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(54) **Liquid laundry detergent composition**

(57) Liquid laundry detergent compositions comprising amphiphilic graft polymers and opacifiers

EP 2 980 197 A1

Description

FIELD OF THE INVENTION

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

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] Opacifiers are also formulated into liquid laundry detergents. Addition of an opacifier offers an aesthetic element to the composition that is preferred by consumers.

15 **[0004]** However, the stability of the opacifier can be negatively impacted by the presence of amphiphilic graft polymers. The opacifier often degrades resulting in an undesirable yellow colouration.

[0005] Therefore, there remains a need for a liquid laundry detergent composition that comprises an amphiphilic graft polymer and an opacifier and that exhibits improved ingredient stability than seen with known compositions.

20 **[0006]** The Inventors surprisingly found that a laundry detergent composition comprising an amphiphilic graft polymer according to the present invention, and an opacifier, exhibited improved ingredient stability than seen with known compositions.

SUMMARY OF THE INVENTION

25 **[0007]** The present invention is to a liquid laundry detergent composition comprising;

(i) 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; and

(ii) an opacifier.

40 **[0008]** The present invention is also to a water-soluble unit dose article comprising a water-soluble film and the liquid laundry detergent composition described above, contained therein.

DETAILED DESCRIPTION OF THE INVENTION

45 Composition

[0009] 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 herein mean a composition that can be used in a laundry wash and/or rinse operation. A laundry detergent composition
50 can also be a laundry pretreatment composition.

[0010] 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
55 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.

[0011] The liquid laundry detergent composition comprises an amphiphilic graft polymer. Suitable graft copolymers

are described in more detail below.

[0012] The liquid laundry detergent composition comprises an opacifier. Suitable opacifiers are described in more detail below.

[0013] The ratio of amphiphilic graft polymer to opacifier is preferably between 0.05:80 and 1:4, preferably between 1:5 and 1:2, more preferably between 1:3 and 1:2.

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 1wt% to 7.5wt% or even from 2wt% to 5.5wt% 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 Plurion® 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] It was also surprisingly found that compositions comprising the amphiphilic graft polymer of the present invention exhibited improved visible clarity as to compositions comprising amphiphilic graft polymers in the art, especially wherein the composition comprised an opacifier. In other words, compositions comprising the amphiphilic graft polymer of the present invention were less 'cloudy' or 'hazy' as compared to compositions comprising amphiphilic graft polymers known in the art. 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 and opacifier that exhibits improved clarity versus compositions known in the art that comprise amphiphilic graft polymers and opacifiers.

Opacifier

[0042] The liquid laundry detergent composition of the present invention comprises an opacifier.

[0043] An opacifier according to the present invention is a solid, inert compound which does not dissolve in the composition and refracts, scatters or absorbs most light wavelengths. Suitable opacifiers have a refractive index (RI) substantially different from the system in which it is incorporated. The colour of a composition can be accurately and reliably measured using the Hunter L, a, b colour scale. The Hunter scale has been in existence since the 1950s and is a well recognized colour measuring technique known in the art. The Hunter colour space is organized as a cube. The L axis runs from top to bottom; the maximum L being 100 which is white and the minimum value is zero, which is black. The a and b axes have no specific numerical limits, however positive a is red, negative a is green, positive b is yellow and negative b is blue (see figure 1). Delta values (ΔL , Δa and Δb) can be measured and are associated with a colour change. The total colour difference, ΔE , can also be calculated. The ΔE is a single value that takes into account the differences between the L, a and b of test and comparison samples. The ΔE is calculated as follows;

Using L_1 , a_1 , b_1 and L_2 , a_2 and b_2

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}$$

[0044] A just noticeable difference (JND) is characterized as a ΔE of greater than 2.3. The JND is the smallest detectable difference possible with the human eye between a starting and secondary level of a particular sensory stimulus.

