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(54) **EXTERNALLY STRUCTURED AQUEOUS ISOTROPIC LIQUID DETERGENT COMPOSITIONS**

EXTERN STRUKTURIERTE, WÄSSRIGE, ISOTROPE
FLÜSSIGWASCHMITTELZUSAMMENSETZUNGEN

COMPOSITIONS DÉTERGENTES LIQUIDES ISOTROPES AQUEUSES STRUCTURÉES DE
FAÇON EXTERNE

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EP 2 841 551 B1

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DescriptionTECHNICAL FIELD

5 **[0001]** This invention relates to externally structured aqueous isotropic liquid detergent compositions.

BACKGROUND

10 **[0002]** Isotropic liquid detergent compositions have no innate ability to suspend solid particles, for example cues and encapsulates. A suspending medium may be achieved by appropriate manipulation of the surfactant and electrolyte levels. However this imposes undesirable constraints on the composition. Use of so-called external structurants can achieve the required suspending duty without imposing such constraints on the composition.

15 **[0003]** Citrus fibre and its uses for structuring of foodstuffs and personal care compositions are described in US2004/0086626, US2009/269376, and WO2010/069732. The compatibility of an activated citrus fibre structured detergent liquid with detergent and care enzymes is described in WO2012/052306. Its use with cationic deposition polymer (Jaguar quaternised guar gum) for anti dandruff shampoo is disclosed in WO2012/019934.

20 **[0004]** US 7981855 discloses detergent liquid surfactant compositions comprising up to 15 wt% surfactant, including at least 1% anionic surfactant, up to 2 wt% bacterial cellulose (preferably MFC) and from 0.001 to 5 wt% citrus fibres. In one embodiment the bacterial cellulose may be partially coated with a polymeric thickener using the method disclosed in US 2007/0027108.

25 **[0005]** When activated citrus fibre is used and especially when it is used at a sufficiently high level to suspend solid particles (i.e. it has a sufficiently high yield stress) there is a problem with residues that are left behind as the externally structured liquid detergent composition drains down the inside of the liquid composition's container under gravity e.g. after some liquid has been poured from the container. These drainage residues are unsightly and deplete the liquid detergent composition of the external structurant.

[0006] It is an object of the present invention to reduce drainage residues of a liquid detergent composition comprising activated citrus fibre external structurant.

SUMMARY OF THE INVENTION

30 **[0007]** According to the present invention there is provided an externally structured aqueous isotropic liquid detergent composition comprising:

- at least 10 wt% water,
- 35 - at least 3 wt% mixed deterative surfactant comprising anionic surfactant,
- at least 0.025 wt% of activated citrus fibre external structurant, characterised in that the liquid further comprises at least 0.1 wt% of water swellable polyacrylate thickening polymer and the viscosity of the liquid at 20 s⁻¹ and 25°C is at least 0.3 Pa.s.

40 **[0008]** The viscosity at 20 s⁻¹ and 25°C is selected because it is indicative of the shear that is applied to a liquid when it is being poured from a bottle in normal use. Without wishing to be bound by theory it is believed that the increase in pour viscosity helps to keep the activated citrus fibre network entrained in the liquid as it drains down a container wall. This reduces the deposition of the activated citrus fibre external structurant onto the wall of a container, particularly when the externally structured detergent liquid drains down the wall under gravity.

45 **[0009]** Preferably, for suspending duty, the composition has a yield stress of at least 0.3 Pa, more preferably at least 0.4 Pa, and further comprises at least 0.1 wt% of suspended particulate material. At the higher levels of activated citrus fibre needed to provide suspending duty, the on-wall drainage problem is very noticeable. Residues left on drainage also reduce with increased level of activation of citrus fibre. Because higher levels of activation allow less citrus fibre to be used to achieve a given structuring effect the preferred lower limit of the citrus fibre will depend on the activation process, the nature and amount of the material to be suspended and the presence or absence of co-structurants. There is always reduced on wall drainage residue when the activated citrus fibre is combined with polymer to increase the viscosity at 20 s⁻¹.

[0010] Preferably the composition comprises at least 0.5 wt% activated citrus fibre, more preferably at least 0.8 wt%.

55 **[0011]** Preferably the composition is provided in a transparent container. For example PET with a shrink sleeve. The advantages of the compositions are at their greatest when the on-wall residues are visible through a transparent container. However, the advantage of not leaving the activated citrus fibre behind on the wall to dry out and cause loss of structuring is present whether the container is transparent or opaque. It is common to use a colorant and or opacifier in detergent liquids and the invention provides further advantages in this case due to the lower level of on drainage residues.

[0012] The externally structured and polymer thickened compositions have the ability to suspend a wide range of solid particulate benefit ingredients: including encapsulated ingredients such as fragrance, enzymes, visual beads/cues, mica/pearlescer, silicone, etc. The suspended material preferably comprises encapsulates and most preferably it comprises perfume encapsulates. In this specification the term solid particulate encompasses liquids contained in a solid shell. Alternatively, or additionally, the solid particulate material may comprise visual cues (film) which may have benefit ingredient embedded or located within them. In one embodiment the solid particulate material may comprise abrasive material, for example ground olive stones.

[0013] The composition is desirably free from cationic polymers, as these can destabilise an otherwise isotropic composition.

