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(54) **PROCESS TO THICKEN A LIQUID DETERGENT COMPOSITION**

VERFAHREN ZUM EINDICKEN EINER FLÜSSIGEN REINIGUNGSMITTELZUSAMMENSETZUNG

PROCÉDÉ POUR ÉPAISSIR UNE COMPOSITION DE DÉTERGENT LIQUIDE

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DescriptionTECHNICAL FIELD

[0001] This invention relates to a process to make a polyacrylate copolymer thickened liquid laundry detergent composition containing amine neutralised anionic surfactant, in particular amine neutralised linear alkyl benzene sulfonate.

BACKGROUND

[0002] Acrylate polymers are well known for thickening detergent compositions used for personal care. Typically, anionic surfactant added to such compositions is pre-neutralised. For the manufacture of detergent compositions for laundry it is the normal practice to neutralise the acid precursor of the anionic surfactant linear alkyl benzene sulfonate (LAS) *in situ* and to use the heat generated by this exothermic reaction to assist with processing. When making liquid laundry detergent compositions the acid precursor of LAS (LAS acid) and fatty acids are often neutralised using caustic to give Sodium LAS and soap in the resulting liquid. It is also known to neutralise and/or to adjust the pH of the liquid using amines, for example monoethanolamine (MEA), triethanolamine (TEA) and mixtures of the two.

[0003] US 2010/0197557 A1 (Dial) describes an abrasive cleaner composition thickened with a HASE (hydrophobically modified alkali swellable emulsion) associative polymer. Compositions 2 and 4 in Table 1 comprise sodium dodecyl benzene sulfonate (LAS) in addition to MEA. Both fail the stability test. The presence of the sodium salt of the LAS in addition to the MEA used for pH adjustment suggests that the LAS has been neutralised with caustic in a separate process prior to adding to this composition. The solution as claimed is to avoid the use of cross-linked thickening polymers and to have a relatively high composition pH (>10). Thus in the examples the associative polymer used is always a HASE polymer. Acusol™ 820 was found to be one of the better associative thickening polymers for use in these compositions. It is clearly taught by the examples that to obtain more stable compositions the inventors removed the LAS from the compositions.

[0004] Dow Chemicals supply the Acusol™ range of acrylate thickeners and have published the following formulation guidelines for incorporation of Acusol™ 820. "ACUSOL 820 thickener is compatible with surfactants, solvents, oils, salts and other ingredients commonly found in detergent and cleaner products. Formulators of detergents and cleaners will have no difficulty in discovering the best way to incorporate ACUSOL 820 into their own specific products. Operating flexibility is provided by the physical characteristics of the product (low viscosity liquid before neutralisation), and its high thickening efficiency allows varying operating procedures. The following mixing procedure meets most formulating needs:

1. Introduce ACUSOL 820 into the formulation water. This should provide at least a threefold dilution of the polymer.
2. Add the nonionic surfactants (if any).
3. Add the anionic surfactants (if any) - low pH first. (In the case of strongly acidic components, such as sulfonic acids, it is preferable to disperse this component in the system and partially neutralize (e.g. - to pH about 4-5) prior to addition of the polymer).
4. Add builders, fillers, particulates.
5. Add dyes, then perfume.
6. Neutralize with the chosen alkali.

[0005] We found that the resulting liquids were unstable and phase separated when this published mixing procedure was followed for a liquid where LAS acid was neutralised with MEA during manufacture. Contrary to this publication we did, in fact, encounter difficulties in determining a modified incorporation process that gave stable compositions when they included amine neutralised LAS.

[0006] WO2011/117427 (Lamberti) discloses liquid aqueous detergent compositions comprising as thickeners and suspending agents cross-linked alkali swellable polyacrylates containing one or more acetoacetyl or cyanoacetyl groups. These types of cross-linked polymers may be referred to as CASE polymers. The compositions also contain from 5 to 60 wt% of a detergent system selected from anionic surfactants, amphoteric surfactants, cationic surfactants, zwitterionic surfactants, non-ionic surfactants and mixture thereof. The examples in WO2011/117427 all use pre-neutralised anionic surfactant and do not use any LAS (or MEA). The pH information in the examples shows that the dispersion of polyacrylates when mixed with the pre-neutralised surfactant produces an acidic mixture which is then adjusted to a mildly acidic final pH with sodium hydroxide. We have determined that whilst MEA pre-neutralised LAS could be used by making a number of non-obvious adaptations to the process described in WO2011/117427 even then the resulting process cannot be used as a substitute for one where LAS is conventionally neutralised *in situ* and other changes are still needed to arrive at the process of the present invention.

[0007] It is desirable to use a manufacturing process that enables consistent large scale production of stable liquids comprising amine neutralised LAS thickened with alkali swellable polymers, including crosslinked polymers of the type

described in WO2011/117427.

[0008] US6376446 (Melaleuca) discloses the addition of acrylate polymers as a final stage of a detergent manufacturing process (along with dye). We have shown that such a process whilst possible at lab scale is not suited to large scale production equipment where the in situ neutralisation of linear alkyl benzene sulfonic acid is being carried out. It is not fully clear whether such sulfonic acid is being used in US6376446. The amount of MEA used in Example 1 is insufficient to neutralise LAS acid and is most likely added only for pH adjustment.

SUMMARY OF THE INVENTION

[0009] According to the present invention there is provided a process to manufacture a liquid detergent composition thickened with 0.1 % to no more than 10 % by weight of the composition of a linear and or cross linked alkali swellable polyacrylate copolymer wherein the composition comprises anionic surfactant comprising linear alkylbenzene sulfonate formed by neutralisation of linear alkylbenzene sulfonic acid during the process by one or more amines, the process comprising the steps of:

- a) Mixing the alkali swellable polyacrylate copolymer with water, then
- b) Further mixing at least one amine with the mixture of step a) the amount of amine being more than sufficient to neutralise the linear alkyl benzene sulfonic acid, and then
- c) Adding the linear alkylbenzene sulfonic acid to the thickened mixture of step b) thereby to form the corresponding anionic surfactant by neutralisation.