[0045] The measurements of the present invention are taken on a HunterLab colour measurement instrument (Hunter Lab Color Quest XE), set as follows;

Illuminant: D65

Angle of observer: 10°

Mode: reflection

[0046] The instrument is used as per the manufacturers instructions. A sample of 20mL are tested in an optically clear glass cell having a fixed path length of 10mm and dimensions 55mm by 57mm. The measurement type is reflectance measurement RSIN, which measures the diffuse and specular reflectance of the sample at the port. The measurements are made with the specular exclusion port door closed.

[0047] Fresh Hunter colour value is a measure of the colour parameters of a fresh sample, immediately after preparation.

[0048] 2 day storage Hunter value, is to mean that the colour of the sample is measured after 2 days storage at 50°C.

[0049] 5 day storage Hunter value, is to mean that the colour of the sample is measured after 5 days storage at 50°C.

[0050] 10 day storage Hunter value, is to mean that the colour of the sample is measured after 10 days storage at 50°C.

[0051] A delta hunter value or ΔE is equally measured fresh, and after 2, 5 and 10 days storage. In these calculations the comparison samples (L_1 , a_1 , b_1) are the values as measured fresh.

[0052] Sufficient opacifier may be added to the composition to result in a fresh hunter L value of greater than 70, more preferably greater than 72, more preferably greater than 75. The first composition preferably has a 10 day storage Hunter L value of greater than 70, more preferably greater than 72, most preferably greater than 75. The first composition has a b value of less than 4, more preferably less than 1. Preferably the ΔE at 10 days storage of the first compartment versus fresh is less than 7, more preferably less than 5, more preferably less than 2, most preferably less than 1.

[0053] The opacifier is preferably selected from the group consisting of styrene/acrylate latexes, titanium dioxide, Tin dioxide, any forms of modified TiO₂, for example carbon modified TiO₂ or metallic doped (e.g. Platinum, Rhodium) TiO₂ or stannic oxide, bismuth oxychloride or bismuth oxychloride coated TiO₂/Mica, silica coated TiO₂ or metal oxide coated and mixtures thereof. Particularly preferred styrene/acrylate latexes are those available from the Rohm & Haas Company sold under the trademark Acusol. The latexes are characterized by preferably having pH of about 2 to about 3, having approximately 40% solids in water, with particle size of about 0.1 to about 0.5 micron. Specifically preferred Acusol.RTM. polymers include Acusol.RTM. OP301 (styrene/acrylate) polymer, Acusol.RTM. OP302, (Styrene/Acrylate/Divinylbenzene Copolymer), Acusol.RTM. OP303 (Styrene/Acrylamide Copolymer), OP303B (Styrene/Acrylamide Copolymer), Acusol.RTM. OP305 (Styrene/PEG-10 Maleate/Nonoxynol-10 Maleate/Acrylate Copolymer) and (Styrene/Acrylate/PEG-10 Dimaleate Copolymer) and mixtures thereof. Preferred species have molecular weight of from 1000 to 1 000 000, more preferably from 2000 to 500 000, most preferably from 5000 to 20 000. The opacifier may comprise a Styrene/PEG-10 Maleate/Nonoxynol-10 Maleate/Acrylate copolymer (Acusol.RTM. OP305). The opacifier may comprise a Styrene/Acrylamide Copolymer (OP303/OP303B).

[0054] Suitable opacifiers can be selected from the group comprising styrene/acrylic acid copolymers, styrene/acrylic acid/maleic acid terpolymers, titanium dioxide, tin dioxide, any forms of modified TiO₂, e.g. carbon modified TiO₂ or metallic doped (e.g. Platinum, Rhodium) TiO₂ or stannic oxide, bismuth oxychloride or bismuth oxychloride coated TiO₂/Mica, silica coated TiO₂ or metal oxide coated and mixtures thereof.

[0055] The opacifier may be selected from a styrene/acrylic acid copolymer, styrene/acrylic acid/maleic acid terpolymer, or a mixture thereof.