[0014] The preferred thickening polymers are linear/crosslinked alkali swellable acrylic copolymers/ ASE/ HASE/ C-HASE. Polymers that require alkaline conditions to swell and so to provide thickening of the detergent liquid should be added such that they are exposed to alkaline conditions at least during the manufacture of the liquid. It is not essential that the finished liquid is alkaline. It is preferred that the citrus fibre is subjected to mechanical shear in the absence of polymer. This can be done by way of a premix of the activated citrus fibre which can then be added to the main mix after the thickening polymer.

[0015] Preferably the composition comprises at least 0.5 wt% thickening polymer, more preferably at least 1 wt%.

[0016] Alkaline swellable hydrophobically modified polymers (HASE) give very stable liquids when used with the activated citrus fibre external structuring. Cross-linked non-hydrophobically modified polymers (CASE) are highly stable when used with water swellable thickening clays. A suitable type of clay is a synthetic hectorite clay sold as Laponite by Rockwood. The composition may comprise a co-structurant which may be selected from other fibrous structurants, clay and other solid particulate materials, including encapsulates. The amount of the co-structurant when present preferably lies in the range 0.5 to 2 wt%.

[0017] Addition of thickening polymer to the citrus fibre structured composition also has the further advantage that the increased pour viscosity at 20°C slows down the rate of separation and development of either bottom or top clear layer separation if the fibre structuring network has negative or positive buoyancy; possibly induced by it holding high levels of less or more dense than the detergent liquid solid particulate materials in suspension. Thus the compositions have increased storage stability and the suspended particles remain evenly dispersed to provide a uniformly representative dose of encapsulated fragrance or other suspended benefit ingredient for each dose, over the time of use.

[0018] The necessary increase in the level of activated citrus fibre to give a detergent liquid with the same yield stress (suspending power) as one having a mixture of activated citrus fibre and thickening polymer means that the liquid with the combination of activated citrus fibre and thickening polymer is clearer. This is a particular advantage if visual cues are suspended in the liquid.

DETAILED DESCRIPTION OF THE INVENTION

Water

[0019] The detergent compositions are aqueous and water forms the majority of the solvent in the composition. Hydrotropes such as propylene glycol and glycerol/glycerine may be included as co-solvents in a lesser amount than the water. Water is needed in the composition in order to keep the surfactant, any polymers, soluble builders, enzymes etc in solution. The water amount stated includes both free and any bound water. The amount of water in the composition is preferably at least 20 wt%, more preferably at least 30 wt%.

Mixed surfactant system

[0020] Due to the robust properties of the novel external structuring system there are few limitations on the type or the amount of the mixed surfactant system. Synthetic surfactants preferably form a major part of the surfactant system. Mixtures of synthetic anionic and nonionic surfactants, or a wholly anionic mixed surfactant system or admixtures of anionic surfactants, nonionic surfactants and amphoteric or zwitterionic surfactants may all be used according to the choice of the formulator for the required cleaning duty and the required dose of the detergent composition.

[0021] The surfactants forming the mixed surfactant system may be chosen from the surfactants described in 'Surface Active Agents' Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, 'McCutcheon's Emulsifiers and Detergents' published by Manufacturing Confectioners Company or in 'Tenside Taschenbuch', H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

[0022] The amount of surfactant in the composition may range from 3 to 75 wt%, preferably 10 to 60 wt%, more preferably from 16 to 50 wt%. The skilled worker will appreciate that the optimum surfactant concentration will largely depend on the product type and the intended mode of use.

[0023] The anionic surfactant may include soap (salt of fatty acid). A preferred soap is made by neutralisation of

hydrogenated coconut fatty acid, for example Prifac® 5908 (ex Croda). Mixtures of saturated and unsaturated fatty acids may also be used.

[0024] Nonionic detergent surfactants are well-known in the art. A preferred nonionic surfactant is a C12-C18 ethoxylated alcohol, comprising 3 to 9 ethylene oxide units per molecule. More preferred are C12-C15 primary, linear ethoxylated alcohols with on average 5 to 9 ethylene oxide groups, more preferably on average 7 ethylene oxide groups.

[0025] Examples of suitable synthetic anionic surfactants include sodium lauryl sulphate, sodium lauryl ether sulphate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, ammonium lauryl ether sulphate, sodium cocoyl isethionate, sodium lauroyl isethionate, and sodium N-lauryl sarcosinate. Mostly preferred the synthetic anionic surfactants comprise the synthetic anionic surfactant linear alkylbenzene sulphonate (LAS). Another synthetic anionic surfactant suitable in the present invention is sodium alcohol ethoxy-ether sulphate (SAES), preferably comprising high levels of sodium C12 alcohol ethoxy-ether sulphate (SLES). It is preferred for the composition to comprise LAS.

[0026] A preferred mixed surfactant system comprises synthetic anionic with nonionic detergent active materials and optionally amphoteric surfactant, including amine oxide.

[0027] Another preferred mixed surfactant system comprises two different anionic surfactants, preferably linear alkyl benzene sulphonate and a sulphate, for example LAS and SLES.

[0028] Synthetic anionic surfactants can be present, for example, in amounts in the range from about 5% to about 70 wt% of the mixed surfactant system.