[0010] Preferably hydrotrope, most preferably monopropylene glycol - MPG - is also mixed with the polymer in step a). Most preferably nonionic surfactant is mixed with the polymer in step a). Fluorescer may also be mixed with the polymer in step a). The surfactant acids comprise LAS acid or combinations of LAS acid and fatty acid. It is preferred that the pH is less than 8 at the time of addition of the polyacrylate copolymer to the mix. Having too high a pH causes a rapid build in viscosity to a level which is incompatible with processing equipment that is normally available for economic large scale production of liquid detergent compositions. By large scale is meant that the batch size is at least 500 Kg, most preferably at least 1 tonne. By holding all of the amine base back until the polyacrylate copolymer has been added in full the pH is kept sufficiently low. Some amine could be added prior to the polyacrylate copolymer provided the pH is not allowed to rise too high. However, this is a less preferred process option.

[0011] Preferably the amine comprises monoethanolamine, optionally in combination with triethanolamine. Sufficient amine is preferably mixed with the mixture of step a) during step b) to thicken the polyacrylate copolymer and to be available to neutralise the linear alkylbenzene sulfonic acid in step c). In the case that the anionic surfactant comprises LAS and soap at least sufficient amine to neutralise the LAS acid to form the LAS is used. Further base, preferably also amine, optionally a different one, may be dosed after neutralisation of the LAS acid to adjust the pH. The soap is preferably formed by neutralisation of fatty acid by amine.

[0012] Citric acid may be added between the LAS acid and fatty acid.

[0013] Preferably, any alkyl ether sulfate (AES) anionic surfactant, in particular sodium lauryl ether sulfate (SLES), is added after step b). More preferably after step c). Other components that are preferably added after step c) are sequestrants (Dequest), cleaning polymers, for example ethoxylated polyethylene imine, preservatives, colorants and opacifiers, shading dyes, enzymes and perfume.

[0014] Sufficient agitation (energy input) is preferably used during step b) when amine is mixed with polyacrylate copolymer mix a) to ensure that there are not localised highly alkaline regions in the mix which would cause localised high viscosity build and a difficult to handle "lumpy" mixture.

DETAILED DESCRIPTION OF THE INVENTION

Surfactants

[0015] For effective laundry detergency the compositions have total active deterative surfactant levels of at least 10 wt%, preferably at least 15 wt% and most preferably at least 25 wt%. For the purposes of this amount any polymeric materials like EPEI are excluded and soap is included. It is essential that the compositions comprise anionic surfactant that is neutralised using amine during the process. The amount of anionic surfactant preferably forms from 20 to 50 % of the total surfactant system.

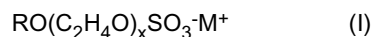
[0016] Surfactants assist in removing soil from the textile materials and also assist in maintaining removed soil in solution or suspension in the wash liquor. Anionic or blends of anionic and nonionic surfactants are a preferred feature of the compositions. The amount of amine neutralised anionic surfactant is at least 5 wt%.

Anionic

[0017] The anionic surfactants in the total surfactant system comprise alkylbenzene sulfonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅. The counter ion for the anionic surfactants is an amine, for example MEA or TEA can be used.

[0018] Suitable linear alkyl benzene sulphonate surfactants include Detal LAS with an alkyl chain length of from 8 to 15, more preferably 12 to 14.

[0019] It is further desirable that the composition comprises an alkyl polyethoxylate sulphate anionic surfactant of the formula (I):



where R is an alkyl chain having from 10 to 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and x averages from 1 to 15.

[0020] Preferably R is an alkyl chain having from 12 to 16 carbon atoms, M is Sodium and x averages from 1 to 3, preferably x is 3; This is the anionic surfactant sodium lauryl ether sulphate (SLES). It is the sodium salt of lauryl ether sulphonic acid in which the predominantly C12 lauryl alkyl group has been ethoxylated with an average of 3 moles of ethylene oxide per mole. This ethoxylated surfactant is preferably added in pre-neutralised form after the addition of any LAS acid to the amine and polymer.

Nonionic

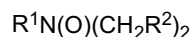
[0021] Nonionic surfactants include primary and secondary alcohol ethoxylates, especially C₈-C₂₀ aliphatic alcohol ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkyl polyglycosides, glycerol monoethers and polyhydroxy amides (glucamide). Mixtures of nonionic surfactant may be used. When included therein the composition contains from 0.2 wt% to 40 wt%, preferably 1 wt% to 20 wt%, more preferably 5 to 15 wt% of a non-ionic surfactant, for example alcohol ethoxylate, nonylphenol ethoxylate, alkylpolyglycoside, alkylidimethylamineoxide, ethoxylated fatty acid monoethanolamide, fatty acid monoethanolamide, polyhydroxy alkyl fatty acid amide, or N-acyl N-alkyl derivatives of glucosamine ("glucamides").

[0022] Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 35 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol.

[0023] Nonionic surfactant is preferably added to the process before the thickening polymer and desirably also before the acid form of the anionic surfactant is added in step c).

Amine Oxide

[0024] The composition may comprise up to 10 wt% of an amine oxide of the formula:



[0025] In which R¹ is a long chain moiety each CH₂R² are short chain moieties. R² is preferably selected from hydrogen, methyl and -CH₂OH. In general R¹ is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R¹ is a primary alkyl moiety. R¹ is a hydrocarbyl moiety having chain length of from about 8 to about 18.

[0026] Preferred amine oxides have R¹ is C₈-C₁₈ alkyl, and R² is H. These amine oxides are illustrated by C₁₂-C₁₄ alkylidimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide.