[0056] The opacifier is preferably present in sufficient amount to leave the composition, in which it is incorporated, white. The composition may comprise between 0.001wt% to 5 wt%, or even 0.1wt% to 2.5wt%, or even from 0.5wt% to 2wt% opacifier.

[0057] Where the opacifier is an inorganic opacifier (e.g. TiO₂, or modifications thereof) the opacifier is preferably present at a level of from 0.001% to 1%, more preferably from 0.01% to 0.5%, most preferably from 0.05% to 0.15% by weight of the composition.

[0058] Where the opacifier is an organic opacifier (e.g. styrene/acrylate latexes), the opacifier is preferably present at a level of from 0.001% to 2.5%, more preferably from 1% to 2.2%, most preferably from 1.4% to 1.8% by weight of the composition.

Solvent

[0059] 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.

[0060] 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

[0061] 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, alkoxyated polyamines, polyethyleneimines, alkoxyated polyethyleneimines, soil release polymers, surfactants, solvents, dye transfer inhibitors, chelants, enzymes, perfumes, encapsulated perfumes, perfume delivery agents, suds suppressor, brighteners, polycarboxylates, structurants, deposition aids and mixtures thereof.

[0062] 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

[0063] 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.

[0064] 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.

[0065] 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 .

[0066] The initiators can be used as such or dissolved in a solvent. Preference is given to using the initiators dissolved in a suitable solvent.

[0067] 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 peroxyvalerate and tert-butyl peroxy-2-ethylhexanoate. Further preferred initiators that are especially suited for temperatures above 120°C are tert-butyl peroxybenzoate, di-cumylperoxid, di-tert-butyl peroxide, especially preferred di-tert-butyl peroxide.

[0068] 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).

[0069] 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.

[0070] 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%.

[0071] 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

[0072] 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.

[0073] 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.

[0074] 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.

[0075] 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.

[0076] 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.

[0077] 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.

[0078] 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.

[0079] 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.

[0080] 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.

[0081] 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.

[0082] 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.

[0083] 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.

[0084] 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.

[0085] 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.

[0086] 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.

[0087] 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.

[0088] 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.

[0089] The area of print may comprise inks, pigments, dyes, blueing agents or mixtures thereof. The area of print may be opaque, translucent or transparent.

[0090] 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.

[0091] 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.

[0092] 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.

[0093] 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.

[0094] 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.

[0095] 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.

5 Process of making

[0096] 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.

10 Method of Use

[0097] The composition or unit dose article of the present invention can be added to a wash liquor to which h 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. 15 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.

EXAMPLES

20 **[0098]** The stability of opacifier in liquid laundry detergent compositions when in the presence of different amphiphilic graft polymers was determined.

Sample preparation

25 Materials used

[0099]

- Base composition containing surfactants such as LAS, AE3S and non-ionic, polymers, chelants, water and perfume
- 30 - Amphiphilic graft polymer premix (see below)
- Opacifier premix (see below)
- Hydrogenated Castor Oil Rheology modifier

Equipment used

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[0100]

- Balance, 0.01g precision
- Mixer (ref IKA EURO-ST-P-CV)
- 40 - 2L beaker, (ref Nalgene 1203-2000)
- Pitched blade turbine Impeller 4 blade, 45deg, 10cm diameter, width 10mm
- 28mL Vials, 22.5mm diameter

Procedure

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[0101] A master batch of the base was prepared in advance using equipment above.

[0102] This batch was split to screen in parallel different compositions.

Table 1

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Component	Weights used in grams
base	845.1
PEG/VAC polymer premix	82.4
Opacifier premix	66.7
Rheology modifier	22.5

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Preparation of amphiphilic graft polymer premix

[0103] In a 2L beaker, 700g of amphiphilic graft polymer was and pre-heated to and maintained at 50°C. 300g of propanediol was added and mixed for 15min at 200rpm.