[0029] The detergent compositions may further comprise an amphoteric surfactant, wherein the amphoteric surfactant is present in a concentration of 1 to 20 wt%, preferably 2 to 15 wt% more preferably 3 to 12 wt% of the mixed surfactant system. Typical examples of suitable amphoteric and zwitterionic surfactants are alkyl betaines, alkylamido betaines, amine oxides, aminopropionates, aminoglycinates, amphoteric imidazolium compounds, alkyldimethylbetaines or alkyldipolyethoxybetaines.

Activated Citrus fibre

[0030] The albedo of citrus fruits is used to make powdered citrus fibre. It has a 'spongy microstructure'. Citrus fruits (mainly lemons and limes) are dejuiced to leave the insoluble plant cell wall material and some internally contained sugars and pectin. It is dried and sieved and then washed to increase the fibre content. Dried materials are large (100's micron cell fragment, consisting of tightly bound/ bonded fibrils). After milling a powdered citrus fibre material is obtained. The process used leaves much of the natural cell wall intact while the sugars are removed. The resulting highly swelling citrus fibre materials are typically used as food additives and have been used in low fat mayonnaise. The pH of the dispersed powder is acidic.

[0031] Microscopy shows that powdered citrus fibre is a heterogeneous mixture of particles with various sizes and shapes. The majority of the material consists of aggregated lumps of cell walls and cell wall debris. However, a number of tube-like structures with an open diameter of about 10 micron, often arranged in clusters, can be identified. These, so called, xylem vessels are water transport channels that are mainly located in the peel of citrus fruits. The xylem vessels consist of stacks of dead cells, joined together to form relatively long tubes, 200 to 300 micron long. The outsides of the tubes are reinforced by lignin, which is often laid down in rings or helices, preventing the tubes from collapse due to the capillary forces acting on the tube walls during water transport.

[0032] A preferred type of powdered citrus fibre is Herbafoods' Herbacel AQ+ type N citrus fibre. This citrus fibre has a total (soluble and insoluble) fibre content of greater than 80% and soluble fibre content of greater than 20%. It is supplied as a fine dried powder with low colour and has a water binding capacity of about 20 kg water per kg of powder.

[0033] To obtain adequate structure powdered citrus fibre is activated (hydrated and opened up structurally) via a high shear dispersion at a low concentration in water to form a premix. Because the dispersed activated citrus fibre is biodegradable, it is advantageous to include a preservative into the premix.

[0034] The shear should not be high enough to lead to defibrillation. If a high-pressure homogeniser is used it should be operated between 200 and 600 bar. The more shear that is applied the less dense the resulting particles. Whilst the morphology is changed by the high shear, process aggregate size appears not to be changed. The fibres break down and then fill the water phase. The shear also rubs loose the outer parts of the cell walls and these are able to form a matrix that structures the water outside of the volume of the original fibre.

[0035] An activated citrus fibre structuring premix may alternatively be made by milling using a high shear mixer, such as a Silverson. The premix may be passed through several sequential high-shear stages in order to ensure full hydration and dispersal of the citrus fibre to form the activated citrus fibre dispersion.

[0036] The premix may be left to hydrate further (age) after the high shear dispersal. The activated premix is preferably used fresh.

[0037] High Pressure Homogenised premixes are preferred over milled premixes, as they are more weight effective to provide sufficient suspending duty to liquids. Increasing the homogenisation pressure gives further increased weight efficacy to the premix. A suitable operational pressure is about 500 barg.

[0038] The level of activated citrus fibre in a premix preferably lies in the range 1 to 5 wt%, more preferably 1.5 to 2.5 wt%. The concentration of activated citrus fibre in the pre-mix depends on the ability of the equipment to deal with the higher viscosity due to higher concentrations. Preferably the amount of water in the premix is at least 20 times greater than the amount of citrus fibres, more preferably at least 25 times even as much as 50 times. It is advantageous that

there is excess water in order to hydrate the activated citrus fibre fully.

[0039] Preferred premixes have a measured yield stress of at least 70 Pa measured using an Anton Paar serrated cup and bob geometry at 25°C.

[0040] When added to a detergent liquid composition activated citrus fibre boosts the yield stress and the pour viscosity of the composition at 20^{s-1} and the composition is a shear thinning liquid. Yield stress and viscosity at 20^{s-1} increase generally in line with the level of activated citrus fibre.

[0041] Activated citrus fibre is compatible with enzymes used in laundry and household care detergent compositions.

[0042] The premix may either be added to the detergent liquid as a post dosed ingredient, or alternatively the composition can be formed by starting with the premix and then adding the other ingredients to it. Some high shear is required to disperse the premix in the composition fully but the duty is not as demanding as for the premix preparation.

[0043] The activated citrus fibre should be used at a high enough level to ensure that the external structuring network does not settle under its own weight. If the network settles then any suspended solid particles settle with the network. To avoid air entrapment in the structuring network the amount of activated citrus fibre is preferably reduced to close to the minimum required to suspend the solid particles, for example encapsulated fragrance or ground olive stones for house-hold cleaning compositions. The clay portion of the external structuring system assists in reduction of the level of the activated citrus fibre needed. Activated citrus fibre benefits from air free processing as this improves the stability of the resulting liquid compositions, especially to bottom clear layer separation.

