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(54) **Detergent compositions**

(57) The present invention relates to a detergent composition wherein the composition is enclosed by a pouch made of a water-soluble film, said composition comprising:

- (a) a surfactant; and
- (b) at least one particle comprising benefit agent wherein the particle floats in de-ionized water at 20°C.

In the compositions of the present invention the particle(s) comprising the benefit agent survive well in the wash liquor and, therefore, it is easier to control the release of the active.

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Description**Technical Field**

5 **[0001]** The present invention relates to detergent compositions. In particular, the present invention relates to shaped detergent compositions comprising surfactant and at least one particle comprising benefit agent.

Background to the Invention

10 **[0002]** Shaped detergent compositions are well known in the art. Usually such compositions take the form of a tablet or a water-soluble pouch. It is understood that these detergent compositions hold several advantages over detergent compositions in particulate or liquid form, such as ease of dosing, handling, transportation and storage.

[0003] One advantage of shaped compositions is that they allow essentially incompatible ingredients to be formulated in a single dosage unit. The shaped compositions can be designed to keep incompatible ingredients physically separate and to sequentially release those ingredients. For example, it is desirable to formulate a single-dose composition that comprises both surfactant and fabric softener. However, many of the commonly used surfactants will form complexes with the fabric softener materials leading to poor cleaning, poor softening and, possibly, residues on the fabric. Therefore, any composition comprising both materials must either be formulated using a limited number of compatible materials or be designed to sequentially release said ingredients, thereby avoiding the problems of incompatibility. For example, WO-A-99/40171 discloses a detergent tablet for fabric washing where there is a fabric conditioning agent present in one zone of the tablet at a greater concentration than in another zone. It is claimed that the conditioning agent may be a softening agent in a zone or region, which disintegrates later than another zone or region of the tablet. It is alleged that this delayed disintegration can be achieved through blocking access of water to the zone, which is intended to disintegrate later or by adding disintegration enhancing materials to the zone, which is intended to disintegrate first. WO-A-00/06683 discloses a tablet composition for use in the washing machine that has at least one particle that is made up of at least one nucleus comprising at least one substance that acts mainly during the rinsing process of the washing machine in addition to a coat that fully surrounds the nucleus and comprises at least one compound whose solubility increases when the concentration of a specific ion in the ambient medium is reduced. WO-A-00/04129 describes multi-phase detergent tablets where there is a first phase that is in the form of a shaped body having at least one mould therein and a second phase in the form of a particulate solid compressed within said mould. In preferred embodiments of the multi-phase tablets of WO-A-00/04129 the second phase (and any subsequent phases) dissolves before the first phase.

[0004] However, prior art compositions often do not effectively control of the delivery of the actives. Frequently, the particles containing active are expelled from the wash before the rinse cycle along with the wash liquor from the main wash. This means they do not have a chance to release the active(s). Also, many of the actives work most effectively when released towards the end of the laundry cycle. When the actives are released early it can lead to degradation, loss of active by being washed away with the wash liquor and/or to essentially incompatible phases being released at the same time causing undesirable residues or loss of efficacy. In addition, due to their chemical and physical properties, the prior art compositions often do not disintegrate quickly and disintegrate into large particles. This means it can be difficult to dose the compositions via the dispensing drawer since, when dispensed via the drawer, the particle size of the disintegrated composition must be such that it can pass from the drawer, through the pipe and into the drum often through small holes.

[0005] It is an object of the present invention to provide a pouch detergent composition that can be formulated to delay the delivery of an active until the appropriate time in the laundry cycle. It is a further object of the present invention to provide a pouch detergent composition that is not only sufficiently robust to withstand handling and transportation, but is also convenient to dose via the dispensing drawer. Other objects and advantages shall become apparent as the description proceeds.

Summary of the Invention

50 **[0006]** The present invention relates to a detergent composition wherein the composition is enclosed by a pouch made of a water-soluble film, said composition comprising:

(a) a surfactant; and

(b) at least one particle comprising benefit agent wherein the particle floats in deionised water at 20°C.

[0007] It is highly preferred that the compositions of the present invention comprise a plurality of discrete particles comprising benefit agent. It is preferred to have a plurality of discrete particles as this causes the benefit agent to be

more evenly distributed around the wash thus helping to ensure a more uniform application of the benefit to the fabrics.

[0008] In the compositions of the present invention, the particles comprising the benefit agent survive well in the wash liquor and, therefore, it is easier to control the release of the active.

[0009] While not wishing to be bound by theory it is believed that having particles comprising benefit agent float means that the particles are more likely to remain in the drum during the wash cycle. For example, many benefit agents perform best when they are added during the rinse cycle. However, during a normal wash cycle the wash liquor is pumped out of the machine at the end of the main wash cycle any particles that do not float are likely to be lost with the water. Also, floating particles reduce the risk of these particles being caught up in the mechanism of the washing machine or in the fabrics thus avoiding mechanical stresses that can cause premature release of the benefit agent. This means that the formulator can more accurately control when the benefit agent is released into the wash liquor. Moreover, having particles that float reduces the risk of residue being left when the composition is dosed via the dispensing drawer.

[0010] In a preferred aspect of the present invention there is a plurality of particles comprising benefit agent. Preferably the particles comprising the benefit agent have a average particle size of from 0.5mm to 10mm, more preferably from 1.5mm to 5mm, even more preferably from 2mm to 4mm.

Detailed Description of the Invention

[0011] The pouch detergent compositions of the present invention comprise surfactant and at least one particle comprising benefit agent. These elements will be described in more detail below.

Pouch and material thereof

[0012] The pouch of the invention, herein referred to as "pouch", is typically a closed structure, made of a water-soluble film described herein, enclosing a volume space which comprises a composition. Said composition is described in more detail herein. The pouch can be of any form, shape and material which is suitable to hold the composition, e.g. without allowing the release of the composition from the pouch prior to contact of the pouch to water. The exact execution will depend on for example, the type and amount of the composition in the pouch, the number of compartments in the pouch, the characteristics required from the pouch to hold, protect and deliver or release the compositions.

[0013] The pouch may be of such a size that it conveniently contains either a unit dose amount of the composition herein, suitable for the required operation, for example one wash, or only a partial dose, to allow the consumer greater flexibility to vary the amount used, for example depending on the size and/or degree of soiling of the wash load.

[0014] It may be preferred that the water-soluble film is stretched during formation and/or closing of the pouch, such that the resulting pouch is at least partially stretched. This is to reduce the amount of film required to enclose the volume space of the pouch. When the film is stretched the film thickness decreases. The degree of stretching indicates the amount of stretching of the film by the reduction in the thickness of the film. For example, if by stretching the film, the thickness of the film is exactly halved then the stretch degree of the stretched film is 100%. Also, if the film is stretched so that the film thickness of the stretched film is exactly a quarter of the thickness of the unstretched film then the stretch degree is exactly 200%. Typically and preferably, the thickness and hence the degree of stretching is non-uniform over the pouch, due to the formation and closing process. For example, when a water-soluble film is positioned in a mould and an open compartment is formed by vacuum forming (and then filled with the components of a composition and then closed), the part of the film in the bottom of the mould, furthest removed from the points of closing will be stretched more than in the top part. Preferably, the film which is furthest away from the opening, e.g. the film in the bottom of the mould, will be stretched more and be thinner than the film closest by the opening, e.g. at the top part of the mould.

[0015] Another advantage of using stretching the pouch is that the stretching action, when forming the shape of the pouch and/or when closing the pouch, stretches the pouch non-uniformly, which results in a pouch which has a non-uniform thickness. This allows control of the dissolution of water-soluble pouches herein, and for example sequential release of the components of the detergent composition enclosed by the pouch to the water.

[0016] Preferably, the pouch is stretched such that the thickness variation in the pouch formed of the stretched water-soluble film is from 10 to 1000%, preferably 20% to 600%, or even 40% to 500% or even 60% to 400%. This can be measured by any method, for example by use of an appropriate micrometer. Preferably the pouch is made from a water-soluble film that is stretched, said film has a stretch degree of from 40% to 500%, preferably from 40% to 200%.

[0017] The pouch is made from a water-soluble film. It is preferred that the pouch as a whole comprises material which is water-dispersible or more preferably water-soluble. Preferred water-soluble films are polymeric materials, preferably polymers which are formed into a film or sheet. The material in the form of a film can for example be obtained by casting, blow-moulding, extrusion or blow extrusion of the polymer material, as known in the art.

[0018] Preferred water-dispersible material herein has a dispersability of at least 50%, preferably at least 75% or

even at least 95%, as measured by the method set out hereinafter using a glass-filter with a maximum pore size of 50 microns.

[0019] More preferably the material is water-soluble and has a solubility of at least 50%, preferably at least 75% or even at least 95%, as measured by the method set out hereinafter using a glass-filter with a maximum pore size of 50 microns, namely:

[0020] Gravimetric method for determining water-solubility or water-dispersability of the material of the compartment and/or pouch:

[0021] 50 grams $\pm$ 0.1 gram of material is added in a 400 ml beaker, whereof the weight has been determined, and 245ml $\pm$ 1ml of distilled water is added. This is stirred vigorously on magnetic stirrer set at 600 rpm, for 30 minutes. Then, the mixture is filtered through a folded qualitative sintered-glass filter with the pore sizes as defined above (max. 50 micron). The water is dried off from the collected filtrate by any conventional method, and the weight of the remaining polymer is determined (which is the dissolved or dispersed fraction). Then, the % solubility or dispersability can be calculated.

[0022] Preferred polymer copolymers or derivatives thereof are selected from polyvinyl alcohols, polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts, polyaminoacids or peptides, polyamides, polyacrylamide, copolymers of maleic/acrylic acids, polysaccharides including starch and gelatine, natural gums such as xanthum and carragum. More preferably the polymer is selected from polyacrylates and water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose sodium, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltodextrin, polymethacrylates, most preferably polyvinyl alcohols, polyvinyl alcohol copolymers and hydroxypropyl methyl cellulose (HPMC). Preferably, the level of a type polymer (e.g., commercial mixture) in the film material, for example PVA polymer, is at least 60% by weight of the film.

[0023] The polymer can have any weight average molecular weight, preferably from about 1000 to 1,000,000, or even from 10,000 to 300,000 or even from 15,000 to 200,000 or even from 20,000 to 150,000.

[0024] Mixtures of polymers can also be used. This may in particular be beneficial to control the mechanical and/or dissolution properties of the compartment or pouch, depending on the application thereof and the required needs. For example, it may be preferred that a mixture of polymers is present in the material of the compartment, whereby one polymer material has a higher water-solubility than another polymer material, and/or one polymer material has a higher mechanical strength than another polymer material. It may be preferred that a mixture of polymers is used, having different weight average molecular weights, for example a mixture of PVA or a copolymer thereof of a weight average molecular weight of 10,000- 40,000, preferably around 20,000, and of PVA or copolymer thereof, with a weight average molecular weight of about 100,000 to 300,000, preferably around 150,000.

[0025] Also useful are polymer blend compositions, for example comprising hydrolytically degradable and water-soluble polymer blend such as polylactide and polyvinyl alcohol, achieved by the mixing of polylactide and polyvinyl alcohol, typically comprising 1-35% by weight polylactide and approximately from 65% to 99% by weight polyvinyl alcohol, if the material is to be water-dispersible, or water-soluble. It may be preferred that the PVA present in the film is from 60-98% hydrolysed, preferably 80% to 90%, to improve the dissolution of the material.

[0026] Most preferred are films, which are water-soluble and stretchable films, as described above. Highly preferred water-soluble films are films which comprise PVA polymers and that have similar properties to the film known under the trade reference M8630, as sold by Chris-Craft Industrial Products of Gary, Indiana, US.

[0027] The water-soluble film herein may comprise other additive ingredients than the polymer or polymer material. For example, it may be beneficial to add plasticisers, for example glycerol, ethylene glycol, diethyleneglycol, propylene glycol, sorbitol and mixtures thereof, additional water, disintegrating aids. It may be useful that the pouch or water-soluble film itself comprises a detergent additive to be delivered to the wash water, for example organic polymeric soil release agents, dispersants, dye transfer inhibitors.

[0028] The pouch is made by a process comprising the steps of contacting a composition herein to a water-soluble film in such a way as to partially enclose said composition to obtain a partially formed pouch, optionally contacting said partially formed pouch with a second water-soluble film, and then sealing said partially formed pouch to obtain a pouch.

[0029] A water-soluble film may be vacuum pulled into the mould so that said film is flush with the inner walls of the mould. A composition herein may then be poured into the mould, a second water-soluble film may be placed over the mould with the composition and the pouch may then be sealed, preferably the partially formed pouch is heat sealed. The film is preferably stretched during the formation of the pouch.

