cP.

[0089] Naturally, different film material and/or films of different thickness may be employed in making the compartments of the present invention. A benefit in selecting different films is that the resulting compartments may exhibit different solubility or release characteristics.

[0090] The film material herein can also comprise one or more additive ingredients. For example, it can be beneficial to add plasticisers, for example glycerol, ethylene glycol, diethyleneglycol, propylene glycol, sorbitol and mixtures thereof. Other additives may include water and functional detergent additives, including surfactant, to be delivered to the wash water, for example organic polymeric dispersants, etc.

[0091] The film may be opaque, transparent or translucent. The film may comprise a printed area. The printed area may cover between 10 and 80% of the surface of the film; or between 10 and 80% of the surface of the film that is in contact with the internal space of the compartment; or between 10 and 80% of the surface of the film and between 10 and 80% of the surface of the compartment.

[0092] The area of print may cover an uninterrupted portion of the film or it may cover parts thereof, i.e. comprise smaller areas of print, the sum of which represents between 10 and 80% of the surface of the film or the surface of the film in contact with the internal space of the compartment or both.

[0093] The area of print may comprise inks, pigments, dyes, blueing agents or mixtures thereof. The area of print may be opaque, translucent or transparent.

[0094] The area of print may comprise a single colour or maybe comprise multiple colours, even three colours. The area of print may comprise white, black, blue, red colours, or a mixture thereof. The print may be present as a layer on the surface of the film or may at least partially penetrate into the film. The film will comprise a first side and a second side. The area of print may be present on either side of the film, or be present on both sides of the film. Alternatively, the area of print may be at least partially comprised within the film itself.

[0095] The area of print may comprise an ink, wherein the ink comprises a pigment. The ink for printing onto the film has preferably a desired dispersion grade in water. The ink may be of any color including white, red, and black. The ink may be a water-based ink comprising from 10% to 80% or from 20% to 60% or from 25% to 45% per weight of water. The ink may comprise from 20% to 90% or from 40% to 80% or from 50% to 75% per weight of solid.

[0096] The ink may have a viscosity measured at 20°C with a shear rate of 1000s⁻¹ between 1 and 600 cPs or between 50 and 350 cPs or between 100 and 300 cPs or between 150 and 250 cPs. The measurement may be obtained with a cone-plate geometry on a TA instruments AR-550 Rheometer.

[0097] The area of print may be achieved using standard techniques, such as flexographic printing or inkjet printing. Preferably, the area of print is achieved via flexographic printing, in which a film is printed, then moulded into the shape of an open compartment. This compartment is then filled with a detergent composition and a second film placed over the compartment and sealed to the first film. The area of print may be on either or both sides of the film.

[0098] Alternatively, an ink or pigment may be added during the manufacture of the film such that all or at least part of the film is coloured.

[0099] 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 2000ppm.

Adjunct ingredients

[0100] The composition may comprise an adjunct ingredient. The adjunct laundry detergent ingredient may be selected from bleach, bleach catalyst, dye, hueing dye, cleaning polymers including alkoxylated polyamines and polyethyleneimines, soil release polymer, surfactant, solvent, dye transfer inhibitors, chelant, enzyme, perfume, encapsulated perfume, polycarboxylates, structurant, opacifier and mixtures thereof.

Hueing Dye: The liquid laundry detergent composition may comprise a hueing dye. The hueing dyes employed in the present laundry care compositions may comprise polymeric or non-polymeric dyes, pigments, or mixtures thereof. Preferably the hueing dye comprises a polymeric dye, comprising a chromophore constituent and a polymeric constituent. The chromophore constituent is characterized in that it absorbs light in the wavelength range of blue, red, violet, purple, or combinations thereof upon exposure to light. In one aspect, the chromophore constituent exhibits an absorbance spectrum maximum from about 520 nanometers to about 640 nanometers in water and/or methanol, and in another aspect, from about 560 nanometers to about 610 nanometers in water and/or methanol.

[0101] Although any suitable chromophore may be used, the dye chromophore is preferably selected from benzodifuranes, methine, triphenylmethanes, naphthalimides, pyrazole, naphthoquinone, anthraquinone, azo, oxazine, azine, xanthene, triphenyldioxazine and phthalocyanine dye chromophores. Mono and di-azo dye chromophores are preferred.

[0102] The hueing dye may comprise a dye polymer comprising a chromophore covalently bound to one or more of

at least three consecutive repeat units. It should be understood that the repeat units themselves do not need to comprise a chromophore. The dye polymer may comprise at least 5, or at least 10, or even at least 20 consecutive repeat units.

