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(54) **Structuring detergent liquids with hydrogenated castor oil**

Strukturierung von Waschmittelflüssigkeiten mit hydriertem Castoröl

Structuration de liquides détergents avec de l'huile de ricin hydrogénée

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EP-A1- 2 216 391	**WO-A1-2005/012475**
WO-A1-2008/114226	**WO-A1-2010/034736**

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Description

TECHNICAL FIELD

[0001] This invention relates to a process for the structuring of aqueousliquid detergent formulations using hydrogenated castor oil (HCO).

BACKGROUND

[0002] Hydrogenated castor oil (HCO, Thixcin R®, castor wax, trihydroxystearin) has been used as a rheology-modifying agent or external structurant for many years.

[0003] In Example 1 of US3354091 Colgate disclose a system where the HCO is mixed with another material to form a premelt or blend. The blend is added at 71 °C to other components of a substantially homogeneous, pourable, heavy-duty aqueous liquid detergent composition comprising 5-30 wt% alkali metal anionic organic sulfonated detergent, 10-30 wt% potassium polyphosphate, 4-12 wt% hydrotrope, 0.1-1 wt% alkali metal carboxymethyl cellulose normally tending to separate from the solution of detergent and phosphate. The HCO (0.01-1 wt%) is added to inhibit the separation of the carboxymethyl cellulose salt. The composition may optionally further comprise a fatty acid alkanolamide to improve detergency and modify foaming power. When used the solid alkanolamide and the castor wax (hydrogenated castor oil) are preferably added as a mixture in molten form. In example 1 lauric isopropanolamide and castor wax are premelted and added as a blend at 71 °C with stirring. The melting point of the castor wax is given as 84-87 °C and the melting point of the alkanolamide would have been about 65-66 °C. Insufficient information is given in this document to know if the castor wax melted or if it dissolved in the melted isopropanolamide. From our investigation of use of nonionic as a solvent for hydrogenated castor oil we believe that the castor wax would have dissolved in the nonionic once it became liquid above 66 °C. Evidence for the existence of a solution is that the liquid is clear. No details are given about the cooling rate. The technical problem is the stabilisation of water-soluble sodium carboxymethyl cellulose in the presence of phosphate builder. In this publication the castor wax solution is added to the bulk remainder of the formulation in order to crystallise it in situ in that formulation.

[0004] In WO2010/034736 we employed a variant of the Colgate solvent addition route to form a structuring system without any requirement to melt the HCO. This patent application describes a process that solves the problem of reliable suspension of perfume encapsulates.

[0005] It claims a method for the production of a phosphate free liquid detergent composition, comprising the steps of:

a) preparation of a first premix by adding surfactants and a base to water under agitation at a temperature at least 55°C, having a pH from 7.5 to 11;
b) preparation of a second premix by adding hydrogenated castor oil to a liquid non-aqueous organic solvent at a temperature of at least 70°C under agitation to dissolve the hydrogenated castor oil in the liquid non-aqueous organic solvent;
c) addition of the warm HCO solution that comprises the second premix from step b) to the first premix from step a) at a temperature of at least 55°C under mixing, at a weight ratio of b) to a) of from 1:40 to 1:10; whereby the hydrogenated castor oil remains in solution;
d) cooling of the mix of step c) to a temperature below 50°C and subsequently storing this mix until the hydrogenated castor oil has crystallised from solution, and
e) then adding encapsulated fragrance with particle size up to 200 micrometre to the cooled externally structured liquid from step d) under mixing.

[0006] In step b) the solvent is conveniently chosen from materials that would be in the eventual liquid. The examples use fatty acid, but nonionic solvents are also contemplated. Following the concept described by Colgate this process adds the HCO premix to a system that comprises the bulk of the remainder of the formulation so that the structuring system is created *in situ.* Attempts to adapt this process to reduced surfactant compositions designed to work with high polymer levels as described in WO09153184 have met with problems due to less surfactant (and more water) being used. The amount of nonionic available to dissolve the HCO is reduced and coupled with the reduced exotherm from neutralisation of the anionic surfactant acid. Insufficient structuring develops when the process is applied to such formulations.

[0007] An alternative process for structuring with HCO has been described in a number of publications. Here the HCO is added in molten form and emulsified before the mixture is cooled to form the structuring system. This process is said to produce a unique "thread like" structurant. Hereinafter it is referred to as the "hot melt process". It can be shown that taking the HCO above its melting point leads to a different type of structure when it is subsequently cooled. In particular "seeding" is promoted.

[0008] WO96/25144 (P&G) represents an early disclosure of this hot melt process. The process comprises four steps. Firstly, the trihydroxystearin (a major component of HCO) is added to distilled water and allowed to mix until fully hydrated. Then the surfactants (anionic, amphoteric, cationic and nonionic) are added and the mixture is heated to 88°C until the trihydroxystearin is fully melted and dissolved. While heating the mixture is subjected to shear via a medium to high agitator speed. Then the trihydroxystearin dispersion is fast cooled utilising a plate and frame heat exchanger to a temperature of about 43°C to 27°C to form trihydroxystearin crystals. Perfume is then added. The mixture is continuously stirred at a medium speed. Polymer and silicones may subsequently be mixed in.

[0009] The hot melt process may be used to make a concentrated HCO premix. In some variants nonionic is used, but it is never used as a solvent for the HCO.

[0010] EP1396535 (P&G) discloses at paragraph 87 a preferred premix preparation process comprising the following steps:

(1) Dissolving the anionic emulsifier in water, preferably in demineralised water;
(2) Adding the nonionic emulsifier;
(3) Optionally, but preferably, heating up the mixture, preferably to a temperature above the melting point of the structuring agent;
(4) Adding the structuring agent;
(5) Allowing the mixture to emulsify, preferably either by stirring for approximately 1 hour or more preferably by mixing under high shear mixing conditions for less than one hour, preferably less than 30 minutes.
(6) Optionally, but preferably, cooling the emulsion down to a temperature, preferably to a temperature below the melting point of the structuring agent at a constant cooling rate of a least 1°C per minute and most preferably not exceeding 2.5°C per minute.

[0011] In practice when HCO is used it is always added in molten form. No explanation is given for how it could be added any other way and it is believed that although application of heat is optional in step 3 the addition to the structuring agent to a system where it is liquid to enable emulsification is essential and the disclosure is non-enabling for any other option.

[0012] WO 2005/012474 (P&G) gives a further disclosure on page 31 for incorporation of a twin external structuring system into a detergent liquid intended to suspend visible beads. The first structurant may be HCO, the second structurant is a polymeric structurant such as a polyacrylate or a polymer gum. The aqueous liquid compositions herein can generally be prepared by first forming a pre-mix within which the structurants are dispersed in a portion of the water eventually used to comprise the aqueous liquid matrix of the compositions herein. This pre-mix is formed in such a way that it comprises a structured aqueous liquid. It is thought that this is only made possible by the presence of the second (polymeric) structurant. HCO on its own would only form a structuring system in water if melted and used with surfactant. To this structured pre-mix can be added, while the pre-mix is under agitation, surfactant(s) and any other ingredient, along with water. Any convenient order of addition of these materials, or for that matter, simultaneous addition of these composition components to the pre-mix can be carried out.

[0013] In closely related WO 2005/012475 (P&G) it is made clear that to activate the HCO it is necessary to do more than add it to water. A preferred pre-mix process is given on page 26.

[0014] A premix is formed by combining the crystalline, hydroxyl-stabilizing agent, preferably in an amount of from about 0.1 percent to about 5 percent by weight of the premix, with water which comprises at least 20 percent by weight of the premix, and one or more of the surfactants to be used in the composition, and optionally, any salts which are to be included in the detergent composition. The pre-mix formed is heated to above the melting point of the crystalline, hydroxyl-containing structurant and then cooled to form the structuring system. In Example I a solution of neutralised LAS acid is first heated to 90°C then the HCO is added and emulsified before cooling to form the structurant pre-mix. Thus the HCO is melted, as in previous hot melt processes.

[0015] More recently WO 2008/114226 (P&G) makes a similar disclosure on page 42:

1) A premix is formed by combining the crystalline, hydroxyl-stabilizing agent, preferably in an amount of from about 0.1 percent to about 5 percent by weight of the premix, with water which comprises at least 20 percent by weight of the premix, and one or more of the surfactants to be used in the composition, and optionally, any salts which are to be included in the detergent composition.
2) The pre-mix formed in Step 1) is heated to above the melting point of the crystalline, hydroxyl-containing structurant.
3) The heated premix is cooled under agitation to form the structuring system.

