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(54) Structuring detergent liquids with hydrogenated castor oil

(57) A process to manufacture an externally structured aqueous liquid detergent composition comprising 7 to 40 wt% surfactant, of which at least 2 wt% is nonionic surfactant, optionally 2 to 30 wt% water soluble polymer, and more than 0.4 to 2.5 wt% Hydrogenated Castor oil (HCO) external structurant, the process comprising the step of formation of a structured water premix which is then mixed with an unstructured liquid and optional further components to form the externally structured liquid detergent composition, characterised in that the structured water premix is formed by:
a) mixing more than 0.4 to 2.5 wt% HCO (based on the liquid detergent composition), with 2 to 10 wt% nonionic surfactant (based on the liquid detergent composition),
b) heating this mixture to 65 to 84°C to prepare a solution of HCO in nonionic surfactant, then
c) mixing the isotropic solution from step b) with a liquid comprising water, and optionally further comprising anionic surfactant, to form a hot structured water premix precursor and holding this premix precursor at a temperature of at least 55°C for from 5 to 30 minutes before allowing the temperature to drop to below 40°C to form a structured water premix.

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Description

TECHNICAL FIELD

[0001] This invention relates to a process for the structuring of aqueous liquid 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] No explanation is given for how HCO could be added any other way than molten and it is believed that although application of heat is optional in step 3 the addition of the structuring agent to a system in molten form to enable emulsification of this liquid 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. 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.

[0014] 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.

[0015] 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 an anionic emulsifier, 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 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.

[0016] It is an object of the present invention to find an alternative process to form an HCO premix that solves these problems and allows the formulation of compositions structured with high levels of HCO, for instance levels greater than 0.4 wt%, even greater than 0.5 wt%. Such higher levels of HCO are desirable for suspending duty, particularly when viscosity reducing polymers are present in the composition.

SUMMARY OF THE INVENTION

[0017] According to the present invention there is provided a process to manufacture an externally structured aqueous liquid detergent composition comprising 7 to 40 wt% surfactant, of which at least 2 wt% is nonionic surfactant, optionally 2 to 30 wt% water soluble polymer, and more than 0.4 to 2.5 wt% Hydrogenated Castor oil (HCO) external structurant, the process comprising the step of formation of a structured water premix which is then mixed with an unstructured liquid and optional further components to form the externally structured liquid detergent composition, characterised in that the structured water premix is formed by:

a) mixing more than 0.4 to 2.5 wt% HCO (based on the liquid detergent composition), with 2 to 10 wt% nonionic surfactant (based on the liquid detergent composition),
b) heating this mixture to 65 to 84°C to prepare a solution of HCO in nonionic surfactant, then
c) mixing the isotropic solution from step b) with a liquid comprising water, and optionally further comprising anionic surfactant, to form a hot structured water premix precursor and holding this premix precursor at a temperature of at least 55°C for from 5 to 30 minutes before allowing the temperature to drop to below 40°C to form a structured water premix.

[0018] Preferably the hot structured water premix in step c) is held at a temperature of at least 60°C, most preferably about 65°C. The temperature must be kept below the melting point of HCO (85°C plus) or the crystal growth will not proceed effectively and poor structuring will result. Provided this rule is obeyed heat generated from neutralisation of surfactants and formation of any soap does not appear detrimental to maintenance of structure.

[0019] The nonionic surfactant used to dissolve the HCO in step b) is preferably used alone, but it may be used in admixture with anionic surfactant, cationic surfactant and/or soap. Of these anionic surfactant is preferred. Ion pairs of anionic and cationic surfactants are useful.

[0020] The amount of nonionic in the structured water premix is preferably more than the amount of HCO, Preferably it is at least 2 times, more preferably at least 4 times, even more preferably at least 8 times, and even up to 15 times or more as much as the amount of HCO in the premix. Viscosity build appears to be related to relative levels of nonionic and HCO present in the premix although the mode of addition to the main mix and the way the structured water premix temperature is controlled before addition can also affect the viscosity build.

