Some of the rinse composition is delayed until the rinse step. Unit dose products for use in the method are also claimed.
CLEANING AND RINSING OF TEXTILE FABRICS

FIELD OF THE INVENTION

[0001] The present invention relates to the cleaning and rinsing of textile fabrics, wherein both wash and rinse compositions are placed in a wash liquor with the fabric, and then a rinsing step is carried out in a rinse liquor, whereby release of at least some of the rinse composition is delayed until the rinse.

BACKGROUND OF THE INVENTION

[0002] U.S. Pat. No. 4,801,636 discloses a comminuted wash additive in a water soluble polymeric film envelope or in microcapsules of the water soluble polymer, or in a water-insoluble envelope sealed with the water soluble polymer. The water soluble polymer typically comprises polyvinyl alcohol and alkyl cellulose monomer units together with a cross-linking agent. The polymer is insoluble at higher pH but becomes increasingly soluble as the pH is reduced.

[0003] It is also known from U.S. Pat. No. 4,108,600 to coat fabric conditioner particles with a coating, the solubility of which is pH dependent. The coating comprises a water soluble polymer, preferably a polyvinyl alcohol or gelatin of defined molecular weight and isoelectric point. These particles have a particle size up to about 1,500 microns and are disposed in a porous receptacle having porous openings which are smaller than the particle size e.g., up to 120 microns. A pH control agent (insolubilising agent) is kept separate from the coated fabric conditioner particles, e.g. in a separate receptacle or separate compartment of the same receptacle. Typical pH control agents are common organic or inorganic acids, bases or buffering agents.

[0004] The delayed release of a fabric softening clay component into the wash liquor, from a detergent tablet containing a washing composition, is disclosed in WO-A-99/40171, although delay until the rinse cycle is not envisaged.

[0005] It has now been found possible to utilise formulations adapted for delayed release in the rinse, in such a way as to improve delivery of the product into the process. This has been achieved by formulating a delayed release rinse composition in unit dose form and to be dosed in a receptacle such as a net bag and/or also dosing the main wash composition in that receptacle, into the washing machine or other wash environment.


[0008] Definition of the Invention

[0009] Thus, in a first aspect, the present invention provides a method of washing and rinsing a textile fabric, the method comprising:

(a) placing in a water permeable receptacle, a wash composition and a rinse composition;

(b) a washing step comprising bringing the receptacle and the fabric into contact with a wash liquor; and

(c) subsequent to the washing step (b), a rinse step comprising contacting the receptacle and the fabric with a rinse liquor;

wherein the rinse composition is formulated such that release of at least some of the rinse composition is delayed until the rinse step.

[0014] A second aspect of the present invention provides a method of rinsing a textile fabric, the method comprising:

(a) placing in a water permeable receptacle, at least one unit dose unit comprising a rinse composition; and

(b) effecting a rinse step of contacting the water permeable receptacle and the fabric with a rinse liquor;

wherein the rinse composition is formulated such that release of a substantial amount of rinse composition cannot occur during a prior wash step.

[0018] A third aspect of the present invention provides a unit dose product for washing and rinsing of a textile fabric comprising a wash composition, a rinse composition and means for inhibiting release of the rinse composition during washing, until the rinse.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Unit Dose Forms

[0020] Suitable unit dose forms include tablets, water soluble sachets and water soluble capsules. Each can be made by a specific technology. Tablets are suitable for solid compositions whereas, sachets and capsules are suitable for solid or liquid compositions, although in the later case, some care has to be taken to ensure long term stability of the composition with the material used to form the tablet, sachet or capsule.

[0021] As mentioned above, dosing of delayed release coated particles up to 1,500 microns in a water permeable receptacle is known from U.S. Pat. No. 4,108,600. A unit dose certainly has at least one dimension (e.g. diameter, length, width or height), greater than 1,500 microns but preferably at least 0.5 cm, more preferably at least 1 cm, for example no more than 5 cm, preferably no more than 2.5 cm.

[0022] However, it is preferred that the delayed release rinse composition is formulated as a component such as a tablet layer, capsule(s) (whether such capsule is free or incorporated in a tablet layer), a sachet or gel matrix which substantially sustains its physical integrity until the rinse step and has a size large enough not to pass through mesh of a net or bag which constitutes the water permeable receptacle. In the case of a whole tablet layer or non-spherical capsule, preferably it has at least one dimension greater than the mesh size. In the case of a capsule which is substantially spherical, preferably its diameter is greater than the mesh size.
[0023] (a) Tablets

[0024] Tableting Entails Compaction of a Particulate Composition.