[0103] The repeat unit can be derived from an organic ester such as phenyl dicarboxylate in combination with an oxyalkyleneoxy and a polyoxyalkyleneoxy. Repeat units can be derived from alkenes, epoxides, aziridine, carbohydrate including the units that comprise modified celluloses such as hydroxyalkylcellulose; hydroxypropyl cellulose; hydroxypropyl methylcellulose; hydroxybutyl cellulose; and, hydroxybutyl methylcellulose or mixtures thereof. The repeat units may be derived from alkenes, or epoxides or mixtures thereof. The repeat units may be C2-C4 alkyleneoxy groups, sometimes called alkoxy groups, preferably derived from C2-C4 alkylene oxide. The repeat units may be C2-C4 alkoxy groups, preferably ethoxy groups.

[0104] For the purposes of the present invention, the at least three consecutive repeat units form a polymeric constituent. The polymeric constituent may be covalently bound to the chromophore group, directly or indirectly via a linking group. Examples of suitable polymeric constituents include polyoxyalkylene chains having multiple repeating units. In one aspect, the polymeric constituents include polyoxyalkylene chains having from 2 to about 30 repeating units, from 2 to about 20 repeating units, from 2 to about 10 repeating units or even from about 3 or 4 to about 6 repeating units. Non-limiting examples of polyoxyalkylene chains include ethylene oxide, propylene oxide, glycidol oxide, butylene oxide and mixtures thereof.

Chelant: The compositions herein may also optionally contain one or more copper, iron and/or manganese chelating agents. If utilized, chelating agents will generally comprise from about 0.1% by weight of the compositions herein to about 15%, or even from about 3.0% to about 15% by weight of the compositions herein. Suitable chelants may be selected from: diethylene triamine pentaacetate, diethylene triamine penta(methyl phosphonic acid), ethylene diamine-N,N'-disuccinic acid, ethylene diamine tetraacetate, ethylene diamine tetra(methylene phosphonic acid), hydroxyethane di(methylene phosphonic acid), and any combination thereof. A suitable chelant is ethylene diamine-N,N'-disuccinic acid (EDDS) and/or hydroxyethane diphosphonic acid (HEDP). The laundry detergent composition may comprise ethylene diamine-N,N'-disuccinic acid or salt thereof. The ethylene diamine-N,N'-disuccinic acid may be in S,S enantiomeric form. The composition may comprise 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt, glutamic acid-N,N-diacetic acid (GLDA) and/or salts thereof, 2-hydroxypyridine-1-oxide, Trilon P™ available from BASF, Ludwigshafen, Germany. Suitable chelants may also be calcium carbonate crystal growth inhibitors. Suitable calcium carbonate crystal growth inhibitors may be selected from the group consisting of: 1-hydroxyethanediphosphonic acid (HEDP) and salts thereof; N,N-dicarboxymethyl-2-aminopentane-1,5-dioic acid and salts thereof; 2-phosphonobutane-1,2,4-tricarboxylic acid and salts thereof; and any combination thereof.

[0105] The composition may comprise a calcium carbonate crystal growth inhibitor, such as one selected from the group consisting of: 1-hydroxyethanediphosphonic acid (HEDP) and salts thereof; N,N-dicarboxymethyl-2-aminopentane-1,5-dioic acid and salts thereof; 2-phosphonobutane-1,2,4-tricarboxylic acid and salts thereof; and any combination thereof.

Polymers: Suitable polymers include carboxylate polymers, polyethylene glycol polymers, polyester soil release polymers such as terephthalate polymers, amine polymers, cellulosic polymers, dye transfer inhibition polymers, dye lock polymers such as a condensation oligomer produced by condensation of imidazole and epichlorhydrin, optionally in ratio of 1:4:1, hexamethylenediamine derivative polymers, and any combination thereof.

[0106] Other polymers include hydroxyethyl cellulose polymer. Preferably, the hydroxyethyl cellulose polymer is derivatised with trimethyl ammonium substituted epoxide. The cellulose polymer may have a molecular weight of between 100,000 and 800,000 daltons. The hydroxyethyl cellulose polymer may be added to the composition as a particle. It may be present in the composition of the particle or may be also be present as a liquid, or a mixture thereof. **Enzymes:** The compositions can comprise one or more detergent enzymes which provide cleaning performance and/or fabric care benefits. Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxi-dases, lipoxigenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, and amylases, or mixtures thereof. A typical combination is a cocktail of conventional applicable enzymes like protease, lipase, cutinase and/or cellulase in conjunction with amylase.