[0021] 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 84°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 undesirable seeding occurs and the HCO is not maintained in solution. If the water temperature is too low (<55°C) creaming and phase separation occur in the final liquid. The preferred water temperature is 60 to 70°C preferably about 65°C.

[0022] The amount of water affects the viscosity of the structured water premix. It needs to be greater than 2 times the weight of HCO plus nonionic and is even more preferably greater than 4 times the weight of nonionic plus HCO. Thus the level of water used in the premix is in the range 2 to 30 times the level of HCO in the premix. It is possible to use all of the available nonionic in the premix. Use of all the available free water is possible too, but it may be desirable, or even necessary, to retain some water for formation of the main mix, especially if the process is configured to make the main mix before late addition of the structured water premix.

[0023] The premix formed in step c) may be maintained above 55°C for a holding period of longer than 15 minutes, e.g. as long as 30 minutes before it is cooled. However, 15 minutes has been found to be long enough in most cases. This holding period 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 2 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 thins the liquid to make it difficult to develop a rheology suitable for suspending duty, the compositions made using the process of the invention with greater than 0.4 wt% HCO retain acceptable structuring properties. The water soluble polymers preferably comprise ethoxylated polyethylene imine and/or other anti redeposition polymers and/or soil release polymers as described below.

[0025] The process is particularly useful for structuring compositions comprising less than 40 wt% surfactant, even more preferably less than 35 wt% surfactant, as they have proved problematic to structure effectively using a prior art 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 and is especially useful when the polymers have the effect of reducing the low shear viscosity of the liquid.

[0026] The main utility of the HCO structuring system is for suspending duty. The components to be suspended may range from invisible microcapsules, for example perfume encapsulates, to visible visual cues, for example cues made from film material or large capsule type visual cues with a diameter of at least 2mm.

[0027] We have found that when formulating compositions comprising viscosity reducing polymers the level of HCO must be increased to greater than 0.4 wt% in order to achieve the required rheological profile and suspending duty. The process described in our copending EP10003640 has therefore been adapted to allow use of these higher levels of HCO in the composition. In particular this modified process facilitates the use of from more than 0.4 to 2.5% HCO in the composition, preferably from 0.41 to 2.5 wt%, more preferably from 0.5 to 2.1 wt% and most preferably from 0.6 to 1.5 wt% HCO.

[0028] The viscosity of the structured water premix formed in step c) is preferably at most 200 cp.

[0029] 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

[0030] 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 2 to 30 wt% water soluble polymers which thin the composition and work against the normal structuring effect of HCO.

[0031] 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.

[0032] Surprisingly by using the process of the invention it is possible to form stable 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 having greater than 0.4% HCO which gives them the required rheology and in particular the ability to suspend solid materials such as visual cues and microcapsules. The structured fabric cleaning compositions comprising high levels of 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) and thereby to provide consumers uniform fragrance delivery in every dose.

[0033] The process facilitates stable thickened and suspending detergent formulations that include cleaning polymers, including anti redeposition polymers, soil release polymers and dye transfer inhibition polymers. Particular polymers that require inclusion of the higher levels of HCO afforded by the process of the present invention are EPEI and polyester soil release polymers. Addition of these polymers reduces low shear viscosity to 0.1 Pa.s, or even as low as 0.001 Pa.s, due to polymer surfactant interactions between cleaning polymers/surfactant and structurant. 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 shear viscosities 50 to 10 000 Pas 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 in order to obtain consistent suspending duty (i.e. the liquid has a yield stress).

[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, if any are present. Most preferred is to use a process where the structured water premix is made from HCO, nonionic surfactant and water only.