[0030] The present compositions can be a single compartment pouch or a multicompartment pouch. When the pouch has multiple compartments the beads and the surfactant may be located in the same compartment or in separate compartments, preferably they are located in separate compartments. Pouches for use herein can contain detergent compositions in any suitable form as long as the compositions comprise surfactant and beads. In particular, the pouches can comprise powders, liquids, solids, gels, foams, and combinations thereof. Preferably, the pouches comprise powder, liquids, and mixtures thereof. Some preferred pouches according to the present invention include:

- single compartment pouch with powder and beads in 2 distinct layers,
- single compartment pouch with powder and beads mixed together,
- single compartment pouch with liquid and beads mixed together,
- dual compartment pouch with powder and beads in separate compartments,
- dual compartment pouch with liquid and beads in separate compartments,
- dual compartment pouch with liquid in one compartment and powder plus beads in the other,
- dual compartment pouch with liquid plus beads in one compartment and powder in the other,
- dual compartment pouch with liquid plus beads in one compartment and powder plus beads in the other.

Surfactant

[0031] An essential feature of the compositions of the present invention is that they comprise surfactant. Any suitable surfactant may be used. Preferred surfactants are selected from anionic, amphoteric, zwitterionic, nonionic (including semi-polar nonionic surfactants), cationic surfactants and mixtures thereof.

[0032] The compositions preferably have a total surfactant level of from 0.5% to 75% by weight, more preferably from 1% to 50% by weight, most preferably from 5% to 30% by weight of total composition.

[0033] Preferably the particles comprising surfactant in the present compositions are at least about 90% dissolved in the wash liquor, at the latest, within ten minutes of the start of the main wash cycle of the washing machine. This allows the agents for use in the main wash cycle to enter the wash liquor quickly. It is preferred that the surfactant reaches its peak concentration in the wash liquor within the first ten minutes, preferably within the first five minutes, more preferably within the first two minutes of the main wash cycle of a washing machine.

[0034] Detergent surfactants are well known and fully described in the art (see, for example, "Surface Active Agents and Detergents", Vol. I & II by Schwartz, Perry and Beach). Some non-limiting examples of suitable surfactants for use herein are:

Nonionic surfactants

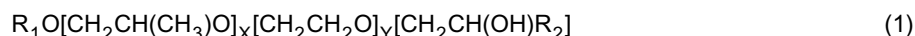
[0035] Essentially any nonionic surfactants useful for deterative purposes can be included in the present detergent compositions. Preferred, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic ethoxylated alcohol surfactant

[0036] The alkyl ethoxylate condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

End-capped alkyl alkoxyate surfactant

[0037] A suitable endcapped alkyl alkoxyate surfactant is the epoxy-capped poly(oxyalkylated) alcohols represented by the formula:

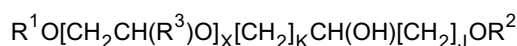


wherein R_1 is a linear or branched, aliphatic hydrocarbon radical having from 4 to 18 carbon atoms; R_2 is a linear or branched aliphatic hydrocarbon radical having from 2 to 26 carbon atoms; x is an integer having an average value of from 0.5 to 1.5, more preferably 1; and y is an integer having a value of at least 15, more preferably at least 20.

[0038] Preferably, the surfactant of formula (I) comprises at least 10 carbon atoms in the terminal epoxide unit $[CH_2CH(OH)R_2]$. Examples of suitable surfactants according to formula (I) include Olin Corporation's POLY-TERGENT® SLF-18B nonionic surfactants, as described, for example, in WO-A-94/22800.

Ether-capped poly(oxyalkylated) alcohols

[0039] Preferred nonionic surfactants for use herein include ether-capped poly(oxyalkylated) alcohols having the formula:



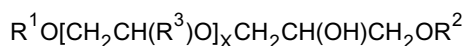
wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 30, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12, and more preferably 1 to 5.

[0040] R^1 and R^2 are preferably linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 6 to 22 carbon atoms with 8 to 18 carbon atoms being most preferred. H or a linear aliphatic hydrocarbon radical having from 1 to 2 carbon atoms is most preferred for R^3 . Preferably, x is an integer having an average value of from 1 to 20, more preferably from 6 to 15.

[0041] As described above, when, in the preferred embodiments, and x is greater than 2, R^3 may be the same or different. That is, R^3 may vary between any of the alkyleneoxy units as described above. For instance, if x is 3, R^3 may be selected to form ethyleneoxy (EO) or propyleneoxy (PO) and may vary in order of (EO)(PO)(EO), (EO)(EO)(PO); (EO)(EO)(EO); (PO)(EO)(PO); (PO)(PO)(EO) and (PO)(PO)(PO). Of course, the integer three is chosen for example only and the variation may be much larger with a higher integer value for x and include, for example, multiple (EO) units and a much small number of (PO) units.

[0042] Particularly preferred nonionic surfactants as described above include those that have a low cloud point of less than 20°C. These low cloud point surfactants may then be employed in conjunction with a high cloud point surfactant as described in detail below for superior grease cleaning benefits.

[0043] Most preferred ether-capped poly(oxyalkylated) alcohol surfactants are those wherein k is 1 and j is 1 so that the surfactants have the formula:



wherein R^1 , R^2 and R^3 are defined as above and x is an integer with an average value of from 1 to 30, preferably from 1 to 20, and even more preferably from 6 to 18. Most preferred are surfactants wherein R^1 and R^2 range from 9 to 14, R^3 is H forming ethyleneoxy and x ranges from 6 to 15.

[0044] The ether-capped poly(oxyalkylated) alcohol surfactants comprise three general components, namely a linear or branched alcohol, an alkylene oxide and an alkyl ether end cap. The alkyl ether end cap and the alcohol serve as a hydrophobic, oil-soluble portion of the molecule while the alkylene oxide group forms the hydrophilic, water-soluble portion of the molecule.

[0045] These surfactants exhibit significant improvements in spotting and filming characteristics and removal of greasy soils, when used in conjunction with high cloud point surfactants, relative to conventional surfactants.

[0046] Generally speaking, the ether-capped poly(oxyalkylene) alcohol surfactants of the present invention may be produced by reacting an aliphatic alcohol with an epoxide to form an ether which is then reacted with a base to form a second epoxide. The second epoxide is then reacted with an alkoxyated alcohol to form the novel compounds of the present invention.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

[0047] The ethoxylated C_6 - C_{18} fatty alcohols and C_6 - C_{18} mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C_{10} - C_{18} ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C_{12} - C_{18} ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO condensates with propylene glycol

[0048] The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from 1500 to 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

[0049] The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from 2500 to 3000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Mixed Nonionic Surfactant System

[0050] In a preferred embodiment of the present invention the detergent tablet comprises a mixed nonionic surfactant system comprising at least one low cloud point nonionic surfactant and at least one high cloud point nonionic surfactant.

[0051] "Cloud point", as used herein, is a well known property of nonionic surfactants which is the result of the surfactant becoming less soluble with increasing temperature, the temperature at which the appearance of a second phase is observable is referred to as the "cloud point" (See Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed. Vol. 22, pp. 360-379).

[0052] As used herein, a "low cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of less than 30°C, preferably less than 20°C, and most preferably less than 10°C. Typical low cloud point nonionic surfactants include nonionic alkoxyethylated surfactants, especially ethoxylates derived from primary alcohol, and polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers. Also, such low cloud point nonionic surfactants include, for example, ethoxylated-propoxylated alcohol (e.g., Olin Corporation's Poly-Tergent™ SLF18), epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent™ SLF18B series of nonionics, as described, for example, in WO-A-94/22800.) and the ether-capped poly(oxyalkylated) alcohol surfactants.

[0053] Nonionic surfactants can optionally contain propylene oxide in an amount up to 15% by weight. Other preferred nonionic surfactants can be prepared by the processes described in US-A-4,223,163.

[0054] Low cloud point nonionic surfactants additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound. Block polyoxyethylene-polyoxypropylene polymeric compounds include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Certain of the block polymer surfactant compounds designated PLURONIC™, REVERSED PLURONIC™, and TETRONIC™ by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention. Preferred examples include REVERSED PLURONIC™ 25R2 and TETRONIC™ 702. Such surfactants are typically useful herein as low cloud point nonionic surfactants.

[0055] As used herein, a "high cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of greater than 40°C, preferably greater than 50°C, and more preferably greater than 60°C. Preferably the nonionic surfactant system comprises an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from 8 to 20 carbon atoms, with from 6 to 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis. Such high cloud point nonionic surfactants include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

[0056] It is also preferred for purposes of the present invention that the high cloud point nonionic surfactants further have a hydrophile-lipophile balance ("HLB"; see Kirk Othmer hereinbefore) value within the range of from 9 to 15, preferably 11 to 15. Such materials include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

[0057] Another preferred high cloud point nonionic surfactant is derived from a straight or preferably branched chain or secondary fatty alcohol containing from 6 to 20 carbon atoms (C₆-C₂₀ alcohol), including secondary alcohols and branched chain primary alcohols. Preferably, high cloud point nonionic surfactants are branched or secondary alcohol ethoxylates, more preferably mixed C_{9/11} or C_{11/15} branched alcohol ethoxylates, condensed with an average of from 6 to 15 moles, preferably from 6 to 12 moles, and most preferably from 6 to 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

Anionic surfactants

[0058] Essentially any anionic surfactants useful for deterative purposes are suitable for use herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

[0059] Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

[0060] Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₁₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

[0061] Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₁₀-C₁₈ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

[0062] Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates, which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate, which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

[0063] A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in WO-A-93/18124.

Anionic sulfonate surfactant

[0064] Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

[0065] Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

[0066] Suitable alkyl ethoxy carboxylates include those with the formula RO(CH₂CH₂O)_xCH₂COO-M⁺ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20% and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula RO-(CHR₁-CHR₂-O)-R₃ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R₃ is selected from hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

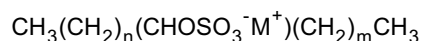
[0067] Suitable soap surfactants include the secondary soap surfactants, which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

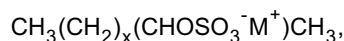
[0068] Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON(R')CH₂COOM, wherein R is a C₅-C₁₇ linear or branched alkyl or alkenyl group, R' is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Secondary Alkyl Sulphate surfactants

[0069] Secondary alkyl sulphate surfactants suitable for use herein include those disclosed in US-A-6,015,784. Preferred secondary alkyl sulphate surfactants are those materials which have the sulphate moiety distributed randomly along the hydrocarbyl "backbone" of the molecule. Such materials may be depicted by the structure:



wherein m and n are integers of 2 or greater and the sum of m+n is typically from 9 to 17, and M is a water-solubilising cation. Preferred secondary alkyl surfactants for use herein have the formula:



and



wherein x and (y+1) are integers of at least 6, and preferably range from 7 to 20, more preferably from 10 to 16. M is a cation, such as alkali metal, ammonium, alkanolammonium, alkaline earth metal or the like. Sodium is typically used. Secondary alkyl surfactants suitable for use herein are described in more detail in US-A-6015784.

Amphoteric surfactants

[0070] Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

[0071] Suitable amine oxides include those compounds having the formula $\text{R}^3(\text{OR}^4)_x\text{N}^0(\text{R}^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10} - C_{18} acylamido alkyl dimethylamine oxide.

[0072] A suitable example of an alkyl amphocarboxylic acid is Miranol™ C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactants

[0073] Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

[0074] Suitable betaines are those compounds having the formula $\text{R}(\text{R}^1)_2\text{N}^+\text{R}^2\text{COO}^-$ wherein R is a C_6 - C_{18} hydrocarbyl group, each R^1 is typically C_1 - C_3 alkyl, and R^2 is a C_1 - C_5 hydrocarbyl group. Preferred betaines are C_{12} - C_{18} dimethyl-ammonio hexanoate and the C_{10} - C_{18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Cationic surfactants

[0075] Cationic ester surfactants used in this invention are preferably water dispersible compound having surfactant properties comprising at least one ester (i.e.-COO-) linkage and at least one cationically charged group. Other suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US-A-4228042, US-A-4239660 and US-A-4260529.

[0076] Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C_6 - C_{16} , preferably C_6 - C_{10} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

[0077] Preferred surfactants for use herein are selected from anionic sulphonate surfactants (particularly linear alkylbenzene sulphonates), anionic sulphate surfactants (particularly C_{12} - C_{18} alkyl sulphates), secondary alkyl sulphate surfactants, nonionic surfactants and mixtures thereof.

Benefit Agent

[0078] Another essential feature of the compositions of the present invention is that they comprise at least one particle

comprising benefit agent that floats in deionised water at 20°C. Preferably the compositions herein comprise a plurality of particles comprising benefit agent. The particles comprising benefit agent can be in the form of granules, beads, noodles, pellets, compressed tablets, filled sachets, and mixtures thereof. Preferably the particles are in the form of beads. It is preferred that the particles that comprise the benefit agent are substantially spherical in shape.

