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(54) Detergent compositions

(57) The present invention relates to a shaped detergent composition comprising:

(a) a surfactant; and
(b) at least one particle comprising benefit agent wherein the particle floats in deionised 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. In addition, the present shaped compositions can be effectively dosed via the dispensing drawer of standard washing machines

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Description

Technical Field

[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

[0002] Shaped detergent compositions are known in the art. Usually such compositions take the form of a tablet. It is understood that detergent compositions in tablet form hold several advantages over detergent compositions in particulate form, such as ease of dosing, handling, transportation and storage. Consumers particularly like the convenience of a shaped detergent composition that they can dose via the dispensing drawer.

[0003] Shaped detergent compositions are usually prepared by pre-mixing components of a detergent composition and forming the pre-mixed detergent components into a tablet using any suitable equipment, preferably a tablet press. Tablets are typically formed by compression of the components of the detergent composition so that the tablets produced are sufficiently robust to be able to withstand handling and transportation without sustaining damage. In addition to being robust, tablets must also dissolve sufficiently fast so that the detergent components are released into the wash water as soon as possible at the beginning of the wash cycle.

[0004] Multi-phase detergent tablets described in the prior art are typically prepared by compressing a first composition in a tablet press to form a substantially planar first layer. A further detergent composition is then delivered to the tablet press on top of the first layer. This second composition is then compressed to form another substantially planar second layer. Thus the first layer is generally subjected to more than one compression as it is also compressed during the compression of the second composition. Typically the first and second compression forces are in the same order of magnitude. The Applicant has found that where this is the case, because the compression force must be sufficient to bind the first and second compositions together, the force used in both the first and second compression steps must be in the range of from about 2,000N to about 200,000N (assuming a tablet cross-section of about 16 cm^2). A consequence of this is a slower rate of tablet dissolution. Other multi-phase tablets exhibiting differential dissolution are prepared such that the second layer is compressed at a lower force than the first layer. However, although the dissolution rate of the second layer is improved, the second layer is soft in comparison to the first layer and is therefore vulnerable to damage caused by handling and transportation.

[0005] One of the advantages of multi-phase tablets is that they allow essentially incompatible ingredients to be formulated in a single dosage unit. The tablet 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.

[0006] EP-A-481547 discloses a dishwashing detergent tablet which, it is alleged, can provide sequential release of a dishwashing composition and a rinse aid composition. The tablets of EP-A-481547 have an inner layer which is completely surrounded on all sides by a barrier layer which, in turn, is completely surrounded by an outer layer. 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.

[0007] However, prior art tablets 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). When the actives are released early it can lead to essentially incompatible phases being released at the same time. Also, many of the actives work most effectively when released towards the end of the laundry cycle so they are not degraded or washed away by the wash liquor. In addition, due to their chemical and physical properties, the prior art tablets often do not disintegrate quickly. This means it can be difficult to dose the tablets via the dispensing drawer and there is a risk of residues remaining on the clothes. Moreover, 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.

[0008] It is an object of the present invention to provide a shaped 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 shaped 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

[0009] The present invention relates to a shaped detergent composition comprising:

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

[0010] 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. It is also preferred that the compositions herein comprise two phases, the first phase in the form of a shaped body having at least one mould therein and the second phase is in the form of a compressed or shaped body contained, for example by physical or chemical adhesion, within the mould of the first phase.

[0011] 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. In addition, the present shaped compositions can be effectively dosed via the dispensing drawer of standard washing machines.

[0012] 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.

[0013] 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

[0014] The shaped 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. The detergent compositions herein can be any suitable shape such as hexagonal, square, rectangular, cylindrical, spherical etc.

[0015] The shaped detergent compositions herein can be of uniform composition. Alternatively, the detergent compositions herein may comprise one or more regions with the concentration of benefit agent and surfactant differing in different regions. It is preferred, but not necessarily essential, that the detergent compositions herein comprise a first phase and the second, and/or any subsequent phase, are spatially distinct in the form of, for example, two layers. As used herein the term "phase" means a distinct, but not necessary homogenous, fraction of the whole composition.

Surfactant

[0016] 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.

[0017] 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.

[0018] 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.

[0019] 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

[0020] Essentially any nonionic surfactants useful for detersive purposes can be included in the present detergent compositions. Preferred, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic ethoxylated alcohol surfactant

[0021] 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 alkoxylate surfactant

[0022] A suitable endcapped alkyl alkoxylate surfactant is the epoxy-capped poly(oxyalkylated) alcohols represented by the formula:

$$R_1O[CH_2CH(CH_3)O]_X[CH_2CH_2O]_Y[CH_2CH(OH)R_2] \qquad (I)$$

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.

[0023] 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

[0024] Preferred nonionic surfactants for use herein include ether-capped poly(oxyalkylated) alcohols having the formula:

$$R^1O[CH_2CH(R^3)O]_X[CH_2]_KCH(OH)[CH_2]_JOR^2$$

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.

[0025] 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.

[0026] 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 alklyeneoxy units as described above. For instance, if x is 3, R^3 may be selected to form ethlyeneoxy (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, mulitple (EO) units and a much small number of (PO) units.

[0027] 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.

[0028] 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:

$$R^1O[CH_2CH(R^3)O]_xCH_2CH(OH)CH_2OR^2$$

where 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.

[0029] 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.

[0030] 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.

[0031] 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 alkoxylated alcohol to form the novel compounds of the present invention.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

[0032] 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

[0033] 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 t 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

[0034] 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

[0035] 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.

[0036] "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).

[0037] 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 alkoxylated 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.

[0038] 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.

[0039] 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.

[0040] 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).

[0041] It is also preferred for purposes of the present invention that the high cloud point nonionic surfactant 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).

[0042] 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 (C_6-C_{20} 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

[0043] Essentially any anionic surfactants useful for detersive 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.

[0044] 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 C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} 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

[0045] 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 C_5-C_{17} acyl-N-(C_1-C_{14} alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

[0046] Alkyl sulfate surfactants are preferably selected from the linear and branched primary C_{10}-C_{18} alkyl sulfates, more preferably the C_{11}-C_{15} branched chain alkyl sulfates and the C_{12}-C_{14} linear chain alkyl sulfates.

[0047] Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10}-C_{18} 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 C_{11}-C_{18}, most preferably C_{11}-C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

[0048] 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

[0049] Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

[0050] 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.

[0051] Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_20)_X$ $CH_2C00^-M^+$ wherein R is a C_6 to C_{18} 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 $RO\text{-}(CHR_1\text{-}CHR_2\text{-}O)\text{-}R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

[0052] 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

[0053] Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R\text{-}CON\ (R^1)\ CH_2\ COOM$, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 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

[0054] 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:

$$CH_3(CH_2)_n(CHOSO_3^-M^+)(CH_2)_mCH_3$$

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

$$CH_3(CH_2)_x(CHOSO_3^-M^+)CH_3,$$

and

$$CH_3(CH_2)_y(CHOSO_3^-M^+)CH_2CH_3$$

wherein x and (y+1) are intergers 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

[0055] Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

[0056] Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ 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.

[0057] A suitable example of an alkyl aphodicarboxylic acid is Miranol™ C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactants

[0058] 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.

[0059] Suitable betaines are those compounds having the formula $R(R^1)_2N^+R^2COO^-$ 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

[0060] 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.

[0061] 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.

[0062] Preferred surfactants for use herein are selected from anionic sulphonate surfactnats (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

[0063] 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 of the subsequent phase that comprise the benefit agent are substantially spherical in shape.

[0064] 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.

[0065] 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.

[0066] 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 0.5x.0.5mm should be used.

[0067] 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.

[0068] 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.

[0069] 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.

[0070] 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.

[0071] Some examples of preferred benefit agents are given below.

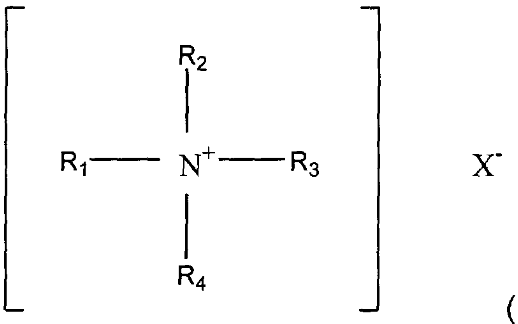
Cationic Softening Agents

[0072] 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.

[0073] 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.