[0025] A variety of tableting machinery is known, and can be used. Generally it will function by stamping a quantity of the particulate composition which is confined in a die.

[0026] Tableting machinery able to carry out such operations is known. For example, suitable tablet presses are available from Fette and from Korsch.

[0027] Tableting may be carried out at ambient temperature or at a temperature above ambient which may allow adequate strength to be achieved with less applied pressure during compaction. In order to carry out the tableting at a temperature which is above ambient, the particulate composition is preferably supplied to the tableting machinery at an elevated temperature. This will of course supply heat to the tableting machinery, but the machinery may be heated in some other way also.

[0028] It is known to make tablets using microwave radiation. WO 96/06156 mentions that hydrated materials are useful in this special circumstance to cause sintering.

[0029] For the present invention, if any heat is supplied, it is envisaged that this will be supplied conventionally, such as by passing the particulate composition through an oven, rather than by any application of microwave energy.

[0030] The size of a tablet will suitably range from 10 to 100 grams (g), preferably from 15 to 60 g, depending on the conditions of intended use, and whether the tablet represents a dose for an average load in a fabric washing or a fractional part of such a dose. The tablets may be of any shape. However, for ease of packaging they are preferably blocks of substantially uniform cross-section, such as cylinders or cuboids.

[0031] The overall density of a tablet is preferably 1040 or 1050 gm/liter, better 1100 gm/liter, up to 1300 or 1350 gm/liter or even more. The tablet density may well lie in a range up to no more than 1250 or even 1200 gm/liter.

[0032] Thus the starting particulate composition may suitably have a bulk density of at least 400 g/liter, preferably at least 500 g/liter, and advantageously at least 700 g/liter. Granular detergent compositions of high bulk density prepared by granulation and densification in a high-speed mixer/granulator, as described and claimed in EP 340013A (Unilever), EP 352135A (Unilever), and EP 425774A (Unilever), or by the continuous granulation/densification processes described and claimed in EP 367339A (Unilever) and EP 390251A (Unilever), are inherently suitable for use in the present invention.

[0033] Tablets in which the rinse composition is held in a central cavity (the body of the tablet) containing a wash composition may be formed using an appropriately shaped die.

[0034] (b) Sachets

[0035] Sachets may be water permeable envelopes made of woven or non woven fabric. Preferably, however, they are formed of water soluble polymer.

[0036] The envelope forming the sachet is most preferably formed by horizontal or vertical form-film-seal of a water soluble polymer film. The film preferably incorporates a stabilizer.

[0037] As will be elucidated in more detail hereinbelow, the water soluble film may be formed from a variety of different materials. The plasticiser will depend on the nature of the film in question. Therefore, preferred plasticisers will be recited in more detail in the section of this description dealing with these film materials. However, the preferred amount of plasticiser is from 0.2% to 40%, preferably from 10% to 20% by weight of the substantially non-aqueous liquid composition. One or more plasticisers may independently be incorporated in the film and in the liquid composition.

[0038] However, it is preferred for the identity of the plasticiser(s) in the film and in the liquid composition to be substantially the same.

[0039] The plasticiser system influences the way the polymer chains react to external factors such as compression and extensional forces, temperature and mechanical shock by controlling the way that the chains distort/realign as a consequences of these intrusions and their propensity to revert or recover to their former state. The key feature of plasticisers is that they are highly compatible with the film, and are normally hydrophilic in nature.

[0040] As used herein, the term “water soluble polymer” refers to a polymer which dissolves and dispenses completely in water within 5 minutes with agitation, e.g. by means of hand, stick or other stirrer or under the action of a mechanical washing machine and at a relevant temperature. A “relevant temperature” is one at which the consumer will need to dissolve or disperse the polymer component at the beginning of, or during a cleaning process. A polymer is to be regarded as dissolving or dispersing at a “relevant temperature” if it does so under the aforementioned conditions at a temperature anywhere in the range of from 20° C. to 60° C.