[0016] We have found that a problem with formation of a premix using the hot melt process is that the high temperature, especially in combination with caustic used to neutralise the anionic emulsifier, used can lead to degradation of some of the components of the HCO. Furthermore, the need to create a high concentration oil in water emulsion for formation of the crystallisation mix leads to use of higher than desirable levels of HCO in the final liquid detergent composition. This is believed to be due to use of very low levels of water in the highly concentrated HCO premix, which means that the premix is heavily diluted on addition to the main composition, with a subsequent loss of structuring which must be compensated for by "overdosing" the HCO.

[0017] It is an object of the present invention to find an alternative process to form an HCO premix that solves these problems.

SUMMARY OF THE INVENTION

[0018] According to the present invention there is provided a process to manufacture a structured aqueous liquid detergent composition comprising 7 to 40 wt% surfactant, of which at least 2 wt% is nonionic surfactant, optionally, and preferably, 4 to 30 wt% water soluble polymer, and 0.1 to 0.4 wt% Hydrogenated Castor oil (HCO) external structurant, the process comprising the step of formation of a structured premix which is then mixed in an amount of 40 to 80 vol% with an unstructured liquid comprising 20 to 60 vol% of the liquid detergent composition, characterised in that:

the structured water premix is formed by:

a) adding 0.1 to 0.4, preferably about 0.25 wt%, HCO (based on the liquid detergent composition), to 2 to 7 wt% surfactant (based on the liquid detergent composition),
b) heating this mixture to 70 to 84°C to prepare a molecularly dispersed transparent solution of a minor part of HCO in a major part of nonionic surfactant, then
c) adding the solution from step b) to a liquid comprising demineralised water at a temperature of at least 55°C optionally further comprising anionic surfactant, but not base, to form a warm structured water premix precursor and allowing this precursor to cool to below 40°C to form a structured water premix;
d) optionally aging the structured water premix prior to its combination with additional surfactant, the optional water soluble polymers and other liquid detergent ingredients to form an externally structured aqueous detergent composition.

[0019] Generated exotherm from neutralisation of surfactants and formation of any soap does not appear detrimental to maintenance of structure provided the exotherm does not exceed the melt temperature of the HCO structuring phase (85°C plus).

[0020] The surfactant used to dissolve the HCO in step b) is preferably selected from anionic surfactant, nonionic surfactant, cationic surfactant and soap. Ion pairs of anionic and cationic surfactants are useful. Nonionic surfactant is preferred, either used alone or with another surfactant, especially anionic surfactant.

[0021] When used the amount of nonionic is preferably at least 15 times as much as the amount of HCO in the premix. Using only 8 times as much nonionic as HCO in the structured water premix proved insufficient to provide a structure to suspend cues. Thus, viscosity build appears to be related to relative levels of nonionic and HCO present in the premix when nonionic is used as the main solvent for the HCO.

[0022] In step c) use of demineralised water at 65°C provides a good structured water premix. The demineralised water to which the HCO solution is added may be higher than 65°C provided the HCO/NI premix is added in at 70 to 85°C under conditions of high shear (250rpm or higher, e.g. using an L4R Silverson, mixer). Use of lower temperatures than 65°C for the demineralised water significantly reduce the degree of external structuring both for the structured water premix and for the final fully formulated liquid detergent compositions. If the temperature of the water to which solvated HCO is added is too high (above the melting point of HCO) then we see seeding effects. If the water temperature is too low (<55°C) we see creaming and phase separation in the final liquid. The preferred water temperature is 60-70°C preferably about 65°C.

[0023] Advantageously, the premix formed in step c) is maintained above 55°C for a holding period of at least 30 minutes before it is cooled. This facilitates development of the required structuring system in the premix. Provided that supersaturation is achieved by use of this holding period, quench cooling has been found to yield good structure, as has slow cooling. Rapid (crash) cooling appears to lead to significant loss of structure. The preferred cooling rate, especially after a holding period, is between 1.5 and 2.5 °C per minute, to allow the correct crystallisation to develop for best structuring effect for suspending duty.

[0024] Advantageously 4 to 30 wt% of polymer solution (solids basis) is dosed to the detergent liquid before or after the structuring system is added. The structuring system provides the advantage that in liquids where such polymer solution addition would provide thinning of the liquid and loss of structuring the compositions of the invention retain acceptable structuring properties. The water soluble polymers preferably comprise ethoxylated polyethylene imine or other anti redeposition polymers and/or soil release polymers as described below.

[0025] Preferably the volume of the structured water premix is greater than the volume of the remainder of the composition.

[0026] The process is particularly useful for structuring compositions comprising less than 40% surfactant, even more preferably less than 35 wt% surfactant, as they have proved problematic to structure effectively using a process in which a warm HCO solution in fatty acid is added direct to the bulk of the remainder of the composition. The process according to the present invention provides highly structured fabric cleaning liquids having non-Newtonian rheology. The structuring will also suspend insoluble benefit agents. The structurant may be used in conjunction with high levels of soluble polymers.

[0027] The main utility of the HCO structuring system is for suspending duty. The components to be suspended may range from invisible microcapsules, such as perfume encapsulates, to visible visual cues such as cues made from film material or large capsule type visual cues with a diameter of at least 2mm.

[0028] The amount of HCO in the liquids preferably ranges from 0.2 to 0.4 wt% to achieve this suspending duty. Preferably the level of HCO in the final composition is less than 0.35, most preferably less than 0.3 wt%.

[0029] The viscosity of the structured water premix formed in step c is preferably at most 200 cp.

[0030] Ideally the structured water premix will have been formed from part of the ingredients that would already have been included in the liquid detergent. How these are mixed with the remaining ingredients of the liquid detergent is relatively flexible.

DETAILED DESCRIPTION OF THE INVENTION

[0031] This process to overcome the problem of structuring low active, high water, concentrated liquids uses a "structured water" premix. This process is especially useful for liquid compositions including 4 to 30 wt% water soluble polymers, which tend to thin the composition and work against the normal structuring effect of hydrogenated castor oil.

[0032] Water may be structured by adding a solution of HCO in nonionic surfactant to warm water. The advantage of adding the HCO as a solution rather than a hot melt form is that it can be liquefied and therefore formed into a colloidal dispersion at a temperature below 90°C, preferably below 87°C, even below 85°C. This is significant. HCO is a complex mix of components and their lowest melting point is 85°C. By operating below that melting point, the HCO is not melted and emulsified into an aqueous medium. The cooled colloidal dispersion formed by the process according to the present invention is stable and can subsequently used as a premix to provide excellent structuring. This is thought to be due to the large amount of liquid used for the structured premix in comparison to the amount of liquid in the remainder of the composition to which it is added,. The loss of structuring that must be compensated by high levels of HCO that is observed when using high dilutions of a structured premix are overcome. Surprisingly by using the process of the invention it is possible to form stable low concentration structured premixes without the complexity of the systems of the prior art. These premixes can then be easily converted to full structured liquid detergent formulations with the required rheology and the ability to suspend solid materials such as visual cues and microcapsules. The structured fabric cleaning compositions containing cleaning polymers may also contain optional functional/non functional/visual cues and/or stable fragrance encapsulates for which significant rheology modification/structuring afforded by this invention is intended to prevent their sedimentation or creaming (under different storage conditions) to provide consumers uniform fragrance delivery in every dose per wash.

[0033] Of particular interest are full formulations that include cleaning polymers, such as anti redeposition polymers, soil release polymers and dye transfer inhibition polymers. Particularly EPEI and polyester soil release polymers. Addition of these polymers does cause a low shear viscosity reduction (0.001 to 0.1 Pas)-due to polymer surfactant interactions between cleaning polymers/surfactant and structurant - but the process according to the invention provides unexpectedly high levels of structuring despite this. The structured liquid may also provide a stable network through which dispersed encapsulates may be prevented from re-aggregating.

[0034] The structured water premix has an opaque appearance and is storage stable at ambient to 37°C. The premix route solves the problem of manufacturing liquids with low to moderate 50 to 10 000 Pas low shear viscosities and having a critical stress consistent with suspending duty. The low level of surfactants and use of polymers in such liquids requires the presence of a rheology modifier such as HCO.

[0035] The hot water to which the HCO solution is added may comprise other ingredients predissolved in the water. Anionic surfactant, and soap are preferred pre-additives to the water ,

[0036] The structured water may be added to other components to manufacture a full structured liquid detergent at various points in the process flow for the manufacture of a full liquid. It is preferably added before any polymers. Usually it is added after any neutralisation reactions have been completed. The temperature of addition does not seem to be critical which leads to good process flexibility. We have added with success using structured water at temperatures from 20 to 40°C.

[0037] The invention may be carried out as a simple batch process. The structured water premix may be produced off line as needed or convenient and does not need to be closely coordinated with the main process plant requirements. The HCO solvent is preferably a functional component of the formulation, typically comprising but not limited to 2 to 7% non-ionic surfactant. It is added to the warm (65°C to 75°C) water under stirring using a Heidolph/IKA stirrer or higher shear mixer such as a L4R Silverson 'dip-in' mixer, or an in line static mixer, and cooled to room temperature with slow stirring (<150rpm).