[0074] Preferred cationic softening agents for use herein are selected from:

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



$$\left[R_1 - \overset{\displaystyle R_2}{\underset{\displaystyle R_4}{N^+}} - R_3 \right] X^-$$

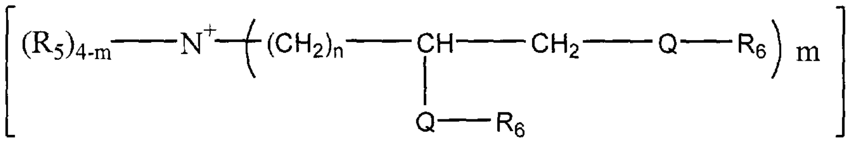
(I)

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):

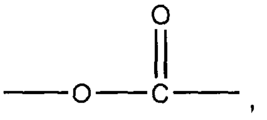
$$\left[(R_5)_{4-m} - N^+ \left((CH_2)_n - Q - R_6 \right)_m \right] X^- \quad \text{(II)}$$



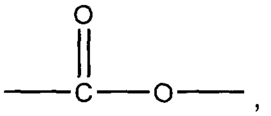
$$\left[(R_5)_{4-m} - N^+ \left((CH_2)_n - \underset{\underset{Q-R_6}{|}}{CH} - CH_2 - Q - R_6 \right)_m \right] X^-$$

(III)

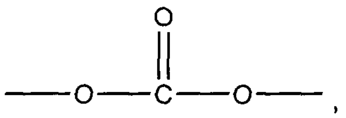
wherein, each R_5 unit is independently selected from hydrogen, branched or straight chain C_1-C_6 alkyl, branched or straight chain C_1-C_6 hydroxyalkyl and mixtures thereof, preferably methyl and hydroxyethyl; each R_6 unit is independently linear or branched C_{11}-C_{22} alkyl, linear or branched 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:



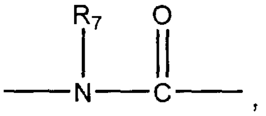
$$-O-\overset{\overset{O}{\|}}{C}- ,$$



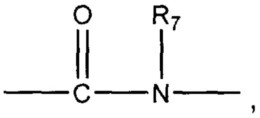
$$-\overset{\overset{O}{\|}}{C}-O- ,$$



$$-O-\overset{\overset{O}{\|}}{C}-O- ,$$

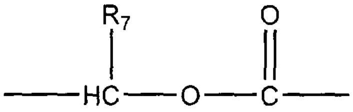


$$-\overset{\overset{\displaystyle R_7}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-,$$



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R_7}{|}}{N}-,$$

and



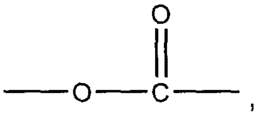
$$-\overset{\overset{\displaystyle R_7}{|}}{HC}-O-\overset{\overset{\displaystyle O}{\|}}{C}-$$

wherein R_7 is hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and mixtures thereof.

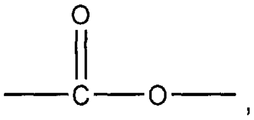
In the above quaternary ammonium compound example, the unit -QR_6 contains a fatty acyl unit which is typically derived from a triglyceride source. The triglyceride source is preferably derived from tallow, partially hydrogenated tallow, lard, partially hydrogenated lard, vegetable oils and/or partially 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:

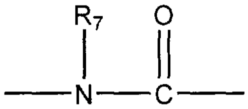


$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-,$$



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-,$$

and



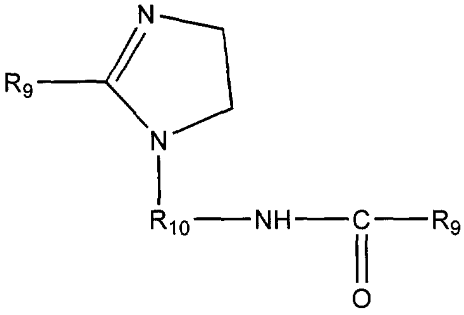
$$-N(R_7)-C(=O)-$$

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.

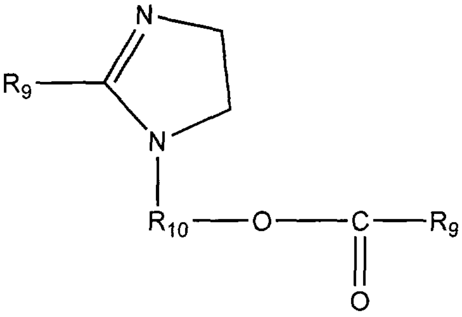
The counterion, X^-, can be chloride, bromide, methylsulfate, formate, sulfate, nitrate, and mixtures thereof. In fact, the anion, X, is merely present as a counterion of the positively charged quaternary ammonium compounds. The scope of this invention is not considered limited to any particular anion.

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):



(IV)

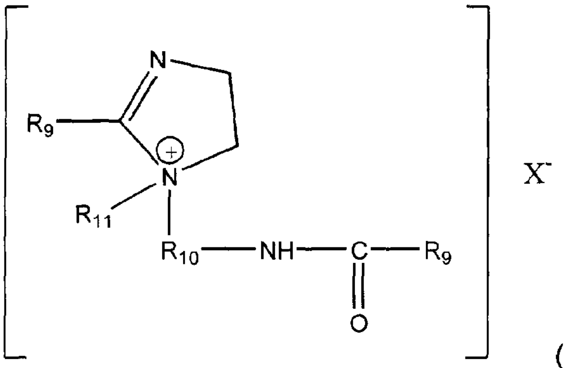


(V)

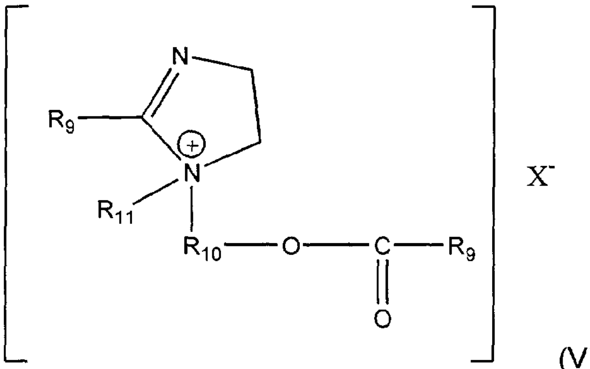
wherein R_9 is an acyclic aliphatic C_{15}-C_{21} hydrocarbon group and R_{10} is a C_1-C_6 alkyl or alkylene group.

These ammonium compounds, having a pKa 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):



(VI)

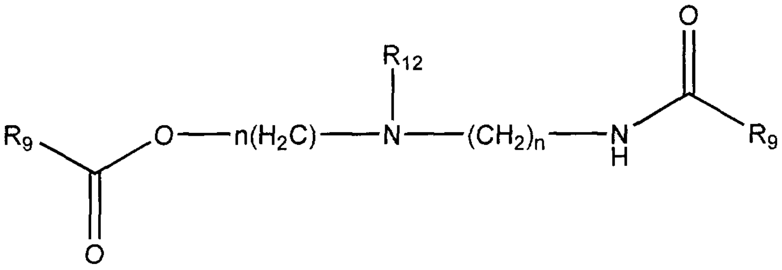


(VII)

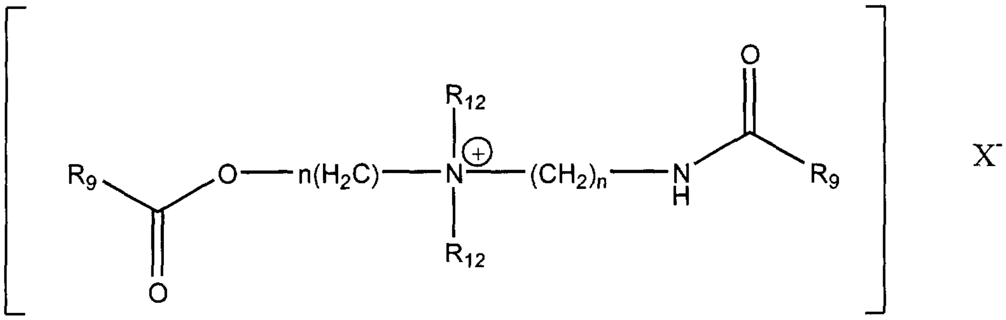
wherein R_9 & R_{10} are as specified hereinabove and R_{11} is selected from C_1-C_4 alkyl and hydroxyalkyl groups.