Fatty acid: The composition of the present invention may comprise a fatty acids or fatty acid salts. The fatty acids are carboxylic acids which are often with a long unbranched aliphatic tail, which is either saturated or unsaturated. Suitable fatty acids or salts of the fatty acids for the present invention are preferably sodium salts, preferably C12-C18 saturated and/or unsaturated fatty acids more preferably C12-C14 saturated and/or unsaturated fatty acids and alkali or alkali earth metal carbonates preferably sodium carbonate.

[0107] Preferably the fatty acids are selected from the group consisting of lauric acid, myristic acid, palmitic acid, stearic acid, topped palm kernel fatty acid, coconut fatty acid and mixtures thereof.

[0108] Solvent: The composition may comprise a solvent. The solvent preferably has molecular weight of less than 1500, more preferably less than 1000, even more preferably less than 700. The solvent preferably has a molecular weight of greater than 10, more preferably greater than 100. The solvent preferably has a cLog P of greater than -1.0

and more preferably less than +10. The solvent preferably has a Hydrogen bonding component (δ_H) of less than 20.5, and preferably greater than 10.

[0109] The solvent may be selected from alcohols, diols, monoamine derivatives, glycols, polyalkylene glycols, such as polyethylene glycol, propane diol, monoethanolamine or mixtures thereof.

[0110] The solvent may be selected from the group comprising of polyethylene glycol (PEG) polymer having molecular weight between 300 and 600, dipropylene glycol (DPG), nbutoxy propoxy propanol (nBPP) and mixtures thereof. More preferably the solvent may be selected from the group comprising polyethylene glycol (PEG) polymer having molecular weight between 400 and 600, dipropylene glycol (DPG), nbutoxy propoxy propanol (nBPP) and mixtures thereof.

Process of making

[0111] Any suitable process can be used to make the composition of the present invention. Those skilled in the art will know suitable process known the art.

Method of Use

[0112] The composition or unit dose article of the present invention can be added to a wash liquor to which laundry is already present, or to which laundry is added. It may be used in an washing machine operation and added directly to the drum or to the dispenser drawer. The washing machine may be an automatic or semi-automatic washing machine. It may be used in combination with other laundry detergent compositions such as fabric softeners or stain removers. It may be used as pre-treat composition on a stain prior to being added to a wash liquor.

EXAMPLE

Example 1

[0113] Below are liquid detergent compositions with different PEG/VAC polymers.

Ingredients (All levels are in weight percent of the composition.)	A	B	C
Linear C ₉ -C ₁₅ Alkylbenzene sulfonic acid	24.2	24.2	24.2
C12-14 alkyl ethoxy 3 sulfate	16.5	16.5	16.5
C ₁₂₋₁₄ alkyl 7-ethoxylate	4.0	4.0	4.0
Citric Acid	1.7	1.7	1.7
Fatty acid	6.8	6.8	6.8
Chelants	1.3	1.3	1.3
polymer 1 - Mw graft base 6000-40/60, pol distribution 0.3-0.34	5.6		
polymer 2 - Mw graft base 6000-40/60, pol distribution 0.45-0.65		5.6	
polymer 3 - Mw graft base 4000-60/40, pol distribution 0.3-0.34			5.6
cleaning polymers	1.9	1.9	1.9
Opacifier	1.8	1.8	1.8
Enzymes	0.1	0.1	0.1
HCO structurant	0.1	0.1	0.1
Solvent system*	22.3	22.3	22.3
Perfume	2.2	2.2	2.2
water	10.1	10.1	10.1
Mono-ethanolamine or NaOH (or mixture thereof)	neutralize to pH to about 7.4		
Other laundry adjuncts / minors	to 100%		
*May include, but not limited to propanediol, glycerol, ethanol, dipropyleneglycol, polyetheyleneglycol, polypropyl- eneglycol.			

[0114] Polymer 1 is an amphiphilic graft copolymer outside of the scope of the claims. Polymers 2 and 3 are amphiphilic graft copolymer according to the present invention.

[0115] 1000g of formulation A and B were prepared in the lab using a balance at 0.01g precision, a mixer type IKA EURO-ST-P-CV and pitched blade turbine impeller 4 blade.

[0116] The formulations were poured at 2/3rd of the height in 3 x 28mL glass vials with diameter of 22mm and stored in an oven with constant temperature at 20. Same procedure was used for formulation stored at 35C.