Thickening Polymer

[0044] The thickening polymer is a water swellable polyacrylate. Such polymers may be alkali swellable copolymers (ASE) optionally with a hydrophobic modification on at least one of the monomers (HASE) or with crosslinking groups (CASE) and possibly with both hydrophobic modification and crosslinking (C-HASE).

[0045] 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 (B), and hydroxyethyl acrylate (HEA), as well as other alkyl esters of AA or MAA.

[0046] Preferably, acrylic polymers have at least 75% of monomer residues derived from (meth)acrylic acid or (meth)acrylate monomers, more preferably at least 90%, 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.

[0047] 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 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 copolymer, and preferably, for satisfactory performance in a wide range of liquid compositions.

[0048] The amount of lipophilically-modified component in the copolymers 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%.

[0049] 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.

[0050] 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.

[0051] Preferably, the 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 sulphonic acid functionality. Examples of hydrophilic comonomers include 2-hydroxyethyl (meth)acrylate (HEMA or HEA), itaconic acid and acrylamido-2-methylpropanesulfonic acid.

[0052] The aqueous compositions of the present invention contain from 0.1 % and preferably no more than 10% of thickening polymer; i.e., the total amount of copolymer(s) is in this range. Preferably, the amount of copolymer 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 copolymer in the aqueous composition is no more than 7%, more preferably no more than 5%, and most preferably no more than 3%. Preferably, the copolymer is an acrylic polymer. The copolymer, in aqueous dispersion or in the dry form, may be blended into an aqueous system to be thickened followed, in the case of a pH-responsive thickener, by a suitable addition of acidic or basic material if required. In the case of copolymeric pH-responsive thickeners, the pH of the system to be thickened is at, or is adjusted to, at least 5, preferably at least 6, more preferably at least 7; preferably the pH is adjusted to no more than 13. The neutralizing agent is preferably a base such as an amine base or an alkali metal or ammonium hydroxide, most preferably sodium hydroxide, ammonium hydroxide or triethanolamine (TEA). Alternatively, the copolymer may first be neutralized in aqueous dispersion and then blended. The surfactant preferably is blended into the aqueous composition separately from the copolymer prior to neutralization. The molecular weight of uncrosslinked polymer is typically in the range of about 100,000 to 1 million.

[0053] In the case that the polymer is crosslinked, a crosslinking 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 crosslinking 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.

[0054] The copolymer may be prepared in the presence of a chain transfer agent when a crosslinking 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-, isoctyl- 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 crosslinking 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.

[0055] Hydrophobically modified polyacrylate thickening polymers are available as Acusol polymers from Dow.

[0056] An alternative or additional polymer type that may be utilised is described in WO2011/117427 (Lamberti). These 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.

5 [0057] Such crosslinked 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.

10 Suspended particles

15 [0058] The composition preferably comprises suspended particles. These particles are preferably solid; that is to say they are neither liquid nor gas. However, within the term solid we include particles with either rigid or deformable solid shells which may then contain fluids. For example the solid particles may be microcapsules such as perfume encapsulates, or care additives in encapsulated form. The particles may take the form of insoluble ingredients such as silicones, quaternary ammonium materials, insoluble polymers, insoluble optical brighteners and other known benefit agents as described, for example, in EP1328616. The amount of suspended particles may be from 0.001 to up to 10 or even 20 wt%. One type of solid particle to be suspended is a visual cue, for example the type of flat film cue described in EP13119706. The cue may itself contain a segregated component of the detergent composition. Because the cue must be water-soluble, yet insoluble in the composition, it is conveniently made from a modified polyvinyl alcohol that is insoluble in the presence of the mixed surfactant system. In that case, the detergent composition preferably comprises at least 5 wt% anionic surfactant.

20 [0059] The suspended particles can be any type. This includes perfume encapsulates, care encapsulates and/ or visual cues or suspended solid opacifier such as mica or other suspended pearlescent materials and mixtures of these materials. The closer the match of the density of the suspended particles to that of the liquid and the thicker the liquid before addition of the external structurant, the greater the amount of particles that may be suspended. Typically, up to 5 wt% of suspended particles may be suspended stably using the mixed external structuring system; however, amounts up to 20 wt% are possible.

25 [0060] Suspension is achieved through providing a yield stress. The yield stress needs to be larger than the stress imposed on the network by the microcapsules or cues otherwise the network is disrupted and the particles can sink or float depending on whether or not they are denser than the base liquid. Perfume microcapsules are almost neutrally buoyant and small, so the required yield stress is low. Air bubbles are bigger and have the biggest density difference and so require a high yield stress (>0.5 Pa, depending on bubble size). If the yield stress is not too high the air bubbles can escape by floating and disengaging from the surface.

30 [0061] Microcapsules preferably comprise a solid shell. Microcapsules carrying an anionic charge should be well dispersed to avoid agglomeration issues. Microcapsules with a cationic charge may also be used. The microcapsule may have a melamine formaldehyde shell. Other suitable shell material may be selected from (poly)urea, (poly)urethane, starch/ polysaccharide, xyloglucan and aminoplasts.