[0079] Preferably, the compositions herein comprise less than 70%, more preferably less than 50%, by weight of total compositions, of particles comprising benefit agent

[0080] The particle in the subsequent phase comprising the benefit agent must float in deionised water at 20°C. In general, particles that are less dense than water will float.

[0081] The ability of the particles to resist dissolution can be measure using the 'Sieve Test' method. The method uses the apparatus as described in the United States Pharmacopoeia (USP) 711 Dissolution test. The particles are weighed and then introduced into a glass vessel as described in the 'Apparatus 1' section (page 1942, USP 24) filled with 1 litre of de-ionized water at 20°C. As soon as the particles are introduced, the paddle-stirring element described in the 'Apparatus 2' section of the USP 711 Dissolution test is activated at a speed of 100 rotations per minute for the required test time. The preferred distance between the bottom of the vessel and the paddle is 25mm but can be adapted if necessary. The preferred vessel volume capacity should be 1 litre but a vessel of 2 litre capacity can also be used if necessary. A common apparatus used to perform this test is the Sotax® AT7.

[0082] At the end of the required test time, in this case 5, 10 or 15 minutes, the mechanical agitation is stopped and the stirring element is removed from the vessel. In order to recuperate the particles that didn't dissolve, the solution and all the undissolved particles are poured through a sieve that will retain the required particle size: in this case, a mesh size of 0.5x0.5mm should be used.

[0083] In order to calculate the dry percentage of remaining undissolved particles in solution, the particles that were retained in the required mesh size sieve are dried at 35°C for at least 12 hours. After this drying step, the particles are weighted and the percentage calculated.

[0084] Preferably the particles comprising benefit agent remain at least 75% undissolved for at least 5 minutes, preferably at least 10 minutes, more preferably at least 20 minutes after the start of the main wash cycle of the washing machine. It is highly preferred that the particles comprising benefit agents remain at least 50%, more preferably at least 75%, undissolved until the start of the rinse cycle of the washing machine.

[0085] As used herein the term "benefit agent" means a compound or mixture of compounds that provides the present compositions with a property that consumers find desirable. The subsequent phase of the present compositions can comprise more than one benefit agent where each agent provides a different benefit.

[0086] Preferably the benefit agent for use herein is selected from cationic softening agents, soil-release agents, perfumes, suds-suppressing system, wrinkle reducing agents, chelating agents, chloride scavengers, dye fixing agents, fabric abrasion reducing polymers, and mixture thereof. More preferably the benefit agent for use herein is selected from cationic softening agents, perfumes, suds-suppressing system and mixtures thereof. Even more preferably the benefit agent for use herein is selected from cationic softening agents, perfumes and mixtures thereof. Highly preferred benefit agents for use herein are cationic softening agents.

[0087] Some examples of preferred benefit agents are given below.

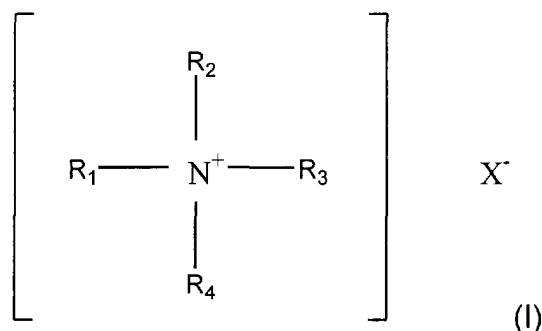
Cationic Softening Agents

[0088] Cationic softening agents are one of the preferred benefit agents for use in the subsequent phase. Any suitable cationic softening agents may be used herein but preferred are quaternary ammonium agents. As used herein the term "quaternary ammonium agent" means a compound or mixture of compounds having a quaternary nitrogen atom and having one or more, preferably two, moieties containing six or more carbon atoms. Preferably the quaternary ammonium agents for use herein are selected from those having a quaternary nitrogen substituted with two moieties wherein each moiety comprises ten or more, preferably 12 or more, carbon atoms.

[0089] Preferably the present compositions comprise from 0.1% to 40%, more preferably from 0.5% to 15%, by weight of total composition, of cationic softening agent. It is highly preferred that any cationic softening agent be concentrated in the second and/or subsequent phases. Therefore, when present, preferably at least 60%, more preferably at least 80%, even more preferably at least 95% of the total quaternary ammonium compound is concentrated in the second and/or subsequent phases.

[0090] Preferred cationic softening agents for use herein are selected from:

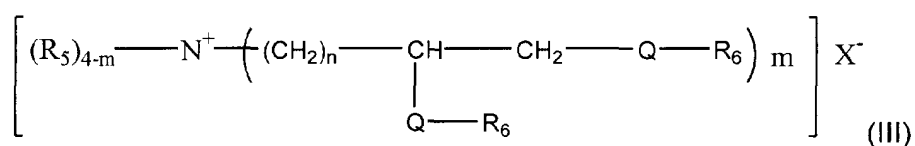
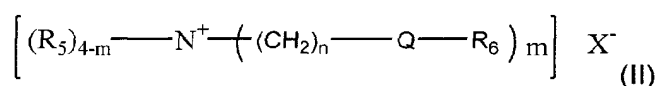
- (a) quaternary ammonium compounds according to general formula (I):



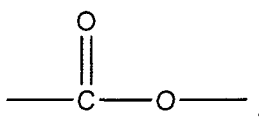
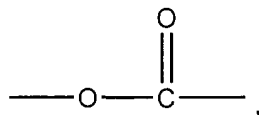
wherein, R_1 & R_2 are each C_1 - C_4 alkyl or C_1 - C_4 hydroxyalkyl groups or hydrogen. R_3 & R_4 are each alkyl or alkenyl groups having from about 8 to about 22 carbon atoms. X^- is a salt forming anion, compatible with quaternary ammonium compounds and other adjunct ingredients.

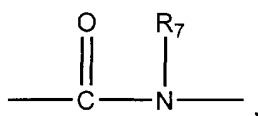
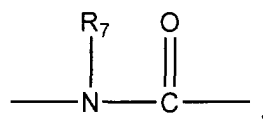
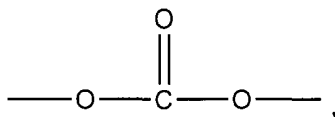
Preferred quaternary ammonium compounds of this type are quaternised amines having the general formula (I) where R_1 & R_2 are methyl or hydroxyethyl and R_3 & R_4 are linear or branched alkyl or alkenyl chains comprising at least 11 atoms, preferably at least 15 carbon atoms.

(b) quaternary ammonium compounds according to general formula (II) or (III):

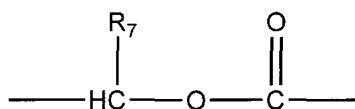


wherein, each R_5 unit is independently selected from hydrogen, branched or straight chain C_1 - C_6 alkyl, branched or straight chain C_1 - C_6 hydroxyalkyl and mixtures thereof, preferably methyl and hydroxyethyl; each R_6 unit is independently linear or branched C_{11} - C_{22} alkyl, linear or branched C_{11} - C_{22} alkenyl, and mixtures thereof; X^- is an anion which is compatible with skin care actives and adjunct ingredients; m is from 1 to 4, preferably 2; n is from 1 to 4, preferably 2 and Q is a carbonyl unit selected from:





and

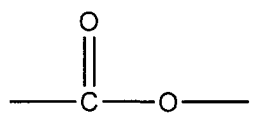
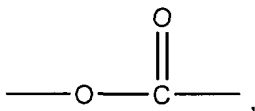


wherein R₇ is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and mixtures thereof.

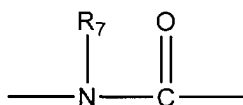
In the above quaternary ammonium compound example, the unit -QR₆ contains a fatty acyl unit, which is typically derived from a triglyceride source. The triglyceride source is preferably derived from tallow, partially hydrogenated tallow, lard, partially hydrogenated lard, vegetable oils and/or partially hydrogenated vegetable oils, such as, canola oil, safflower oil, peanut oil, rapeseed oil, sunflower oil, corn oil, soybean oil, tall oil, rice bran oil, etc. and mixtures of these oils.

The counterion, X⁻ in the above compounds, can be any compatible anion, preferably the anion of a strong acid, for example, chloride, bromide, methylsulfate, ethylsulfate, sulfate, nitrate and the like, more preferably chloride or methyl sulfate. The anion can also, but less preferably, carry a double charge in which case X⁻ represents half a group.

The preferred quaternary ammonium compounds of the present invention are the diester and/or diamide Quaternary Ammonium (DEQA) compounds, the diesters and diamides having general formula (II), wherein the carbonyl group Q is selected from:



and

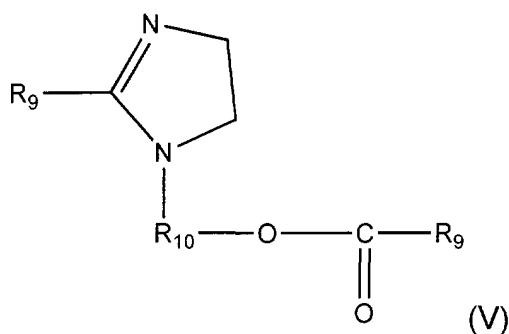
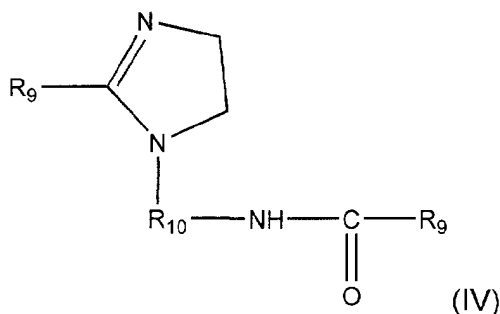


Tallow, canola and palm oil are convenient and inexpensive sources of fatty acyl units, which are suitable for use in the present invention as R_6 units.

The counterion, X^- , can be chloride, bromide, methylsulfate, formate, sulfate, nitrate, and mixtures thereof. In fact, the anion, X , is merely present as a counterion of the positively charged quaternary ammonium compounds. The scope of this invention is not considered limited to any particular anion.

As used herein, when the diester is specified, it will include the monoester and triester that are normally present as a result of the manufacture process.

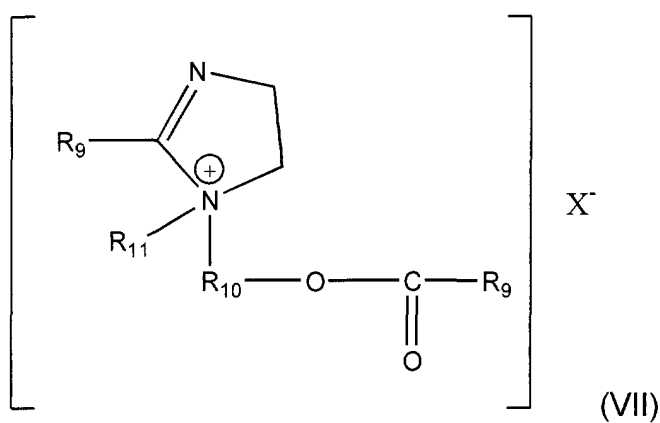
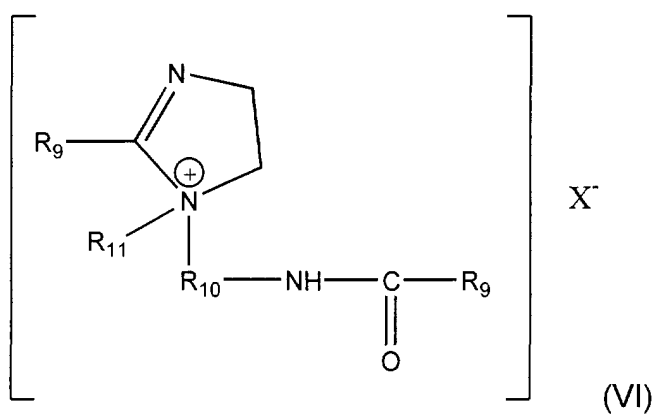
(c) quaternary ammonium compounds according to general formula (IV) or (V):



wherein R_9 is an acyclic aliphatic $\text{C}_{15}\text{--C}_{21}$ hydrocarbon group and R_{10} is a $\text{C}_1\text{--C}_6$ alkyl or alkylene group.

These ammonium compounds, having a pK_a value of not greater than about 4, are able to generate a cationic charge in situ when dispersed in an aqueous solution, providing that the pH of the final composition is not greater than about 6.