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):



(VIII)



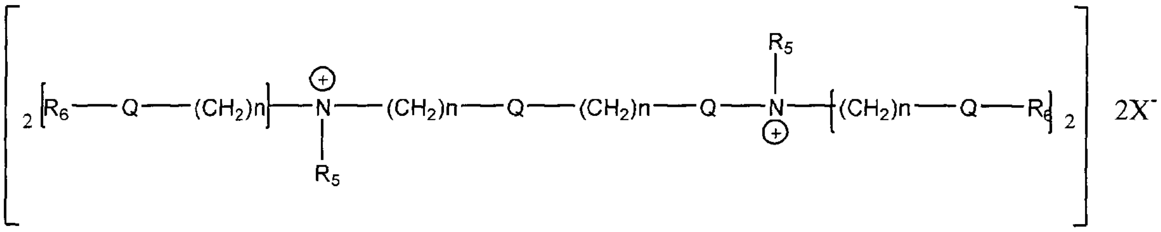
(IX)

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.

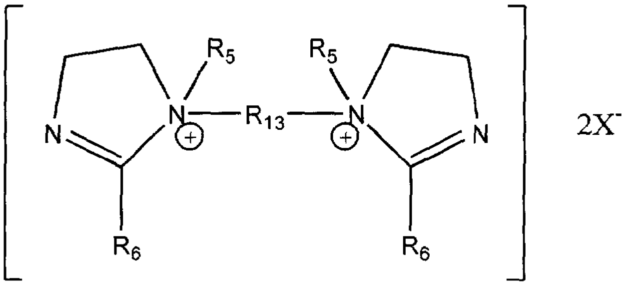
These ammonium compounds (VIII), having a pKa value of not greater than about 4, are able to generate a cationic charge in situ when dispersed in an aqueous solution, providing that the pH of the final composition is not greater than about 6.

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.

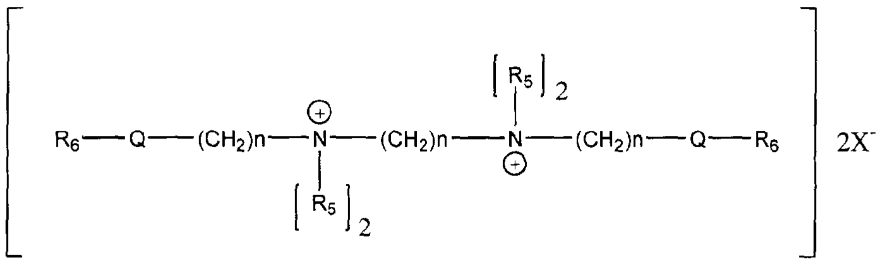
(f) diquaternary ammonium compounds according to general formula (X), (XI), (XII) or (XIII):



(X)

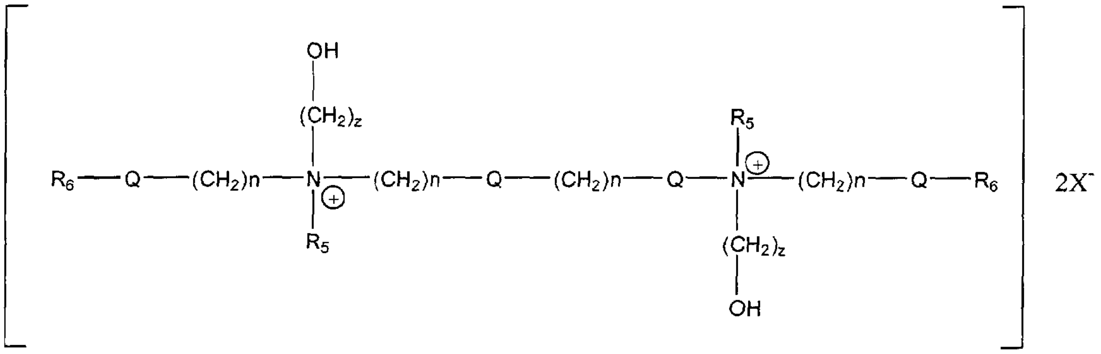


(XI)



$$\left[R_6-Q-(CH_2)n-\underset{[R_5]_2}{\overset{\oplus}{N}}-(CH_2)n-\underset{\oplus}{\overset{[R_5]_2}{N}}-(CH_2)n-Q-R_6\right]2X^-$$

(XII)



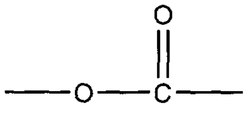
$$\left[R_6-Q-(CH_2)n-\underset{R_5}{\overset{OH-(CH_2)_z}{N^{\oplus}}}-(CH_2)n-Q-(CH_2)n-Q-\underset{(CH_2)_z-OH}{\overset{R_5}{N^{\oplus}}}-(CH_2)n-Q-R_6\right]2X^-$$

(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.

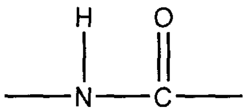
(g) mixtures of the above quaternary ammonium compounds.

[0075] 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:



$$-O-\overset{O}{\overset{\|}{C}}-$$

[0076] 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:



$$-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-$$

[0077] 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.

[0078] 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, palmyl, 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

[0079] 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) C_3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C_3 oxyalkylene terephthalate units is 2:1 or lower, (ii) C_4-C_6 alkylene or oxy C_4-C_6 alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate, having a degree of polymerization of at least 2, or (iv) C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, or a combination of (a) and (b).

[0080] 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 C_4-C_6 alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as $MO_3S(CH_2)_nOCH_2CH_2O$-, where M is sodium and n is an integer from 4-6, as disclosed in US-A-4,721,580.

[0081] 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 C_1-C_4 alkyl and C_4 hydroxyalkyl cellulose; see US-A-4,000,093.

[0082] Soil release agents characterized by poly(vinylester) hydrophobe segments include graft copolymers of poly (vinyl ester), e.g., C_1-C_6 vinyl esters, preferably poly(vinylacetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See EP-A-219 048.

[0083] 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.

[0084] 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.

[0085] 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 sulfoarolyl, end-capped terephthalate esters.

[0086] 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

[0087] 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.

[0088] 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.

[0089] 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 sequestrant is preferably at least 1:1.

[0090] 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.

[0091] Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

[0092] 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

[0093] 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.

[0094] 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 WO-A-93/08876 and EP-A-705 324.

Perfume

[0095] The perfume component of the present invention may comprise an encapsulate perfume, a properfume, neat perfume materials, and mixtures thereof.

[0096] 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.

[0097] 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.

[0098] 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 doors. Examples of suitable malodour counteractants are disclosed in U.S. Patent No. 3,102,101, issued August 27, 1963, to Hawley et al.

[0099] 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.

[0100] A wide variety of capsules exist which will allow for delivery of perfume effect at various times during the use of the detergent compositions.

[0101] 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.

[0102] 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.

[0103] The encapsulating materials of the perfumed particles is preferably a water-soluble or water-dispersible encapsulating material.

[0104] 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.

[0105] 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.

[0106] Other suitable water soluble or water dispersible encapsulating materials comprise dextrins derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in U.S. 3,455,838. These acid-ester dextrins 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.

[0107] 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.

[0108] 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.

[0109] 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).

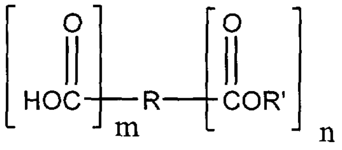
c) the mixture is spray-dried in a co-current tower fitted with a spinning disk atomizer. The drying air inlet temperature is low 150-200°C. This type of spray-drying ensures minimum loss of perfume and high drying rate. The granules have a particulate size of 50-150 microns.

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.

[0110] 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.

[0111] 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 Borcher et al. Issued August 18, 1992 and U.S. Patent No 5,234,610 Gardlik et al. Issued Aug 10, 1993.

[0112] 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



$$\left[\mathrm{HO}\overset{\displaystyle O}{\overset{\|}{C}}\right]_m\!\!-R-\left[\overset{\displaystyle O}{\overset{\|}{C}}\mathrm{OR'}\right]_n$$

wherein R is selected from the group consisting of substituted or unsubsitued C_1-C_{30} 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.

[0113] 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 eterfied ester of a perfume alcohol.

[0114] Preferably, R is selected from the group consisting of substituted or unsubstituted C_1-C_{20} straight, branched or cyclic alkyl, alkenyl, alkynyl, alkylaryl, aryl group or ring containing a herteroatom. 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, (b-citronellyl) maleate, nonadol maleate, phenoxanyl maleate, (3,7-dimethyl-1-octanyl) succinate, (cyclohexylethyl) maleate, florally succinate, (b-citronellyl) phthalate and (phenylethyl) adipate.

[0115] Pro-perfumes suitable for use herein include 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.

[0116] 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.

[0117] 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

[0118] 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 quaterinised 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.

[0119] 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.