[0038] For the best results the mix should be held at a temperature above 55°C, more preferably above 60°C and below the melting point of the hydrogenated castor oil for at least 15 minutes before the main cooling and crystallisation commences. Such a batch can be crash cooled in less than an hour and still provide excellent structuring.

[0039] Preferably, the structured water premix is maintained above 55°C, more preferably above 60°C, for at least 30 minutes and even up to 1 hour, for supersaturation nucleation to take place before it is cooled to room temperature to effect crystallisation (which can be varied according to cooling rates/scale) with stirring/shear or without stirring/shear. The optimum cooling rate lies in the range 1.5 to 2.5 °C per minute. However, different cooling rates are possible and total batch mixing times range from 16h using slow cooling to 1hr using quench cooling.

[0040] Alternative 'solvents' include other nonionic surfactants. Fatty acid solvents as used in prior art processes are less preferred for this process, due to the need to neutralise them on addition of the HCO solution to the warm water. Such neutralisation may affect the rheology and is a limitation on process flexibility. It is preferred that the structured water does not contain any alkali, such as caustic if it would affect the structuring; this can easily be checked by a simple test. Anionic surfactants may also be suitable solvents, especially in admixture with the nonionic surfactant and optionally also in admixture with cationic surfactants and/or soap (neutralised fatty acid).

[0041] Typical fabric cleaning liquid detergent ingredients, such as alkali/buffers, hydrotropes, dyes, fragrance, etc. are added to the structured water premix after the structure is formed to complete the composition. Fabric cleaning and fabric treatment polymers are preferably added. These additional components are described in more detail below.

Liquid detergent compositions

[0042] The process provides liquid detergent compositions, wherein the hydrogenated castor oil is present at a concentration of from 0.1 to 0.4% by weight of the total composition. Preferably, the concentration of hydrogenated castor oil is from 0.15 to 0.35% by weight, even more preferably from 0.2 to 0.3%, and most preferably about 0.25% by weight of the total composition.

[0043] Without wishing to be limited by theory, we envisage that when the concentration of hydrogenated castor oil is too high in the liquid detergent composition obtainable by the method of the invention, this liquid detergent composition will be thick and viscous and not well pourable, leading to dispensing problems and dissolution properties when in use. When the concentration of hydrogenated castor oil is too low, the structured liquid cannot stably suspend particles in the formulation.

[0044] Preferably, the concentration of surfactants in the liquid detergent compositions made according to the invention is from 7 to 40% by weight, more preferred from 10 to 35% by weight, and most preferably from 15 to 30% by weight of the total composition.

[0045] The liquid cleaning composition may be formulated as a concentrated cleaning 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.

[0046] Whilst the compositions made according to the present invention may be used for cleaning any suitable substrate, the preferred substrate is a laundry fabric. 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

[0047] The liquid detergent compositions obtained by the method according to the present invention are preferably concentrated liquid cleaning compositions. The liquid compositions have a physical form that preferably ranges from a pourable liquid, a pourable gel to a non-pourable gel. These forms are conveniently characterised by the product viscosity. In these definitions, and unless indicated explicitly to the contrary, throughout this specification, all stated viscosities are those measured at a shear rate of 21 s-1 and at a temperature of 25°C. 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. For suspending duty the fully formulated structured liquids may also be characterised as having a critical stress. Typical yield stresses for liquids according to the invention lie in the range 0.1 to 0.8 Pa.

[0048] Pourable liquid detergent compositions preferably have a viscosity of not more than 1,500 mPa.s, more preferably not more than 1,000 mPa.s, still more preferably, not more than 500 mPa.s. Typically, the viscosity is lower than 500 mPa.s at 21 s-1.

[0049] Pourable gels, preferably have a viscosity of at least 1,500 mPa.s but no more than 6,000 mPa.s, more preferably no more than 4,000 mPa.s, still more preferably no more than 3,000 mPa.s and especially no more than 2,000 mPa.s.

[0050] Non-pourable gels, preferably have a viscosity of at least 6,000 mPa.s but no more than 12,000 mPa.s, more preferably no more than 10,000 mPa.s, still more preferably no more than 8,000 mPa.s and especially not more than 7,000 mPa.s.

[0051] Compared with the prior art thread-like structuring systems the viscosity at a shear stress of 5 Pa is about 1 Pa.s compared with 0.3 Pa.s and at the higher shear of 10 Pa it is 0.7 Pa.s versus 0.2 Pa.s. On the other hand, the viscosity at low shear stress (0.1 Pa) is similar for the two types of structuring. This means that the tendency for any suspended materials to separate out in transportation is lower for the products according to the invention.

[0052] For the purpose of this invention a composition is considered to be physically stable when it remains homogeneous over a period of about 3 months at temperatures from 5 to 50°C.

Hydrogenated Castor Oil

[0053] Castor oil, also known as ricinus oil, is a vegetable oil obtained from the bean of the castor plant (Ricinus communis). Castor oil is a colourless to very pale yellow liquid with mild or no odour or taste. It is a triglyceride in which approximately ninety percent of fatty acid chains are ricinoleic acid (12-hydroxy-9-cis-octadecenoic acid). Oleic and linoleic acids are the other significant components. The controlled hydrogenation of castor oil yields fully hydrogenated castor oil, which is used in the method and products according to the present invention. At room temperature, hydrogenated castor oil is a hard white wax that melts at a temperature of about 86 to 88°C. Suppliers are, for example, Hindustan Unilever, supplying flakes or granules, Cognis (powder), Vertellus (flakes) or Elementis (flakes or granules), or any mixture thereof. A hydrogenated castor oil suitable in the present invention is for example Thixcin® R available from Elementis.

Water

[0054] The process of the invention is ideally suited to manufacture of compositions with a relatively high level of water. Such compositions include the dilute types of formulations commonly found in the prior art. However, significantly, the invention is also suited to a new type of concentrated formulation, which has a low level of surfactant and high levels of soluble cleaning polymers. These compositions may have high levels of water also and they have proved problematic to manufacture using the known HCO structuring processes. Thus the invention is particularly suited for the manufacture of compositions comprising more than 50 wt% water, especially more than 55 wt% water and up to 80, even 90 wt% water.

Surfactants

[0055] The liquid detergent composition of the invention may comprise from 7 to 40 wt%, more preferred from 10 to 35 wt%, and most preferably from 15 to 30 wt% of a surfactant, preferably selected from anionic, nonionic, cationic, zwitterionic active detergent materials or mixtures thereof.

[0056] In general, the surfactants of the 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, in the current edition of 'McCutcheon's Emulsifiers and Detergents' published by Manufacturing Confectioners Company or in 'Tenside Taschenbuch', H. Stache, 2nd Edn., Carl Hanser Verlag, 1981.

[0057] In addition to the surfactants mentioned above, a preferred compound in the liquid detergent composition according to the invention is soap (salt of fatty acid). Preferably, the organic non-aqueous solvent used in step b) of the method of the invention comprises a fatty acid. Preferably the fatty acid comprises linear alkyl saturated C12-C18 fatty acids. Examples of fatty acids suitable for use of the present invention include pure or hardened fatty acids derived from palmitoleic, safflower, sunflower, soybean, oleic, linoleic, linolenic, ricinoleic, rapeseed oil or mixtures thereof. An example of a preferred fatty acid is a hydrogenated coconut fatty acid, for example Prifac 5908 (supplied by Uniqema, Gouda, Netherlands). Mixtures of saturated and unsaturated fatty acids can also be used herein.

[0058] It will be recognised that the fatty acid will be present in the (final) liquid detergent composition primarily in the form of a soap. Suitable cations include sodium, potassium, ammonium, monoethanol ammonium diethanol ammonium, triethanol ammonium, tetraalkyl ammonium, e.g. tetra methyl ammonium up to tetradecyl ammonium cations.

[0059] The amount of fatty acid will vary depending on the particular characteristics desired in the final liquid detergent composition. Preferably 0 to 30%, more preferably 1 to 20% most preferably 2 to 10 wt% of fatty acid is present in the liquid detergent compositions made according to the invention.

[0060] Mixtures of synthetic anionic and nonionic surfactants are especially useful in a liquid detergent compositions made using the invention.