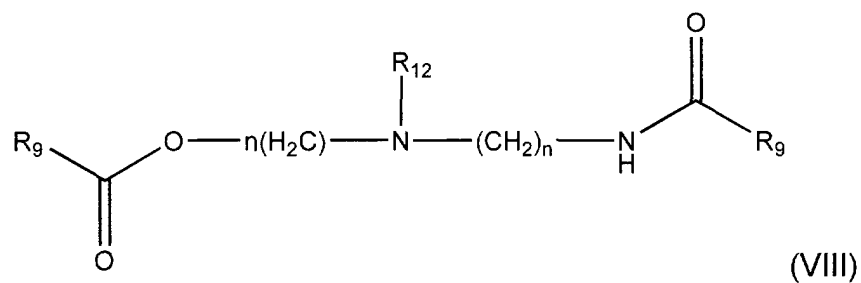
(d) quaternary ammonium compounds according to general formula (VI) or (VII):

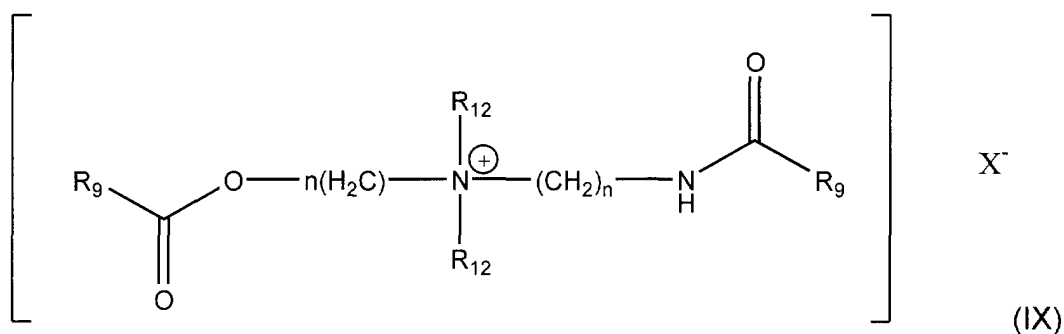


wherein R_9 & R_{10} are as specified hereinabove and R_{11} is selected from C_1 - C_4 alkyl and hydroxyalkyl groups.

The counterion, X^- , can be chloride, bromide, methylsulfate, formate, sulfate, nitrate, and mixtures thereof. In fact, the anion, X , is merely present as a counterion of the positively charged quaternary ammonium compounds. The scope of this invention is not considered limited to any particular anion.

(e) quaternary ammonium compounds according to general formula (VIII) or (IX):



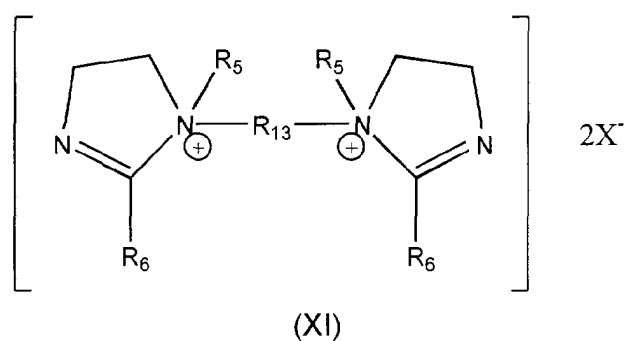
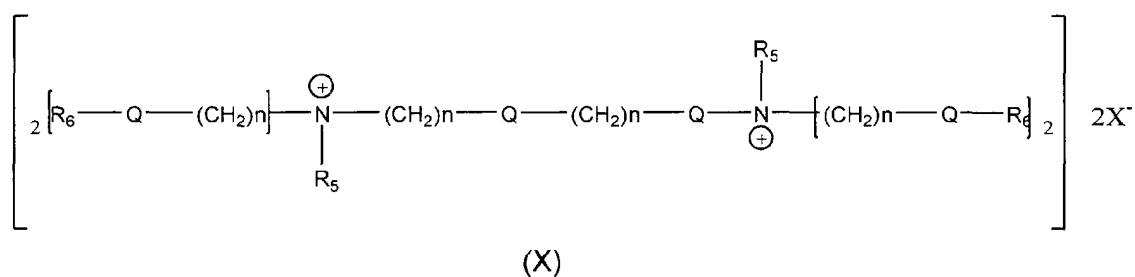


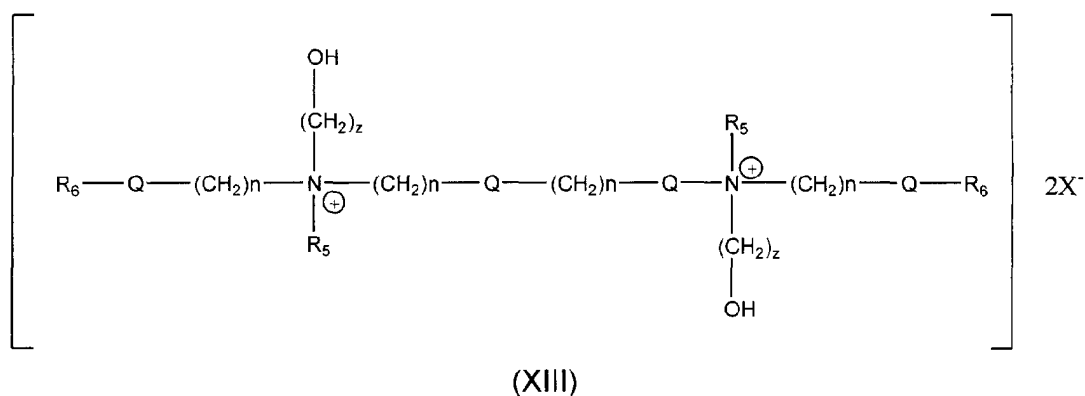
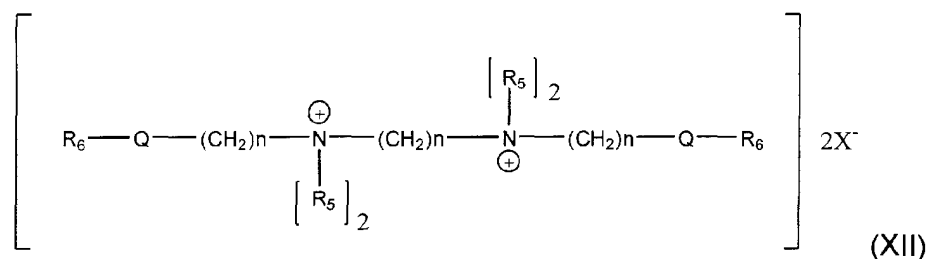
wherein, n is from 1 to 6, R_9 is selected from acyclic aliphatic C_{15} - C_{21} hydrocarbon groups and R_{12} is selected from C_1 - C_4 alkyl and hydroxyalkyl groups.

These ammonium compounds (VIII), having a pK_a value of not greater than about 4, are able to generate a cationic charge in situ when dispersed in an aqueous solution, providing that the pH of the final composition is not greater than about 6.

The counterion, X^- (IX), can be chloride, bromide, methylsulfate, formate, sulfate, nitrate, and mixtures thereof. In fact, the anion, X , is merely present as a counterion of the positively charged quaternary ammonium compounds. The scope of this invention is not considered limited to any particular anion.

(f) diquaternary ammonium compounds according to general formula (X), (XI), (XII) or (XIII):

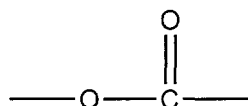




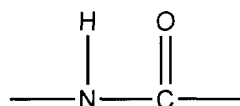
wherein R_5 , R_6 , Q , n & X^- are as defined hereinabove in relation to general formula (II) and (III), R_{13} is selected from C_1 - C_6 alkylene groups, preferably an ethylene group and z is from 0 to 4.

(g) mixtures of the above quaternary ammonium compounds.

[0091] The preferred quaternary ammonium agents for use in the present invention are those described in section (b) hereinabove. In particular, diester and/or diamide quaternary ammonium (DEQA) compounds according to general formula (II) hereinabove are preferred. Preferred diesters for use herein are those according to general formula (II) wherein R_5 , R_6 , and X^- are as defined hereinabove and Q is:



[0092] Preferred diamides for use herein are those according to general formula (II) wherein R_5 , R_6 , and X^- are as defined hereinabove and Q is:



[0093] Preferred examples of quaternary ammonium compounds suitable for use in the compositions of the present invention are N,N-di(canolyl-oxy-ethyl)-N,N-dimethyl ammonium chloride, N,N-di(canolyl-oxy-ethyl)-N-methyl,N-(2-hydroxyethyl) ammonium methyl sulfate, N,N-di(canolyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride and mixtures thereof. Particularly preferred for use herein is N,N-di(canolyl-oxy-ethyl)-N-methyl,N-(2-hydroxyethyl) ammonium methyl sulfate.

[0094] Although quaternary ammonium compounds are derived from "canolyl" fatty acyl groups are preferred, other

suitable examples of quaternary ammonium compounds are derived from fatty acyl groups wherein the term "canolyl" in the above examples is replaced by the terms "tallowyl, cocoyl, palmlyl, lauryl, oleyl, ricinoleyl, stearyl, palmityl" which correspond to the triglyceride source from which the fatty acyl units are derived. These alternative fatty acyl sources can comprise either fully saturated, or preferably at least partly unsaturated chains.

Soil Release Agents

[0095] Suitable polymeric soil release agents include those soil release agents having: (a) one or more nonionic hydrophile 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 hydrophile 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 30 oxypropylene units, said hydrophile segments preferably comprising at least 25% oxyethylene units and more preferably, especially for such components having 20 to 30 oxypropylene units, at least 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C₃ oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C₃ oxyalkylene terephthalate units is 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 hydroxy-alkyl ether cellulose derivatives, or mixtures therein, or a combination of (a) and (b).

[0096] Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from 200, although higher levels can be used, preferably from 3 to 150, more preferably from 6 to 100. Suitable oxy C₄-C₆ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as MO₃S (CH₂)_nOCH₂CH₂O-, where M is sodium and n is an integer from 4-6, as disclosed in US-A-4,721,580.

[0097] Polymeric soil release agents useful herein also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₁-C₄ alkyl and C₄ hydroxyalkyl cellulose; see US-A-4,000,093.

[0098] Soil release agents characterized by poly(vinylester) hydrophobe segments include graft copolymers of poly (vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinylacetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See EP-A-219 048.

[0099] Another suitable 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 25,000 to 55,000. See US-A-3,959,230 and US-A-3,893,929.

[0100] Another suitable 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.

[0101] Another suitable polymeric soil release agent is a sulfonated 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 US-A-4,968,451. Other suitable polymeric soil release agents include the terephthalate polyesters of US-A-4,711,730, the anionic end-capped oligomeric esters of US-A-4,721,580, and the block polyester oligomeric compounds of US-A-4,702,857. Other polymeric soil release agents also include the soil release agents of US-A-4,877,896 which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

[0102] Another 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 one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from 1.7 to 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate.

Chelants/Heavy Metal Ion Sequestrant

[0103] The compositions of the invention preferably contain as an optional component a chelants or heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components, which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

[0104] Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1%

to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

[0105] Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water-soluble. The molar ratio of said counter cation to the heavy metal ion sequesterant is preferably at least 1:1.

[0106] Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates. Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

[0107] Other suitable heavy metal ion sequesterant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

[0108] Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof.

Suds Suppressing System

[0109] The compositions of the present invention preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

[0110] Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl and alcanol antifoam compounds. Preferred suds suppressing systems and antifoam compounds are disclosed in WO-A-93/08876 and EP-A-705 324.

Perfume

[0111] The perfume component of the present invention may comprise an encapsulate perfume, a properfume, neat perfume materials, and mixtures thereof.

[0112] In the context of this specification, the term "perfume" means any odoriferous material or any material, which acts as a malodour counteractant. In general, such materials are characterized by a vapour pressure greater than atmospheric pressure at ambient temperatures. The perfume or deodorant materials employed herein will most often be liquid at ambient temperatures, but also can be solids such as the various tamphoraceous perfumes known in the art. A wide variety of chemicals are known for perfumery uses, including materials such as aldehydes, ketones, esters and the like. More commonly, naturally occurring plant and animal oils and exudates comprising complex mixtures of various chemicals components are known for use as perfumes, and such materials can be used herein. The perfumes herein can be relatively simple in their composition or can comprise highly sophisticated, complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odour.

[0113] Perfumes, which are normally solid can also be employed in the present invention. These may be admixed with a liquefying agent such as a solvent prior to incorporation into the particles, or may be simply melted and incorporated, as long as the perfume would not sublime or decompose upon heating.

[0114] The invention also encompasses the use of materials, which act as malodour counteractants. These materials, although termed "perfumes" hereinafter, may not themselves have a discernible odour but can conceal or reduce any unpleasant odors. Examples of suitable malodour counteractants are disclosed in U.S. Patent No. 3,102,101, issued August 27, 1963, to Hawley et al.