[0036] The structured water premix is mixed with other components to manufacture a full structured liquid detergent. This addition may take place at various points in the process flow for the manufacture of a full liquid. It can be added as the first ingredient or it can be added later in the process to an unstructured liquid formed from some of the other ingredients and preferably including the thinning polymers. Only heat sensitive ingredients such as enzymes and perfume are desirably added after the structured water premix has been mixed with the unstructured part of the composition. However, as the structured water premix may be added cool it may even be added after those ingredients if so desired. This provides the advantage of considerable 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, comprising, but not limited to, 2 to 10% nonionic surfactant. It is preferably added to the warm (e.g. 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 10, even 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] It can be even more advantageous if the structured water premix is maintained above 55°C, more preferably above 60°C, for at least 10, even at least 15 minutes 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 16 hours using slow cooling to 1 hour using quench cooling.

[0040] In addition to the essential nonionic 'solvent' for the HCO, which includes mixtures of nonionic surfactants, some anionic surfactants may additionally be used. 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 premix does not contain any alkali, for example caustic, if it would affect the structuring; this can easily be checked by a simple test. Subject to this limitation anionic surfactants may optionally be used in admixture with cationic surfactants and/or soap (neutralised fatty acid).

Liquid detergent compositions

[0041] The process enables the production of liquid detergent compositions comprising high levels of viscosity reducing polymer and HCO present at a concentration of from more than 0.4% to 2.5 wt% by weight of the total composition. Preferably, the concentration of HCO oil is from 0.41 to 2.5% by weight, more preferably 0.5 to 2 wt% and even more preferably from 0.6 to 1.5%.

[0042] If the concentration of HCO is too low, the structured liquid cannot stably suspend solid or gaseous particles in the formulation. The inclusion of high levels of viscosity reducing polymer, in particular EPEI and most particularly the nonionic EPEI known as PEI(600)20EO and sold under the name Sokalan HP 20 by BASF generates a reduction in composition viscosity that may be offset by use of the relatively high levels of HCO in the compositions made possible by use of the process of the invention. Suitably the composition comprises more than 2 wt% of nonionic EPEI, preferably more than 2.5 wt% and even more preferably more than 3 wt%.

[0043] Suitable modified polyethyleneimine polymers, are 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.

[0044] 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).

[0045] Preferably, the concentration of surfactants in the liquid detergent composition made according to the process of the invention is from 7 to 40 wt%, more preferred from 10 to 35 wt%, and most preferably from 15 to 30 wt% of the total composition.

[0046] The liquid cleaning compositions 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.

[0047] Whilst the composition made by the method 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 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

[0048] The liquid detergent compositions obtainable 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 made using the process 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 or yield stress. Typical yield stresses for liquids according to the invention are in the range 0.1 to 0.8 Pa.

[0049] Pourable liquid detergent compositions made according to the invention preferably have a pouring viscosity of 300 to 1000 mPa.s, more preferably not more than 800 mPa.s at 21 s^{-1}.

[0050] 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. Furthermore suspended particles will remain suspended and the formulation undergoes minimal colour change, even in the presence of enzymes, including pectate lyase.

[0051] The compositions may be provided in a bottle for multidose use. They may alternatively be supplied as unit dose formulations in a suitable container, for example a polymer film pouch. The non Newtonian rheology of the contained liquid having the advantages already taught in the prior art for such unit dose formats.

Hydrogenated Castor Oil

[0052] 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

[0053] 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 20 wt% water, especially more than 35 wt% water and up to 60, even 90 wt% water.

Surfactants

[0054] The liquid detergent compositions made in accordance with the process 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 surfactant, preferably selected from anionic, nonionic, cationic, zwitterionic active detergent materials or mixtures thereof.

[0055] 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 tensile Taschenbuch', H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

[0056] In addition to the surfactants mentioned above, a preferred ingredient in the liquid detergent composition made using the invention is soap (salt of fatty acid). Preferably the soap is formed by neutralisation of 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. 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.

[0057] The amount of fatty acid will vary depending on the particular characteristics desired in the final liquid detergent composition. Preferably 0 to 30 wt%, more preferably 1 to 20 wt% most preferably 2 to 10 wt% of fatty acid is present in the pre-neutralised liquid detergent composition.