[0061] Nonionic detergent surfactants are well-known in the art. They normally consist of a water-solubilising polyalkoxylene or a mono- or di-alkanolamide group in chemical combination with an organic hydrophobic group derived, for example, from alkylphenols in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols, primary, secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof), preferably having from 8 to 20 carbon atoms, monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylene. Also common are fatty acid mono- and dialkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkyloyl group having from 1 to 3 carbon atoms. In any of the mono- and dialkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule. In all polyalkoxylene containing surfactants, the polyalkoxylene moiety preferably consists of from 2 to 20 groups of ethylene oxide or of ethylene oxide and propylene oxide groups. Amongst the latter class, particularly preferred are those described in EP 225 654 A. Also preferred are those ethoxylated nonionics that are the condensation products of fatty alcohols with from 9 to 18 carbon atoms condensed with from 3 to 11 moles of ethylene oxide. Examples of these are the condensation products of C9-18 alcohols with on average 3 to 9 moles of ethylene oxide. Preferred for use in the liquid detergent compositions made using the invention are C12-C15 primary, linear alcohols with on average 3 to 9 ethylene oxide groups.

[0062] Preferably a nonionic surfactant that may be used in the present invention 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.

[0063] Suitable synthetic anionic surfactants for the detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals, including alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkoyl sarcosinates, alkyl ether carboxylates, alpha-olefin sulphonates and acyl methyl taurates, especially their sodium, magnesium ammonium and mono, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 22 carbon atoms, preferably 8 to 18 carbon atoms, still more preferably 12 to 15 carbon atoms and may be unsaturated. The alkyl ether sulphates and alkyl ether carboxylates may contain from one to ten ethylene oxide or propylene oxide units per molecule, and preferably contain one to three ethylene oxide units per molecule.

[0064] Examples of suitable synthetic anionics 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.

[0065] Preferred surfactant systems are mixtures of synthetic anionic with nonionic detergent active materials and additionally cationic or amphoteric surfactant. Especially preferred is a surfactant system that is a mixture of alcohol ethoxy-ether sulphate (AES) and a C12-C15 primary ethoxylated alcohol 3-9 EO ethoxylate and a quaternary ammonium cationic surfactant.

[0066] Preferred surfactant systems are mixtures of synthetic anionic with nonionic detergent active materials and soap, additionally with cationic or amphoteric surfactant. Synthetic anionic surfactants can be present for example in amounts in the range from about 5% to about 70 wt% of the total surfactant material.

[0067] In a preferred embodiment of the invention, the detergent composition also comprises a cationic surfactant or an amphoteric surfactant, wherein the cationic or amphoteric surfactant is present in a concentration of 1 to 20%, preferably 2 to 15% more preferably 3 to 12 wt% of the total surfactant.

[0068] Suitable cationic surfactants that may be used are, substituted or unsubstituted, straight-chain or branched quaternary ammonium salts. Preferably the cationic surfactant is of the formula:

$$R1R2R3R4N+ X-$$

wherein R1 is C8-C22-alkyl, C8-C22-alkenyl, C8-C22-alkylalkenylamidopropyl or C8-C22-alkoxyalkenylethyl, R2 is C1-C22-alkyl, C2-C22-alkenyl or a group of the formula -A-(OA)n-OH, R3 and R4 are C1-C22-alkyl, C2-C21-alkenyl or a group of the formula -A-(OA)n-OH, A is -C2H4- and/or -C3H6- and n is a number from 0 to 20 and X is an anion. A commercially available and preferred example of this type of cationic surfactant is a compound of the formula above, where R1 is a C12/14 alkyl group, R2 is a group of the formula -A-(OA)n-OH, wherein A is -C2H4- and n is nil, and R3 and R4 are both -CH3 (i.e. C1-alkyl). This type of cationic surfactant is commercially available from e.g. Clariant under the name Praepagen® HY.

[0069] Typical examples of suitable amphoteric and zwitterionic surfactants are alkyl betaines, alkylamido betaines, amine oxides, aminopropionates, aminoglycinates; amphoteric imidazolinium compounds, alkyldimethylbetaines or alkyldipolyethoxybetaines.

Optional ingredients

[0070] The compositions herein can further comprise a variety of optional ingredients. A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, etc.

Carriers

[0071] Liquid detergent compositions of the invention may contain various solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Other suitable carrier materials are glycols, such as mono-, di-, tri-propylene glycol, glycerol and polyethylene glycols (PEG) having a molecular weight of from 200 to 5000. The compositions may contain from 1 % to 50%, typically 5% to 30%, preferably from 2% to 10%, by weight of such carriers.

Detergency builder

[0072] One or more detergency builders may suitably be present in the liquid detergent composition of the invention. However, phosphate builders are not used. The dendritic structuring system may not form in the same way when high levels of dissolved phosphate are present in the solution prior to crystallisation of the hydrogenated castor oil.

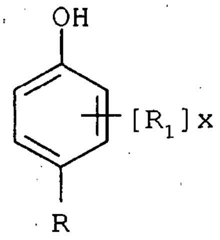
[0073] Examples of suitable organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates; carboxylates, polycarboxylates, polyacetyl carboxylates, carboxymethyloxysuccinates, carboxymethyloxymalonates, ethylene diamine-N,N-disuccinic acid salts, polyepoxysuccinates, oxydiacetates, triethylene tetramine hexa-acetic acid salts, N-alkyl imino diacetates or dipropionates, alpha sulpho- fatty acid salts, dipicolinic acid salts, oxidised polysaccharides, polyhydroxysulphonates and mixtures thereof.

[0074] Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamino-tetraacetic acid, nitrilo-triacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid, tartrate mono succinate and tartrate di succinate.

Antioxidants

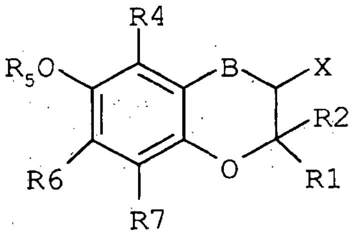
[0075] The liquid detergent compositions obtainable by the method according to the present invention preferably comprise from 0.005 to 2% by weight of an anti-oxidant. Preferably, the anti-oxidant is present at a concentration in the range of 0.01 to 0.08% by weight.

[0076] Anti-oxidants are substances as described in Kirk-Othmer (Vol 3, pg 424) and in Uhlmans Encyclopedia (Vol 3, pg 91). One class of anti-oxidants that could be used in the present invention is alkylated phenols having the general formula:



wherein R is C1-C22 linear or branched alkyl, preferably methyl or blanched C3-C6 alkyl; C3-C6 alkoxy, preferably methoxy; R1 is a C3-C6 branched alkyl, preferably tert-butyl; x is 1 or 2. Hindered phenolic compounds are a preferred type of alkylated phenols according to this formula. A preferred hindered phenolic compound of this type is 2, 6-di-tert-butyl-hydroxy-toluene (BHT).

[0077] A further class of anti-oxidants which could be suitable for use in the present invention is a benzofuran or benzopyran derivative having the formula:



wherein R1 and R2 are each independently alkyl or R1 and R2 can be taken together to form a C5-C6 cyclic hydrocarbyl moiety; B is absent or CH2; R4 is C1-C6 alkyl; R5 is hydrogen or -C(O)R3 wherein R3 is hydrogen or C1-C19 alkyl; R6 is C1-C6 alkyl; R7 is hydrogen or C1-C6 alkyl; X is CH2OH, or CH2A wherein A is a nitrogen comprising unit, phenyl, or substituted phenyl. Preferred nitrogen comprising A units include amino, pyrrolidino, piperidino, morpholino, piperazino, and mixtures thereof.

[0078] Anti-oxidants such as tocopherol sorbate, butylated hydroxy benzoic acids and their salts, gallic acid and its alkyl esters, uric acid and its salts and alkyl esters, sorbic acid and its salts, and dihydroxy fumaric acid and its salts may also be used.

[0079] Preservatives, such as Proxel may advantageously be included. They may be added to the water in step c).

Fragrances

[0080] The liquid detergent compositions obtainable by the method according to the present invention preferably comprise from 0.001 to 3% by weight of the total composition of a perfume composition, preferably from 0.01 to 2% by weight of the total composition. Said perfume composition preferably comprises at least 0.01% by weight based on the liquid compositions of a perfume component selected from terpenes, ketones, aldehydes and mixtures thereof. The perfume composition may fully consist of the perfume component but generally the perfume composition is a complex mixture of perfumes of various differing perfume classifications. In this regard, the perfume composition preferably comprises at least 0.1 %, more preferably at least 1.0%, still more preferably at least 5% by weight of the perfume component.

[0081] At least part of the perfume component comprises encapsulated fragrances like perfume microcapsules. The entirety of the perfume may be provided in this form. The preferred perfume microcapsules utilised in the present invention are 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 perfume (including any liquid carrier therefor).

[0082] In the context of the present invention, core-in-shell microcapsules preferably have a d4,3 average particle size of from 1 to 100 micrometer.

[0083] Microcapsules as described in US-A-5 066 419 have a friable coating which is 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% by weight of the particles.

[0084] Core-in-shell perfume microcapsules of other kinds are also suitable for use in the present invention. Ways of making such other microencapsulates of 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.