[0115] By encapsulated perfumes it is meant perfumes that are encapsulated within a capsule comprising an encapsulating material or a perfume, which is loaded onto a, preferably porous, carrier material, which is then preferably encapsulated within a capsule comprising an encapsulating material.

[0116] A wide variety of capsules exist which will allow for delivery of perfume effect at various times during the use of the detergent compositions.

[0117] Examples of such capsules with different encapsulated materials are capsules provided by microencapsulation. Here the perfume comprises a capsule core, which is coated completely with a material, which may be polymeric. U.S. Patent 4,145,184, Brain et al, issued March 20, 1979, and U.S. Patent 4,234,627, Schilling, issued November 18, 1980, teach using a tough coating material, which essentially prohibits the diffusions out of the perfume.

[0118] The choice of encapsulated material to be used in the perfume particles of the present invention will depend to some degree on the particular perfume to be used and the conditions under which the perfume is to be released. Some perfumes will require a greater amount of protection than others and the encapsulating material to be used

therewith can be chosen accordingly.

[0119] The encapsulating materials of the perfumed particles is preferably a water-soluble or water-dispersible encapsulating material.

[0120] Nonlimiting examples of suitable water-soluble coating materials include such substances as methyl cellulose, maltodextrin and gelatin. Such coatings can comprise from 1 % to 25 % by weight of the particles.

[0121] Especially suitable water-soluble encapsulating materials are capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB-A-1,464,616.

[0122] Other suitable water-soluble or water dispersible encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in U.S. 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials are N-Lok®, manufactured by National Starch, Narlex® (ST and ST2), and Capsul E®. These encapsulating materials comprise pregelatinised waxy maize starch and, optionally, glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

[0123] For enhanced protection of the perfume particles in a liquid product, it may be more effective to encapsulate the perfume with a material that is pH sensitive, i.e., a material that will remain as a coating on the particle in one pH environment but which would be removed from the particle in a different pH environment. This would allow for further protection of perfume in especially liquid or gel compositions over long storage periods, i.e., the perfume would not diffuse out of the particle in the liquid medium as readily. Diffusion of the perfume out of the stripped particle would then take place after the particles were brought into contact with a different pH environment.

[0124] The encapsulated perfume particles can be made by mixing the perfume with the encapsulating matrix by spray-drying emulsions containing the encapsulating material and the perfume. In addition, the particle size of the product from the spray-drying tower can be modified. These modifications can comprise specific processing steps such as post-tower agglomeration steps (e.g. fluidized bed) for enlarging the particle size and/or processing steps wherein the surface properties of the encapsulates are modified, e.g. dusting with hydrophobic silica in order to reduce the hygroscopicity of the encapsulates.

[0125] A particularly preferred encapsulation process is an emulsification process followed by spray-drying and finally dusting with silica. The emulsion is formed by:

a) dispersing the starch matrix in water at room temp. in a 1:2 ratio. It is preferred that the starch is pregelatinised so that the emulsion can be carried out at this temperature. This in turn minimizes perfume loss. There must be a "low viscosity" starch to achieve high starch concentrations in water and high perfume loadings.

b) the perfume oil is then added to the above mixture in the ratio of 0.8-1.05 : 1:2, and the mixture is then emulsified using a high shear mixer. The shearing motion must produce oil droplets below 1 micron and the emulsion must be stable in this form for at least 20 mins (the function of the starch is to stabilize the emulsion once it's mechanically made).

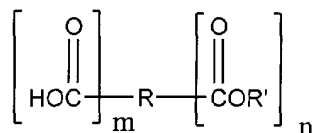
c) the mixture is spray-dried in a co-current tower fitted with a spinning disk atomizer. The drying air inlet temperature is low 150-200°C. This type of spray-drying ensures minimum loss of perfume and high drying rate. The granules have a particulate size of 50-150 microns.

d) the resulting dried encapsulates can contain up to 5 % unencapsulated oil at the surface of the granules. To improve the flow characteristics up to 2 % hydrophobic silica can be optionally added to the encapsulates via a ribbon blender.

[0126] Alternatively the perfume may be loaded onto a carrier and then optionally encapsulated. Suitable carriers are porous and do not react with the perfume. A suitable carrier is zeolite as described in WO-A-94/28107.

[0127] The perfume component may alternatively comprise a pro-perfumes. Pro-perfumes are perfume precursors, which release the perfume on interaction with an outside stimulus for example, moisture, pH, chemical reaction. Suitable pro-perfumes include those described in U.S. Patent No. 5,139,687 Borchert et al. Issued August 18, 1992 and U.S. Patent No 5,234,610 Gardlik et al. Issued Aug 10, 1993.

[0128] Examples of suitable pro-perfumes comprise compounds having an ester of a perfume alcohol. The esters includes at least one free carboxylate group and has the formula



wherein R is selected from the group consisting of substituted or unsubstituted C₁-C₃₀ straight, branched or cyclic alkyl, alkenyl, alkynyl, alkylaryl or aryl group; R' is a perfume alcohol with a boiling point at 760 mm Hg of less than about 300°C; and n and m are individually an integer of 1 or greater.

[0129] The perfume component may further comprise an ester of a perfume alcohol wherein the ester has at least one free carboxylate group in admixture with a fully esterified ester of a perfume alcohol.

[0130] Preferably, R is selected from the group consisting of substituted or unsubstituted C₁-C₂₀ straight, branched or cyclic alkyl, alkenyl, alkynyl, alkylaryl, aryl group or ring containing a heteroatom. R' is preferably a perfume alcohol selected from the group consisting of geraniol, nerol, phenoxanol, floralol, β-citronellol, nonadol, cyclohexyl ethanol, phenyl ethanol, phenoxyethanol, isoborneol, fenchol, isocyclogeraniol, 2-phenyl-1-propanol, 3,7-dimethyl-1-octanol, and combinations thereof and the ester is preferably selected from maleate, succinate adipate, phthalate, citrate or pyromellitate esters of the perfume alcohol. The most preferred esters having at least one free carboxylate group are then selected from the group consisting of geranyl succinate, neryl succinate, (□-citronellyl) maleate, nonadol maleate, phenoxanyl maleate, (3,7-dimethyl-1-octanyl) succinate, (cyclohexylethyl) maleate, florally succinate, (□-citronellyl) phthalate and (phenylethyl) adipate.

[0131] Pro-perfumes suitable for use herein include those known in the art. Suitable pro-perfumes can be found in the art including U.S. Pat. Nos.: 4,145,184, Brain and Cummins, issued Mar. 20, 1979; 4,209,417, Whyte, issued June 24, 1980; 4,545,705, Moeddel, issued May 7, 1985; and 4,152,272, Young, issued May 1, 1979.

[0132] It may be desirable to add additional perfume to the composition, as is, without protection via the capsules. Such perfume loading would allow for aesthetically pleasing fragrance of the detergent tablet itself.

[0133] The detergent tablet preferably comprises perfume component at a level of from 0.05 % to 15 %, preferably from 0.1 % to 10 %, most preferably from 0.5% to 5% by weight.

Dye Fixing Agent

[0134] The compositions of the present invention can comprise dye fixing agents (fixatives). These are well-known, commercially available materials, which are designed to improve the appearance of dyed fabrics by minimising the loss of dye from the fabrics due to washing. Many dye fixatives are cationic and are based on quaternised nitrogen compounds or on nitrogen compounds having a strong cationic charge, which is formed *in situ* under the conditions of usage. Cationic fixatives are available under various trade names from several suppliers. Representative trade names include CROSCOLOR PMF and CROSCOLOR NOFF from Crosfield, INDOSOL E-50 from Sandoz, SANDOFIX TPS from Sandoz, SANDOFIX SWE from Sandoz, REWIN SRF, REWIN SRF-O and REWIN DWE from CHT-Beitlich GmbH, Tinofix ECO, Tinofix FRD and Solfin from Ciba-Geigy.

[0135] Other suitable cationic dye fixing agents are described in "Aftertreatments for Improving the Fastness of Dyes on Textile Fibres", Christopher C. Cook, *Rev. Prog. Coloration*, Vol. XII (1982). Dye fixing agents suitable for use in the present compositions include ammonium compounds such as fatty acid-diamine condensates *inter alia* the hydrochloride, acetate, metosulphate and benzyl hydrochloride salts of diamine esters. Non-limiting examples include oleyldiethyl aminoethylamide, oleylmethyl diethylenediamine methosulphate, monostearylethylene diamino-trimethylammonium methosulphate. In addition, the N-oxides of tertiary amines, derivatives of polymeric alkyldiamines, polyamine cyanuric chloride condensates, aminated glycerol dichlorohydrins, and mixture thereof.

[0136] Another class of dye fixing agents suitable for use herein are cellulose reactive dye fixing agents. The cellulose reactive dye fixatives may be suitably combined with one or more dye fixatives described herein above in order to comprise a "dye fixative system". The term "cellulose reactive dye fixing agent" is defined herein as a dye fixing agent that reacts with the cellulose fibres upon application of heat or upon a heat treatment either *in situ* or by the formulator. Cellulose reactive dye fixatives are described in more detail in WO-A-00/15745.

Chlorine Scavengers

[0137] The compositions of the present invention can comprise one or more chlorine scavengers. Suitable scavengers include ammonium salts having the formula:



wherein each R is independently hydrogen, C₁-C₄ alkyl, C₁-C₄ substituted alkyl and mixtures thereof, preferably R is hydrogen or methyl, more preferably hydrogen. R¹ is selected from hydrogen, C₁-C₉ alkyl, C₁-C₉ substituted alkyl and mixtures thereof, preferably hydrogen. X is a compatible anion, preferably chloride. Non-limiting examples of preferred chlorine scavengers include ammonium chloride, ammonium sulphate, and mixtures thereof. Preferably ammonium chloride.

Fabric Abrasion Reducing Polymers

[0138] The compositions herein can comprise fabric abrasion reducing polymers. Any suitable fabric abrasion reducing polymers may be used herein. Some examples of suitable polymers are described in WO-A-00/15745.

Wrinkle Reducing Agents

[0139] The compositions herein can comprise wrinkle reducing agents. Any suitable wrinkle reducing agents may be used herein. Some examples of suitable agents are described in WO-A-99/55953.

Optional Ingredients

[0140] There are a variety of optional ingredients that may be used in the compositions herein. Any suitable ingredient or mixture of ingredients may be used. Non-limiting examples of these optional ingredients are given below

[0141] The present compositions can comprise a disintegration aid. As used herein, the term "disintegration aid" means a substance or mixture of substances that has the effect of hastening the dispersion of the matrix of the present compositions on contact with water. Any suitable disintegration aid can be used but preferably they are selected from disintegrants, effervescent, binders, clays, highly soluble compounds, cohesive compounds, and mixtures thereof.

[0142] The compositions of the present invention can comprise enzymes. Where present said enzymes are preferably selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof. Preferred enzymes include protease, amylase, lipase, peroxidases, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

[0143] The compositions of the present invention may comprise a bleaching system. Bleaching systems typically comprise a "bleaching agent" (source of hydrogen peroxide) and an "initiator" or "catalyst". When present, bleaching agents will typically be at levels of from about 1%, preferably from about 5% to about 30%, preferably to about 20% by weight of the composition. If present, the amount of bleach activator will typically be from about 0.1%, preferably from about 0.5% to about 60%, preferably to about 40% by weight, of the bleaching composition comprising the bleaching agent-plus-bleach activator.

Bleaching Agents -

[0144] Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms.

[0145] The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

[0146] A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

[0147] Compositions of the present invention may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC").

However, chlorine-type bleaches are less preferred for compositions, which comprise enzymes.

(a) Bleach Activators -

[0148] Preferably, the peroxygen bleach component in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01%, preferably from about 0.5%, more preferably from about 1% to about 15%, preferably to about 10%, more preferably to about 8%, by weight of the composition. Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoyl-caprolactam, benzoyloxybenzene sulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C₁₀-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C₈-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

[0149] Preferred hydrophobic bleach activators include, but are not limited to, nonanoyloxybenzenesulphonate (NOBS), 4-[N-(nonaoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS) an example of which is described in U.S. Patent No. 5,523,434, dodecanoyloxybenzenesulphonate (LOBS or C₁₂-OBS), 10-undecenoyloxybenzenesulfonate (UDOBS or C₁₁-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA).

[0150] Preferred bleach activators are those described in U.S. 5,698,504 Christie et al., issued December 16, 1997; U.S. 5,695,679 Christie et al. issued December 9, 1997; U.S. 5,686,401 Willey et al., issued November 11, 1997; U.S. 5,686,014 Hartshorn et al., issued November 11, 1997; U.S. 5,405,412 Willey et al., issued April 11, 1995; U.S. 5,405,413 Willey et al., issued April 11, 1995; U.S. 5,130,045 Mitchel et al., issued July 14, 1992; and U.S. 4,412,934 Chung et al., issued November 1, 1983, and copending patent applications U. S. Serial Nos. 08/709,072, 08/064,564, all of which are incorporated herein by reference.