[0027] A preferred amine oxide material is Lauryl dimethylamine oxide, also known as dodecylidimethylamine oxide or DDAO. Such an amine oxide material is commercially available from Huntsman under the trade name Empigen® OB. Amine oxides suitable for use herein are also available from Akzo Chemie and Ethyl Corp. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers.

[0028] Whereas in certain of the preferred embodiments R² is H, it is possible to have R² slightly larger than H. Specifically, R² may be CH₂OH, for example: hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide.

[0029] Preferred amine oxides have the formula:



where R¹ is C₁₂₋₁₆ alkyl, preferably C₁₂₋₁₄ alkyl; Me is a methyl group.

Zwitterionic

[0030] Nonionic-free systems with up to 95 %wt LAS can be made provided that some zwitterionic surfactant, for example carbobetaine, is present. A preferred zwitterionic material is a carbobetaine available from Huntsman under the name Empigen® BB. Betaines and / or amine oxides, improve particulate soil detergency in the compositions.

[0031] Any amine oxide and zwitterionic surfactant is preferably added after step c)

Additional surfactants

[0032] Other surfactants than the preferred LAS, SLES, and nonionic may be added to the mixture of deterative surfactants. However cationic surfactants are preferably substantially absent.

Amines

[0033] The presence of amine is required to neutralise the anionic surfactant acid and to provide buffering and pH control; preferred amines are MEA, and TEA. If present these amines are preferably used in the composition at levels of from 1 to 15 wt%. The composition is preferably alkaline, more preferably the final pH is at least 8.

Thickening Polymers

[0034] The thickening polymers are linear and / or crosslinked alkali swellable polyacrylate copolymers. Such alkali swellable copolymers (ASE) optionally have a hydrophobic modification on at least one of the monomers (HASE) or have cross-linking groups (CASE) and possibly have both hydrophobic modification and cross-linking (C-HASE).

[0035] As used herein the term "(meth)acrylic" refers to acrylic or methacrylic, and "(meth)acrylate" refers to acrylate or methacrylate. The term "acrylic polymers" refers to polymers of acrylic monomers, i.e., acrylic acid (AA), methacrylic acid (MAA) and their esters, and copolymers comprising at least 50% of acrylic monomers. Esters of AA and MAA include, but are not limited to, methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), hydroxyethyl methacrylate (HEMA), methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), and hydroxyethyl acrylate (HEA), as well as other alkyl esters of AA or MAA.

[0036] Preferred polyacrylic copolymers have at least 75% of monomer residues derived from (meth)acrylic acid or (meth)acrylate monomers, more preferably at least 90%, even more preferably at least 95%, and most preferably at least 98%. The term "vinyl monomer" refers to a monomer suitable for addition polymerization and containing a single polymerizable carbon-carbon double bond.

[0037] Hydrophobic properties may be imparted by use of lipophilically-modified (meth)acrylate residues each of which may contain either one, or a plurality of, lipophilic groups. Such groups are suitably in the same copolymer component as, and attached to, hydrophilic chains, such as for example polyoxyethylene chains. Alternatively the thickening polyacrylic copolymer may contain a vinyl group which may be used to copolymerize the polymer to other vinyl-containing entities to alter or improve the properties of the polymer. Polymerizable groups may be attached to lipophilic groups directly, or indirectly for example via one or more, for example up to 60, preferably up to 40, water-soluble linker groups, for example, -CH[R]CH₂O- or -CH[R]CH₂NH- groups wherein R is hydrogen or methyl. Alternatively, the polymerizable group may be attached to the lipophilic group by reaction of the hydrophilic, for example polyoxyethylene, component with a urethane compound containing unsaturation. The molecular weight of the lipophilic-modifying group or groups is preferably selected together with the number of such groups to give the required minimum lipophilic content in the thickening polymer, and preferably, for satisfactory performance in a wide range of liquid compositions.

[0038] The amount of lipophilically-modified component in the thickening polymers preferably is at least 5%, more preferably at least 7.5%, and most preferably at least 10%; and preferably is no more than 25%, more preferably no more than 20%, more preferably no more than 18%, and most preferably no more than 15%.

[0039] The lipophilic-modifying groups themselves are preferably straight chain saturated alkyl groups, but may be aralkyl or alkyl carbocyclic groups such as alkylphenyl groups, having at least 6, and up to 30 carbon atoms although branched chain groups may be contemplated. It is understood that the alkyl groups may be either of synthetic or of natural origin and, in the latter case particularly, may contain a range of chain lengths.

[0040] The chain length of the lipophilic-modifying groups is preferably below 25, more preferably from 8 to 22, and most preferably from 10 to 18 carbon atoms. The hydrophilic component of the lipophilically-modified copolymer may

suitably be a polyoxyethylene component preferably comprising at least one chain of at least 2, preferably at least 5, more preferably at least 10, and up to 60, preferably up to 40, more preferably up to 30 ethylene oxide units. Such components are usually produced in a mixture of chain lengths.

[0041] Preferably, any C2-C4 alkyl (meth)acrylate residues in the copolymer are C2-C3 alkyl (meth)acrylate residues, and most preferably EA. Preferably, the amount of C2-C4 alkyl (meth)acrylate residues is at least 20%, more preferably at least 30%, more preferably at least 40% and most preferably at least 50%. Preferably, the amount of C2-C4 alkyl (meth)acrylate residues is no more than 75%, more preferably no more than 70%, and most preferably no more than 65%. Preferably, the amount of acrylic acid residues in the copolymer used in the present invention is at least 5%, more preferably at least 7.5%, more preferably at least 10%, and most preferably at least 15%. Preferably, the amount of acrylic acid residues is no more than 27.5%, more preferably no more than 25%, and most preferably no more than 22%. Acrylic acid residues are introduced into the copolymer by inclusion of either acrylic acid, or an acrylic acid oligomer having a polymerizable vinyl group, in the monomer mixture used to produce the copolymer. Preferably, the copolymer contains residues derived from methacrylic acid in an amount that provides a total acrylic acid plus methacrylic acid content of at least 15%, more preferably at least 17.5%, and most preferably at least 20%. Preferably, the total acrylic acid plus methacrylic acid content of the copolymer is no more than 65%, more preferably no more than 50%, and most preferably no more than 40%. Optionally, the copolymer also contains from 2% to 25%, preferably from 5% to 20%, of a hydrophilic comonomer, preferably one having hydroxyl, carboxylic acid or sulphonate functionality. Examples of hydrophilic comonomers include 2-hydroxyethyl (meth)acrylate (HEMA or HEA), itaconic acid and acrylamido-2-methylpropanesulfonic acid.