[0104] Different amphiphilic graft polymer premixes were made according to the present invention, but which differed in molecular weight.

Preparation of opacifier premix

[0105] In a 100mL beaker, 60g of Opacifier OP301 was added and mixed for 5min at 200rpm with 40g of propanediol.

Preparation of samples

[0106] First the base was added and afterwards, the relevant amphiphilic graft polymer was premixed at 250rpm for 3 min before the opacifier-premix was added. This was mixed for 1 min before adding the rheology modifier. The rheology modifier was added at 500rpm and mixed for 30s.

Preparation for physical stability storage

[0107] Within 3 hours after making, 28mL vials of compositions to be tested were prepared and filled at 2/3rd of the height. These were placed them in constant storage rooms at 20°C.

Test Methods

[0108] The samples were checked visually under a lamp for failure for stability after one week. If no separation or phase split was observed, the sample was considered stable. Results can be seen in Table 2.

Table 2

MW of graft base	Visual stability determination
6000	Unstable
4000	Stable

[0109] As can be seen from Table 1, after 1 week storage the composition with the amphiphilic graft polymer having a molecular weight outside of the scope of the present invention was seen to phase split. However, the composition comprising the amphiphilic graft polymer within the scope of the present invention was still stable.

[0110] 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;

(i) 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; 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; and

(ii) an opacifier.

2. The liquid laundry detergent composition according to claim 1, wherein the opacifier is selected from the group comprising styrene/acrylic acid copolymers, styrene/acrylic acid/maleic acid terpolymers, titanium dioxide, tin dioxide, any forms of modified TiO₂, e.g. carbon modified TiO₂ or metallic doped (e.g. Platinum, Rhodium) TiO₂ or stannic oxide, bismuth oxychloride or bismuth oxychloride coated TiO₂/Mica, silica coated TiO₂ or metal oxide coated and mixtures thereof.
3. The liquid laundry detergent composition according to claim 2, wherein the opacifier is selected from a styrene/acrylic acid copolymer, styrene/acrylic acid/maleic acid terpolymer, or a mixture thereof.
4. 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.
5. 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.
6. The composition according to any preceding claims, wherein the polymer has a polydispersity M_w/M_n of less than or equal to 3.
7. 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.
8. The composition according to any preceding claims, wherein the polymer comprises less than 10% by weight of polyvinyl ester (B) in ungrafted form.
9. The composition according to any preceding claims, wherein the polymer comprises less than 30% ungrafted polyethylene glycol.
10. The composition according to any preceding claims, wherein the polymer comprises from 25 to 60% by weight of the graft base (A) and from 40 to 75% by weight of the vinyl ester component (B).
11. The liquid laundry detergent composition according to any preceding claims, wherein the composition comprises between 0.1wt% to 10wt%, or even from 1wt% to 7.5wt% or even from 2wt% to 5.5wt% amphiphilic graft polymer.
12. The liquid laundry detergent composition according to any preceding claims, wherein the composition comprises between 0.001wt% to 5 wt%, or even 0.1wt% to 2.5wt%, or even from 0.5wt% to 2wt% opacifier.
13. The liquid laundry detergent composition according to any preceding claims, wherein the ratio of amphiphilic graft polymer to opacifier is preferably between 0.05:80 and 1:4, preferably between 1:5 and 1:2, more preferably between 1:3 and 1:2.
14. The liquid laundry detergent composition according to any preceding claims comprising an adjunct material and wherein the adjunct material is 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, structurants, deposition aids and mixtures thereof.
15. The liquid laundry detergent composition according to any preceding claims comprising a solvent preferably selected from the group comprising, glycerol, p-diol, dipropylene glycol, polypropylene glycol, diethylene glycol, ethanol, isopropanol, butanol and mixtures thereof.
16. A water-soluble unit dose article comprising a water-soluble film and the liquid laundry detergent composition according to any preceding claims contained therein.



EUROPEAN SEARCH REPORT

Application Number
EP 14 17 9397

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