[0058] Mixtures of synthetic anionic and nonionic surfactants are especially useful in a liquid detergent composition made according to the invention.

[0059] 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 in which 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 di-alkanolamide 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 composition of the invention are C12-C15 primary, linear alcohols with on average 3 to 9 ethylene oxide groups.

[0060] A preferred 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.

[0061] 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.

[0062] 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.

[0063] 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 linear alkylbenzene sulphonate (LAS), alcohol ethoxy-ether sulphate sodium salt (AES), particularly SLES, and a C12-C15 primary ethoxylated alcohol 3-9 EO ethoxylate nonionic.

[0064] Preferred surfactant systems are mixtures of synthetic anionic with nonionic detergent active materials and soap, additionally with cationic or amphoteric surfactant, preferably amphoteric. 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.

[0065] Preferred detergent compositions also comprises a cationic surfactant or an amphoteric surfactant, wherein the cationic or amphoteric surfactant is present in a concentration of 1 to 20 wt%, preferably 2 to 15 wt% more preferably 3 to 12 wt% of the total surfactant.

[0066] 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.

[0067] 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

[0068] The detergent compositions can further comprise a variety of optional ingredients including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, etc.

Carriers

[0069] 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-, tripropylene 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

[0070] One or more detergency builders may 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 HCO.

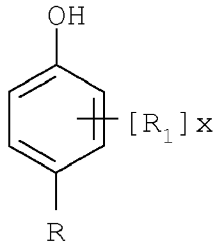
[0071] Examples of suitable organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates, carboxymethyloxysuccinates, carboxymethyloxymalonates, ethylene diamine-N,N-disuccinic acid salts, 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.

[0072] 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

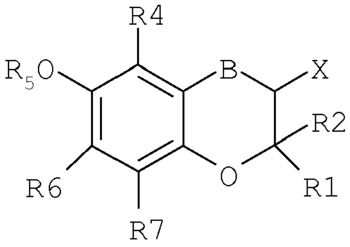
[0073] The liquid detergent compositions obtainable by the method according to the present invention preferably comprise from 0.005 to 2% by weight of an anti-oxidant. Preferably, the anti-oxidant is present at a concentration in the range of 0.01 to 0.08% by weight.

[0074] 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 branched 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).

[0075] 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.

[0076] 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.

[0077] Preservatives, such as Proxel may advantageously be included. They may be added to the water in step c).

Fragrances

[0078] The liquid detergent compositions obtainable by the method according to the present invention preferably comprise from 0.001 to 3 wt% of the total composition of a perfume composition, preferably from 0.01 to 2 wt% of the total composition. Said perfume composition preferably comprises at least 0.01 wt% based on the liquid composition 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 wt% of the perfume component.

[0079] At least part of the perfume component may advantageously comprise encapsulated fragrances like perfume microcapsules. The entirely 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).

[0080] In the context of the present invention, core-in-shell microcapsules preferably have a $d_{4,3}$ average particle size of from 1 to 100 micrometer.

[0081] 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.

[0082] 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.

[0083] Other patent applications specifically relating to use of melamine-formaldehyde core-in-shell microcapsules suitable for use in the liquids made according tot the present invention are WO-A-98/28396, WO02/074430, EP-A-1 244 768, US-A-2004/0071746 and US-A-2004/0142868.

[0084] Preferably, perfume is added to the compositions after the premix is added to the main mix and after the liquid has been cooled. 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

[0085] '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 present invention include proteases, amylases, cellulases, peroxidases, and mixtures thereof, of any suitable origin, such as vegetable, animal bacterial, fungal and yeast origin. Preferred cocktails or mixtures are selected according to 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.

[0086] Enzymes are normally incorporated into the 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 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 wt% of enzymes.

[0087] Protease enzymes are usually present in enzyme 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.