35 [0062] The average particle diameter of the microcapsules lies in the range from 1 to 100 micrometer and at least 90 wt% of the microcapsules preferably has a diameter in this range. More preferably, 90 wt% of the microcapsules have a diameter in the range 2 to 50 micrometers, even more preferably 5 to 50 micrometers. Most preferred are microcapsules with diameters less than 30 micrometers.

40 [0063] It is advantageous to have a very narrow particle size distribution, for instance 90 wt% of microcapsules in the range 8 to 11 microns. Microcapsules in the range 2 to 5 microns cannot be dispersed so effectively due to the high surface area of the smaller particles.

45 [0064] Preferably the composition comprises at least 0.01 wt% of microcapsules, preferably with an anionic charge. Such microcapsules may deliver a variety of benefit agents by deposition onto substrates such as laundry fabric. To obtain maximum benefit they should be well dispersed through the liquid detergent composition and the vast majority of the microcapsules must not be significantly agglomerated. Any microcapsules that become agglomerated during manufacture of the liquid remain so in the container and will thus be dispensed unevenly during use of the composition. This is highly undesirable. The contents of the microcapsules are normally liquid. For example, fragrances, oils, fabric softening additives and fabric care additives are possible contents. Preferred microcapsules are particles termed core-in-shell microcapsules. As used herein, the term core-in-shell microcapsules refers to encapsulates whereby a shell which is substantially or totally water-insoluble at 40 °C surrounds a core which comprises or consists of a benefit agent (which is either liquid or dispersed in a liquid carrier).

50 [0065] Suitable microcapsules are those described in US-A-5 066 419 which have a friable coating, preferably an aminoplast polymer. Preferably, the coating is the reaction product of an amine selected from urea and melamine, or mixtures thereof, and an aldehyde selected from formaldehyde, acetaldehyde, glutaraldehyde or mixtures thereof. Preferably, the coating is from 1 to 30 wt% of the particles.

5 [0066] Core-in-shell microcapsules of other kinds are also suitable for use in the present invention. Ways of making such other microcapsules of benefit agents such as perfume include precipitation and deposition of polymers at the interface such as in coacervates, as disclosed in GB-A-751 600, US-A-3 341 466 and EP-A-385 534, as well as other polymerisation routes such as interfacial condensation, as described in US-A-3 577 515, US-A-2003/0125222, US-A-6 020 066 and WO-A-03/101606. Microcapsules having polyurea walls are disclosed in US-A-6 797 670 and US-A-6 586 107. Other patent applications specifically relating to use of melamine-formaldehyde core-in-shell microcapsules in aqueous liquids are WO-A-98/28396, WO02/074430, EP-A-1 244 768, US-A-2004/0071746 and US-A-2004/0142868.

[0067] Perfume encapsulates are a preferred type of microcapsule suitable for use in the present invention.

10 [0068] A preferred class of core-in-shell perfume microcapsule comprises those disclosed in WO 2006/066654 A1. These comprise a core having from about 5% to about 50 wt% of perfume dispersed in from about 95% to about 50 wt% of a carrier material. This carrier material preferably is a non-polymeric solid fatty alcohol or fatty ester carrier material, or mixtures thereof. Preferably, the esters or alcohols have a molecular weight of from about 100 to about 500 and a melting point from about 37°C to about 80°C, and are substantially water-insoluble. The core comprising the perfume and the carrier material are coated in a substantially water-insoluble coating on their outer surfaces. Similar microcapsules are disclosed in US 5,154,842 and these are also suitable.

15 [0069] The microcapsules may attach to suitable substrates, e.g. to provide persistent fragrance that is desirably released after the cleaning process is complete.

Liquid detergent compositions

20 [0070] The detergent compositions have sufficient yield stress, also called critical stress, of at least 0.08 Pa, preferably at least 0.09 Pa, more preferably at least 0.1 Pa, even at least 0.15 Pa measured at 25°C. These increasing levels of yield stress are capable of suspending particles of increasingly different density from the bulk liquid. A yield stress of 0.09 Pa has been found sufficient to suspend most types of perfume encapsulates. Pure clay is unstable and cannot provide effective structuring of an aqueous isotropic detergent liquid composition. The mixed external structuring system also stays dispersed; neither floating (to give bottom clear layer separation) nor sinking (to give top clear layer separation). This self suspension is achieved by ensuring that the structuring system wants to occupy all the volume of the detergent liquid. This is a function of the amounts of clay and activated citrus fibre used. To obtain this from activated citrus fibre alone has been found to generate a yield stress so high that air bubbles are suspended and these then destabilise the structuring network.

25 [0071] The detergent liquid may be formulated as a concentrated detergent liquid for direct application to a substrate, or for application to a substrate following dilution, such as dilution before or during use of the liquid composition by the consumer or in washing apparatus.

30 [0072] Cleaning may be carried out by simply leaving the substrate in contact for a sufficient period of time with a liquid medium constituted by or prepared from the liquid cleaning composition. Preferably, however, the cleaning medium on or containing the substrate is agitated.

Product Form

40 [0073] The liquid detergent compositions are preferably concentrated liquid cleaning compositions. The liquid compositions are pourable liquids.