[0120] 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

[0121] The compositions of the present invention can comprise one or more chlorine scavengers. Suitable scavengers include ammonium salts having the formula:

$$[R_3R^1N]^+X^-$$

wherein each R is independently hydrogen, C_1-C_4 alkyl, C_1-C_4 substituted alkyl and mixtures thereof, preferably R is hydrogen or methyl, more preferably hydrogen. R^1 is selected from hydrogen, C_1-C_9 alkyl, C_1-C_9 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

[0122] 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

[0123] 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

[0124] 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

Disintegration Aid

[0125] It is highly preferred that the compositions of the present invention 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. This can take the form of a substances which hastens the disintegration itself or substances which allow the tablet to be formulated or processed in such a way that the disintegrative effect of the water itself is hastened. For example, suitable disintegration aid include clays that swell on contact with water (hence breaking up the matrix of the compositions) and coatings which increase tablet integrity allowing lower compression forces to be used during manufacture (hence the tablets are less dense and more easily dispersed.

[0126] Any suitable disintegration aid can be used but preferably they are selected from disintegrants, coatings, effervescents, binders, clays, highly soluble compounds, cohesive compounds, and mixtures thereof.

Disintegrant

[0127] The shaped compositions herein can comprise a disintegrant that will swell on contact with water. Possible disintegrants for use herein include those described in the Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include clays such as bentonite clay; starch: natural, modified or pregelatinised starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum; croscarmylose sodium, crospovidone, cellulose, carboxymethyl cellulose, algenic acid and its salts including sodium alginate, silicone dioxide, polyvinylpyrrolidone, soy polysaccharides, ion exchange resins, and mixtures thereof.

Coating

[0128] Preferably the shaped compositions of the present invention are coated. The coating can improve the mechanical characteristics of a shaped composition while maintaining or improving dissolution. This very advantageously applies to multi-layer tablets, whereby the mechanical constraints of processing the multiple phases can be mitigated though the use of the coating, thus improving mechanical integrity of the tablet. The coating can also slow or stop the shaped compositions from absorbing moisture. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. The coating for use herein is preferably brittle so that the tablet breaks up quickly when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material dissolves under alkaline conditions, or is readily emulsified by surfactants. This contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also avoids deposition of undissolved particles or lumps of coating material on the wash load.

[0129] Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

[0130] The preferred coatings and methods for use herein are described in EP-A-846,754, herein incorporated by reference.

[0131] As specified in EP-A-846,754, preferred coating ingredients are for example dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof. Most preferred is adipic acid.

[0132] A coating of any desired thickness can be applied. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

[0133] Preferably the coating comprises a disintegrant, as described hereinabove, that will swell on contact with water and break the coating into small pieces.

[0134] In a preferred embodiment, the coating comprises an acid having a melting temperature of at least 145°C, such as adipic acid for example, as well as a clay, such as a bentonite clay for example, whereby the clay is used as a disintegrant and also to render the structure of adipic acid more favourable for water penetration, thus improving the dispersion of the adipic acid in a aqueous medium. Preferred are clays having a particle size of less than 75 μm, more preferably of less than 53 μm, in order to obtain the desired effect on the structure of the acid. Preferred are bentonite clays. Indeed the acid has a melting point such that traditional cellulosic disintegrants undergo a thermal degradation during the coating process, whereas such clays are found to be more heat stable. Further, traditional cellulosic disintegrant such as Nymcel™ for example are found to turn brown at these temperatures.

[0135] A preferred optional materials for use in the coating herein is cation exchange resins, typically as described in *Kirk-Othmer's Encyclopedia of Chemical Technology,* 4th Edition, Volume 14, pp 738-740. Any suitable cation-exchange resin may be used herein including strong acid cation-exchange resins, weak acid cation exchange resins. and mixtures thereof. Commercially available cation exchange resins include those that are generally composed of an insoluble poly(styrene-divinylbenzene) co-polymer which has been functionalised with sulfonic acid groups such as *Amberlite*® IR-120(plus), *Amberlite*® IR-120(plus) sodium form and *Amberlite*® IRP-69 (Rohm & Haas) and *Dowex*® 50WX8-100, *Dowex*® HCR-W2 (Dow Chemicals). Other examples of commercially available cation-exchange resins are those composed of co-polymers of a suitable alkenyl carboxylic acid (e.g. acrylic acid or methacrylic acid) such as *Amberlite*® IRP-64 (Rohm & Haas), *Dowex*® CCR-3(plus) (Dow Chemical). The preferred cation-exchange resins for use herein are those sold by Purolite under the names *Purolite*® C100NaMR, a sodium salt sulfonated poly(styene-divinylbenzene) co-polymer and *Purolite*® C100CaMR, a calcium salt sulfonated poly(styene-divinylbenzene) co-polymer.

[0136] The preferred coatings and methods for use herein are described in EP-A-846,754, herein incorporated by reference.

Effervescent

[0137] The shaped compositions of the present invention preferably comprise an effervescent. As used herein, effervescency means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas. An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent improves the disintegration time of the tablet. The amount will preferably be from 0.1% to 20%, more preferably from 5% to 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separate particles.

Tensile Strength

[0138] Depending on the composition of the starting material and the shape of the tablets the compacting force may be adjusted to not affect the tensile strength and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape. For a cylindrical tablet, the tensile strength corresponds to the diametrical fracture stress (DFS) which is a way to express the strength of a tablet, and is determined by the following equation:

$$\mathrm{DFS} = \frac{2F}{\pi Dt}$$

where F is the maximum force (Newton) to cause tensile failure (fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell Industries Inc. D is the diameter of the tablet and t is the thickness of the tablet. A tablet having a DFS of less than 20kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A DFS of at least 25kPa is preferred. Similarly, this applies to non-cylindrical tablets, to define the tensile strength, whereby the cross-section normal to the height of the tablet is non-round, and whereby the force applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non-round cross-section.

[0139] Due to the gas created by the effervescency in the tablet, the tablet can have a higher DFS and still have the same disintegration profile as a tablet without effervescency. When the DFS of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

[0140] Further dispesion aid could be provided by using compounds such as sodium acetate, nitrilotriacetic acid and salts thereof or urea. A list of suitable dispersion aid may also be found in Pharmaceutical Dosage Forms: Tablets, Vol. 1, 2nd Edition, Edited by H. A. Lieberman et al, ISBN 0-8247-8044-2.

Binders

[0141] Non-gelling binding can be integrated to the particles forming the tablet in order to facilitate dispersion. If non-gelling binder are used they are preferably selected from synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacetates, water-soluble acrylate copolymers, and mixtures thereof. The handbook of Pharmaceutical Excipients 2nd Edition has the following binder classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar Gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferred binder also have an active cleaning function in the wash such as cationic polymers. Examples include ethoxylated hexamethylene diamine quaternary compounds, bishexamethylene triamines or other such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

[0142] Non-gelling binder materials are preferably sprayed on and hence preferably have a melting point of below 90°C, preferably below 70°C, more preferably below 50°C so as not the damage or degrade the other active materials in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

[0143] Non-gelling binder materials are preferably used in an amount of from 0.1% to 15%, by weight of total composition.

Clays

[0144] The compositions herein may also comprise clays. Preferred clays are expandable clays. As used herein the term "expandable" means clays with the ability to swell (or expand) on contact with water. These are generally three-layer clays such as aluminosilicates and magnesium silicates having an ion exchange capacity of at least 50 meq/ 100g of clay. The three-layer expandable clays used herein are classified geologically as smectites.

[0145] There are two distinct classes of smectite-type clays. In the first, aluminium oxide is present in the silicate crystal lattice (general formula - $Al_2(Si_2O_5)_2(OH)_2$) and, in the second, magnesium oxide is present in the silicate crystal lattice (general formula - $Mg_3(Si_2O_5)_2(OH)_2$). It is recognised that the range of water hydration in the above formulae can vary with the processing to which the clay has been subjected. This is immaterial to the use of the smectite clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while the metal cations such as Na^+, Ca^{2+}, as well as H^+, can be co-present in the water of hydration to provide electrical neutrality. Except as noted hereinafter, such cation substitutions are immaterial to the use of the clays herein since the desirable physical properties of the clays are not substantially altered thereby. The three-layer alumino-silicates generally have a dioctahedral crystal lattice while the three-layer magnesium silicates generally have a trioctahedral crystal lattice.