[0088] Other suitable proteases include Alcalase® and Savinase® Relase® from Novozymes and Maxatase® from International Bio-Synthetics, Inc., The Netherlands.

[0089] The composition may additionally comprise enzymes as found in WO 01/00768. It may additionally comprise Mannanase.

[0090] Preferably enzymes are added to the compositions after they have been cooled to below 40°C.

Suds Suppressors

[0091] Compounds for reducing or suppressing the formation of suds can be incorporated into the liquids. 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.

[0092] 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).

[0093] The detergent liquids 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.

[0094] 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.

[0095] 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.

[0096] 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 wt% of suds suppressor.

[0097] If high sudsing is desired, suds boosters such as the C10-C16 alkanolamides or amine oxides can be incorporated into the compositions, typically at 1%- 10 wt% levels. The C10-C14 monoethanol and diethanol amides illustrate a typical class of such suds boosters. If desired, soluble magnesium salts such as $MgCl_2$, $MgSO_4$, and the like, can be added at levels of, typically, 0.1 %-2 wt%, to provide additional suds and to enhance grease removal performance.

Chelating Agents

[0098] The liquid detergent compositions herein 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.

[0099] 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 w% by weight of such compositions. Preferred chelating agents are available under the DEQUEST name. For example Dequest® 2066 and Dequest® 2010.

Polymers:

[0100] The composition preferably comprises one or more polymers, especially polymers that result in a thinning of the composition. 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:

[0101] 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.

[0102] 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.

[0103] 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.

[0104] Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof. The N-O 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.

[0105] 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.

[0106] 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.

[0107] 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. PVPs 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.

[0108] The amount of dye transfer inhibition agent in the composition according to the present invention will be from 0.01 to 10 wt%, preferably from 0.02 to 8wt%, or even to 5 wt%, more preferably from 0.03 to 6 wt&, or even to 2 wt%, of the composition. 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:

[0109] 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 methylene-malonic 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 wt% of the polymer.

[0110] 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.

[0111] 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 0 terpolymer of acrylic/maleic/ vinyl alcohol.

[0112] 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.

[0113] 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 hydrophilise 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.

[0114] 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 wt%, of the composition.

[0115] A particularly preferred class of polymer are the ethoxylated polyethylene imines, also termed 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.

[0116] 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, 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 C1-C4 alkyl or mixtures thereof; or

c) a combination thereof.

[0117] Modified, especially ethoxylated, polyethyleneimine polymer (EPEI) is preferably present in the composition at a level of between 0.01 and 25 wt%, but more preferably at a level of at least 2 wt% and/or less than 9.5 wt% , most preferably from 3 to 9 wt% and with a ratio of EPEI to non-soap surfactant of from 1:2 to 1:7, preferably from 1:3 to 1:6, or even to 1:5.

[0118] Preferably, the composition according to the present invention comprises a dye transfer inhibition agent selected from polyvinylpyrridine N-oxide (PVNO), polyvinyl pyrrolidone (PVP), polyvinyl imidazole, N-vinylpyrrolidone and N-vinylimidazole copolymers (PVPVI), copolymers thereof, and mixtures thereof.

Soil Release Polymers:

[0119] Generally the soil release polymers for polyester will comprise polymers of aromatic dicarboxylic acids and alkylene glycols (including polymers containing polyalkylene glycols).

[0120] 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 therein,

(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).

[0121] 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.

[0122] 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).

[0123] 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.

[0124] 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.

[0125] 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.

[0126] Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl 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. 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.

[0127] 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); US 6242404 (Rhodia); WO 2001023515 (Rhodia); WO 9941346 (Rhodia); 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).

[0128] Particularly preferred are combinations of relatively high levels of EPEI (>2 wt% on the composition) with soil release polymers (SRP), especially, but not exclusively, if betaine is included in the surfactant system.

[0129] 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.