[0151] The mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1, more preferably from about 10:1 to about 1:1, preferably to about 3:1.

[0152] Quaternary substituted bleach activators may also be included. The present laundry compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in U.S. 5,686,015 Willey et al., issued November 11, 1997; U.S. 5,654,421 Taylor et al., issued August 5, 1997; U.S. 5,460,747 Gosselink et al., issued October 24, 1995; U.S. 5,584,888 Miracle et al., issued December 17, 1996; and U.S. 5,578,136 Taylor et al., issued November 26, 1996; all of which are incorporated herein by reference.

[0153] Highly preferred bleach activators useful herein are amide-substituted as described in U.S. 5,698,504, U.S. 5,695,679, and U.S. 5,686,014 each of which are cited herein above. Preferred examples of such bleach activators include: (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl) oxybenzene sulfonate, (6-decanamidocaproyl)oxybenzenesulfonate and mixtures thereof.

[0154] Other useful activators, disclosed in U.S. 5,698,504, U.S. 5,695,679, U.S. 5,686,014 each of which is cited herein above and U.S. 4,966,723 Hodge et al., issued October 30, 1990, include benzoxazin-type activators, such as a C₆H₄ ring to which is fused in the 1,2-positions a moiety --C(O)OC(R¹)=N-.

[0155] Depending on the activator and precise application, good bleaching results can be obtained from bleaching systems having with in-use pH of from about 6 to about 13, preferably from about 9.0 to about 10.5. Typically, for example, activators with electron-withdrawing moieties are used for near-neutral or sub-neutral pH ranges. Alkalis and buffering agents can be used to secure such pH.

[0156] Acyl lactam activators, as described in U.S. 5,698,504, U.S. 5,695,679 and U.S. 5,686,014, each of which is cited herein above, are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A) and acyl valerolactams (see U.S. 5,503,639 Willey et al., issued April 2, 1996 incorporated herein by reference).

(b) Organic Peroxides, especially Diacyl Peroxides -

[0157] These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming.

(c) Metal-containing Bleach Catalysts -

[0158] The present invention compositions and methods may utilize metal-containing bleach catalysts that are effective for use in bleaching compositions. Preferred are manganese and cobalt-containing bleach catalysts.

[0159] One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of de-

fined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrate having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed

Manganese Metal Complexes -

[0160] If desired, the compositions herein can be catalyzed by means of a manganese compound. Such compounds and levels of use are well known in the art and include, for example, the manganese-based catalysts disclosed in U. S. Patent Nos. 5,576,282; 5,246,621; 5,244,594; 5,194,416; and 5,114,606; and European Pat. App. Pub. Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1; preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-triacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})-(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Patent Nos. 4,430,243 and U.S. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following: U.S. Patent Nos. 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Cobalt Metal Complexes -

[0161] Cobalt bleach catalysts useful herein are known, and are described, for example, in U.S. Patent Nos. 5,597,936; 5,595,967; and 5,703,030; and M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", *Adv. Inorg. Bioinorg. Mech.*, (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[\text{Co}(\text{NH}_3)_5\text{OAc}] \text{ T}_y$, wherein "OAc" represents an acetate moiety and "T_y" is an anion, and especially cobalt pentaamine acetate chloride, $[\text{Co}(\text{NH}_3)_5\text{OAc}]\text{Cl}_2$; as well as $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{OAc})_2$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{PF}_6)_2$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{SO}_4)$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{BF}_4)_2$; and $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{NO}_3)_2$ (herein "PAC").

[0162] These cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. Patent Nos. 5,597,936; 5,595,967; and 5,703,030; in the Tobe article and the references cited therein; and in U.S. Patent 4,810,410; *J. Chem. Ed.* (1989), 66 (12), 1043-45; *The Synthesis and Characterization of Inorganic Compounds*, W. L. Jolly (Prentice-Hall; 1970), pp. 461-3; *Inorg. Chem.*, 18, 1497-1502 (1979); *Inorg. Chem.*, 21, 2881-2885 (1982); *Inorg. Chem.*, 18, 2023-2025 (1979); *Inorg. Synthesis*, 173-176 (1960); and *Journal of Physical Chemistry*, 56, 22-25 (1952).

Transition Metal Complexes of Macropolycyclic Rigid Ligands -

[0163] Compositions herein may also suitably include as bleach catalyst a transition metal complex of a macropolycyclic rigid ligand. The amount used is a catalytically effective amount, suitably about 1 ppb or more, for example up to about 99.9%, more typically about 0.001 ppm or more, preferably from about 0.05 ppm to about 500 ppm (wherein "ppb" denotes parts per billion by weight and "ppm" denotes parts per million by weight). Transition-metal bleach catalysts of Macropolycyclic Rigid Ligands which are suitable for use in the invention compositions can in general include known compounds where they conform with the definition herein, as well as, more preferably, any of a large number of novel compounds expressly designed for the present laundry or laundry uses, and non-limitingly illustrated by any of the following:

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)
 Dichloro-5,12-diethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)
 Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(II) Hexafluorophosphate
 Diaquo-5,12-diethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(II) Hexafluorophosphate
 Aquo-hydroxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III) Hexafluorophosphate
 Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(II) Tetrafluoroborate
 Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(III) Hexafluorophosphate
 Dichloro-5,12-diethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(III) Hexafluorophosphate
 Dichloro-5,12-di-n-butyl-1,5,8,12-tetraaza bicyclo[6.6.2]hexadecaneManganese(II)
 Dichloro-5,12-dibenzyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(II)
 Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II)
 Dichloro-5-n-octyl-1 2-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II)
 Dichloro-5-n-butyl-1 2-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II).

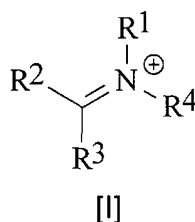
[0164] As a practical matter, and not by way of limitation, the compositions and laundry processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic washing process, typical compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the bleaching compositions.

(d) Other Bleach Catalysts -

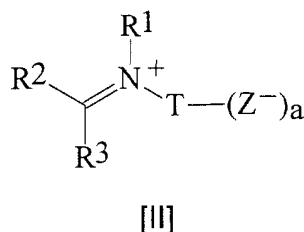
[0165] The compositions herein may comprise one or more other bleach catalysts. Preferred bleach catalysts are zwitterionic bleach catalysts, which are described in U.S. Patent No. 5,576,282 (especially 3-(3,4-dihydroisoquinolinium) propane sulfonate. Other bleach catalysts include cationic bleach catalysts are described in U.S. Patent Nos. 5,360,569, 5,442,066, 5,478,357, 5,370,826, 5,482,515, 5,550,256, and WO 95/13351, WO 95/13352, and WO 95/13353.

(e) Bleach Boosting Compounds -

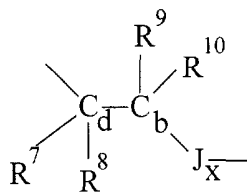
[0166] The compositions herein may comprise one or more bleach boosting compounds. Bleach boosting compounds provide increased bleaching effectiveness in lower temperature applications. The bleach boosters act in conjunction with conventional peroxygen bleaching sources to provide increased bleaching effectiveness. Suitable bleach boosting compounds for use in accordance with the present invention comprise cationic imines, zwitterionic imines, anionic imines and/or polyionic imines having a net charge of from about +3 to about -3, and mixtures thereof. These imine bleach boosting compounds of the present invention include those of the general structure:



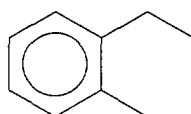
wherein R¹-R⁴ may be a hydrogen or an unsubstituted or substituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals. Preferred bleach boosting compounds include where R¹-R⁴ may be a hydrogen or an unsubstituted or substituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals except that at least one of R¹-R⁴ contains an anionically charged moiety. More preferred bleach boosting compounds include the anionically charged moiety bonded to the imine nitrogen. Such bleach boosting compounds comprise quaternary imine zwitterions represented by the formula:



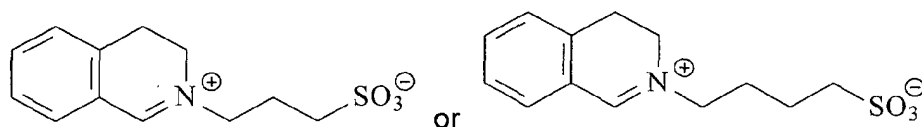
wherein R¹-R³ is hydrogen or an unsubstituted or substituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals; R¹ and R² form part of a common ring; T has the formula:



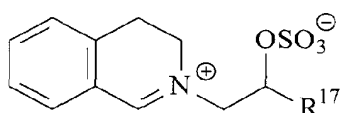
wherein x is equal to 0 or 1; J , when present, is selected $-\text{CR}^{11}\text{R}^{12}$ -, $-\text{CR}^{11}\text{R}^{12}\text{CR}^{13}\text{R}^{14}$ -, and $-\text{CR}^{11}\text{R}^{12}\text{CR}^{13}\text{R}^{14}\text{CR}^{15}\text{R}^{16}$ -, R^7 - R^{16} are individually selected from the group consisting of H, linear or branched C_1 - C_{18} substituted or unsubstituted alkyl, alkylene, oxyalkylene, aryl, substituted aryl, substituted arylcarbonyl groups and amide groups; Z is covalently bonded to J_x when x is 1 and to C_b when x is 0, and Z is selected from the group consisting of $-\text{CO}_2^-$, $-\text{SO}_3^-$ and $-\text{OSO}_3^-$ and a is 1. R_1 and R_2 together may form the non-charged moiety:



[0167] Most preferred bleach boosting compounds include are aryliminium zwitterions wherein R_3 is H, Z is $-\text{SO}_3^-$ or $-\text{OSO}_3^-$, and a is 1. The aryliminium zwitterions may have the formula:

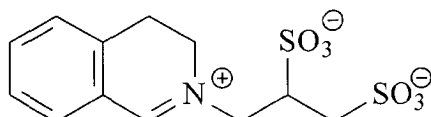


or

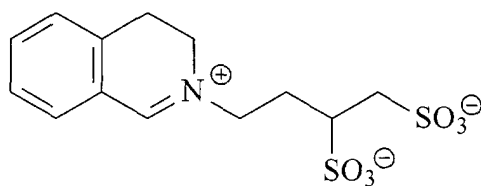


wherein R^{17} is selected from the group consisting of H and linear or branched C_1 - C_{18} substituted or unsubstituted alkyl, preferably C_1 - C_{14} alkyl and even more preferably C_8C_{10} linear alkyl chain.

[0168] The bleach boosting compounds may also comprise an aryliminium polyion having a net negative charge and R^3 is H, T is $-(\text{CH}_2)_b$ - or $-\text{CH}_2(\text{C}_6\text{H}_4)-$, Z is $-\text{SO}_3^-$, a is 2 and b is from 2 to 4. The aryliminium polyion preferably has the formula:



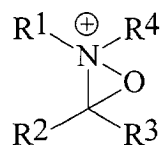
or



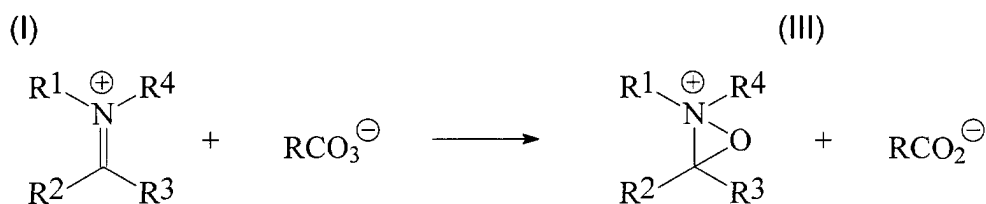
or is a water-soluble salt of these compounds.

[0169] The quaternary imine bleach boosting compounds preferably act in conjunction with a peroxygen source to provide a more effective bleaching system. The bleach boosting compounds react with the peroxygen source to form a more active bleaching species, an oxaziridinium compound. The formed oxaziridinium compounds are either cationic, zwitterionic or polyionic with a net negative charge as was the imine bleach boosting compound. The oxaziridinium compound has an increased activity at lower temperatures relative to the peroxygen compound. The oxaziridinium compound is represented by the formula:

(III)

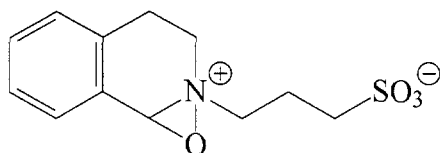


and can be produced from the imine of formula (I) or (II), wherein R^4 is $T-(Z^-)_a$, of the present invention with the reaction:



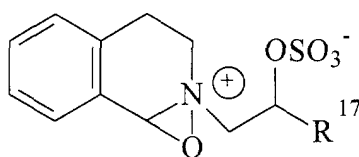
[0170] Thus, the preferred bleach boosting compounds of the present invention represented by the formula (II) produces the active oxaziridinium bleaching species represented by the formula:

(IV)



or

(V)



wherein R¹⁷ is defined as above.