[0146] The clays useful in the present invention preferably have an ion-exchange capacity of at least 50 meq/100g of clay. More preferably at least 60 meq/100g of clay. The smectite clays used herein are all commercially available. For example, clay useful herein include montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconitem, vermiculite and mixtures thereof. The clays herein are available under various tradenames, for example, Thixogel #1 and Gelwhite GP from Georgia Kaolin Co., Elizabeth, NJ, USA; Volclay BC and Volclay #325 from American Colloid Co., Skokie, IL, USA; Black Hills Bentonite BH450 from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R.T. Vanderbilt. It is to be recognised that such smectite-type minerals obtained under the foregoing tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

[0147] The clay is preferably mainly in the form of granules, with at least 50%, preferably at least 75%, more preferably at least 90%, being in the form of granules having a size of at least 100μm. Preferably the granules have a size of from 100μm to 1800μm and more preferably from 150μm to 1180μm.

Highly Soluble Compounds

[0148] The multiphase compositions of the present invention may comprise a highly soluble compound. Such a compound could be formed from a mixture or from a single compound.

A highly soluble compound is defined as follow:

[0149] A solution is prepared as follows comprising de-ionised water as well as 20 grams per litre of a specific compound:

1- 20 g of the specific compound is placed in a Sotax Beaker. This beaker is placed in a constant temperature bath set at 10°C. A stirrer with a marine propeller is placed in the beaker so that the bottom of the stirrer is at 5 mm above the bottom of the Sotax beaker. The mixer is set at a rotation speed of 200 turns per minute.
2- 980 g of the de-ionised water is introduced into the Sotax beaker.
3- 10 s after the water introduction, the conductivity of the solution is measured, using a conductivity meter.
4- Step 3 is repeated after 20, 30, 40, 50, 1min, 2 min, 5 min and 10 min after step 2.
5- The measurement taken at 10 min is used as the plateau value or maximum value.

[0150] The specific compound is highly soluble according to the invention when the conductivity of the solution reaches 80% of its maximum value in less than 10 seconds, starting from the complete addition of the de-ionised water to the compound. Indeed, when monitoring the conductivity in such a manner, the conductivity reaches a plateau after a certain period of time, this plateau being considered as the maximum value. Such a compound is preferably in the form of a flowable material constituted of solid particles at temperatures comprised between 10 and 80°Celsius for ease of handling, but other forms may be used such as a paste or a liquid.

[0151] Examples of preferred highly soluble compounds include salts of acetate, urea, citrate, phosphate, sodium diisobutylbenzene sulphonate (DIBS), sodium toluene sulphonate, and mixtures thereof.

Cohesive Compounds

[0152] The multiphase compositions herein may comprise a compound having a Cohesive Effect on the particulate material of a detergent matrix forming the composition. The Cohesive Effect on the particulate material of a detergent matrix forming the tablet or a layer of the tablet is characterised by the force required to break a tablet or layer based on the examined detergent matrix pressed under controlled compression conditions. For a given compression force, a high tablet or layer strength indicates that the granules stuck highly together when they were compressed, so that a strong cohesive effect is taking place. Means to assess tablet or layer strength (also refer to diametrical fracture stress) are given in Pharmaceutical dosage forms : tablets volume 1 Ed. H.A. Lieberman et al, published in 1989.

[0153] The cohesive effect is measured by comparing the tablet or layer strength of the original base powder without compound having a cohesive effect with the tablet or layer strength of a powder mix which comprises 97 parts of the original base powder and 3 parts of the compound having a cohesive effect. The compound having a cohesive effect is preferably added to the matrix in a form in which it is substantially free of water (water content below 10% (pref. below 5%)). The temperature of the addition is between 10 and 80°C, more pref. between 10 and 40°C.

[0154] A compound is defined as having a cohesive effect on the particulate material according to the invention when at a given compacting force of 3000N, tablets with a weight of 50g of detergent particulate material and a diameter of 55mm have their tablet tensile strength increased by over 30% (preferably 60 and more preferably 100%) by means of the presence of 3% of the compound having a cohesive effect in the base particulate material.

[0155] An example of a compound having a cohesive effect is sodium diisoalkylbenzene sulphonate.

[0156] When integrating a highly soluble compound having also a cohesive effect on the particulate material used for a tablet or layer formed by compressing a particulate material comprising a surfactant, the dissolution of the tablet or layer in an aqueous solution is significantly increased. In a preferred embodiment, at least 1% per weight of a tablet or layer is formed from the highly soluble compound, more preferably at least 2%, even more preferably at lest 3% and most preferably at least 5% per weight of the tablet or layer being formed from the highly soluble compound having a cohesive effect on the particulate material.

[0157] A highly soluble compound having a cohesive effect on the particulate material allows to obtain a tablet having a higher tensile strength at constant compacting force or an equal tensile strength at lower compacting force when compared to traditional tablets. Typically, a whole tablet will have a tensile strength of more than 5kPa, preferably of more than 10kPa, more preferably, in particular for use in laundry applications, of more than 15kPa, even more preferably of more than 30 kPa and most preferably of more than 50 kPa, in particular for use in dish washing or auto dish washing applications; and a tensile strength of less than 300 kPa, preferably of less than 200 kPa, more preferably of less than 100 kPa, even more preferably of less than 80 kPa and most preferably of less than 60 kPa. Indeed, in case of laundry application, the tablets should be less compressed than in case of auto dish washing applications for example, whereby the dissolution is more readily achieved, so that in a laundry application, the tensile strength is preferably of less than 30 kPa.

[0158] This allows to produce tablets or layers which have a solidity and mechanical resistance comparable to the solidity or mechanical resistance of traditional tablets while having a less compact tablet or layer thus dissolving more readily. Furthermore, as the compound is highly soluble, the dissolution of the tablet or layer is further facilitated, resulting in a synergy leading to facilitated dissolution for a tablet according to the invention.

Enzymes

[0159] The compositions of the present invention preferably 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, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

[0160] Preferred enzymes include protease, amylase, lipase, peroxidases, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

[0161] The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 12 and an activity above 50 CEVU (Cellulose Viscosity Unit). Suitable cellulases are disclosed in US-A-4,435,307, JP-A-61078384 and WO-A-96/02653 which disclose fungal cellulases produced respectively from Humicola insolens, Trichoderma, Thielavia and Sporotrichum. EP-A-739 982 describes cellulases isolated from novel Bacillus species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO-A-95/26398.

[0162] Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800. Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in WO-A-91/17243. Also suitable cellulases are the EGIII cellulases from Trichoderma longibrachiatum described in WO-A-94/21801. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in EP-A-495257. Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO-A-91/17244 and WO-A-91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO-A-96/34092, WO-A-96/17994 and WO-A-95/24471. If present, cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

[0163] Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in WO-A-89/099813, WO-A-89/09813 and in EP-A-540784. Also suitable is the laccase enzyme.

[0164] Preferred enhancers are substitued phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO-A-94/12621) and substitued syringates (C_3-C_5 substitued alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide. If present, peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

[0165] Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in GB-A-1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum,* e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli.* Especially suitable lipases are lipases such as M1 Lipase™ and Lipomax™ (Gist-Brocades) and Lipolase™ and Lipolase Ultra™(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitables are the lipolytic enzymes described in EP-A-258068, WO-A-92/05249, WO-A-95/22615, WO-A-94/03578, WO-A-95/35381 and WO-A-96/00292.

[0166] Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e. g. WO-A-88/09367; WO-A-90/09446, WO-A-94/14963 and WO-A-94/14964.

[0167] The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

[0168] Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus,* having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE™ by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB-A-1,243,784 to Novo. Other suitable proteases include ALCALASE™, DURAZYM™ and SAVINASE™ from Novo and MAXATASE™, MAXACAL™, PROPERASE™ and MAXAPEM™ (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in EP-A-292623 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in EP-A-199,404, which refers to a modified bacterial serine protealytic enzyme which is called "Protease A" herein. Suitable is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in WO-A-91/06637. Genetically modified variants, particularly of Protease C, are also included herein.

[0169] A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO-A-95/10591 and in US-A-5677272.

[0170] Also suitable for the present invention are proteases described in patent applications EP-A-251 446 and WO-A-91/06637, protease BLAP™ described in WO-A-91/02792 and their variants described in WO-A-95/23221.

[0171] See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO-A-93/18140. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO-A-92/03529. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO-A-95/07791. A recombinant trypsin-like protease for detergents suitable herein is described in WO-A-94/25583. Other suitable proteases are described in EP-A-516,200.

[0172] Other preferred protease enzymes include protease enzymes which are a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived by replacement of a plurality of amino acid residues of a precursor carbonyl hydrolase with different amino acids, wherein said plurality of amino acid residues replaced in the precursor enzyme correspond to position +210 in combination with one or more of the following residues: +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218 and +222, where the numbered positions correspond to naturally-occurring subtilisin from Bacillus amyloliquefaciens or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins (such as Bacillus lentus subtilisin). Preferred enzymes of this type include those having position changes +210, +76, +103, +104, +156, and +166.