[0130] The most preferred soil release polymers are the water soluble/miscible or dispersible polyesters such as: linear nonionic polyesters sold under the Repel-0-Tex brand by Rhodia (Gerol), nonionic polyesters sold under the Texcare brand by Clariant, especially Texcare SRN170, and branched nonionic polyesters such as those available from Sasol and described in US 7119056.

Clay Soil Removal/Anti-redeposition Agents

[0131] The compositions of the present invention can also optionally contain water- soluble ethoxylated amines having clay soil removal and antiredeposition properties. Liquid detergent compositions typically contain about 0.01 % to about 5 wt% of these agents.

[0132] Other types of preferred antiredeposition agent include the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Brightener

[0133] 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, dibenzothiphene-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).

Fabric Softeners

[0134] 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

[0135] The suspending powder of the HCO thickened liquid allows the option to include in the composition solid phase bleach or bleach system components. 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.

[0136] The 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.

[0137] 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.

[0138] 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.

[0139] Typical examples of activators within these groups are polyacylated alkylene diamines, such N,N,N1N,1-tetraacetylethylene diamine (TAED) and N,N,N1,N1- tetraacetylmethylene diamine (TAMD); acylated glycolurils, such as tetraacetylgylcoluril (TAGU); triacetylcyanurate and sodium sulphophenyl ethyl carbonic acid ester.

[0140] 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.

[0141] 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% by weight, preferably from about 0.1 % to about 0.5% by weight.

[0142] Photobleaches, including singlet oxygen photobleaches, could also be used.

[0143] The invention will now be further described with reference to the following non limiting examples.

EXAMPLES

[0144] In the examples the following materials were used:

HCO	is Thixcin R - Hydrogenated castor oil from Elementis
Nonionic	is Neodol 25-7 C12 - 15 alcohol ethoxylated with 7 moles ethylene oxide ex Shell Chemicals
LAS acid	is acid form of C12-14 linear alkylbenzene sulphonate
SLES 3EO	is C12 -13 alcohol 3-ethoxylate sulphate, Na salt
Fatty acid	is Prifac 5908 C12-18 hardened Lauric Fatty Acid ex Croda
HEDP	is Dequest 2010 Hydroxyl ethylidene (1, 1-diphosphonic acid) ex Thermphos
TEA	is triethanolamine
MEA	is monoethanolamine
EPEI	is PEI(600)E020 - Sokalan® HP20 ex BASF
Perfume	is a free oil pefume
Fluorescer	is Tinopal 5BM GX ex Ciba
Opacifier	is Acusol OP301 ex Dow
MPG	is Monopropylene glycol

Examples 1 to 4 and Comparative example A - Structured water premixes

[0145] We made a range of structured water premixes with different HCO to Nonionic ratios as shown in Table 1 and designed to deliver different amounts of HCO external structurant to the final detergent liquid. The premixes were made by dissolving HCO with agitation in the stated amount of Nonionic at a temperature of 75°C in a fume cupboard. In each case this isotropic premix represented the full amount of the HCO and Nonionic for the final composition (ratio nonionic to HCO).

Table 1

Example	Amount of HCO (final liquid)	Ratio Nonionic:HCO
A	0.25	18:1
1	0.70	6.14:1
2	1.00	4.6:1
3	1.50	3:1
4	2.00	2.3:1

[0146] The 0.25 HCO example is comparative as it is outside the scope of the present invention.

[0147] This warm HCO isotropic premixes were never warmed as far as the melting point of the HCO (85 to 88°C for this material). One part of the isotropic premix was added in less than 30 seconds to about 3 parts 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 at 2 °C per minute to ambient. The Exception to this was Example 4 which was too viscous to use easily at ambient temperature, so it was cooled after 15 mins at 65°C slowly to 60°C and then added hot to the rest of the composition, which was at ambient.

[0148] The structured water premixes so formed were stable and could be kept until needed for use in formulation of concentrated heavy-duty aqueous laundry liquids.

Example 2

[0149] Each of the structured water premixes as prepared in comparative example A and examples 1 to 4 was used to structure a concentrated detergent liquid comprising a high level of thinning polymer and having a composition as shown in table 2.