[0085] 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.

[0086] Preferably, perfume is added to the compositions after the cooling step d) in the method of the invention. All perfume added in the form of encapsulated perfume must be added after the full structured liquid is formed. Normally it would be added after polymers, enzymes etc.

Detersive enzymes

[0087] 'Detersive enzyme', as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry application. Suitable enzymes that could be used in the composition of the present invention include proteases, amylases, cellulases, peroxidases, and mixtures thereof, of any suitable origin, such as vegetable, animal bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity, thermostability, and stability to active bleach detergents, builders and the like. In this respect bacterial and fungal enzymes are preferred such as bacterial proteases and fungal cellulases. Enzymes are included in the present detergent compositions for a variety of purposes, including removal of protein-based, saccharide-based, or triglyceride-based stains, for the prevention of refugee dye transfer, and for fabric restoration.

[0088] Enzymes are normally incorporated into detergent composition at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, or freshness improving effect on the treated substrate. In practical terms for normal commercial operations, typical amounts are up to about 50 mg by weight, more typically 0.01 mg to 30 mg, of active enzyme per gram of detergent composition. Stated otherwise, the composition of the invention may typically comprise from 0.001 to 3%, preferably from 0.01 to 1 % by weight of a commercial enzyme preparation.

[0089] Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent formulations. Suitable examples of proteases are the subtilisins that are obtained from particular strains of B. subtilis and B. licheniformis. One suitable protease is obtained from a strain of Bacillis, having maximum activity throughout the pH-range of 8-12, developed and sold as Esperase® by NovoZymes of Denmark.

[0090] Other suitable proteases include Alcalase® and Savinase® Relase® from Novozymes and Maxatase® from International Bio-Synthetics, Inc., The Netherlands.

[0091] The composition may additionally comprise enzymes as found in WO 01/00768. It may additionally comprise Mannanase.

[0092] Preferably enzymes are added to the compositions after the cooling step d) in a preferred method of the invention.

Suds Suppressors

[0093] Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in US-A-4,489,455 and US-A-4,489,574 and in front-loading European-style washing machines.

[0094] A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430- 447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See US-A-2,954,347. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts. Favourable anti-foaming results were obtained with fatty acid mixtures comprising lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid and behenic acid. A preferred fatty acid of this type is Prifac 5908 (trademark ex Uniqema).

[0095] The detergent compositions may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C18-C40 ketones (e.g., stearone), etc.

[0096] The preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in US-A-4,265,779.

[0097] For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine.

[0098] Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines. The compositions herein will generally comprise from 0.1% to about 5% of suds suppressor.

[0099] If high sudsing is desired, suds boosters such as the C10-C16 alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C10-C14 monoethanol and diethanol amides illustrate a typical class of such suds boosters. If desired, soluble magnesium salts such as MgCl2, MgSO4, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Chelating Agents

[0100] The liquid detergent compositions may also optionally contain one or more iron, copper and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally- substituted aromatic chelating agents and mixtures therein, all as hereinafter defined.

[0101] If utilised, these chelating agents will generally comprise from about 0.1 % to about 10% by weight of the detergent compositions herein. More preferably, if utilised the chelating agents will comprise from about 0.1 % to about 3.0% by weight of such compositions.

Polymers

[0102] The composition preferably comprises one or more polymers. Polymers can assist in the cleaning process by helping to retain soil in solution or suspension and/or preventing the transfer of dyes. Polymers can also assist in the soil removal process. Dye transfer, anti-redeposition and soil-release polymers are described in further detail below.

Dye transfer inhibitors:

[0103] Detergent compositions often employ polymers as so-called 'dye-transfer inhibitors'. These prevent migration of dyes, especially during long soak times. Any suitable dye-transfer inhibition agents may be used in accordance with the present invention. Generally, such dye-transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof.

[0104] Nitrogen-containing, dye binding, DTI polymers are preferred. Of these polymers and co-polymers of cyclic amines such as vinyl pyrrolidone (PVP), and/or vinyl imidazole (PVI) are preferred.

[0105] Polyamine N-oxide polymers suitable for use herein contain units having the following structural formula: R-AX-P; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is an aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic group or combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups, or the N-O group can be attached to both units.

[0106] Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof. The NO group can be represented by the following general structures: N(O)(R')0-3, or =N(O)(R')0-1, wherein each R' independently represents an aliphatic, aromatic, heterocyclic or alicyclic group or combination thereof; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa<10, preferably pKa<7, more preferably pKa< 6.

[0107] Any polymer backbone can be used provided the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamides, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferably 1,000 to 500,000; most preferably 5,000 to 100,000. This preferred class of materials is referred to herein as "PVNO". A preferred polyamine N-oxide is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

[0108] Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (as a class, referred to as PVPVI) are also preferred. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000, as determined by light scattering as described in Barth, et al., Chemical Analysis, Vol. 113. "Modern Methods of Polymer Characterization". The preferred PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched. Suitable PVPVI polymers include Sokalan(TM) HP56, available commercially from BASF, Ludwigshafen, Germany.

[0109] Also preferred as dye transfer inhibition agents are polyvinylpyrrolidone polymers (PVP) having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 2000,000, and more preferably from about 5,000 to about 50,000. PVP's are disclosed for example in EP-A-262,897 and EP-A-256,696. Suitable PVP polymers include Sokalan(TM) HP50, available commercially from BASF. Compositions containing PVP can also contain polyethylene glycol (PEG) having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

[0110] The amount of dye transfer inhibition agent in the composition according to the present invention will be from 0.01 to 10 %, preferably from 0.02 to 8, or even to 5 %, more preferably from 0.03 to 6, or even to 2 %, by weight of the composition.

[0111] It will be appreciated that the dye transfer inhibition agents will assist in the preservation of whiteness by preventing the migration of dyes from place to place. This preservation of whiteness assists in cleaning and counteracts the reduction in surfactants present in the wash liquor.

Anti-redeposition polymers:

[0112] Anti-redeposition polymers are typically polycarboxylate materials. Polycarboxylate materials, which can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, are preferably admixed in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight of the polymer.

[0113] Particularly suitable polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Pat. No. 3,308,067, issued Mar. 7, 1967. In the present invention, the preferred polycarboxylate is sodium polyacrylate.

[0114] Acrylic/maleic-based copolymers may also be used as a preferred component of the anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published Dec. 15, 1982, as well as in EP 193,360, published Sep. 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful polymers maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

[0115] Polyethylene glycol (PEG) can act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 3,000 to about 10,000. Polyaspartate and polyglutamate dispersing agents may also be used.

[0116] Any polymeric soil release agent known to those skilled in the art can optionally be employed in compositions according to the invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibres, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibres and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

[0117] The amount of anti redeposition polymer in the composition according to the present invention will be from 0.01 to 10 %, preferably from 0.02 to 8 %, more preferably from 0.03 to 6 %, by weight of the composition.

[0118] Also suitable are modified polyethyleneimine polymers, as disclosed for example in WO-A-0005334. These modified polyethyleneimine polymers are water-soluble or dispersible, modified polyamines. Modified polyamines are further disclosed in US-A-4,548,744; US-A-4,597,898; US-A- 4,877,896; US-A- 4,891, 160; US-A-4,976,879; US-A-5,415,807; GB-A-1,537,288; GB-A-1,498,520; DE-A-28 29022; and JP-A-06313271.

[0119] The modified ethoxylated polyamines (EPEI) are described above and are generally linear or branched poly (>2) amines. The amines may be primary, secondary or tertiary. A single or a number of amine functions are reacted with one or more alkylene oxide groups to form a polyalkylene oxide side chain. The alkylene oxide can be a homopolymer (for example ethylene oxide) or a random or block copolymer. The terminal group of the alkylene oxide side chain can be further reacted to give an anionic character to the molecule (for example to give carboxylic acid or sulphonic acid functionality).

[0120] Another particularly preferred class of polymer is polyethylene imine, preferably modified polyethylene imine. Polyethylene imines are materials composed of ethylene imine units -CH2CH2NH- 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 such as carbon dioxide, sodium bisulfite, sulfuric 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.

[0121] Preferentially, these comprise a polyethyleneimine backbone of about 300 to about 10000 weight average molecular weight; wherein the modification of the polyethyleneimine backbone is:

a) one or two alkoxylation modifications per nitrogen atom in the polyethyleneimine backbone, the alkoxylation modification comprising the replacement of a hydrogen atom by a polyalkoxylene chain having an average of about 1 to about 40 alkoxy moieties per modification, wherein the terminal alkoxy moiety of the alkoxylation modification is capped with hydrogen, a C1-C4 alkyl, an anionic group or mixtures thereof;

b) a substitution of one C1-C4 alkyl moiety and one or two alkoxylation modifications per nitrogen atom in the polyethyleneimine backbone, the alkoxylation modification comprising the replacement of a hydrogen atom by a polyalkoxylene chain having an average of about 1 to about 40 alkoxy moieties per modification wherein the terminal alkoxy moiety is capped with hydrogen, a C_1-C_4 alkyl, an anionic group or mixtures thereof; or

c) a combination thereof.