[0041] Preferred water soluble polymers are those capable of being cast into a film or solid mass and may for example as described in Davidson and Sittig, Water-Soluble Resins, Van Nostrand Reinhold Company, New York (1968). The water-soluble polymer should have proper characteristics, such as strength and pliability, to permit machine handling. Preferred water-soluble resins include polyvinyl alcohol, cellulose ethers, polyethylene oxide, starch, polyvinylpyrrolidone, polyacrylamide, polyvinyl methyl ether-maleic anhydride, polyethylene oxide, hydroxyethylcellulose, methylcellulose, polyethylene glycols, carboxymethylcellulose, polyacrylic acid salts, alginates, acrylate copolymers, guar gum, casein, ethylene maleic anhydride resin series, polyethyleneimine, ethyl hydroxyethylcellulose, ethyl methylcellulose, hydroxyethyl methylcellulose or blends of polymers mentioned above. Lower molecular weight water-soluble, polyvinyl alcohol film-forming resins are preferred.

[0042] Generally, preferred water-soluble, polyvinyl alcohol film-forming polymers should have relatively low average molecular weight and low levels of hydrolysis in water. Polyvinyl alcohols preferred for use therein have a weight average molecular weight between 1,000 and 300,000, preferably between 2,000 and 200,000, most preferably between 30,000 and 150,000. Hydrolysis, or alcoholysis, is defined as the percent completion of the reaction where acetate groups on the resin are substituted with hydroxyl, —OH, groups. A hydrolysis range of from 60-99% of polyvinyl alcohol...
film-forming resin is preferred, while a more preferred range of hydrolysis is from about 70-95% for water-soluble, polyvinyl alcohol film-forming resins. The most preferred range of hydrolysis is 80-92%. As used in this application, the term “polyvinyl alcohol” includes polyvinyl acetate compounds with levels of hydrolysis disclosed herein. The water-soluble resin film should be formulated so as to substantially completely dissolve in 130° F. water with agitation within about five minutes, preferably within about 3 minutes in 100° F. water with agitation, and most preferably within about 1 minute in 100° F. water with agitation.

[0043] All of the above polymers include the aforementioned polymer classes whether as single polymers or as copolymers formed of monomer units or as copolymer formed of monomer units derived from the specified class or as copolymers wherein those monomer units are copolymerised with one or more comonomer units.

[0044] A preferred plastics film is a polyvinyl alcohol film, especially one made of a polyvinyl alcohol copolymer having a comonomer having a carboxylate function.

[0045] PVA can be made by the polymerisation of vinyl acetate, followed by hydrolysis, conveniently by reaction with sodium hydroxide. However, the resulting film has a highly symmetrical, hydrogen-bonded structure and depends on the particular PVA composition, is not necessarily readily soluble in cold water. PVA films which are suitable for the formation of water-soluble packages are typically polymers produced from copolymerisation of vinyl acetate and another comonomer which contains a carboxylic function. Examples of such comonomers include monocarboxylates, such as acrylic acid, and dicarboxylates, such as itaconic acid, which may be present during polymerisation as esters. Alternatively, the anhydride of maleic acid may be used as the copolymer. The inclusion of the comonomer reduces the symmetry of and degree of hydrogen bonding in the final film and renders the film soluble even in cold water. Partially hydrolysed PVA can also be used to deliberately adapt the film to be cold water soluble.

[0046] Suitable PVA films for use in a package according to the invention are commercially available and described, for example, in EP-B-0 291 198. PVA films for use in a package according to the invention can be made by the copolymerisation of vinyl acetate and a carboxylate-containing monomer (for example acrylic, maleic or itaconic acid or acid ester), followed by either partial (for example up to about 90%) or complete hydrolysis with sodium hydroxide.

[0047] In order to make the water solubility of PVA ionic strength and/or pH dependent, so it is soluble in the rinse liquor but not in the wash liquor, it may be blended with one or more other substances, e.g. with an alkyl cellulose and a metallic cross-linker such as a boron compound, as described in U.S. Pat. No. 4,801,636.

[0048] Plasticizers can be included in the polymer to improve the physical stability of the film. The preferred amount of plasticiser is from 0.2% to 20%, preferably from 5% to 10% by weight of the substantially non-aqueous liquid composition.