[0074] Throughout this specification, all stated viscosities are those measured at a shear rate of 20 s⁻¹ and at a temperature of 25°C unless stated to be otherwise. This shear rate is the shear rate that is usually exerted on the liquid when poured from a bottle. The liquid detergent compositions according to the invention are shear-thinning liquids.

Manufacturing process

50 [0075] At the higher levels of activated citrus fibre required to suspend heavier particles the amount of water that may be removed from the base to make up the premix separately becomes too large so post dosing of a structuring premix is not a viable option. Instead structured detergent compositions may be prepared starting with the activated fibre to which the other ingredients are added in their normal order of addition. In addition to enabling the incorporation of the higher level of activated fibre into the detergent liquid this has the further advantage that dispersion of the activated fibre by high shear continues during the addition of the later ingredients (including the later added clay) rather than as a post shearing step, thereby reducing the batch time. We have found that the best practice is to de-aerate the liquid composition before filling it into containers. However, the external structuring system allows for more process flexibility and this step is not essential.

Optional ingredients

[0076] Activated citrus fibre has been found to be compatible with usual ingredients that may be found in detergent liquids. Among which there may be mentioned, by way of example: thickening clays; enzymes, particularly: lipase, cellulase, protease, mannanase, amylase and pectate lyase; cleaning polymers, including ethoxylated polyethylene imines (EPEI) and polyester soil release polymers; chelating agents or sequestrants, including HEDP (1-Hydroxyethylidene-1,1,-diphosphonic acid) which is available, for example, as Dequest® 2010 from Thermphos; detergency builders; hydrotropes; neutralising and pH adjusting agents; optical brighteners; antioxidants and other preservatives, including Proxel®; other active ingredients, processing aids, dyes or pigments, carriers, fragrances, suds suppressors or suds boosters, chelating agents, clay soil removal/ anti-redeposition agents, fabric softeners, dye transfer inhibition agents, and transition metal catalyst in a composition substantially devoid of peroxygen species.

[0077] These and further possible ingredients for inclusion are further described in WO2009 153184.

Packaging

[0078] The compositions may be packaged in any form of container. Typically a plastic bottle with a detachable closure/pouring spout. The bottle may be rigid or deformable. A deformable bottle allows the bottle to be squeezed to aid dispensing. If clear bottles are used they may be formed from PET. Polyethylene or clarified polypropylene may be used. Preferably the container is clear enough that the liquid, with any visual cues therein, is visible from the outside. The bottle may be provided with one or more labels, or with a shrink wrap sleeve which is desirably at least partially transparent, for example 50% of the area of the sleeve is transparent. The adhesive used for any transparent label should not adversely affect the transparency.

EXAMPLES

[0079] The invention will now be further described with reference to the following nonlimiting examples.

Rheology Flow Curve Measurement

[0080] Rheology flow curves are generated using the following three step protocol:-

Instrument - Paar Physica - MCR300 with Automatic Sample Changer (ASC)

Geometry - CC27, profiled DIN concentric cylinder

Temperature - 25 °C

[0081] Step 1 - Controlled stress steps from 0.01 to 400 Pa; 40 steps logarithmically spaced in stress with 40 s being spent at each point to measure the shear rate (and hence viscosity); Step 1 is terminated once a shear rate of 0.1 s⁻¹ is reached.

[0082] Step 2 - Controlled shear rate steps from 0.1 to 1200s⁻¹; 40 steps logarithmically spaced in shear rate with 6 seconds being spent at each point to determine the stress required to maintain the shear rate and hence the viscosity.

[0083] Step 3 - Controlled shear rate steps from 1200 to 0.1 s⁻¹; 40 steps logarithmically spaced in shear rate with 6 seconds being spent at each point to determine the stress required to maintain the shear rate and hence the viscosity.

[0084] The results of the first two steps are combined being careful to remove any overlap and to ensure that the required shear rates were achieved at the start of the step.

[0085] The yield stress in Pa is taken to be the value of the stress at a shear rate of 0.1 s⁻¹. I.e. the equivalent of the y-axis intercept in a Herschel-Buckley plot of shear stress vs. shear rate. The yield stress was taken as the point at which the data cut the viscosity = 10 Pa.s and the pour viscosity was taken as the viscosity at 20 s⁻¹, both at 25 °C.

[0086] Abbreviations used in these examples have the following meanings:

- A820 is Acusol 820 thickening polymer (ex: Dow).
- A805S is Acusol 805S thickening polymer (ex: Dow).
- Viscolam CK57 is a crosslinked thickening polymer (CASE) ex Lamberti, as described in WO2011/117427.
- ACF is activated citrus fibre 2 wt% premix (500 Barg).
- Water is Demineralised Water.
- 5BMGX is Tinopal Fluorescer ex Ciba.
- Glycerol is a hydrotrope.