Table 2 - Composition of Detergent Liquid

Ingredient (100%)	**Wt%**
HCO’	0.70
Nonionic’	4.58
Water’	17
Balance Water (Total water 40.82)	to 100
LAS acid	8.75
SLES 3EO	6.82
Fatty Acid	3.00
MPG	11.00
Glycerol	5.00
MEA	7.00
TEA	2.50
Citric Acid	3.90
HEDP	1.50
EPEI (thinning polymer)	3.00
Fluorescer	0.10
Perfume	0.78
Sodium Sulphite	0.25
Opacifier	1.00
^{1} means the ingredient is used to make the structured water premix	

[0150] The perfume and sodium sulphite was added after the structured water premix has been mixed with the other ingredients. Table 3 shows the viscosities of the resulting liquids using the different structured water premixes.

Table 3 -viscosity data for liquids with different levels of HCO

HCO level In final liquids (premix used)	Viscosity Pa 21 s-^{1}	Yield stress Pa (Indicates ability to suspend)
%		
0.25 (A)	0.13	0.55
0.70 (1)	0.32	1.88

(continued)

HCO level In final liquids (premix used)	Viscosity Pa 21 s^{-1}	Yield stress Pa (Indicates ability to suspend)
%		
1.00 (2)	0.35	3.07
1.50 (3)	0.53	8.00
2.00 (4)	0.81	7.80

[0151] It can be seen that the low shear viscosity is much improved for the liquids with above the comparative level of 0.25% HCO and these liquids with more than 0.4 wt% HCO external structurant could suspend insoluble solid cues without an segregation, sedimentation or creaming, even in the presence of 3 wt% of the thinning polymer EPEI.

Claims

1. A process to manufacture an externally structured aqueous liquid detergent composition comprising 7 to 40 wt% surfactant, of which at least 2 wt% is nonionic surfactant, optionally 2 to 30 wt% water soluble polymer, and more than 0.4 to 2.5 wt% Hydrogenated Castor oil (HCO) external structurant, the process comprising the step of formation of a structured water premix which is then mixed with an unstructured liquid and optional further components to form the externally structured liquid detergent composition, **characterised in that** the structured water premix is formed by:

a) mixing more than 0.4 to 2.5 wt% HCO (based on the liquid detergent composition), with 2 to 10 wt% nonionic surfactant (based on the liquid detergent composition),
b) heating this mixture to 65 to 84°C to prepare a solution of HCO in nonionic surfactant, then
c) mixing the isotropic solution from step b) with a liquid comprising water, and optionally further comprising anionic surfactant, to form a hot structured water premix precursor and holding this premix precursor at a temperature of at least 55°C for from 5 to 30 minutes before allowing the temperature to drop to below 40°C to form a structured water premix.

2. A process according to claim 1 in which the hot structured water premix in step c is held at a temperature of at least 60°C.

3. A process according to claim 2 in which the hot structured water premix in step c is held at a temperature of at least 65°C.

4. A process according to any preceding claim in which the amount of nonionic is at least 3 times as much as the amount of HCO in the premix formed in step c).

5. A process according to any preceding claim in which the liquid comprises 2 to 30% water soluble polymers.

6. A process according to any preceding claim in which the polymers comprise water soluble polymers selected from ethoxylated polyethylene imine (EPEI), soil release polymers and mixtures thereof.

7. A process according to claim 6 in which the amount of EPEI is at least 2 wt%.

8. A process according to claim 7 in which the amount of EPEI is at least 2.5 wt%.

9. A process according to claim 8 in which the amount of EPEI is at least 3 wt%.

10. A process according to any preceding claim in which particles are added to the structured aqueous detergent liquid and suspended in it.

11. A process according to claim 10 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.

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EUROPEAN SEARCH REPORT

Application Number
EP 11 15 6942

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	11 August 2011	Richards, Michael

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A : technological background
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