[0049] Generally speaking, plasticisers suitable for use with PVA-based films have —OH groups in common with the —CH2—CH(OH)2—CH2—CH(OH)—polymer chain of the film polymer.

[0050] Their mode of functionality is to introduce short chain hydrogen bonding with the chain hydroxyl groups and thus weaken adjacent chain interactions which inhibits swelling of the aggregate polymer mass—the first stage of film dissolution.

[0051] Water itself is a suitable plasticiser for PVOH films but other common plasticisers include:

[0052] Polyhydroxy compounds, e.g. glycerol, trimethylolpropane, diethylene glycol, triethylene glycol, dipropylene glycol, sorbitol

[0053] Starches e.g. starch ether, esterified starch, oxidized starch and starches from potato, tapioca and wheat

[0054] Celluloses/carbohydrates, e.g. amylopectin, dextrin carboxymethylcellulose and pectin.

[0055] Polyvinylpyrrolidone (PVP), another preferred polymer for use in the articles of the present invention, may be cast from a variety of solvents to produce films which are clear, glossy, and reasonably hard at low humidities. These polyvinylpyrrolidone films exhibit excellent adhesion to a wide variety of surfaces, including glass, metals, and plastics. Unmodified films of polyvinylpyrrolidone are hydroscopic in character. Dry polyvinylpyrrolidone film has a density of 1.25 and a refractive index of 1.53. Tackiness at higher humidities may be minimized by incorporating compatible, water-insensitive modifiers into the polyvinylpyrrolidone film, such as 10% of an aryl-sulfonamide-formaldehyde resin.

[0056] Suitable plasticisers for PVP-based films may be chosen from one or more of those specified above for PVA.

[0057] Preferred water-soluble films may also be prepared from polyethylene oxide (PEO) resins by standard calendering, molding, casting, extrusion, and other conventional techniques. The polyethylene oxide films may be clear or opaque, and are inherently flexible, tough, and resistant to most oils and greases. These polyethylene oxide resin films provide better solubility than other water-soluble plastics without sacrificing strength or toughness. The excellent ability to lay flat, stiffness, and sealability of water-soluble polyethylene oxide films make good for machine handling characteristics.

[0058] Suitable plasticisers for PEO-based films may be selected from one or more of those specified for PVA and PVP.

[0059] Sachet Forming Methods

[0060] Horizontal Form-Fill-Sea


[0062] By way of example, a thermoforming process is now described where a number of packages according to the invention are produced from two sheets of water soluble material. In this regard recesses are formed in the film sheet using a forming die having a plurality of cavities with dimensions corresponding generally to the dimensions of the
packages to be produced. Further, a single heating plate is used for thermoforming the film for all the cavities, and in the same way a single sealing plate is described.

[0063] A sheet of polyvinyl alcohol film is drawn over a forming die so that the film is placed over the plurality of forming cavities in the die. In this example each cavity is generally dome shape having a round edge, the edges of the cavities further being radiussed to remove any sharp edges which might damage the film during the forming or sealing steps of the process. Each cavity further includes a raised surrounding flange. In order to maximise package strength; the film is delivered to the forming die in a crease free form and with minimum tension. In the forming step, the film is heated to 100 to 120°C, preferably approximately 110°C, for up to 5 seconds, preferably approximately 700 micro seconds. A heating plate is used to heat the film, which plate is positioned to superpose the forming die. During this preheating step, a vacuum of 0.5 bar is pulled through the pre-heating plate to ensure intimate contact between the film and the pre-heating plate. This intimate contact ensuring that the film is heated evenly and uniformly (the extent of the vacuum is dependant of the thermoforming conditions and the type of film used, however in the present context a vacuum of less than 0.6 bar was found to be suitable). Non-uniform heating results in a formed package having weak spots. In addition to the vacuum, it is possible to blow air against the film to force it into intimate contact with the preheating plate.