[0122] The polyethyleneimine polymer is present in the composition provided in step (a), prior to the dilution step (b), preferably at a level of between 0.01 and 25 wt%, but more preferably at a level of at least 3 wt% and/or less than 9.5 wt%, most preferably from 4 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.

[0123] Preferably, the composition comprises a dye transfer inhibition agent selected from polyvinylpyrridine N-oxide (PVNO), polyvinyl

[0124] pyrrolidone (PVP), polyvinyl imidazole, N-vinylpyrrolidone and N-vinylimidazole copolymers (PVPVI), copolymers thereof, and mixtures thereof.

Soil Release Polymers:

[0125] Generally the soil release polymers for polyester will comprise polymers of aromatic dicarboxylic acids and alkylene glycols (including polymers containing polyalkylene glycols).

[0126] The polymeric soil release agents useful herein especially include those soil release agents having:

(a) one or more nonionic hydrophilic components consisting essentially of:

(i) polyoxyethylene segments with a degree of polymerization of at least 2, or

(ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophilic segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or

(iii)a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophilic component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fibre surfaces upon deposit of the soil release agent on such surface, said hydrophilic segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or

(b) one or more hydrophobic components comprising:

(i) C3 oxyalkylene terephthalate segments, wherein, if said hydrophobic components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C3 oxyalkylene terephthalate units is about 2:1 or lower,

(ii) C4 -C6 alkylene or oxy C4 -C6 alkylene segments, or mixtures thereof,

(iii)poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or
(iv) C1 -C4 alkyl ether or C4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C1 -C4 alkyl ether or C4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C1 -C4 alkyl ether and/or C4 hydroxyalkyl ether units to deposit upon conventional polyester synthetic fibre surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fibre surface, to increase fibre surface hydrophilicity, or a combination of (a) and (b).

[0127] Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C4 -C6 alkylene hydrophobic segments include, but are not limited to, end-caps of polymeric soil release agents such as MO3 S(CH2)n OCH2 CH2 O--, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to Gosselink.

[0128] Soil release agents characterized by poly(vinyl ester) hydrophobic segments include graft copolymers of poly(vinyl ester), e.g., C1 -C6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published Apr. 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

[0129] One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Pat. No. 3,959,230 to Hays, issued May 25, 1976 and U.S. Pat. No. 3,893,929 to Basadur issued Jul. 8, 1975.

[0130] Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from DuPont) and MILEASE T (from ICI). See also U.S. Pat. No. 4,702,857, issued Oct. 27,1987 to Gosselink.

[0131] Another preferred polymeric soil release agent is a sulphonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Pat. No. 4,968,451, issued Nov. 6, 1990 to J.J. Scheibel and E. P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Pat. No. 4,711,730, issued Dec. 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Pat. No. 4,702,857, issued Oct. 27,1987 to Gosselink.

[0132] Preferred polymeric soil release agents also include the soil release agents of U.S. Pat. No. 4,877,896, issued Oct. 31,1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

[0133] If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent composition, typically greater than or equal to 0.2 wt% even from 3 wt% to 9 wt%, but more preferably they are used at greater than 1 wt%, even greater than 2 wt% and most preferably greater than 3 wt%, even more preferably greater than 5 wt%, say 6 to 8 wt% in the composition.

[0134] Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

[0135] Suitable soil release polymers are described in WO 2008095626 (Clariant); WO 2006133867 (Clariant); WO 2006133868 (Clariant); WO 2005097959 (Clariant); WO 9858044 (Clariant); WO 2000004120 (Rhodia Chimie); US 6242404 (Rhodia Inc); WO 2001023515 (Rhodia Inc); WO 9941346 (Rhodia Chim); WO 9815346 (Rhodia Inc); WO 9741197 (BASF); EP 728795 (BASF); US 5008032 (BASF); WO 2002077063 (BASF); EP 483606 (BASF); EP 442101 (BASF); WO 9820092 (Proctor & Gamble); EP 201124 (Proctor & Gamble); EP 199403 (Proctor & Gamble); DE 2527793 (Proctor & Gamble); WO 9919429 (Proctor & Gamble); WO 9859030 (Proctor & Gamble); US 5834412 (Proctor & Gamble); WO 9742285 (Proctor & Gamble); WO 9703162 (Proctor & Gamble); WO 9502030 (Proctor & Gamble); WO 9502028 (Proctor & Gamble); EP 357280 (Proctor & Gamble); US 4116885 (Proctor & Gamble); WO 9532232 (Henkel); WO 9532232 (Henkel); WO 9616150 (Henkel); WO 9518207 (Henkel); EP 1099748 (Henkel); FR 2619393 (Colgate Palmolive); DE 3411941 (Colgate Palmolive); DE 3410810 (Colgate Palmolive); WO 2002018474 (RWE-DEA MINERALOEL & CHEM AG; SASOL GERMANY GMBH); EP 743358 (Textil Color AG); PL 148326 (Instytut Ciezkiej Syntezy Organicznej "Blachownia", Pol.); JP 2001181692 (Lion Corp); JP 11193397 A (Lion Corp); RO 114357 (S.C. "Prod Cresus" S.A., Bacau, Rom.); and US 7119056 (Sasol).

[0136] Particularly preferred are combinations of relatively high levels of EPEI (>3wt% on the composition) with soil release polymers, especially, but not exclusively, if betaine is included in the surfactant system.

[0137] Combination of EPEI and soil release polymers of the above types enables increased performance at lower in wash surfactant levels compared to 1.0g/L or higher non soap surfactant wash liquors with betaine but without either EPEI or SRP. SRP performance is enhanced significantly by repeated pre-treatment. There is some evidence of a build-up effect of EPEI performance.

[0138] The most preferred soil release polymers are the water soluble/miscible or dispersible polyesters such as: linear polyesters sold under the Repel-O-Tex brand by Rhodia (Gerol), polyesters sold under the Texcare brand by Clariant, especially Texcare SRN170, and heavily branched polyesters such as those available from Sasol and described in US 7119056.

Clay Soil Removal/Anti-redeposition Agents

[0139] The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties.

[0140] Liquid detergent compositions typically contain about 0.01 % to about 5% of these agents.

[0141] One preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in US-A-4,597,898.

[0142] Other types of preferred antiredeposition agent include the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Brightener

[0143] Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the liquid detergent compositions herein. Commercial optical brighteners, which may be useful in the present invention, can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered- ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

[0144] Optical brighteners are preferably added to the water in step c) to dissolve them easily.

Fabric Softeners

[0145] Various through-the-wash fabric softeners, especially the impalpable smectite clays of US-A-4,062,647 as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in US-A-4,375,416 and US-A-4,291,071.

Bleaches

[0146] Optionally, the composition according to the present invention may contain a bleach or bleach system. This bleach or bleach system may be, for example: (a) a peroxygen bleach species alone and/or in combination with a bleach activator and/or a transition metal catalyst; and (b) a transition metal catalysts in a composition substantially devoid of peroxygen species.

[0147] Bleaching catalysts for stain removal have been developed over recent years and may be used in the present invention. Examples of transition metal bleaching catalysts that may be used are found, for example, in: WO-01/48298, WO-00/60045, WO-02/48301, WO-00/29537 and WO-00/12667. The catalyst may alternatively be provided as the free ligand that forms a complex in situ.

[0148] Bleach activators are also well known in the art. The exact mode of action of bleach activators for peroxybleach compounds is not known, but it is believed that peracids are formed by reaction of the activators with the inorganic peroxy compound, which peracids then liberate active-oxygen by decomposition. They are generally compounds which contain N-acyl or O-acyl residues in the molecule and which exert their activating action on the peroxy compounds on contact with these in the washing liquor.

[0149] Typical examples of activators within these groups are polyacylated alkylene diamines, such N,N,N1,N1-tetraacetylethylene diamine (TAED) and N,N,N1,N1-tetraacetylmethylene diamine (TAMD); acylated glycolurils, such as tetraacetylglycoluril (TAGU); triacetylcyanurate and sodium sulphophenyl ethyl carbonic acid ester.

[0150] Peroxygen bleaching agents are also well known in the art, for example, peracids (e.g., PAP), perborates, percarbonates, peroxyhydrates, and mixtures thereof. Specific preferred examples include: sodium perborate, commercially available in the form of mono- and tetra-hydrates, and sodium carbonate peroxyhydrate. Other examples of peroxyl species and activators as well as other transition metal catalyst are found in WO 02/077145.