[0171] Peroxygen sources are well-known in the art and the peroxygen source employed in the present invention may comprise any of these well known sources, including peroxygen compounds as well as compounds which under consumer use conditions provide an effective amount of peroxygen in situ. The peroxygen source may include a hydrogen peroxide source, the in situ formation of a peracid anion through the reaction of a hydrogen peroxide source and a bleach activator, preformed peracid compounds or mixtures of suitable peroxygen sources. Of course, one of ordinary skill in the art will recognize that other sources of peroxygen may be employed without departing from the scope of the invention.

[0172] The bleach boosting compounds, when present, are preferably employed in conjunction with a peroxygen source in the bleaching compositions of the present invention. In such a composition, the peroxygen source is preferably present at a level of from about 0.1% to about 60% by weight of the composition, and more preferably from about 1% to about 40% by weight of the composition. In the composition, the bleach boosting compound is preferably present at a level of from about 0.01% to about 10% by weight of the composition, and more preferably from about 0.05% to about 5% by weight of the composition.

(f) Preformed Peracids -

[0173] Also suitable as bleaching agents are preformed peracids, such as phthalimido-peroxy-caproic acid ("PAP"). See for example U.S. Patent Nos. 5,487,818, 5,310,934, 5,246,620, 5,279,757 and 5,132,431.

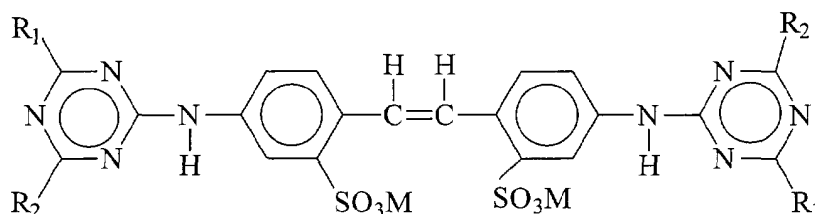
[0174] The compositions of the present invention can comprise polymeric dye transfer inhibiting agents. If present, the pouch compositions herein preferably comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of total composition of polymeric dye transfer inhibiting agents.

[0175] The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

[0176] The compositions of the present invention can comprise builders. Suitable water-soluble builder compounds for use herein include water soluble monomeric polycarboxylates or their acid forms, homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, and mixtures thereof.

[0177] The compositions of the present invention can comprise optical brighteners. If present, pouch compositions herein preferably contain from 0.005% to 5% by weight of total composition of hydrophilic optical brighteners.

[0178] Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

[0179] When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-

Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

[0180] When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

[0181] When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

[0182] Other preferred optical brighteners are those known as Brightener 49 available from Ciba-Geigy.

[0183] The compositions of the present invention can comprise a clay softening system. Any suitable clay softening system may be used but preferred are those comprising a clay mineral compound and optionally a clay flocculating agent. If present, pouch compositions herein preferably contain from 0.001% to 10% by weight of total composition of clay softening system.

[0184] The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US-A-3,862,058, US-A-3,948,790, US-A-3,954,632 and US-A-4,062,647. Also, EP-A-299,575 and EP-A-313,146 in the name of the Procter & Gamble Company describe suitable organic polymeric clay flocculating agents.

[0185] The compositions of the present invention can comprise organic polymeric compounds. By organic polymeric compound it is meant essentially any polymeric organic compound commonly found in detergent compositions having dispersant, anti-redeposition, or other detergency properties.

[0186] Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.01% to 30%, preferably from 0.05% to 15%, most preferably from 0.1% to 10% by weight of the compositions.

[0187] Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids, modified polycarboxylates or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of molecular weight 2000-10000 and their copolymers with any suitable other monomer units including modified acrylic, fumaric, maleic, itaconic, aconitic, mesaconic, citraconic and methylenemalononic acid or their salts, maleic anhydride, acrylamide, alkylene, vinylmethyl ether, styrene and any mixtures thereof. Preferred are the copolymers of acrylic acid and maleic anhydride having a molecular weight of from 5000 to 100 000, more preferably from 20,000 to 100,000.

[0188] Preferred commercially available acrylic acid containing polymers having a molecular weight below 15,000 include those sold under the tradename Sokalan PA30, PA20, PA15, PA10 and Sokalan CP10 by BASF GmbH, and those sold under the tradename Acusol 45N, 480N, 460N by Rohm and Haas.

[0189] Preferred acrylic acid containing copolymers include those which contain as monomer units: a) from 90% to 10%, preferably from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, preferably from 20% to 80% by weight of a substituted acrylic monomer or its salts having the general formula- $[CR_2-CR_1(CO-O-R_3)]$ - wherein at least one of the substituents R_1 , R_2 or R_3 , preferably R_1 or R_2 is a 1 to 4 carbon alkyl or hydroxyalkyl group, R_1 or R_2 can be a hydrogen and R_3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R_1 is methyl, R_2 is hydrogen (i.e. a methacrylic acid monomer). The most preferred copolymer of this type has a molecular weight of 3500 and contains 60% to 80% by weight of acrylic acid and 40% to 20% by weight of methacrylic acid.

[0190] The polyamine and modified polyamine compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

[0191] Other optional polymers may polyvinyl alcohols and acetates both modified and non-modified, cellulose and modified cellulose, polyoxyethylenes, polyoxypropylenes, and copolymers thereof, both modified and non-modified, terephthalate esters of ethylene or propylene glycol or mixtures thereof with polyoxyalkylene units.

[0192] Suitable examples are disclosed in US-A-5,591,703, US-A-5,597,789 and US-A-4,490,271.

[0193] An alkali metal silicate can be a component of the compositions of the present invention. A preferred alkali metal silicate is sodium silicate having an $SiO_2:Na_2O$ ratio of from 1.8 to 3.0, preferably from 1.8 to 2.4, most preferably 2.0. Sodium silicate is preferably present at a level of less than 20%, preferably from 1% to 15%, most preferably from 3% to 12% by weight of SiO_2 . The alkali metal silicate may be in the form of either the anhydrous salt or a hydrated salt.

[0194] Alkali metal silicate may also be present as a component of an alkalinity system.

[0195] The alkalinity system also preferably contains sodium metasilicate, present at a level of at least 0.4% SiO_2 by weight. Sodium metasilicate has a nominal $SiO_2:Na_2O$ ratio of 1.0. The weight ratio of said sodium silicate to said sodium metasilicate, measured as SiO_2 , is preferably from 50:1 to 5:4, more preferably from 15:1 to 2:1, most preferably from 10:1 to 5:2.

[0196] The present compositions can comprise colourant. The term 'colourant', as used herein, means any substance that absorbs specific wavelengths of light from the visible light spectrum. Such colourants when added to a detergent

composition have the effect of changing the visible colour and thus the appearance of the detergent composition. Colourants may be for example either dyes or pigments. Preferably the colourants are stable in composition in which they are to be incorporated. Thus in a composition of high pH the colourant is preferably alkali stable and in a composition of low pH the colourant is preferably acid stable.

[0197] The first and/or second and/or optionally further phases may contain a colourant, a mixture of colourants, coloured particles or mixture of coloured particles such that the various phases have different visual appearances. Preferably one of either the first or the second phases comprises a colourant. Where both the first and second and/or subsequent phases comprise a colourant it is preferred that the colourants have a different visual appearance.

[0198] Examples of suitable dyes include reactive dyes, direct dyes, azo dyes. Preferred dyes include phthalocyanine dyes, anthraquinone dye, quinoline dyes, monoazo, disazo and polyazo. More preferred dyes include anthraquinone, quinoline and monoazo dyes. Preferred dyes include SANDOLAN E-HRL 180% (tradename), SANDOLAN MILLING BLUE (tradename), TURQUOISE ACID BLUE (tradename) and SANDOLAN BRILLIANT GREEN (tradename) all available from Clariant UK, HEXACOL QUINOLINE YELLOW (tradename) and HEXACOL BRILLIANT BLUE (tradename) both available from Pointings, UK, ULTRA MARINE BLUE (tradename) available from Holliday or LEVAFIX TURQUOISE BLUE EBA (tradename) available from Bayer, USA.

[0199] The colourant may be incorporated into the phases by any suitable method. Suitable methods include mixing all or selected detergent components with a colourant in a drum or spraying all or selected detergent components with the colourant in a rotating drum.

[0200] Colourant when present as a component of the first phase is present at a level of from 0.001% to 1.5%, preferably from 0.01% to 1.0%, most preferably from 0.1% to 0.3%. When present as a component of the second and/or optionally further phases, colourant is generally present at a level of from 0.001% to 0.1%, more preferably from 0.005% to 0.05%, most preferably from 0.007% to 0.02%.

[0201] The compositions of the present invention may contain a lime soap dispersant compound, preferably present at a level of from 0.1% to 40% by weight, more preferably 1% to 20% by weight, most preferably from 2% to 10% by weight of the compositions.

[0202] A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. Preferred lime soap dispersant compounds are disclosed in WO-A-93/08877.

Method of Use

[0203] The present invention includes methods of washing in a washing machine comprising charging a washing machine with a pouch composition according to the present invention and washing in a conventional manner. Methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent tablet composition in accord with the invention.

pH of the compositions

[0204] The pouch compositions of the present invention are preferably not formulated to have an unduly high pH. Preferably, the compositions of the present invention have a pH, measured as a 1% solution in distilled water, of from 7.0 to 12.5, more preferably from 7.5 to 11.8, most preferably from 8.0 to 11.5.

Examples

EXAMPLE 1:

[0205] The following example describes a dual compartment pouch having one compartment comprising a solid detergent composition and one separate compartment comprising the beads.

Solid detergent composition:	
	% by weight, of total composition
Anionic agglomerates 1	7.1
Anionic agglomerates 2	17.5
Nonionic agglomerates	2.0
Cationic agglomerates	4.6
Layered silicate	9.7

(continued)

Solid detergent composition:	
	% by weight, of total composition
Sodium percarbonate	12.2
Bleach activator agglomerates	6.1
Sodium carbonate	10.82
EDDS/Sulphate particle	0.5
Tetrasodium salt of Hydroxyethane	0.6
Diphosphonic acid	
Soil release polymer	0.3
Fluorescer	0.2
Zinc Phthalocyanine sulphonate encapsulate	0.03
Soap powder	1.2
Suds suppresser	2.8
Citric acid	4.5
Protease	1
Lipase	0.35
Cellulase	0.2
Amylase	1.1
Perfume spray on	0.1
DIBS (Sodium diisobutylbenzene sulphonate)	2.1
Anionic agglomerates 1 comprise 40% anionic surfactant, 27% zeolite and 33% carbonate; Anionic agglomerates 2 comprise 40% anionic surfactant, 28% zeolite and 32% carbonate; Nonionic agglomerate comprise 26% nonionic surfactant, 6% Lutensit K-HD 96 ex BASF, 40% sodium acetate anhydrous, 20% carbonate and 8% zeolite; Cationic agglomerate comprise 20% cationic surfactant, 56% zeolite and 24% sulfate Layered silicate comprises of 95% SKS 6 and 5% silicate; Bleach activator agglomerates comprise 81% Tetraacetyethylene diamine (TAED), 17% acrylic/maleic copolymer (acid form) and 2% water; EDDS/Sulphate particle particle comprise 58% of Ethylene diamine-N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water; Zinc phthalocyanine sulphonate encapsulates are 10% active; Suds suppresser comprises 11.5% silicone oil (ex Dow Corning), 59% zeolite and 29.5% H₂O.	

Bead composition:	
	% by weight, of total composition
Softener and perfume bead	15.0 %

[0206] Perfume beads composition contains 56% expancel 091DE80, 7% silica, 8% perfume, 5% crosslinked polyvinylalcohol (PVA)-borate, 5% water, 18% cationic softener N,N-di(candyl-oxy-ethyl)-N-methyl,N-(2-hydroxyethyl) ammonium methyl sulfate and 1% of laundry compatible Zeneca Monastral blue.

MANUFACTURING:

Manufacturing of the solid composition

[0207] The detergent active composition of the first phase was prepared by admixing the granular components in a mixing drum for 5 minutes to create an homogenous particle mixture. During this mixing, the spray-ons were carried out with a nozzle and hot air using the binder composition described above.