[0117] Vials were checked visually under office lamp for physical change such as discoloration, phase changes. Formulation is considered stable when it shows a homogeneous milky white color.

Results:

[0118]

	20C storage temperature				
polymer	1 week	2 weeks	3 weeks	4 weeks	8 weeks
polymer 1	OK	OK	OK	OK	OK
Polymer 2	OK	OK	OK	OK	OK
Polymer 3	OK	OK	OK	OK	OK

	35C storage temperature				
polymer	1 week	2 weeks	3 weeks	4 weeks	8 weeks
polymer 1	OK	OK	Phase split	Phase split	Phase split
Polymer 2	OK	OK	OK	OK	OK
Polymer 3	OK	OK	OK	OK	OK

[0119] As can be seen from the results, the change of polarity distribution from 0.3-0.34 to 0.45-65 or of a specific molecular weight of the present invention provided improved physical stability of the compositions at 35°C. Although all polymers performed well at 20°C storage, at higher temperatures of 35°C as would be experienced by products during storage and shipping and/or storage within the home, the compositions comprising the amphiphilic graft copolymer outside of the scope of the claims phase split. Compositions comprising amphiphilic graft copolymers according to the present invention performed well across a range of storage temperatures experienced by consumer goods.

[0120] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

Claims

1. A liquid laundry detergent composition comprising;
an amphiphilic graft polymer, wherein the polymer is based on water-soluble polyalkylene oxides (A) as a graft base and side chains formed by polymerization of a vinyl ester component (B), and comprising;

- i. from 15% to 70% by weight of a water-soluble polyalkylene oxide as a graft base and
- ii. side chains formed by free-radical polymerization of from 30 to 85% by weight of a vinyl ester component composed of

(B1) from 70 to 100% by weight of vinyl acetate and/or vinyl propionate and

(B2) from 0 to 30% by weight of a further ethylenically unsaturated monomer; and

wherein the graft base has a mean molecular weight (M_w) of from 3500 to 5500, or wherein the polymer has a

full width at half maximum of the polarity distribution between 0.35 and 1.0, or a mixture thereof.

2. The liquid laundry detergent composition according to claim 1 comprising a structurant.
- 5 3. The liquid laundry detergent composition according to claim 2 wherein the structurant is selected from non-polymeric or polymeric structurants.
4. The liquid laundry detergent composition according to claim 3, wherein the structurant is a non-polymeric structurant, preferably a crystallisable glyceride.
- 10 5. The liquid laundry detergent composition according to claim 3, wherein the structurant is a polymeric structurant, preferably a fibre based polymeric structurant, more preferably a cellulose based fibre-based structurant.
6. The liquid laundry detergent according to any preceding claims, wherein said graft polymer has a maximum of the polarity distribution between about 0.45 and about 1.
- 15 7. The composition according to any preceding claims, wherein the graft base has a mean molecular mass from 3500 to 4500, or even from 3750 to 4250.
8. The composition according to any preceding claims, wherein the polymer has a polydispersity M_w/M_n of less than or equal to 3.
9. The composition according to any preceding claims wherein the polymer has an average of less than or equal to 1 graft site per 50 alkylene oxide units.
- 25 10. The composition according to any preceding claims, wherein the polymer has a polydispersity M_w/M_n of less than or equal to 3.
11. The liquid laundry detergent composition according to any preceding claims, wherein the composition comprises between 0.1wt% to 10wt%, or even from 1.5wt% to 5.5wt% or even from 2wt% to 5wt% amphiphilic graft polymer.
- 30 12. The liquid laundry detergent composition according to any preceding claims comprising an ingredient selected from, bleach, bleach catalyst, dye, hueing agents, cleaning polymers, alkoxylated polyamines, polyethyleneimines, alkoxylated polyethyleneimines, soil release polymers, surfactants, solvents, dye transfer inhibitors, chelants, enzymes, perfumes, encapsulated perfumes, perfume delivery agents, suds suppressor, brighteners, polycarboxylates, opacifiers, deposition aids and mixtures thereof.
- 35 13. The liquid laundry detergent composition according to any preceding claims comprising an anionic surfactant and a non-ionic surfactant, preferably wherein the ratio of anionic surfactant to non-ionic surfactant is between 5:1 and 23:1.
- 40 14. A water soluble unit dose article comprising a water soluble film and a composition according to any preceding claims.
15. The water soluble unit dose article according to claim 12, wherein the unit dose article is a multicompartment unit dose article, preferably a superposed multicompartment unit dose article.
- 45 16. A process of cleaning laundry comprising the step of adding the composition or unit dose article according to any preceding claims to the drum or dispenser drawer washing machine.