[0042] The aqueous compositions contain from 0.1% to no more than 10% of thickening polymer; i.e., the total amount of thickening polymer(s) is in this range. Preferably, the amount of thickening polymer in the aqueous composition is at least 0.3%, more preferably at least 0.5%, more preferably at least 0.7%, and most preferably at least 1%. Preferably, the amount of thickening polymer in the aqueous composition is no more than 7%, more preferably no more than 5%, and most preferably no more than 3%. The molecular weight of uncross-linked polyacrylic copolymer is typically in the range of about 100,000 to 1 million.

[0043] In the case that the polyacrylic copolymer is cross-linked, a cross-linking agent, such as a monomer having two or more ethylenic unsaturated groups, is included with the copolymer components during polymerization. Examples of such monomers include diallyl phthalate, divinylbenzene, allyl methacrylate, diacrylobutylene or ethylene glycol dimethacrylate. When used, the amount of cross-linking agent is typically from 0.01% to 2%, preferably from 0.1 to 1% and more preferably from 0.2 to 0.8%, based on weight of the copolymer components. The thickening polyacrylic copolymer may be prepared in the presence of a chain transfer agent when a cross-linking agent is used. Examples of suitable chain transfer agents are carbon tetrachloride, bromoform, bromotrichloromethane, and compounds having a mercapto group, e.g., long chain alkyl mercaptans and thioesters such as dodecyl-, octyl-, tetradecyl- or hexadecyl-mercaptans or butyl-, isooctyl- or dodecyl-thioglycolates. When used, the amount of chain transfer agent is typically from 0.01 % to 5%, preferably from 0.1 % to 1%, based on weight of the copolymer components. If the cross-linking agent is used in conjunction with a chain transfer agent, which are conflicting operations for polymerization purposes, not only is exceptional efficiency observed but also very high compatibility with hydrophilic surfactants, as manifested by increased product clarity.

[0044] Hydrophobically modified polyacrylate thickening copolymers are available as Acusol polymers from Dow.

[0045] A preferred thickening polyacrylic copolymer type that may be utilised is described in WO2011/117427 (Lamberti). These preferred polymers comprise:

i) from 0.2 to 10 % by weight of a thickening agent which is a crosslinked alkali swellable polyacrylate obtainable by polymerization of:

- a) from 20 to 70% by weight of a monoethylenically unsaturated monomer containing a carboxylic group;
- b) from 20 to 70% by weight of a (meth)acrylic acid ester;
- c) from 0.05 to 3% by weight of an unsaturated monomer containing one or more acetoacetyl or cyanoacetyl groups;
- d) from 0.01 to 3% by weight of a polyethylenically unsaturated monomer; e) from 0 to 10% by weight of a nonionic acrylic associative monomer;

ii) from 5 to 60% by weight of a detergent component consisting of at least one compound selected from anionic surfactants, amphoteric surfactants, cationic surfactants, zwitterionic surfactants, non-ionic surfactants and mixture thereof.

[0046] Such cross-linked alkali swellable polyacrylates containing one or more acetoacetyl or cyanoacetyl groups possess high thickening capability in the presence of surfactants and electrolytes, provide homogeneous and clear

solutions and possess improved suspending and thickening properties in comparison with crosslinked alkali swellable polyacrylates of the prior art. Crosslinked thickening polymers of this type are available as Viscolam thickening polymers from Lamberti.

Optional ingredients

Other Polymers

EPEI

[0047] A particularly preferred class of polymer for use in the composition is polyethylene imine, preferably modified polyethylene imine. Polyethylene imines are materials composed of ethylene imine units $-CH_2CH_2NH-$ and, where branched, the hydrogen on the nitrogen is replaced by another chain of ethylene imine units. These polyethyleneimines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst for example carbon dioxide, sodium bisulphite, sulphuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, and the like. Specific methods for preparing these polyamine backbones are disclosed in U.S. Pat. No. 2,182,306, Ulrich et al., issued Dec. 5, 1939; U.S. Pat. No. 3,033,746, Mayle et al., issued May 8, 1962; U.S. Pat. No. 2,208,095, Esselmann et al., issued Jul. 16, 1940; U.S. Pat. No. 2,806,839, Crowther, issued Sep. 17, 1957; and U.S. Pat. No. 2,553,696, Wilson, issued May 21, 1951.

[0048] Preferably, the EPEI comprises a polyethyleneimine backbone of about 300 to about 10000 weight average molecular weight; wherein the modification of the polyethyleneimine backbone is intended to leave the polymer without quaternisation. Such nonionic EPEI may be represented as PEI(X)YEO where X represents the molecular weight of the unmodified PEI and Y represents the average moles of ethoxylation per nitrogen atom in the polyethyleneimine backbone. The ethoxylation may range from 9 to 40 ethoxy moieties per modification, preferably it is in the range of 16 to 26, most preferably 18 to 22.

[0049] The polyethyleneimine polymer is present in the composition preferably at a level of between 0.01 and 25 wt%, but more preferably at a level of at least 2 wt% and/or less than 9.5 wt%, most preferably from 3 to 9 wt% and with a ratio of non-soap surfactant to EPEI of from 2:1 to 7:1, preferably from 3:1 to 6:1, or even to 5:1.