[0173] The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

[0174] Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO-A-94/02597 describes cleaning compositions which incorporate mutant amylases. See also WO-A-95/10603. Other amylases known for use in cleaning compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US-A-5,003,257; EP-A-252,666; WO-A-/91/00353; FR-A-2,676,456; EP-A-285,123; EP-A-525,610; EP-A-368,341; and GB-A-1,296,839. Other suitable amylases are stability-enhanced amylases described in WO-A-94/18314 and

WO-A-96/05295 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO-A-95/10603. Also suitable are amylases described in EP-A-277,216, WO-A-95/26397 and WO-A-96/23873.

[0175] Examples of commercial α-amylases products are Purafect Ox Am™ from Genencor and Termamyl™, Ban™ ,Fungamyl™ and Duramyl™, Natalase™ all available from Novo Nordisk A/S Denmark. WO-A-95/26397 describes other suitable amylases : α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl™ at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas™ α-amylase activity assay. Suitable are variants of the above enzymes, described in WO-A-96/23873. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO-A-95/35382.

[0176] Preferred amylase enzymes include those described in WO-A-95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056.

[0177] The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition

[0178] In a particularly preferred embodiment, detergent tablets of the present invention comprise amylase enzymes, particularly those described in WO-A-95/26397 and co-pending application by Novo Nordisk PCT/DK96/00056 in combination with a complementary amylase. By "complementary" it is meant the addition of one or more amylase suitable for detergency purposes. Examples of complementary amylases (α and/or β) are described below. WO-A-94/02597 and WO-A-95/10603 describe cleaning compositions which incorporate mutant amylases. Other amylases known for use in cleaning compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US-A-5,003,257; EP-A-252,666; WO-A-91/00353; FR-A-2,676,456; EP-A-285,123; EP-A-525,610; EP-A-368,341; and GB-A-1,296,839. Other suitable amylases are stability-enhanced amylases described in WO-A-94/18314 and WO-A-96/05295 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO-A-95/10603. Also suitable are amylases described in EP-A-277,216. Examples of commercial α-amylases products are Purafect Ox Am™ from Genencor and Termamyl™, Ban™ ,Fungamyl™ and Duramyl™, all available from Novo Nordisk A/S Denmark. WO-A-95/26397 describes other suitable amylases: α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl™ at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas™ α-amylase activity assay. Suitable are variants of the above enzymes, described in WO-A-96/23873. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO-A-95/35382.

[0179] Preferred complementary amylases for the present invention are the amylases sold under the tradename Purafect Ox Am described in WO-A-94/18314, WO-A-96/05295 sold by Genencor; Termamyl™, Fungamyl™, Ban™ Natalase™ and Duramyl™, all available from Novo Nordisk A/S and Maxamyl™ by Gist-Brocades.

[0180] Said complementary amylase is generally incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition. Preferably a weight of pure enzyme ratio of specific amylase to the complementary amylase is comprised between 9:1 to 1:9, more preferably between 4:1 to 1:4, and most preferably between 2:1 and 1:2.

[0181] The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

[0182] Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

[0183] Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in EP-A-553607. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

[0184] A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO-A-93/07263, WO-A-93/07260, WO-A-89/08694 and US-A-3,553,139. Enzymes are further disclosed in US-A-4,101,457 and in US-A-4,507,219. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in US-A-4,261,868. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in US-A-3,600,319, EP-A-199,405 and EP-A-200,586. Enzyme stabilisation systems are also described, for example, in US-A-3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO-A-94/01532.

Bleaching System

[0185] 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 -

[0186] 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.

[0187] 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.

[0188] 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.

[0189] 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 -

[0190] 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 (C_{10}-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C_8-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.

[0191] 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 C_{12}-OBS), 10-undecenoyloxybenzenesulfonate (UDOBS or C_{11}-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA).

[0192] 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.

[0193] 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.

[0194] 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.

[0195] 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.

[0196] 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. 4,966,723Hodge et al., issued October 30, 1990, include benzoxazin-type activators, such as a C_6H_4 ring to which is fused in the 1,2-positions a moiety --C(O)OC(R^1)=N-.

[0197] 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.

[0198] 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 -

[0199] 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 -

[0200] 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.

[0201] One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined 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 in U.S. 4,430,243 Bragg, issued February 2, 1982.

Manganese Metal Complexes -

[0202] 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 Mn^{IV}_2(u-O)$_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$(PF_6)$_2$, Mn^{III}_2(u-O)$_1$(u-OAc)$_2$ (1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$(ClO_4)$_2$, Mn^{IV}_2 (u-O) $_3$(1,4,7-triazacyclononane)$_4$(ClO_4)$_4$, $Mn^{III}Mn^{IV}_4$(u-O)$_1$(u-OAc)$_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$ (ClO_4)$_3$, Mn^{IV}(1,4,7-trimethyl-1,4,7-triazacyclononane)-(OCH_3)$_3$(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 -

[0203] 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 $[Co(NH_3)_5OAc]\ T_y$, wherein "OAc" represents an acetate moiety and "T_y" is an anion, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$ (herein "PAC").

[0204] 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 -

[0205] 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 Macrocyclic 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(ll) Hexafluorophosphate
Diaquo-5,12-diethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(ll) 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-15,8,12-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-1 2-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II)
Dichloro-5-n-octyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II)
Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II).

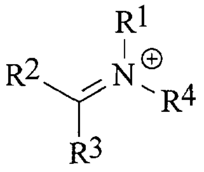
[0206] As a practical matter, and not by way of limitation, the compositions and laundry processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm 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 -

[0207] 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.

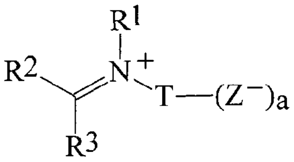
(e) Bleach Boosting Compounds -

[0208] 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:



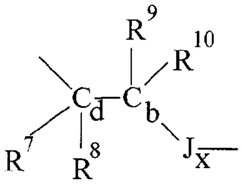
[I]

where R^1-R^4 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 R^1-R^4 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 R^1-R^4 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:

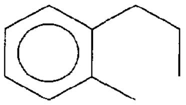


[II]

wherein R^1-R^3 is hydrogen or an unsubstituted or substituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals; R^1 and R^2 form part of a common ring; T has the formula:

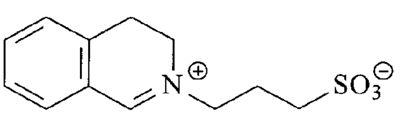


wherein x is equal to 0 or 1; J, when present, is selected $-CR^{11}R^{12}-$,$-CR^{11}R^{12}CR^{13}R^{14}-$, and $-CR^{11}R^{12}CR^{13}R^{14}CR^{15}R^{16}-$; R^7-R^{16} are individually selected from the group consisting of H, linear or branched C_1-C_{18} substituted or unsubstituted alkyl, alkylene, 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 $-CO_2^-$,$-SO_3^-$ and $-OSO_3^-$ and a is 1. R_1 and R_2 together may form the non-charged moiety:

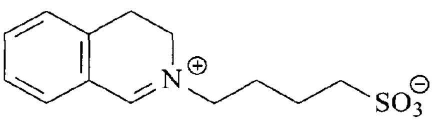


.

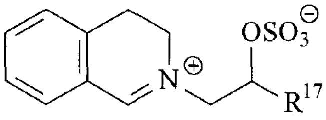
[0209] Most preferred bleach boosting compounds include are aryliminium zwitterions wherein R_3 is H, Z is $-SO_3^-$ or $-OSO_3^-$, and a is 1. The aryliminium zwitterions may have the formula:



or

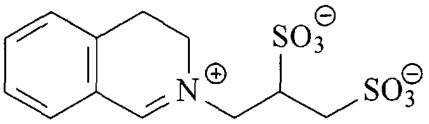


or

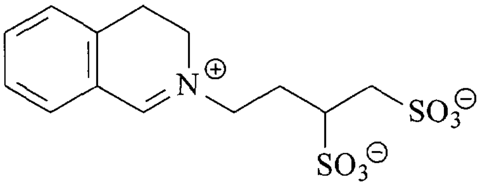


where R^{17} is selected from the group consisting of H and linear or branched C_1-C_{18} substituted or unsubstituted alkyl, preferably C_1-C_{14} alkyl and even more preferably C_8C_{10} linear alkyl chain.