[0064] The thermoformed film is moulded into the cavities blowing the film off the heating plate and/or by sucking the film into the cavities thus forming a plurality of recesses in the film which, once formed, are retained in their thermoformed orientation by the application of a vacuum through the walls of the cavities. This vacuum is maintained at least until the packages are sealed. Once the recesses are formed and held in position by the vacuum, a liquid coating according to the invention is added to each of the recesses. A second sheet of polyvinyl alcohol film is then superposed on the first sheet across the filled recesses and heat-sealed thereto using a sealing plate. In this case the heat sealing plate, which is generally flat, operates at a temperature of about 140 to 160°C, and contacts the films for 1 to 2 seconds and with a force of 8 to 30 kg/cm², preferably 10 to 20 kg/cm². The raised flanges surrounding each cavity ensure that the films are sealed together along the flange to form a continuous seal. The radiussed edge of each cavity is at least partly formed by a resiliently deformable material, such as for example silicone rubber. This results in reduced force being applied at the inner edge of the sealing flange to avoid heat/pressure damage to the film.

[0065] Once sealed, the packages formed are separated from the web of sheet film using cutting means. At this stage it is possible to release the vacuum on the die, and eject the formed packages from the forming die. In this way the packages are formed, filled and sealed while nesting in the forming die. In addition they may be cut while in the forming die as well.

[0066] During the forming, filling and sealing steps of the process, the relative humidity of the atmosphere is controlled to ca. 50% humidity. This is done to maintain the heat sealing characteristics of the film. When handling thinner films, it may be necessary to reduce the relative humidity to ensure that the films have a relatively low degree of plasticisation and are therefore stiffer and easier to handle.

Vertical Form-Fill-Seal

[0067] In the vertical form-fill-seal (VFFS) technique, a continuous tube of flexible plastics film is extruded. It is sealed, preferably by heat or ultrasonic sealing, at the bottom, filled with the liquid composition, sealed again above the liquid film and then removed from the continuous tube, e.g. by cutting.

[0068] Encapsulation methods for other water soluble films such as based on PVP or PEO will be known to those skilled in the art.

[0069] The way that the chains distort/realign as a consequence of these intrusions and their propensity to revert or recover to their former state. The key feature of plasticisers is that they are highly compatible with the film, and are normally hydrophilic in nature.

[0070] (c) Capsules

[0071] Capsules may be made of, for example, gelatin or starch but are preferably based on water soluble polymers used to encapsulate the material in question.

[0072] The material may typically be formed as a granule of bolus and coated by a process is fluidised-bed coating or agglomeration. Other useful options are pan coating, dip coating or rotating disk coating. In these cases the core material may be a capsule, a tablet, or any other form of the material to be encapsulated material may also be encapsulated via film coating.

[0073] Delayed Release

[0074] In the first embodiment of the present invention, the rinse composition must be provided in a form such that release of at least some of the rinse composition is delayed until the rinse step. This is also the case in preferred embodiments of the second invention. It generally entails controlled/triggered release, depending on some parameter which changes between the wash and rinse.

[0075] Release inhibition for the rinse composition can be controlled by various physical chemical triggers like temperature, pH, ionic strength, Ca²⁺ level, osmotic pressure or changes in the concentration of soluble components of wash compositions, e.g. Na⁺ level, due to dissolution in the rinse. Alternatively, release inhibition could be controlled by enzyme release in the rinse phase, the spinning motion or time. Combinations of triggers mentioned above can be used.

[0076] Release inhibiting means for preventing release of the rinse composition is preferably pH and/or ionic strength and/or temperature dependent. The pH in the wash liquor is usually high, i.e. at least 9.5, especially at least 10. However, in the rinse liquor, the pH is usually much lower, i.e. no more than 9, typically no more than 8.5. The ionic strength of the wash liquor is usually at least 4 mS/cm, especially at least 4.5 mS/cm. In the rinse liquor, the ionic strength is lower, at the most 2.5 mS/cm, especially lower than 1.5 mS/cm.

[0077] Typical pH and/or ionic strength dependent release inhibiting means may form all or part of any material used to encapsulate the rinse composition or form a such
containing the rinse composition, or be mixed in a matrix with the rinse conditioner in powder or granular form.

[0078] One preferred form of water soluble polymer, the solubility of which is ionic strength and pH dependent, is a polymer made from vinyl alcohol monomer units, optionally also with one or more other comonomer units such as alkyl cellulose or carboxyl functional monomers such as acrylic, malic or itaconic acids or the equivalent acid esters thereof. As already described, these kinds of polymers are suitable for making sachets from films of those polymers.