Polyester soil release polymer

[0050] The compositions may optionally include 0.3 wt% or more of a soil release polymer which is substantive to polyester fabric. Such polymers typically have a fabric substantive midblock formed from propylene terephthalate repeat units and one or two end blocks of capped polyalkylene oxide, typically PEG 750 to 2000 with methyl end capping.

Other polymer types

[0051] In addition to a soil release polymer there may be used dye transfer inhibition polymers, anti redeposition polymers and cotton soil release polymers, especially those based on modified cellulosic materials.

Hydrotrope

[0052] A hydrotrope is a solvent that is neither water nor conventional surfactant that aids the solubilisation of the surfactants and other components in the aqueous liquid to render it isotropic. Among suitable hydrotropes there may be mentioned as preferred: MPG (monopropylene glycol), glycerol, sodium cumene sulphonate, ethanol, other glycols, e.g. di propylene glycol, diethers and urea.

Enzymes

[0053] It is preferable that at least one or more enzymes may be present in the compositions. Preferably at least two, more preferably at least three different classes of enzymes are used in combination. Preferred enzymes are selected from protease, amylase, mannanase, pectate lyase and cellulase. Notable among the other enzymes that may be used are lipase, phospholipase, cutinase, peroxidase, oxidase. Enzymes are desirably provided in combination with an enzyme stabilizer, particularly the protease enzyme. Suitable enzyme stabilizers include polyols, for example propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative for example 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

Lignin compounds

[0054] When a lipase enzyme is included a lignin compound may be used in the composition in an amount that can be optimised by trial and error. Lignin is a component of all vascular plants, found mostly between cellular structures but also within the cells and in the cell walls.

[0055] Preferred is a modified lignin polymer substituted with a sulfonate group. Preferably the modified lignin sulfonate is substituted with anionic or alkoxy groups. Modified lignin polymers are discussed in WO/2010/033743. Most preferably the modified lignin polymer is lignin sulfonate (lignosulfonate). Lignin sulfonate may be obtained by the Howard process.

Fluorescent Agents

[0056] It can be advantageous to include fluorescer in the compositions. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.5 wt %.

[0057] Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra, Tinopal 5BMGX, and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

[0058] Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-naphthol[1,2-d]triazole, disodium 4,4'-bis[[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino]stilbene-2-2' disulfonate, disodium 4,4'-bis[[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino] stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfostyryl)biphenyl.

Bleach Catalyst

[0059] Compositions may comprise a weight efficient bleach system. Such systems typically do not utilise the conventional percarbonate and bleach activator approach. An air bleach catalyst system is preferred. Suitable complexes and organic molecule (ligand) precursors for forming complexes are available to the skilled worker, for example, from: WO 98/39098; WO 98/39406, WO 97/48787, WO 00/29537; WO 00/52124, and WO00/60045, . An example of a preferred catalyst is a transition metal complex of MeN4Py ligand (N,N-bis(pyridin-2-yl-methyl)-1-,1-bis(pyridin-2-yl)-1-aminoethane). Suitable bispidon catalyst materials and their action are described in WO02/48301. The bleach catalyst may be encapsulated to reduce interaction with other components of the liquid during storage.

[0060] Photobleaches may also be employed. A "photobleach" is any chemical species that forms a reactive bleaching species on exposure to sunlight, and preferably is not permanently consumed in the reaction. Preferred photo-bleaches include singlet oxygen photo-bleaches and radical photo-bleaches. Suitable singlet oxygen photo-bleaches may be selected from, water soluble phthalocyanine compounds, particularly metallated phthalocyanine compounds where the metal is Zn or Al-Z1 where Z1 is a halide, sulphate, nitrate, carboxylate, alkanolate or hydroxyl ion. Preferably the phthalocyanin has 1-4 SO₃X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO2005/014769 (Ciba).

[0061] When present, the bleach catalyst is typically incorporated at a level of about 0.0001 to about 10wt%, preferably about 0.001 to about 5wt%.

Perfume

[0062] The compositions will usually comprise perfume. Preferred are free oil perfumes. Additionally the composition may utilize some encapsulated perfume. Use of a perfume that is encapsulated reduces the amount of perfume vapour that is produced by the composition before it is diluted. This is important when the perfume concentration is increased to allow the amount of perfume per wash to be kept at a reasonably high level.

[0063] It is even more preferable that the perfume is not only encapsulated but also that the encapsulated perfume is provided with a deposition aid to increase the efficiency of perfume deposition and retention on fabrics. The deposition aid is preferably attached to the encapsulate by means of a covalent bond, entanglement or strong adsorption, preferably by a covalent bond or entanglement.

Builders and sequestrants

[0064] The detergent compositions may also optionally contain relatively low levels of organic detergent builder or sequestrant material. Examples include the alkali metal, citrates, succinates, malonates, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other examples are DEQUEST™, organic phosphonate type sequestering agents sold by Thermphos and alkanehydroxy phosphonates.

[0065] Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, for example those sold by BASF under the name SOKALAN™.

[0066] If utilized, the organic builder materials may comprise from about 0.5% to 20 wt%, preferably from 1 wt% to 10 wt%, of the composition. The preferred builder level is less than 10 wt% and preferably less than 5 wt% of the composition. A preferred sequestrant is HEDP (1-Hydroxyethylidene -1,1,-diphosphonic acid), for example sold as Dequest® 2010. Also suitable, but less preferred as it gives inferior cleaning results, is Dequest® 2066 (Diethylenetriamine penta(methylene phosphonic acid or Heptasodium DTPMP).

External Structurants

[0067] The compositions may have their rheology further modified by use of a material or materials that form a structuring network within the composition. Suitable structurants include hydrogenated castor oil, microfibrinous cellulose and natural based structurants, for example citrus pulp fibre. Citrus pulp fibre is particularly preferred especially if lipase enzyme is included in the composition. The presence of an external structurant gives shear thinning rheology and also allows materials such as encapsulates and visual cues to be suspended stably in the liquid.