[0210] The bleach boosting compounds may also comprise an aryliminum polyion having a net negative charge and R^3 is H, T is $-(CH_2)_b-$ or $-CH_2(C_6H_4)-$, Z is$-SO_3^-$, a is 2 and b is from 2 to 4. The aryliminium polyion preferably has the formula:



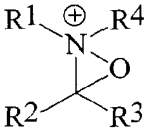
or



or is a water-soluble salt of these compounds.

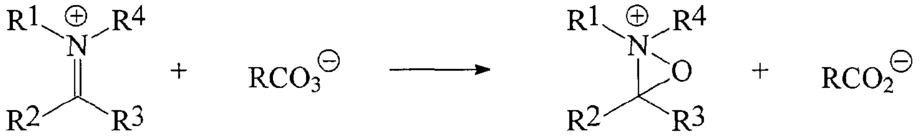
[0211] The quaternary imine bleach boosting compounds preferably act in conjunction with a peroxygen source to provide a more effective bleaching system. The bleach boosting compounds react with the peroxygen source to form a more active bleaching species, an oxaziridinium compound. The formed oxaziridinium 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)



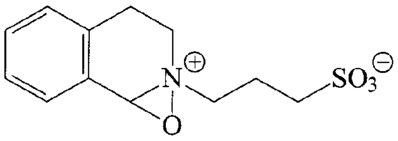
and can be produced from the imine of formula (I) or (II), wherein R^4 is T—$(Z^-)_a$, of the present invention with the reaction:

(I) (III)



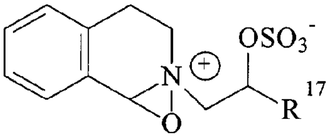
[0212] Thus, the preferred bleach boosting compounds of the present invention represented by the formula (II) produces the active oxaziridinium bleaching species represented by the formula:

(IV)



or

(V)



wherein R^{17} is defined as above.

[0213] 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.

[0214] 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 -

[0215] 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.

Polymeric Dye Transfer Inhibiting Agents

[0216] The compositions of the present invention can comprise polymeric dye transfer inhibiting agents. If present, the shaped 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.

[0217] The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

Builders

[0218] 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.

[0219] The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred. Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in GB-A-1,379,241, lactoxysuccinates described in GB-A-1,389,732, amino-succinates described in NL-A-7205873, the oxypolycarboxylate materials described in GB-A-1,387,447. Polycarboxylates containing four carboxy groups suitable for use herein include those disclosed in GB-A-1,261,829. Polycarboxylates containing sulfo substituents include the sulfosuccinates derivatives disclosed in GB-A-1,398,421, GB-A-1,398,422 and US-A-3,936,448 and the sulfonated pyrolysed citrates described in GB-A-1,439,000. Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, 2,5-tetrahydrofuran-cis-dicarboxylates, 2,2,5,5-tetrahydrofuran-tetracarboxylates, 1,2,3,4,5,6-hexane-hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and phthalic acid derivatives disclosed in GB-A-1,425,343. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates. The parent acids of monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builders. Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultrafine calcium carbonate as disclosed in DE-A-2,321,001.

[0220] Suitable partially water-soluble builder compounds for use herein include crystalline layered silicates as disclosed in EP-A-164,514 and EP-A-293,640. Preferred crystalline layered sodium silicates of general formula:

$$NaMSi_xO_{2+1}.yH_2O$$

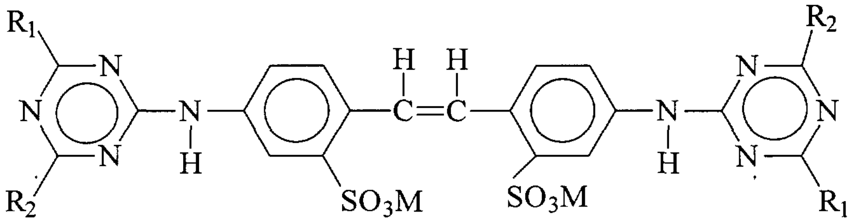
wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type preferably have a two dimensional sheet structure, such as the so called δ-layered structure as described in EP-A-164,514 and EP-A-293,640. Methods of preparation of crystalline layered silicates of this type are disclosed in DE-A-3,417,649 and DE-A-3,742,043. A more preferred crystalline layered sodium silicate compound has the formula δ-$Na_2Si_2O_5$, known as NaSKS-6™ available from Hoeschst AG.

[0221] Suitable largely water-insoluble builder compounds for use herein include the sodium aluminosilicates. Suitable aluminosilicates include the aluminosilicate zeolites having the unit cell formula $Na_z[(AlO_2)_z(SiO_2)_y].xH2O$ wherein z and y are at least 6, the molar ratio of z to y is from 1 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 10% to 22% water in bound form. The aluminosilicate zeolites can be naturally occurring materials but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, and Zeolite HS. Preferred aluminosilicate zeolites are colloidal aluminosilicate zeolites. When employed as a component of a detergent composition colloidal aluminosilicate zeolites, especially colloidal zeolite A, provide ehanced builder performance, especially in terms of improved stain removal, reduced fabric encrustation and improved fabric whiteness maintenance. Mixtures of colloidal zeolite A and colloidal zeolite Y are also suitable herein providing excellent calcium ion and magnesium ion sequestration performance.

Optical Brightener

[0222] The compositions of the present invention can comprise optical brighteners. If present, shaped compositions herein preferably contain from 0.005% to 5% by weight of total composition of hydrophilic optical brighteners.

[0223] Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 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.

[0224] When in the above formula, R_1 is anilino, R_2 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.

[0225] 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.

[0226] 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.

[0227] Other preferred optical brighteners are those known as Brightener 49 available from Ciba-Geigy.

Clay Softening System

[0228] 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, shaped compositions herein preferably contain from 0.001% to 10% by weight of total composition of clay softening system.

[0229] 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.

Organic Polymeric Compounds

[0230] 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.

[0231] 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.

[0232] 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 methylenemalonic 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.

[0233] 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.

[0234] 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-$[CR_2\text{-}CR_1(CO\text{-}O\text{-}R_3)]$- 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.

[0235] 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.

[0236] Other optional polymers may polyvinyl alcohols and acetates both modified and non-modified, cellulosics and modified cellulosics, polyoxyethylenes, polyoxypropylenes, and copolymers thereof, both modified and non-modified, terephthalate esters of ethylene or propylene glycol or mixtures thereof with polyoxyalkylene units.

[0237] Suitable examples are disclosed in US-A-5,591,703, US-A-5,597,789 and US-A-4,490,271.

Alkali Metal Silicate

[0238] An alkali metal silicate is a preferred 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.

[0239] Alkali metal silicate may also be present as a component of an alkalinity system.

[0240] 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.

Colourant

[0241] 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.

[0242] 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.

[0243] 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 TURQUISE BLUE EBA (tradename) available from Bayer, USA.

[0244] 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.

[0245] 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%.

Lime Soap Dispersant Compound

[0246] 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.

[0247] 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.

Process

[0248] The present invention includes processes for making the aforementioned shaped compositions. The compositions of the present invention can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients are used in particulate form. Any liquid ingredients can be incorporated in a conventional manner into solid particulate ingredients. Preferably the shaped compositions of the present invention are compressed at a force of less than 10000 N/cm^2, more preferably not more than 3000 N/cm^2, even more preferably not more than 750 N/cm^2. Indeed, the more preferred embodiments of the present invention are compressed with a force of less than 500 N/cm^2. Generally, the compositions herein will be compressed with relatively low forces to enable them to disintegrate quickly.

[0249] The particulate material used for making the tablet of this invention can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities of 600g/l or lower. Particulate materials of higher bulk density can be prepared by a continuous granulation and densification process (e.g. using Lodige® CB and/or Lodige® KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sentering, etc.

[0250] The components of the particulate material may be mixed together by any conventional means. The shaped compositions may be manufactured by using any compacting process such as tabletting, briquetting or extrusion, preferably tabletting. Suitable equipment includes a standard single stroke or a rotary press (such as is available form Courtoy®, Korsch®, Manesty® or Bonals®). Preferably the tablets are prepared by compression in a tablet press capable of preparing a tablet comprising a mould. The shaped compositions herein preferably have a diameter of between 20mm and 60mm, preferably of at least 35mm and up to 55mm, and a weight of between 25 and 100 grammes. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. In a preferred embodiment according to the invention, the tablet has a density of at least 0.5 g/cc, more preferably at least 1.0 g/cc, and preferably less then 2.0 g/cc, more preferably less than 1.5 g/cc.

[0251] Multi-phase tablets can be made using known techniques.

[0252] A preferred process for making the compositions of the present invention comprises the steps of:

(a) compressing a first phase, comprising surfactant, to form a shaped body comprising a mould;
(b) delivering the subsequent phase into said mould, the subsequent phase comprising at least one benefit agent; and
(c) compressing the subsequent phase within the mould.