[0079] In one preferred class of embodiments, the polymer comprises monomers units selected from one or more vinyl alcohol derivatives, acrylates and alkylacrylates, the acrylates and/or alkylacrylates optionally having basic functionality, said polymer optionally being in admixture with an alkylcellulose and/or a cross-linking agent. Another preferred class is when the polymer is an alkyl substituted cellulose ether. However, other preferred forms of polymer for the delayed release function will now be given.

[0080] The pH dependence of the solubility of such a polymer may be brought about by incorporation therein of a cross-linking agent of the kind described in U.S. Pat. No. 4,801,636. These are so-called "metallic" cross-linking agents.

[0081] A preferred "metallic" cross-linking agent comprising boric acid and its salt. Other potential cross-linkers are for example telluric and asenic acid precursors and salts thereof. Derivatised metalloid oxides may also be possible. Even more cross-linkers are given in the book: "Polyvinylalcohol—Properties and applications, Chapter 9 by C. A. Finch (John Wiley & Sons, New York, 1973"). The cross-linking agent can be present in the polymer itself and/or as part of another component in the same or another composition used at the same time.

[0082] The polymeric material and cross-linking may be in contact with a cationic species having a hydrophobic group. The cationic species may be present in the aqueous wash liquid or can be added to the film or additive materials. Such cationic species may comprise organonitrogen salts, organophosphorous salts, cationic organic sulphonium salts, cationic organic tin compounds, amphoteric surfactants and the like. The organic groups or such salts may be alkyl, aryl, alkenyl or combinations thereof. Quaternary ammonium compounds are the preferred cationic species. For example in the presence of cetyl pyridinium chloride (at a concentration of 0.1 wt %), the dissolution rates of the PVA/alkyl cellulose decrease by a factor of 32 at high borate concentration/high pH, while only by a factor of 3 at low borate ion concentration/low pH.

[0083] A surfactant may be added to the polymer as anti-foam and as a wetting agent. Virtually any surfactant known in the art is suitable for this purpose. Non-limiting examples include ethoxylated aliphatic alcohols, ethoxylated alkylphenols, polyols and C12-15 aliphatic alcohols. Other examples are polyethylene glycol ether and octyl alcohol.

[0084] Other materials, including polymers, the solubility or dispersability of which in an aqueous medium is pH dependent, may be chosen from the following:

- JP-A-60 141 705 discloses a copolymer characterised in that a basis monomer (A) represented by the formula:
  \[ CH₂—C(R\text{COOCH₂CH₃}NR²R³] \]

- (i) (in which R is a hydrogen or a methyl group, and R² and R³ each is an alkyl group having 1-3 carbons), a monomer (B) which is insoluble or hardly soluble in water and a monomer (C) which is soluble in water are copolymerised in such a manner that the amount of (A) is 10-65% by weight, the amount of (B) is 8-45% by weight and the ratio by weight of (B)/(C) is from 2/1 to 1/7.

- This polymer is substantially insoluble in alkaline water of pH of about 9.5 or higher while it is soluble in water of pH of about 8.5 or lower. The ratio between the dissolving time above a pH of 9.5 and that below a pH of 8.5 is large.

- The insoluble monomer (A) is a main monomer component for preparing such pH sensitive copolymers and may for example be selected from from N-N-dimethylamino ethyl acrylate, N,N-dimethylamino ethyl acrylate, N,N-dimethylamino ethyl methacrylate, N,N-dimethylamino ethyl acrylate, N—N-dichloroamino ethyl methacrylate and mixtures thereof.

- Examples for the insoluble monomer (B) are acrylic acid ester, methacrylic acid ester, crotonic acid ester, itaconic acid ester, vinylacetate and styrene. It is preferred that the carbon number of the alkyl group which is ester bonded is from 1 to 8. Methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate and ethyl methacrylate and the particularly preferred examples.

- Water soluble monomer (C) can be selected from N,N-dimethylaminopropylacrylamide (or methacrylic acid amide), N,N-dimethylacrylamide (or methacrylic acid amide), 2-hydroxyethyl acrylate (or methacrylate), 2-hydroxypropyl acrylate (or methacrylate) and an ester of acrylamide or methacrylic acid with polyethylene glycol or methoxy(poly)ethylene glycol (p=2–30).