[0151] It is also preferred to include in the compositions, a stabiliser for the bleach or bleach system, for example ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate or other appropriate organic phosphonate or salt thereof. These stabilisers can be used in acid or salt form which is the calcium, magnesium, zinc or aluminium salt form. The stabiliser may be present at a level of up to about 1 wt%, preferably from about 0.1 % to about 0.5 wt%.

[0152] Since many bleaches and bleach systems are unstable in aqueous liquid detergents and/or interact unfavourably with other components in the composition, e.g. enzymes, they may for example be protected, e.g. by encapsulation or by formulating a structured liquid composition, whereby they are suspended in solid form.

[0153] Photobleaches, including singlet oxygen photobleaches, could, also be used.

[0154] The invention will now be further described with reference to the following non limiting examples.

EXAMPLES

Example 1 - Structured water premix A

[0155] In this example we made I litre of a structured water premix. 2.5g of HCO (Thixcin ® was dissolved in 72.8g Neodol 25-7 nonionic at a temperature of 84°C. This warm HCO solution was never warmed as far as the melting point of the HCO (85 to 88°C for this material). It was added in less than 30 seconds to 572g demineralised water at 65°C stirring with a Heidolph stirrer at 250 rpm for 10 mins and then reducing stirring speed for 30 minutes while maintaining the temperature at 65°C before cooling to room temperature at a rate of 2°C per minute.

[0156] The structured water premix so formed was stable and could be kept until needed for use in formulation of concentrated heavy-duty aqueous laundry liquids. The premix had a low shear viscosity of 625 Pa.s.

Example 2 - Structured water premix B

[0157] Example 1 was repeated except that the amount of nonionic used was reduced to 70g and the amount of water was increased to 800g. The HCO nonionic solution was added to the water at a temperature of 83°C. Cooling to room temperature commenced immediately. The structured water premix formed had a low shear viscosity of 415 Pa.s; and a viscosity at 21s-1 of 0.0957 Pa.s.

Example 3 - Structured water premix C

[0158] In a further variation of example 1 the HCO nonionic solution was prepared in the same way but instead of adding it to hot water it was added to a solution made up by neutralising 48.5g LAS acid, then 17g Prifac 5908 fatty acid by addition to a solution of caustic in the water. To this fully neutralised LAS soap solution was added 24.2g SLES solids under stirring at 250 rpm. To this solution, the HCO/nonionic solution was then added at 83°C. It was held at a temperature of 65°C for 30 minutes before cooling to room temperature to form a structured water premix with very good structuring.

Example 4

[0159] Structured water premix C as prepared in example 3 was used to structure a low active and medium water level liquid comprising a high level of polymers with composition as shown in table 1.

[0160] The yield stress before polymer addition was 0.6 Pa. After polymers were added it dropped to 0.5 Pa. Some 5mm diameter visual film cues made of a modified polyvinyl alcohol polymer were mixed in at low shear. The liquid was subsequently stored for 12 weeks at 37°C. The liquid passed as storage stable under these conditions and no creaming or sedimentation of the film cues was observed.

Example 5

[0161] Example 4 was repeated but using structured water premix A as prepared in Example 1. The yield stress before polymer or visual cues addition was > 0.5 Pa.

Table 1 composition of Examples 4 & 5

Raw Material	**% as 100%**
Demin WATER	57.20
Opacifier	0.100
MPG	15.00
NaOH	0.74
Neodol 25-7	7.28
LAS acid	4.85

(continued)

Raw Material	**% as 100%**
Optical brightener	0.10
Prifac 5908	1.70
Thixcin R (hydrogenated castor oil)	0.25
SLES 3EO	2.42
Dequest 2066	0.50
Colour	0.00078
Enzymes	1.89
Perfume	1.39
Proxel	0.02
EPEI (polymer)	3.10
Betaine	0.86
PET/POET Soil release polymer (polymer)	2.10
Visual cue	0.50
TOTAL	100.0

Example 6

[0162] The process was used to structure another type of low active liquid that had proved difficult to structure using the prior art processes (Table 2). We used structured water premix B comprising the HCO, nonionic and water from table 2 prepared as in example 2 above.

[0163] The yield stress of the resulting liquid was 0.8 Pa and it was found to be capable of suspending visible (5mm diameter) film cues made of a modified polyvinyl alcohol polymer added by low shear mixing. The liquid was stored for 12 weeks at 37°C. The liquid was passed as storage stable under these conditions and no creaming or sedimentation of the film cues was observed.

Table 2 - Composition of Liquid for Example 6

Raw Material	**% (as 100% active)**
Water	80.18
Mono propylene glycol (MPG)	1.00
Optical Brightener	0.020
NaOH (47%)	0.27
Nonionic Neodol 25-7	7.00
SLES 3EO	7.00
Prifac 5908	1.50
Cationic Praepagen HY	1.00
Proxel GXL	0.0160
Dequest 2066 (Heptasodium DTPMP)	1.00
Enzymes	0.38
Colour	0.000495
PERFUME	0.39

(continued)

Raw Material	**% (as 100% active)**
HCO	0.25

Comparative Example A showing failure to structure using prior art process

[0164] An attempt was made to structure the liquid of example 4 (table 1) using a process Route (adapted from WO2010/034736). To the main mixer was added demineralised water (35°C), glycerol, MPG, Optical brightener, NaOH (47%), TEA, Citric Acid (50%), fatty acid, and LAS acid, they were mixed and heated to 65°C.

[0165] Separately a pre-mix of HCO in the Neodol was prepared by heating the mixture to 70 -75°C. The clear HCO solution was then added to the main mixer and mixed in. To this was added SLES 3EO, Dequest 2066, adjusted the pH to 7.5 and the mixture was cooled slowly to 30°C Then we added dyes, microcapsules, perfume, and enzymes to obtain the final product.

[0166] From optical microscopy (10x mag) it could be seen that there was very poor structure. The crystallisation was different from that desired with large spaces/voids. Due to the lack of structure this liquid did not have a yield stress and was incapable of suspending microcapsules or visual cues. The temperature of the main mix was adjusted down to 60 and up to 70°C but without any improvement for the structuring.

Comparative Examples Band C

[0167] These examples show the effect of heating the HCO above its melting point compared with the inventive process when it is kept below its melting point at all times. For example B and C Example 1 was repeated except that the HCO was heated to a temperature in excess of 90°C. For Example B it was then crash cooled for 15 minutes using ice and low shear mixing. For example C it was cooled over about 3 hours, again using low shear mixing. Whereas the Structured water premix made by keeping the HCO below its melting point had the expected structuring and viscosity the crash cooled overheated example B failed to make effective structuring and Example C gave a thick paste. Neither is suitable for use to generate the liquids in accordance with Examples 4 to 6.

Example	**Comments**	**Eta0 / Pa·s**
1	Good structure	625
B	thin liquid	125
C	paste	150000

Claims

1. A process to manufacture a structured aqueous liquid detergent composition comprising 7 to 40 wt% surfactant, of which at least 2 wt% is nonionic surfactant, optionally, and preferably, 4 to 30 wt% water soluble polymers, and 0.1 to 0.4 wt% Hydrogenated Castor oil (HCO) external structurant, the process comprising the step of formation of a structured water premix which is then mixed in an amount of 40 to 80 vol% with an unstructured liquid comprising further surfactant and making up 20 to 60 vol% of the liquid detergent composition, **characterised in that** the structured water premix is formed by:

   a) adding 0.1 to 0.4, preferably about 0.25 wt%, HCO (based on the liquid detergent composition), to 2 to 8 wt% surfactant (based on the liquid detergent composition),
   b) heating this mixture to 70 to 84°C to prepare a molecularly dispersed transparent solution of a minor part of HCO in a major part of surfactant, then
   c) adding the solution from step b) to water at a temperature of at least 55°C, preferably at least 65°C, even at least 75°C optionally further comprising anionic surfactant, but not base, to form a warm structured water premix precursor and allowing this precursor to cool to below 40°C to form a structured water premix;
   d) optionally aging the structured water premix prior to its combination with the unstructured liquid comprising further surfactant and
   e) the optional further addition of additional detergent liquid ingredients, preferably including 4 to 30 wt% water

soluble polymers to form an externally structured aqueous detergent composition, with the proviso that at no time during the process does the temperature of the HCO exceed its melting point.

2. A process according to claim 1, in which the surfactant used to dissolve the HCO in step b) is selected from anionic surfactant, nonionic surfactant, cationic surfactant, soap and mixtures thereof.

3. A process according to any preceding claim in which the amount of nonionic is at least 15 times as much as the amount of HCO in the premix.

4. A process according to any preceding claim in which the premix formed in step c) is maintained above 55°C, preferably at least 60°C, more preferably at least 65°C for a holding period of at least 15 minutes before it is cooled.