EP 2 841 551 B1

MPG	is Monopropylene Glycol (hydrotrope).
NI	is Neodol 25-7 Nonionic ex Shell.
NaOH	is 50% sodium hydroxide base.
LAS acid	is acid form of Linear alkyl benzene sulphonate Anionic Surfactant.
5 MEA	is Monoethanolamine base.
TEA	is Triethanolamine base.
Prifac 5908	is saturated fatty acid (soap) ex Croda.
SLES	is SLES 3EO Anionic Surfactant.
10 Dequest 2066	is Diethylenetriamine penta(methylene phosphonic acid (or Heptasodium DTPMP) sequestrant ex Thermphos.
Dequest 2010	is HEDP (1-Hydroxyethylidene -1,1 , -diphosphonic acid) sequestrant ex Thermphos.
EPEI	is ethoxylated polyethyleneimine PE160020EO Sokalan HP20 ex BASF.
Perfume encaps	is Oasis Cap Det B72 ex Givaudan.
15 Preservative	is Proxel GXL™ antimicrobial preservative, a 20% solution of 1,2 benzisothiazolin-3-one in dipropylene glycol and water ex Arch Chemicals.
Dye	is Patent blue and Acid yellow colorant.
Opacifier	is Acusol OP 301 ex DOW
Perfume	is free oil perfume
20 Enzyme	is Savinase 16 L EX protease ex Novozymes

Activated Citrus Fibre Premix

[0087] A 2 wt% activated citrus fibre premix was prepared using the materials given in Table 1, according to the following method.

Table 1

Material	% As supplied	Weight (g)
Demin. Water	97.92	1958.4
Proxel GXL	0.08	1.6
Herbacel AQ + type N	2.00	40.0

[0088] The demineralised water was stirred using an agitator stirrer with overhead drive operated at 160 rpm. The Proxel GXL preservative was added. Then Herbacel AQ plus N Citrus Fibre (ex: Herbafoods) was added gradually to ensure no clumping. Stirring was continued for a further 15 minutes to allow the fibres to swell sufficiently prior to the activation stage. The activation stage was carried out by high pressure homogenisation (HPH) at 500 barg.

Examples 1 to 4 - Structured detergent liquids

[0089] Detergent liquids as specified in the following examples were made using the 2 wt% activated citrus fibre premix described above. Sufficient freshly made premix was added to a mixer to give the required level of activated citrus fibre in the finished composition and it was milled for 10 minutes. The polymer and remaining ingredients to make up the liquid were then combined with this mix. The fragrance encapsulates were combined last, when used. Dispersion was carried out using an in-line Silverson (L5T).

[0090] The polymer and activated citrus fibre content of the liquids is as given in Table 2. Two detergent bases were used with three different thickening polymers: Base A: Table 3, and Base B: Table 4.

Table 2

Example	Base	ACF wt%	Polymer wt% and type
1	Base A	0.1	1.2 wt% A805S
2	Base B	0.1	1.2% Viscolam CK 57
3	Base B	0.1	1.2% A820
4	Base B	0.1	1.2% A805S

EP 2 841 551 B1

Table 3 - Base A

Component	wt%
Water and minors*	57.84
ACF	0.10
Thickening polymer **	1.20
Glycerol	5.00
MPG	2.00
NI	13.72
LAS acid	9.15
NaOH	1.20
Prifac 5908	1.50
TEA	1.69
Citric Acid	0.00
SLES	4.57
Dequest 2066	0.34
Perfume encapsulates (50% aqueous dispersion)	0.30
Perfume	1.39
	100.00
* dye, fluorescer, opacifier, enzymes	
** Viscolam CK57, Acusol 820, or Acusol A805S	

Table 4 - Base B

Name	wt%
Water and minors*	40.51
ACF	0.10
Thickening polymer**	1.20
MPG	11.00
Glycerol	5.00
NI	4.58
MEA	7.60
LAS acid	8.75
TEA	2.50
Citric Acid	2.50
Prifac 5908	3.00
Dequest 2010	1.50
SLES	6.82
Sodium Sulphite	0.25
EPEI	3.00
Perfume Encapsulates	0.30

EP 2 841 551 B1

(continued)

Name	wt%
Perfume	1.39
TOTAL	100.00
* dye, fluorescer, enzymes ** Viscolam CK57, Acusol 820, or Acusol A805S	

[0091] The mixed activated citrus fibre and polymer co-structurant enables suspension of encapsulated fragrance, or other benefit ingredients, in Examples 1 - 4.

Rheological stability of structured liquids

[0092] The rheology of Example 2 was measured before and after storage at 50°C. The pouring viscosity and yield stress were within about 10% of the original values after storage for 8 weeks. Further examples were made tested and it was confirmed that for 0.15% of activated citrus fibre with 0.8% of Viscolam in Base B the amount of syneresis was low. The same or better stability was found for Base A.

Examples 5, 6 and C drainage residues

[0093] Further compositions were prepared using polymers in Base A. The polymer levels were as given in Table 5. Visible residues were assessed by adding the compositions to transparent Nunc bottles. The bottle was manipulated to ensure that the sample thoroughly wetted the vertical walls and then left for a few minutes to drain. The resulting on wall drainage residue was assessed visually against a comparative liquid C made using the same detergent base and structured with 0.25% activated citrus fibre. In all cases the drainage residues from the activated citrus fibre and polymer examples according to the invention were visibly less than the 0.25 wt% comparative example. 0.25 wt% was chosen as a realistic comparison as that is the amount of citrus fibres needed to suspend perfume encapsulates stably. We also tested further polymers in different isotropic liquid detergent bases and achieved the same result.