EUROPEAN SEARCH REPORT

 Application Number
 EP 14 17 9405

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	WO 2013/134601 A1 (PROCTER & GAMBLE [US]) 12 September 2013 (2013-09-12)	1,6-12, 16	INV. C11D3/37 C11D3/22 C11D17/04 C11D17/00
Y	* page 14, line 26 - page 15; claims 1-12; figure 8 * * page 16, lines 30, 31; examples 24, 25; table 2 * * page 36, line 4 - page 38, line 25 * * page 18, line 30 - page 19, line 2 *	1-16	
X	WO 2007/138054 A1 (PROCTER & GAMBLE [DE]; BOECKH DIETER [DE]; HERRERA TABOADA LIDCAY [BE]) 6 December 2007 (2007-12-06)	1,7-13, 16	
Y	* in example 9 the compositions A-C and F with the graft polymer 5; claim 6; example 9 *	1-16	
X	EP 0 285 037 A2 (BASF AG [DE]) 5 October 1988 (1988-10-05)	1-3,5, 7-12,16	
Y	* polymers 3, 8, 9, 14-20; page 8, line 2 - line 20; table 1 * * claims 1, 4 *	1-16	
Y	EP 2 302 026 A1 (PROCTER & GAMBLE [US]) 30 March 2011 (2011-03-30) * paragraphs [0052] - [0055], [0060], [0071] - [0082]; claims 1, 14, 15 *	1-16	TECHNICAL FIELDS SEARCHED (IPC) C11D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 30 January 2015	Examiner Loiselet-Taisne, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 1
 EPO FORM 1503 03/82 (P04C01)

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

EP 14 17 9405

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.

30-01-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013134601 A1	12-09-2013	CA 2865507 A1	12-09-2013
		CN 104160009 A	19-11-2014
		EP 2823029 A1	14-01-2015
		US 2013252874 A1	26-09-2013
		WO 2013134601 A1	12-09-2013

WO 2007138054 A1	06-12-2007	AT 474868 T	15-08-2010
		AT 474906 T	15-08-2010
		BR PI0711719 A2	29-11-2011
		BR PI0712159 A2	17-01-2012
		CA 2650067 A1	06-12-2007
		CA 2653880 A1	06-12-2007
		CN 101454364 A	10-06-2009
		CN 101473025 A	01-07-2009
		EG 25183 A	11-10-2011
		EP 2024479 A1	18-02-2009
		EP 2029645 A1	04-03-2009
		ES 2349236 T3	29-12-2010
		ES 2349321 T3	29-12-2010
		JP 5542434 B2	09-07-2014
		JP 2009538946 A	12-11-2009
		JP 2009538947 A	12-11-2009
		KR 20090023374 A	04-03-2009
		RU 2008142866 A	10-07-2010
		US 2009176935 A1	09-07-2009
		US 2009298735 A1	03-12-2009
		WO 2007138053 A1	06-12-2007
		WO 2007138054 A1	06-12-2007
		ZA 200808921 A	25-11-2009

EP 0285037 A2	05-10-1988	CA 1302832 C	09-06-1992
		DE 3711298 A1	13-10-1988
		EP 0285037 A2	05-10-1988
		ES 2041721 T3	01-12-1993
		JP 2541616 B2	09-10-1996
		JP S63260994 A	27-10-1988
US 4846995 A	11-07-1989	-----	
EP 2302026 A1	30-03-2011	AR 078367 A1	02-11-2011
		CA 2770037 A1	24-03-2011
		CN 102575202 A	11-07-2012
		EP 2302026 A1	30-03-2011
		JP 2013503964 A	04-02-2013
		RU 2012105131 A	27-10-2013
		WO 2011034761 A1	24-03-2011

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- US 5340390 A [0048]
- WO 2009101545 A1 [0054]
- US 6967027 B [0055]
- US 5207826 A [0055]
- US 4487634 A [0055]
- US 4373702 A [0055]
- US 4863565 A [0055]
- US 20070027108 A [0055] [0056]
- US 61167604 B [0060]
- US 6102999 A [0060]
- US 6166117 A [0087]
- US 6787512 B [0087]
- US 20060213801 A [0087]
- WO 2010119022 A [0087]

Non-patent literature cited in the description

- **THOMAS P. RYAN.** Modern Engineering Statistics.
Wiley-Interscience, John Wiley & Sons, Inc, 2007
[0036]