5. A process according to any preceding claim in which the cooling rate is between 1.5 and 2.5°C per minute.

6. A process according to any preceding claim in which 4 to 30% polymers are added in step e) and the polymers comprise water soluble polymers selected from ethoxylated polyethylene imine, soil release polymers and mixtures thereof.

7. A process according to any preceding claim in which the volume of the structured water premix is greater than the volume of the remainder of the composition.

8. A process according to any preceding claim in which particles are suspended in the liquid.

9. A process according to any preceding claim in which the suspended particles are selected from perfume encapsulates less than 100 micron diameter, and visible visual cues greater than 2 mm diameter and mixtures thereof.

Patentansprüche

1. Verfahren zur Herstellung einer strukturierten, wässrigen, flüssigen Detergenszusammensetzung, die 7 bis 40 Gew.-% oberflächenaktives Mittel, von dem es sich bei mindestens 2 Gew.-% um ein nicht-ionisches oberflächenaktives Mittel handelt, gegebenenfalls und vorzugsweise 4 bis 30 Gew.-% wasserlöslichens Polymeres und 0,1 bis 0,4 Gew.-% hydriertes Rizinusöl (HCO) als externes Strukturierungsmittel umfasst, wobei das Verfahren die Stufe der Bildung eines strukturierten Wasservorgemisches umfasst, das anschließend in einer Menge von 40 bis 80 Vol.-% mit einer unstrukturierten Flüssigkeit, die weiteres oberflächenaktives Mittel umfasst und 20 bis 60 Vol.-% der flüssigen Detergenszusammensetzung ausmacht, vermischt wird, wobei das Verfahren **dadurch gekennzeichnet ist, dass** das strukturierte Wasservorgemisch gebildet wird durch:

   a) Zugeben von 0,1 bis 0,4 Gew.-% und vorzugsweise von etwa 0,25 Gew.-% HCO (bezogen auf die flüssige Detergenszusammensetzung) zu 2 bis 8 Gew.-% oberflächenaktivem Mittel (bezogen auf die flüssige Detergenszusammensetzung),
   b) Erwärmen dieses Gemisches auf 70 bis 84°C, um eine molekular dispergierte, transparente Lösung eines untergeordneten Anteils an HCO in einem übergeordneten Anteil an oberflächenaktivem Mittel herzustellen, anschließend
   c) Zugeben der Lösung von Stufe b) zu Wasser bei einer Temperatur von mindestens 55°C, vorzugsweise von mindestens 65°C und insbesondere von mindestens 75°C, das gegebenenfalls ferner ein anionisches oberflächenaktives Mittel, jedoch keine Base umfasst, zur Bildung einer warmen, strukturierten Wasservorgemisch-Vorstufe und Abkühlenlassen dieser Vorstufe auf eine Temperatur unter 40°C zur Bildung eines strukturierten Wasservorgemisches,
   d) gegebenenfalls Altern des strukturierten Wasservorgemisches vor dessen Vereinigung mit der unstrukturierten Flüssigkeit, die weiteres oberflächenaktives Mittel umfasst, und
   e) gegebenenfalls weitere Zugabe von zusätzlichen Bestandteilen der Detergensflüssigkeit, die vorzugsweise 4 bis 30 Gew.-% wasserlösliche Polymere umfassen, zur Bildung einer extern strukturierten wässrigen Detergenszusammensetzung, mit der Maßgabe, das zu keinem Zeitpunkt während des Verfahrens die Temperatur des HCO dessen Schmelzpunkt übersteigt.

2. Verfahren nach Anspruch 1, wobei das zum Lösen des HCO in Stufe b) verwendete oberflächenaktive Mittel aus anionischen oberflächenaktiven Mitteln, nicht-ionischen oberflächenaktiven Mitteln, kationischen oberflächenakti-

ven Mitteln, Seifen und Gemischen davon ausgewählt ist.

3. Verfahren nach einem der vorstehenden Ansprüche, wobei die Menge des nicht-ionischen Mittels mindestens das 15-fache der Menge des HCO im Vorgemisch beträgt.

4. Verfahren nach einem der vorstehenden Ansprüche, wobei das in Stufe c) gebildete Vorgemisch oberhalb von 55°C, vorzugsweise bei mindestens 60°C und insbesondere bei mindestens 65°C für eine Haltezeit von mindestens 15 Minuten gehalten wird, bevor es abgekühlt wird.

5. Verfahren nach einem der vorstehenden Ansprüche, wobei die Abkühlgeschwindigkeit 1,5 bis 2,5°C pro Minute beträgt.

6. Verfahren nach einem der vorstehenden Ansprüche, wobei 4 bis 30% Polymere in Stufe e) zugesetzt werden und die Polymeren wasserlösliche Polymere umfassen, die aus ethoxyliertem Polyethylenimin, schmutzfreisetzenden Polymeren und Gemischen davon ausgewählt sind.

7. Verfahren nach einem der vorstehenden Ansprüche, wobei das Volumen des strukturierten Wasservorgemisches größer ist als das Volumen der restlichen Zusammensetzung.

8. Verfahren nach einem der vorstehenden Ansprüche, wobei Teilchen in der Flüssigkeit suspendiert sind.

9. Verfahren nach einem der vorstehenden Ansprüche, wobei die suspendierten Teilchen ausgewählt sind aus verkapselten Duftstoffen mit einem Durchmesser von weniger als 100 µm und sichtbaren Signalprodukten mit einem Durchmesser von mehr als 2 mm und Gemischen davon.

Revendications

1. Procédé de fabrication d'une composition de détergent liquide aqueuse structurée comprenant de 7 à 40 % en poids de tensioactif, dont au moins 2 % en poids sont un tensioactif non ionique, éventuellement, et de préférence, de 4 à 30 % en poids de polymères solubles dans l'eau, et de 0,1 à 0,4 % en poids de structurant externe d'huile de ricin hydrogénée (HCO), le procédé comprenant l'étape de formation d'un prémélange d'eau structuré qui est ensuite mélangé dans une quantité de 40 à 80 % en volume avec un liquide non structuré comprenant plus de tensioactif et constituant de 20 à 60 % en volume de la composition de détergent liquide, **caractérisé en ce que** le prémélange d'eau structuré est formé :

a) en ajoutant de 0,1 à 0,4, de préférence environ 0,25 % en poids, de HCO (rapporté à la composition de détergent liquide), à de 2 à 8 % en poids de tensioactif (rapporté à la composition de détergent liquide),
b) en chauffant ce mélange à de 70 à 84°C pour préparer une solution transparente moléculairement dispersée d'une partie mineure de HCO dans une partie majeure de tensioactif, puis
c) en ajoutant la solution de l'étape b) à de l'eau à une température d'au moins 55°C, de préférence d'au moins 65°C, encore mieux d'au moins 75°C comprenant éventuellement de plus un tensioactif anionique, mais pas une base, pour former un précurseur de prémélange d'eau structuré chaud et en laissant ce précurseur refroidir en dessous de 40°C pour former un prémélange d'eau structuré ;
d) en faisant éventuellement vieillir le prémélange d'eau structuré avant sa combinaison avec le liquide non structuré comprenant plus de tensioactif et
e) en ajoutant de plus éventuellement des ingrédients liquides de détergents supplémentaires, comprenant de préférence de 4 à 30 % en poids de polymères solubles dans l'eau pour former une composition de détergent aqueuse structurée de manière externe, à condition qu'à aucun moment pendant le procédé la température du HCO excède son point de fusion.

2. Procédé selon la revendication 1, dans lequel le tensioactif utilisé pour dissoudre le HCO dans l'étape b) est choisi parmi un tensioactif anionique, un tensioactif non ionique, un tensioactif cationique, un savon et des mélanges de ceux-ci.

3. Procédé selon l'une quelconque des revendications précédentes, dans lequel la quantité de non ionique est d'au moins 15 fois celle de la quantité de HCO dans le prémélange.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le prémélange formé dans l'étape c) est maintenu au-dessus de 55°C, de préférence au moins 60°C, encore mieux au moins 65°C pendant une durée de maintien d'au moins 15 minutes avant qu'il soit refroidi.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la vitesse de refroidissement est de 1,5 à 2,5°C par minute.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel de 4 à 30 % de polymères sont ajoutés dans l'étape e) et les polymères comprennent des polymères solubles dans l'eau choisis parmi une polyéthylène imine éthoxylée, des polymères libérant la saleté et des mélanges de ceux-ci.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le volume du prémélange d'eau structuré est supérieur au volume du reste de la composition.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel des particules sont mises en suspension dans le liquide.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel les particules mises en suspension sont choisies parmi des capsules de parfum de diamètre inférieur à 100 microns, et des marques visuelles visibles de diamètre supérieur à 2 mm et des mélanges de celles-ci.

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