Table 5

Example	Base	ACF wt%	Polymer wt% and type	Drainage residues
5	Base A	0.10	1.2 wt% A805S	Visibly reduced
6	Base A	0.10	1.2% A820	Visibly reduced
C	Base A	0.25	0	Severe

Claims

1. An externally structured aqueous isotropic detergent liquid comprising:
 - a) at least 10 wt% water,
 - b) at least 3 wt% mixed deterative surfactant comprising anionic surfactant,
 - c) at least 0.025 wt% of activated citrus fibre external structurant, **characterised in that** the liquid further comprises at least 0.1 wt% of water swellable polyacrylate thickening polymer and the viscosity of the liquid at 20 s⁻¹ and 25°C is at least 0.3 Pa.s.
2. A composition according to claim 1 wherein the viscosity of the liquid at 20 s⁻¹ and 25°C is at least 0.4 Pa.s.
3. A composition according to any preceding claim in a transparent container.
4. A composition according to any preceding claim having a yield stress of at least 0.1 Pa and further comprising at least 0.01 wt% of suspended particles.
5. A composition according to claim 4 wherein the suspended particles comprise microcapsules.

EP 2 841 551 B1

6. A composition according to claim 5 wherein the microcapsules comprise perfume encapsulates.
7. A composition according to claim 4 wherein the suspended particles comprise visual cues.
- 5 8. A composition according to claim 7 wherein the visual cues are lamellar particles formed from sheets of polymer film.
9. A composition according to any preceding claim comprising at least 1 wt% of the thickening polymer.
10. A composition according to any preceding claim further comprising a colorant.

Patentansprüche

1. Extern strukturierte wässrige isotope Waschmittelflüssigkeit, umfassend:

- a) mindestens 10 Gew.-% Wasser
- b) mindestens 3 Gew.-% gemischtes Waschtensid, umfassend anionisches Tensid,
- c) mindestens 0,025 Gew.-% externen Struktureber aus aktivierter Zitrusfaser,

dadurch gekennzeichnet, dass die Flüssigkeit ferner mindestens 0,1 Gew.-% wasserschwellbares Polyacrylat-Verdickungspolymer umfasst und die Viskosität der Flüssigkeit bei 20 s^{-1} und 25°C mindestens 0,3 Pa.s beträgt.

2. Zusammensetzung gemäß Anspruch 1, wobei die Viskosität der Flüssigkeit bei 20 s^{-1} und 25°C mindestens 0,4 Pa.s beträgt.
3. Zusammensetzung gemäß irgendeinem vorhergehenden Anspruch in einem durchsichtigen Behälter.
4. Zusammensetzung gemäß irgendeinem vorhergehenden Anspruch mit einer Fließspannung von mindestens 0,1 Pa und ferner umfassend mindestens 0,01 Gew.-% suspendierte Teilchen.
5. Zusammensetzung gemäß Anspruch 4, wobei die suspendierten Teilchen Mikrokapseln umfassen.
6. Zusammensetzung gemäß Anspruch 5, wobei die Mikrokapseln Riechstoff-Verkapselungen umfassen.
7. Zusammensetzung gemäß Anspruch 4, wobei die suspendierten Teilchen visuelle Hinweise umfassen.
8. Zusammensetzung gemäß Anspruch 7, wobei die visuellen Hinweise aus Folien von Polymerfilm erzeugte lamellare Teilchen sind.
9. Zusammensetzung gemäß irgendeinem vorhergehenden Anspruch, umfassend mindestens 1 Gew.-% von dem Verdickungspolymer.
10. Zusammensetzung gemäß irgendeinem vorhergehenden Anspruch, ferner umfassend ein Farbmittel.

Revendications

1. Liquide de détergent isotope aqueux structuré de manière externe comprenant :

- a) au moins 10 % en poids d'eau,
- b) au moins 3 % en poids de tensioactif détersif mixte comprenant un tensioactif anionique,
- c) au moins 0,025 % en poids de structurant externe de fibre d'agrumes activé,

caractérisé en ce que le liquide comprend de plus au moins 0,1 % en poids de polymère épaississant de polyacrylate gonflable dans l'eau et la viscosité du liquide à 20 s^{-1} et 25°C est d'au moins 0,3 Pa.s.

2. Composition selon la revendication 1, dans laquelle la viscosité du liquide à 20 s^{-1} et 25°C est d'au moins 0,4 Pa.s.

EP 2 841 551 B1

3. Composition selon l'une quelconque des revendications précédentes dans un récipient transparent.
4. Composition selon l'une quelconque des revendications précédentes présentant une limite apparente d'élasticité d'au moins 0,1 Pa et comprenant de plus au moins 0,01 % en poids de particules en suspension.
5. Composition selon la revendication 4, dans laquelle les particules en suspension comprennent des microcapsules.
6. Composition selon la revendication 5, dans laquelle les micro-capsules comprennent des encapsulations de parfum.
7. Composition selon la revendication 4, dans laquelle les particules en suspension comprennent des indices visuels.
8. Composition selon la revendication 7, dans laquelle les indices visuels sont des particules lamellaires formées à partir de feuilles de film polymère.
9. Composition selon l'une quelconque des revendications précédentes comprenant au moins 1 % en poids du polymère épaississant.
10. Composition selon l'une quelconque des revendications précédentes comprenant de plus un colorant.

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REFERENCES CITED IN THE DESCRIPTION

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