Method of Use

[0253] The present invention includes methods of washing in a washing machine comprising charging a washing machine with a shaped 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. By an effective amount of the detergent tablet composition it is meant from 15g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

[0254] Preferably the shaped composition is dosed via the dispensing drawer of the machine but it can be added directly into the wash load. If added directly into the wash load, the shaped composition can be added on its own or in combination with a dispensing device such as a reticulated bag. A dispensing device is not strictly necessary for the shaped compositions of the present invention but consumers have become accustomed to using one due to the poor dissolution profiles of many of the prior art shaped compositions. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method. Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water. To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

[0255] Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle.

[0256] Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European EP-A-018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in EP-A-011500, EP-A-011501, EP-A-011502, and EP-A-011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

pH of the compositions

[0257] The shaped 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:

[0258]

First phase:	
	% by weight, of total composition
Anionic agglomerates 1	7.1
Anionic agglomerates 2	17.5
Nonionic agglomerates	9.1
Cationic agglomerates	4.6
Layered silicate	9.7
Sodium percarbonate	12.2
Bleach activator agglomerates	6.1
Sodium carbonate	7.27
EDDS/Sulphate particle	0.5
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.6
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

(continued)

First phase:	
	% by weight, of total composition
Amylase	1.1
Binder spray on system	3.05
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 sufactant, 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% 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% H_2O

Binder spray on system comprises 0.5 parts of Lutensit K-HD 96 and 2.5 parts of Polyethylene glycols (PEG)

Second phase:	
	% by weight, of total composition
Softerner and perfume bead	8.4

[0259] 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 first phase:

[0260] 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 phase 2:

[0261] 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 were it is operated at 1000 revolutions per minute for 5 minutes were a good spheronization was achieved.

[0262] 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.

[0263] The resulting beads had a density of 950 kg/m^3 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.

Tablet manufacturing:

[0264] The multi-phase tablet composition was prepared using an Instron 4400 testing machine and a standard die for manual tablet manufacturing. 35g of the detergent active composition of the first phase was fed into the dye of 41x41 mm with rounded edges that has a ratio of 2.5 mm. The mix was compressed with a force of 1,500 N with a punch that has a suitable shape to form a concave mould of 25 mm diameter and 10 mm depth in the tablet. The shaped punch was carefully removed leaving the tablet into the dye. 4g of beads that will form the second phase were introduced into the mould left in the first tablet shape and a final compression of 1,700 N was applied to manufacture the multiphase tablet using a flat normal punch. The tablet is then manually ejected from the dye.

[0265] In a following step, the tablet made with the process described above were coated by manually dipping them into a molten mixture of coating at 170°C and let them cool back to room temperature allowing the coating to harden. The composition and percentage of the coating are described in the tablet composition above.

[0266] Several tablets are made in order to perform the tests indicated below.

TESTING:

Assessing the disintegration profile for the tablet:

[0267] In order to test the disintegration time of the tablets, a Sotax AE7 apparatus was used. The tablets were introduced in the glass vessel filled with 1 liter de-ionized water at 20°C. The paddle stirring element was activated at a speed of 100 rotations per minute during 1 minute.

[0268] The solution and all the undissolved particles are poured through a 4x4 mm sieve and no pieces of tablets and particles were retained.

Using the tablets in a washing machine:

[0269] The coated multiphase tablets produced with the method and composition described above were tested in a western European washing machine Bauknecht WA9850 using a standard 40°C wash cycle without pre-wash and comprising a main wash cycle and three rinse cycles.

[0270] After introducing 1.2kg of mixed soiled fabrics in the drum of the washing machine, two tablets are introduced in the main wash dispenser and the washing machine is activated. The two tablets were disintegrated in less than one minute and all the tablet composition was driven inside the drum through the piping of the washing machine. In order to monitor the dissolution of the beads through out the wash, the undissolved particles were collected from the drum and from the clothes at different timings. The test was restarted after each evaluation. One side by side comparisons was done by testing floating beads vs. non floating beads (where the Expancel was replaced by sodium carbonate). The results of the test can be observed in the table below:

Percentage of each phase remaining undissolved in the drum at different periods of the wash and rinse cycle

Washing machine cycle	Floating + rinse release		Non-floating	
Phase:	First	Second	First	Second
2' after start of the wash cycle	80%	96%	81%	94%
End of wash cycle (before the wash liquor gets pumped out)	5%	81%	4%	81%
Beginning of 1st rinse cycle (after water intake)	2%	69%	2%	21%
End of 1st rinse cycle (before the rinse liquor is pumped out)	1%	55%	1%	15%
Beginning of last rinse cycle	-	10%	-	4%
End of the last rinse cycle (after all the water has been pumped out and after last spin)	-	6%	-	2%

[0271] A side by side comparison was achieved with an expert panel to evaluate the performance of the tablets on cotton terry cloth towels. Two trained and qualified judges evaluated dry perfume release and softness performance using a -4 to +4 nine point scale. Each group of tablets was evaluated by a paired comparison with the control tablets (Ariel essential tablets) and the preferred items were given a numerical score, with a -4 corresponding to a strong preference for the precedent item over the current one and a +4 corresponding to a strong preference for the current item over the precedent one, and 0 being no difference.

[0272] An average of the scores obtained in a Bauknecht WA9850 using 1.2 kg of Terry towels in a standard 40°C wash cycle without pre-wash and comprising a main wash cycle and three rinse cycles is shown below:

Tablet used	Softening performance vs control	Perfume release vs control
Control (Ariel Essential tablets)	0	0
Tablets with floating and delayed release beads	3.4	2.2
Tablets with non floating beads	1.2	0.8

EXAMPLE 2:

[0273]

First phase:	
	% 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	21.066
EDDS/Sulphate particle	0.19
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.34
Fluorescer	0.15
Zinc phtalocyanine 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
Binder spray-on	2.0
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

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

Nonionic agglomerate comprise 26% nonionic surfactant, 6% Lutensit K-HD 96, 40% sodium acetate anhydrous, 20% carbonate and 8% zeolite.

Cationic agglomerate comprise of 20% cationic surfactant, 56% zeolite and 24% sulfate

Layered silicate comprises of 95% SKS 6 and 5% silicate

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 diamineN,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

Binder spray on system comprises of 0.5 parts of Lutensit K-HD 96 and 2.5 parts of PEGs

Second phase:	
	% by weight, of total composition
Perfume bead composition	4.9

[0274] Perfume beads composition contains 46% expancel 091DE80, 8% silica, 10% silicate, 15% perfume, 5% crosslinked polyvinylalcohol-borate, 10% water and 7% sodium sulfate.

EXAMPLE 3:

[0275]

First phase:	
	% by weight, of total composition
Clay extrudate	13
Flocculant agglomerate	3.5
Anionic particle	38.2
Sodium percarbonate	8.0
Bleach activator agglomerates	2.3
HPA sodium tripolyphosphate	11.4
Sodium carbonate	10.043
EDDS/Sulphate particle	0.19
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.34
Fluorescer	0.15
Zinc phtalocyanine sulphonate encapsulate	0.027
Soap powder	1.40
Suds suppresser	2.6
Citric acid	1.0
Protease	0.45
Cellulase	0.20
Amylase	0.20
Perfume	1.0
Binder spray-on	2.0

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

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

Layered silicate comprises of 95% SKS 6 and 5% silicate

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 diamineN,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

Binder spray on system comprises of 0.5 parts of Lutensit K-HD 96 and 2.5 parts of PEGs

The anionic particle was a blown powder with: 17.7% sodium linear alkylbenzene sulphonate, 2% Nonionic C35 7EO, 5.9% Nonionic C35 3EO, 0.5% soap, 47.8% sodium tripolyphosphate (Rhodia-phos HPA 3.5 from Rhone Poulenc), 10.8 sodium silicate, 0.4% sodium carboxymethly cellulose, 2.1% Acrylate/maleate co-polymer and 12.9% of moisture and salts.

Second phase:	
	% by weight, of total composition
Perfume bead composition	4.9

[0276] Perfume beads composition contains 46% expancel 091DE80, 8% silica, 10% silicate, 15% perfume, 5% crosslinked polyvinylalcohol-borate, 10% water and 7% sodium sulfate.

Claims

1. A shaped detergent 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 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.

5. 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.

6. 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.

7. 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.

8. 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.

9. 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.

10. A process for producing a detergent composition according to any of Claims 1-8, said process comprising a mixing step and a compression step.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 87 0254

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	16 March 2001	Pfannenstein, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 87 0254

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82