Manufacturing of the beads

[0208] The beads of the second phase were manufactured using a Braun food processor with a standard stirrer

where the dry mixture described above is added. The mixer was operated at high speed during 1 minute and the mix is poured into a Fuji Paudal Dome Gran DGL1 (Japan) extruder with 3 mm diameter holes in the extruder tip plate and operated at 70 revolutions per minute. The resulting product was added into a Fuji Paudal Marumerizer QJ-230 where it is operated at 1000 revolutions per minute for 5 minutes where a good spheronization was achieved.

[0209] In a further step, the beads were coated by a partially insoluble coating described. This was achieved by spraying the beads in a conventional mix drum with 4% (weight beads based) of a mixture of 80% cross linked polyvinyl alcohol-borate and 20% water at 70°C using a spray nozzle and hot air. The beads are then left in a rotating drum for 60 minutes and hot air was injected in order to evaporate part of the water contained in the PVA coating. The final water content in the bead is mentioned in the bead composition above.

[0210] The resulting beads had a density of 950 kg/m³ which floated in de-ionized water at 20°C. The particle size was measured using the ASTM D502-89 method and the calculated average particle size was 2.6 mm.

Pouch making:

[0211] A piece of plastic is placed in a mould to act as a false bottom. The mould consists of a cylindrical shape and has a diameter of 45mm and a depth of 25mm. A 1mm thick layer of rubber is present around the edges of the mould. The mould has some holes in the mould material to allow a vacuum to be applied. With the false bottom in place the depth of the mould is 12mm. A piece of PVA film (Chris-Craft M-8630) is placed on top of this mould and fixed in place. A vacuum is applied to pull the film into the mould and pull the film flush with the inner surface of the mould and the false bottom. The perfume & softener beads are poured into the mould. Next, a second piece of Chris-Craft M-8630 film is placed over the top of the mould with the beads and sealed to the first piece of film by applying an annular piece of flat metal of an inner diameter of 46mm and heating that metal under moderate pressure onto the ring of rubber at the edge of the mould to heat-seal the two pieces of film together to form a compartment comprising the liquid component. The metal ring is typically heated to a temperature of from 135°C to 150°C and applied for up to 5 seconds.

[0212] The compartment comprising the beads is removed from the mould and the piece of plastic acting as a false bottom is also removed from the mould. A third piece of Chris-Craft M-8630 film is placed on top of the mould and fixed in place. A vacuum is applied to pull the film into the mould and pull the film flush with the inner surface of the mould. The rest of the detergent composition is poured into the mould. Next, the compartment comprising the beads is placed over the top of the mould with the detergent composition and is sealed to the third layer of film by applying an annular piece of flat metal of an inner diameter of 46mm and heating that metal under moderate pressure onto the ring of rubber at the edge of the mould to heat-seal the pieces of film together to form a pouch comprising two compartments, where a first compartment comprises the beads and a second compartment comprises the rest of the detergent composition. The metal ring is typically heated to a temperature of from 135°C to 150°C and applied for up to 5 seconds.

[0213] The making of the two compartment described above could of course be made in different molds in order to perform both steps simultaneously.

EXAMPLE 2:

[0214] The following example describes a single compartment pouch with one layer made of a solid detergent composition and one layer made of beads creating two distinct layers within the one pouch compartment.

Solid detergent composition:	
	% by weight, of total composition
Anionic agglomerates 1	7.1
Anionic agglomerates 2	17.5
Nonionic agglomerates	2.0
Cationic agglomerates	4.6
Layered silicate	9.7
Sodium percarbonate	12.2
Bleach activator agglomerates	6.1
Sodium carbonate	10.82
EDDS/Sulphate particle	0.5
Tetrasodium salt of Hydroxyethane	0.6
Diphosphonic acid	
Soil release polymer	0.3

(continued)

Solid detergent composition:	
	% by weight, of total composition
Fluorescer	0.2
Zinc Phthalocyanine sulphonate encapsulate	0.03
Soap powder	1.2
Suds suppresser	2.8
Citric acid	4.5
Protease	1
Lipase	0.35
Cellulase	0.2
Amylase	1.1
Perfume spray on	0.1
DIBS (Sodium diisobutylbenzene sulphonate)	2.1
Anionic agglomerates 1 comprise 40% anionic surfactant, 27% zeolite and 33% carbonate; Anionic agglomerates 2 comprise 40% anionic surfactant, 28% zeolite and 32% carbonate; Nonionic agglomerate comprises 26% nonionic surfactant, 6% Lutensit K-HD 96 ex BASF, 40% sodium acetate anhydrous, 20% carbonate and 8% zeolite; Cationic agglomerate comprises 20% cationic surfactant, 56% zeolite and 24% sulfate; Layered silicate comprises of 95% SKS 6 and 5% silicate; Bleach activator agglomerates comprise 81% Tetraacetylethylene diamine (TAED), 17% acrylic/maleic copolymer (acid form) and 2% water; EDDS/Sulphate particle particle comprise 58% of Ethylene diamine-N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water; Zinc phthalocyanine sulphonate encapsulates are 10% active; Suds suppresser comprises 11.5% silicone oil (ex Dow Corning), 59% zeolite and 29.5% H₂O.	

Bead composition:	
	% by weight, of total composition
Softener and perfume bead	15.0 %

[0215] Perfume beads composition contains 56% expancel 091DE80, 7% silica, 8% perfume, 5% crosslinked polyvinylalcohol (PVA)-borate, 5% water, 18% cationic softener N,N-di(candyl-oxy-ethyl)-N-methyl,N-(2-hydroxyethyl) ammonium methyl sulfate and 1% of laundry compatible Zeneca Monastral blue.

[0216] The manufacturing of the 2 phases is done accordingly to the description in the first example.

Pouch making:

[0217] A piece of Chris-Craft M-8630 film, 38 microns thick, is placed on top of a mould and fixed in place. The mould consists of a cylindrical shape with a diameter of 45 mm and a depth of 25 mm. A 1 mm thick layer of rubber remains present around the edges of the mould. The mould has some holes in the mold material to allow a vacuum to be applied.

[0218] A vacuum is applied to pull the film into the mold and pull the film flush with the inner surface of the mould. The detergent composition (Phase 1) is poured into the mould. This powder mix has a bulk density of 860 g/l prior to being poured into the mould. This is slightly vibrated. The softener and perfume beads (Phase 2) are then poured on top of the detergent composition forming a distinct layer.

Next, a sheet of the same M-8630 film is placed over the top of the mould with the powder and sealed to the first layer of film by applying an annular piece of flat metal of an inner diameter of 46 mm and heating that metal under moderate pressure onto the ring of rubber at the edge of the mould, to heat-seal the two pieces of film together. The metal ring is typically heated to a temperature of 140 - 146 °C and applied for up to 5 seconds. The film is stretched during this process, which can be visualised by using in this example a film material with a grid on it. The thickness variation of the film is between 20 and 40 microns, the bottom being 20 microns, the top being 40 microns and the sides varying between 20 and 40 microns.

EXAMPLE 3:

[0219] The following example describes a single compartment pouch where the beads and the rest of the solid detergent composition are mixed together.

Solid detergent composition:	
	% by weight, of total composition
Clay extrudate	14
Flocculant agglomerate	3.8
Anionic agglomerates 1	32
Anionic agglomerates 2	2.27
Sodium percarbonate	8.0
Bleach activator agglomerates	2.31
Sodium carbonate	23.066
EDDS/Sulphate particle	0.19
Tetrasodium salt of Hydroxyethane	0.34
Diphosphonic acid	
Fluorescer	0.15
Zinc phthalocyanine sulphonate encapsulate	0.027
Soap powder	1.40
Suds suppresser	2.6
Citric acid	4.0
Protease	0.45
Cellulase	0.20
Amylase	0.20
Perfume spray-on	0.1
Clay extrudate comprise 97% of CSM Quest 5A clay and 3% water; Flocculant raw material is polyethylene oxide with an average molecular weight of 300,000; Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate; Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate; Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water; Zinc phthalocyanine sulphonate encapsulates are 10% active; Ethylene diamine-N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine-N, N-disuccinic acid sodium salt, 23% of sulphate and 19% water; Suds suppresser comprises of 11.5% silicone oil (ex Dow Corning), 59% zeolite and 29.5% water;	

Bead composition:	
	% by weight, of total composition
Perfume bead composition	4.9

[0220] Perfume beads composition contains 46% expancel 091DE80, 8% silica, 10% silicate, 15% perfume, 5% crosslinked polyvinylalcohol-borate, 10% water and 7% sodium sulfate.

[0221] The pouch making is done accordingly to the description in example # 2 but this time the beads and the rest of the detergent composition are mixed together forming a single phase.

EXAMPLE 4:

[0222] The following example describes a dual compartment pouch having one compartment comprising a liquid detergent composition and one separate compartment comprising a solid detergent composition and the beads mixed together creating a single phase.

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Liquid detergent composition:	
	% by weight, of total composition
Nonionic surfactant	12.0
Solvent	4.0
Dye	0.1
Nonionic surfactant comprises an ethoxylated alcohol surfactant; Solvent comprises 1,2-Propanediol.	

Solid detergent composition:	
	% by weight, of total composition
Anionic agglomerate	25.0
Cationic agglomerate	5.0
Layered silicate	5.0
Sodium percarbonate	12.2
Bleach activator agglomerates	6.1
Sodium carbonate	12.72
EDDS/Sulphate particle	0.5
Tetrasodium salt of Hydroxyethane	0.6
Diphosphonic acid	
Soil release polymer	0.3
Fluorescer	0.2
Zinc Phthalocyanine sulphonate encapsulate	0.03
Soap powder	1.2
Suds suppresser	2.8
Citric acid	4.5
Protease	1
Lipase	0.35
Cellulase	0.2
Amylase	1.1
Perfume spray on	0.1
Anionic agglomerate comprise 40% anionic surfactant, 27% zeolite and 33% carbonate; Cationic agglomerate comprises 20% cationic surfactant, 56% zeolite and 24% sulfate; Layered silicate comprises of 95% SKS 6 and 5% silicate; Bleach activator agglomerates comprise 81% Tetraacetylethylene diamine (TAED), 17% acrylic/maleic copolymer (acid form) and 2% water; EDDS/Sulphate particle particle comprise 58% of Ethylene diamineN,N-disuccinic acid sodium salt, 23% of sulphate and 19% water; Zinc phthalocyanine sulphonate encapsulates are 10% active; Suds suppresser comprises 11.5% silicone oil (ex Dow Corning), 59% zeolite and 29.5% H₂O;	

Bead composition:	
	% by weight, of total composition
Perfume bead composition	4.9

[0223] Perfume beads composition contains 46% expancel 091DE80, 8% silica, 10% silicate, 15% perfume, 5% crosslinked polyvinylalcohol-borate, 10% water and 7% sodium sulfate.

[0224] The pouch making is done accordingly to the description in example # 1 by which the first compartment of the pouch comprises the liquid detergent composition described above and the second compartment comprises a solid

composition made by mixing the perfume beads and the solid detergent composition described above.

Claims

1. A detergent composition wherein the composition is enclosed by a pouch made of a water-soluble film, said composition comprising:
 - (a) a surfactant; and
 - (b) at least one particle comprising benefit agent wherein the particle floats in deionised water at 20°C.
2. A detergent composition according to Claim 1 wherein the composition comprises a plurality of particles comprising benefit agent.
3. A detergent composition according to Claim 1 or 2 wherein the particles comprising the benefit agent have a average particle size of from 0.5mm to 10mm.
4. A detergent composition according to any preceding claim wherein the water-soluble film has a solubility of at least 50%, preferably at least 75%.
5. A detergent composition according to any of the preceding claims wherein the benefit agent is selected from cationic softening agents, soil-release agents, perfumes, suds-suppressing system, anti-wrinkle agents, chelating agents, chloride scavengers, dye fixing agents, fabric abrasion reducing polymers, and mixture thereof.
6. A detergent composition according to any of the preceding claims wherein the benefit agent is selected from cationic softening agents, perfumes, pro-perfumes and mixtures thereof.
7. A detergent composition according to any of the preceding claims comprising at least two phases, the first phase, comprising surfactant, in the form of a shaped body with at least one mould therein and the second phase, comprising benefit agent, compressed within the mould.
8. A detergent composition according to any of the preceding claims comprising from 0.5% to 75% by weight, preferably from 1% to 50% by weight of surfactant.
9. A detergent composition according to any of the preceding claims wherein the surfactant is selected from anionic sulphonate surfactants, anionic sulphate surfactants, secondary alkyl sulphate surfactants, nonionic surfactants and mixtures thereof.
10. A method of washing in a washing machine comprising charging a washing machine with a shaped detergent composition according to any of the preceding claims and washing in a conventional manner.



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