Further Optional Ingredients

[0068] The compositions may contain one or more further optional ingredients. Such ingredients include: foam boosting agents, preservatives (e.g. bactericides), polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents and ironing aids. The compositions may further comprise colorants, pearlisers and/or opacifiers, and shading dye. A suitable combination of shading would be 0.002wt% Acid Violet 50 (100% active) and 0.0005wt% Solvent Violet 13 (100% active). They would be added either during or after step c), preferably after.

Packaging and use

[0069] Preferably the liquid compositions made using the process are supplied in multiuse plastics packs with a top or bottom closure. A dosing measure may be supplied with the pack either as a part of the cap or as an integrated system. The liquid compositions may be used by measuring a dose of around 35 ml and adding it directly or in a dosing device to a washing machine, for example a front loading automatic washing machine.

[0070] The invention will now be further described with reference to the following nonlimiting examples.

EXAMPLES

Comparative Examples A, B and C

[0071] Unthickened LAS MEA based liquid detergent compositions were made. Then aqueous solutions of three polyacrylate thickening copolymers were added slowly to each composition whilst the compositions were mechanically stirred using a 2 blade stirrer at 350-400 rpm.

[0072] Each of the thickening polymers used were commercially available associative polymers that thicken under alkaline conditions. The polymers were:

- A) Viscolam™ CK57 from Lamberti
- B) Acusol™ 820 from Dow
- C) Acusol™ 805s from Dow

[0073] This process produced clear, stable, thickened detergent compositions A, B and C at lab scale. However, such an energy intensive post-addition process is not feasible for large scale manufacture of polymer thickened detergent liquids due to the difficulty of providing this level of mixing energy at large scale and also due to the inevitable prolongation of batch times.

Comparative Examples D-G

[0074] To try to cut down the process time some process variations where the polymer was added earlier in the process were then made at lab scale (1kg). These also used unrealistically intensive mixing. The different orders of addition are detailed in Table 1 where the number represents the order that the ingredient was added to the composition. All these

process variations resulted in lack of composition stability as evidenced by phase separation or gelation.

Table 1 - Order of addition

Ingredient	Example			
	D	E	F	G
Water & hydrotrope (MPG)	1	1	1	1
Polymer	2	2	4	7
Nonionic	3	3	2	2
LAS acid and SLES	4	4	3	3
Dyes	5	6	6	4
Perfume	6	7	7	5
MEA/TEA	7	5	5	6
Result	Phase separation	Phase separation	Phase separation	Gelation

[0075] Comparative Example D is the process recommended for sulfonic acid containing liquids thickened with Acusol™ 820 by supplier Dow. Comparative Example G is like the process adopted by Lamberti in their patent application WO2011/117427, notwithstanding that they used neither LAS nor MEA/TEA. In all cases the composition was stirred for 20 minutes with the stirrer set at 400 rpm.

Example 1

[0076] We made a separate premix consisting of a blend of nonionic, MPG, thickening polymer and water. Surprisingly, by using this process we produced a stable composition without the need for high energy mixing and without significant increase in process time. A process using such a premix to provide a stable 1 wt% polymer thickened liquid composition is given in Table 2 below.

Table 2

Order of addition	Ingredient	as 100% (%)
1	Demin water	27.81
2	MEA	6.20
3	TEA	4.00
4a	NI 7EO	8.40
4b	MPG	8.00
4c	Thickening Polymer	1.00
4d	Demin water	10.00
5	Citric Acid	2.50
6	Fluorescer	0.25
7	LAS acid	11.20
8	Dequest 2010	1.50
9	Prifac 5908	3.50
10	Sodium Sulfite	0.25
11	SLES 3EO	8.40
12	EPEI	3.00
13	Enzymes and perfume	To 100

[0077] Ingredients with order of addition 4a, 4b, 4c and 4d are formulated as a premixed blend in that order and added as if one ingredient to the full composition.

Key to ingredients

[0078]

MEA	Monoethanolamine (amine base)
TEA	Triethanolamine (amine base)
NI 7EO	C12-15 alcohol ethoxylate 7EO nonionic Neodol® 25-7 (ex Shell Chemicals).
MPG	Monopropylene glycol (hydrotrope)
Thickening Polymer	Acusol™ 820 or Viscolam™ CK57 .
LAS acid	C ₁₂₋₁₄ linear alkylbenzene sulphonic acid (acid precursor of LAS)
Citric acid	Sequestrant
Dequest 2010	Sequestrant, HEDP (1-Hydroxyethylidene -1,1 , -diphosphonic acid) ex Thermphos.
Prifac 5908	Saturated lauric fatty acid ex Croda.
SLES 3EO	Sodium lauryl ether Sulphate with 3 moles EO.
EPEI	Sokalan HP20 - ethoxylated polyethylene imine cleaning polymer: PEI(600) 20EO ex BASF.

[0079] Inclusion of MPG in the nonionic/polymer premix effectively prevented any gelation or polymer precipitation. Stable compositions were made using this process with two thickening polymers: Acusol™ 820 and Viscolam™ CK57 .

Example 2

[0080] The premix process used in Example 1 requires a separate mixing vessel for the polymer premix. Example 2 is a modification of Example 1 to make the same composition using a "one pot" process. The amine addition was split into two separate additions, TEA being added to the polymer mix before the LAS acid and MEA after it. However, provided

the amount of polymer being added is not too high it has been found to be possible to add the entire base to the polymer in advance of introduction of the LAS acid and the order of addition of TEA and MEA is not critical. We have found that adding base to polymer avoids the viscosity peaks being too high as it is possible to control the mixing to ensure that local high pH is avoided and thereby to avoid localised formation of high viscosity "gels".

Example 3

[0081] The order of addition (OOA) for a one pot process using Viscolam™ CK57 polymer and a split addition of the amine base is shown in Table 3. The polymer dispersed readily in the mixture of water MPG and nonionic. Addition of the MEA thickens the mixture to the highest viscosity seen during the process. This viscosity drops again when the LAS acid is added and rises, but not to such a high level as previously, after addition of the TEA. This process option is particularly useful for more viscous compositions.

Table 3

OOA	Ingredient	as 100% (%)
1	Demin water	37.71
2	Fluorescer	0.25
3	MPG	8.00
4	NI 7EO	8.40
5	Viscolam CK57	1.00
6	MEA	6.20
7	LAS acid	11.20
8	TEA	4.00
9	Citric Acid	2.50
10	Prifac 5908	3.50
11	Dequest 2010	1.50
12	Sodium Sulfite	0.25
13	SLES 3EO	8.40
14	EPEI	3.00
15	Enzymes, Free oil perfume, colour and opacifier	to 100

[0082] The final pH of this detergent liquid was 8.2 ± 0.3 and its final measured viscosity at 21 s^{-1} and 20°C was $280 \text{ mPa}\cdot\text{s}$ (280 cP) $\pm 50 \text{ mPa}\cdot\text{s}$ (50 cP). The liquid was phase stable.

Example 4

[0083] A further process variant, in which MEA and TEA are added together before the LAS acid, is detailed in Table 4. This highly time-efficient process is possible for this composition because the higher viscosity peak due to adding all the amines together is not too high.

Table 4

OOA	Ingredient	as 100% (%)
1	demin. water	29.01
2	Fluorescer	0.25
3	MPG	8.00
4	NI 7EO	8.40
5	Viscolam™ CK57 ¹	1.00

(continued)

OOA	Ingredient	as 100% (%)
6	TEA	4.00
7	MEA	6.40
8	LAS acid	11.20
9	Citric acid (50%)	2.50
10	Prifac™ 5908	3.50
11	SLES (3EO)	8.40
12	Dequest™ 2010	1.50
13	EPEI	3.00
14	Sodium Sulfite ²	0.25
15	demin water	6.00
16	Colorant, Opacifier, enzyme and perfume (in water)	6.59
¹ Alkali swellable thickening polymer. ² After addition of sodium sulfite, the batch is cooled to 30 °C before adding further ingredients. The exact order of addition is chosen mainly to minimize batch cycle time.		

Example 5

[0084] An alternative process suitable for higher levels of polymer is given in Table 5. The final viscosity of this liquid was 280 mPa*s (280 cP) @21 s⁻¹ and 20°C (± 50 mPa*s (50 cP)). This is similar to the process used for Example 3.

Table 5

OOA	Ingredient	as 100% (%)
1	Demin water	37.709
2	Fluorescer	0.25
3	MPG	8.00
4	NI 7EO	8.40
5	Viscolam CK57	1.00
6	MEA	6.20
7	LAS acid	11.20
8	TEA	4.00
9	Citric Acid	2.50
10	Prifac 5908	3.50
11	Dequest 2010	1.50
12	Sodium Sulfite	0.25
13	SLES 3EO	8.40
14	EPEI	3.00
15	Enzymes, colour, opacifier and perfume	To 100

Claims

1. A process to manufacture a liquid detergent composition thickened with 0.1 % to no more than 10 % by weight of

the composition of a linear and or cross linked alkali swellable polyacrylate copolymer wherein the composition comprises anionic surfactant comprising linear alkylbenzene sulfonate formed by neutralisation of linear alkylbenzene sulfonic acid during the process by one or more amines, the process comprising the steps of:

- a) Mixing the alkali swellable polyacrylate copolymer with water, then
- b) Further mixing at least one amine with the mixture of step a) the amount of amine being more than sufficient to neutralise the linear alkyl benzene sulfonic acid, and then
- c) Adding the linear alkylbenzene sulfonic acid to the thickened mixture of step b) thereby to form the corresponding anionic surfactant by neutralisation.

2. A process according to claim 1 in which hydrotrope, preferably Monopropylene glycol is also mixed with the water in step a).
3. A process according to any preceding claim in which nonionic surfactant is also mixed with the water in step a).
4. A process according to any preceding claim in which fluorescer is also mixed with the water in step a).
5. A process according to any preceding claim in which the amine comprises monoethanolamine.
6. A process according to any preceding claim in which the amine further comprises triethanolamine.
7. A process according to any preceding claim in which sufficient amine is used in step b) to thicken the polyacrylate copolymer and to neutralise the linear alkylbenzene sulfonic acid.
8. A process according to any preceding claim in which further base, preferably also amine, may be added to the mixture to adjust the pH after neutralisation of the linear alkylbenzene sulfonic acid in step c).
9. A process according to any preceding claim in which preneutralised alkyl ether sulphate surfactant (AES), preferably sodium lauryl ether sulphate (SLES) is added after step c).
10. A process according to any preceding claim in which other components are added after step c), the other components being selected from the group comprising: sequestrants, cleaning polymers, preservatives, shading dyes, enzymes, perfume colorants and opacifiers and mixtures thereof.
11. A process according to any preceding claim in which the composition comprises at least 10 wt%, preferably at least 15 wt% and most preferably at least 25 wt% total surfactant.
12. A process according to any preceding claim in which the anionic surfactant formed by the neutralisation step c) makes up from 20 to 50% of the total surfactant system of the composition.
13. A process according to any preceding claim in which the pH of the final composition is alkaline, preferably greater than 8.

Patentansprüche

1. Verfahren zur Herstellung einer flüssigen Reinigungsmittelzusammensetzung, verdickt mit 0,1 Gewichts-% bis nicht mehr als 10 Gewichts-% der Zusammensetzung eines linearen und/oder vernetzten Alkali-quellbaren Polyacrylatcopolymers, wobei die Zusammensetzung anionisches Tensid umfasst, das lineares Alkylbenzolsulfonat umfasst, gebildet während des Verfahrens durch Neutralisation von linearer Alkylbenzolsulfonsäure mit einem oder mehreren Aminen, wobei das Verfahren die Schritte umfasst:
 - a) Mischen des Alkali-quellbaren Polyacrylatcopolymers mit Wasser, dann
 - b) weiteres Mischen mindestens eines Amins mit der Mischung des Schritts a), wobei die Menge des Amins mehr als ausreichend ist, um die lineare Alkylbenzolsulfonsäure zu neutralisieren, und dann
 - c) Zugeben der linearen Alkylbenzolsäure zu der verdickten Mischung des Schritts b), um dadurch durch Neutralisation das entsprechende anionische Tensid zu bilden.

2. Verfahren nach Anspruch 1, in welchem ein Hydrotrop, vorzugsweise Monopropylenglycol, ebenfalls mit dem Wasser im Schritt a) gemischt wird.
- 5 3. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem nichtionisches Tensid ebenfalls mit dem Wasser im Schritt a) gemischt wird.
4. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem ein Fluoreszenzmittel ebenfalls mit dem Wasser im Schritt a) gemischt wird.
- 10 5. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem das Amin Monoethanolamin umfasst.
6. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem das Amin ferner Triethanolamin umfasst.
- 15 7. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem ausreichendes Amin im Schritt b) verwendet wird, um das Polyacrylatcopolymer zu verdicken und um die lineare Alkylbenzolsulfonsäure zu neutralisieren.
8. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem ferner Base, vorzugsweise auch Amin, zu der Mischung gegeben werden kann, um den pH nach der Neutralisation der linearen Alkylbenzolsulfonsäure im Schritt c) einzustellen.
- 20 9. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem das vorneutralisierte Alkylethersulfat-Tensid (AES), vorzugsweise Natriumlaurylethersulfat (SLES), nach Schritt c) zugegeben wird.
- 25 10. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem nach Schritt c) andere Bestandteile zugegeben werden, wobei die anderen Bestandteile aus der Gruppe ausgewählt sind, die umfasst: Komplexbildner, Reinigungspolymere, Konservierungsmittel, Nuancierfarbstoffe, Enzyme, Parfümfarbmittel und Trübungsmittel und Mischungen davon.
- 30 11. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem die Zusammensetzung mindestens 10 Gew.-%, vorzugsweise mindestens 15 Gew.-% und höchst bevorzugt mindestens 25 Gew.-% gesamtes Tensid umfasst.
12. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem das anionische Tensid, gebildet durch den Neutralisationsschritt c), von 20 bis 50% des gesamten Tensidsystems der Zusammensetzung ausmacht.
- 35 13. Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem der pH der Endzusammensetzung alkalisch, vorzugsweise größer als 8, ist.

Revendications

- 40 1. Procédé de fabrication d'une composition de détergent liquide épaissie avec de 0,1 % à au plus 10 % en masse de la composition d'un copolymère de polyacrylate gonflable par un alcali linéaire et/ou réticulé dans lequel la composition comprend un tensioactif anionique comprenant un alkylbenzènesulfonate linéaire formé par neutralisation d'acide alkylbenzènesulfonique pendant le procédé par une ou plusieurs aminés, le procédé comprenant les étapes de :
45 a) mélange du copolymère de polyacrylate gonflable par un alcali avec de l'eau, puis
b) de mélange supplémentaire d'au moins une amine avec le mélange de l'étape a) la quantité de l'amine étant supérieure à la quantité suffisante pour neutraliser l'acide alkylbenzènesulfonique linéaire, et puis
50 c) d'addition de l'acide alkylbenzènesulfonique linéaire au mélange épaissi de l'étape b) pour former par-là le tensioactif anionique correspondant par neutralisation.
2. Procédé selon la revendication 1 dans lequel un hydrotrope, de préférence du monopropylène glycol est également mélangé avec l'eau dans l'étape a).
- 55 3. Procédé selon l'une quelconque des revendications précédentes dans lequel un tensioactif non-ionique est également mélangé avec l'eau dans l'étape a).

4. Procédé selon l'une quelconque des revendications précédentes dans lequel un fluorescent est également mélangé avec l'eau dans l'étape a).
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'amine comprend la monoéthanolamine.
6. Procédé selon l'une quelconque des revendications précédentes dans lequel l'amine comprend de plus la triéthanolamine.
- 10 7. Procédé selon l'une quelconque des revendications précédentes dans lequel une amine suffisante est utilisée dans l'étape b) pour épaissir le copolymère de polyacrylate et pour neutraliser l'acide alkylbenzènesulfonique linéaire.
8. Procédé selon l'une quelconque des revendications précédentes dans lequel de plus une base, de préférence également une amine, peut être ajoutée au mélange pour ajuster le pH après neutralisation de l'acide alkylbenzènesulfonique linéaire dans l'étape c).
- 15 9. Procédé selon l'une quelconque des revendications précédentes dans lequel un tensioactif d'alkyléther sulfate préneutralisé (AES), de préférence le lauryléther sulfate de sodium (SLES) est ajouté après l'étape c).
- 20 10. Procédé selon l'une quelconque des revendications précédentes dans lequel d'autres constituants sont ajoutés après l'étape c), les autres constituants étant choisis dans le groupe comprenant : des séquestrants, des polymères nettoyants, des conservateurs, des colorants d'ombrage, des enzymes, des colorants de parfum et des opacifiants et des mélanges de ceux-ci.
- 25 11. Procédé selon l'une quelconque des revendications précédentes dans lequel la composition comprend au moins 10 % en masse, de préférence au moins 15 % en masse et encore mieux au moins 25 % en masse de tensioactif total.
12. Procédé selon l'une quelconque des revendications précédentes dans lequel le tensioactif anionique formé par la neutralisation de l'étape c) constitue de 20 à 50 % du système de tensioactif total de la composition.
- 30 13. Procédé selon l'une quelconque des revendications précédentes dans lequel le pH de la composition finale est alcalin, de préférence supérieur à 8.

REFERENCES CITED IN THE DESCRIPTION

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