- (ii) WO-A-00/17311 discloses a material which has a melting point no less than 30°C. and a pKa of no more than 12 and no less than 7.0, preferably between 11.5 and 8.0, most preferably between 10.5 and 9.0. The preferred material is selected so that during the early part of the wash where the wash solution pH is controlled by the detergent around 10, the coating material is substantially neutral without charge and remains relatively water insoluble. During the rinse the material will be protonated to become positively charged and more water soluble.

- Preferred coating materials are, amines, waxes, Schiff base compounds and mixtures thereof. Preferred amines include other than primary fatty amines. Such amines include polymeric aminofunctional homopolymers and/or copolymers and/or ter-polymers. The preferred amines typically do not have exclusively primary amino functionality, rather they typically contain secondary and/or tertiary amino groups, optionally with primary amino moieties also included.

- Waxes can be used as a co-melted blend to improve the filming property. The preferred ratio of wax to amines is no more than 50% wax.
An alternate class of such materials are Schiff bases, i.e. adduct of amines with aldehydes. Only selected types break down at the pH of the current invention. One example is formed between p-amino benzoate with an alkyl aldehyde. A preferred example is the Schiff base made by fusing p-amino benzoate with a n-dodecyl aldehyde.

(iii) WO00/06683 discloses a material which includes at least one compound which is not or only slightly soluble at the end of the main wash cycle of the washing machine (at pH above 10). In the rinsing processes (pH less than 9), however it is dissolved or detached from the nucleus (from the nuclei) to such an extent that at least a partial discharge of the nucleus material takes place. This compound preferably includes a polymer, especially a pH-sensitive polymer, which includes at least one repeating unit, which has at least one basic function, which does not form part of the backbone chain of the polymer. In a preferred implementation the polymer includes at least one repeating unit, which is based on a compound, which has been selected from the group which consists of vinylalcohol derivatives, acrylates or alkylacrylates which include said basic function. In a special implementation of the invention the polymer is carbohydrate which has been functionalised with said basic function.

In an alternative implementation the repeating unit is based on a compound with the following formula:

![Chemical Structure](image)

where G is a connecting group which has been selected from \(-\text{COO}-, \text{O}-\), \(-\text{CONH}-, \text{NHCN}-, \text{NH}-\text{COO}-, \text{OCONH}-\) or \(-\text{COO}-\). R1 and R2 independently of each other is hydrogen or an alkyl group with 1-3 carbon atoms, R3 independent of each other is hydrogen or an alkyl group with 1-5 carbon atoms and x is an integer between 1 and 6.

Preferably, the repeating unit is based on a compound with the following formula IV:

![Chemical Structure](image)

where R1 independent of each other is hydrogen or an alkyl group with 1-3 carbon atoms, R2 independent of each other is hydrogen or an alkyl group with 1-5 carbon atoms and x is an integer between 1 and 6.

Alternatively, a pH sensitive polymer sold as ACEATM ex Sankyo, and having the following formula, may be used:

![Chemical Structure](image)

In other variants, the basic function is an imine or a basic aromatic N-containing group, preferably a pyridine group or an imidazole group or the pH-sensitive component is a polymer obtainable from Chitosan, or the material may contain K-Carrageenan.

(iv) An example of a material that can inhibit dissolution of the rinse material during the main wash, is polyvinyl caprolactam or hydroxybutylmethylcellulose. Those materials are insoluble at temperatures above 35°C, but become soluble in the rinse phase, when water of ambient temperature is introduced in the washing machine.


The Water Permeable Receptacle

The water permeable receptacle is intended to retain the contents thereof during the wash and rinse steps whilst allowing the contents to be wetted by the wash or rinse water or liquor, such that at the relevant time, they may be released by dispersion and/or dissolution.

Although such a receptacle may be formed of a non-woven fabric, preferably it is formed from a woven material, for example a coarse-woven cloth or net. Such a material should have a mesh size which is significantly smaller than the intended contents. As mentioned above, preferably the mesh size should be larger than at least one dimension of any component such as a tablet layer, capsule (whether free or incorporated in a tablet layer), sachet or gel matrix which constitutes a unitary delayed release rinse conditioner component which substantially retains its physical integrity until the rinse step. Substantially spherical such capsules, whether separate or incorporated in a tablet layer, preferably have a diameter larger than the mesh size. Mesh sizes of at least 3 mm, preferably around 5 mm, e.g. up to 7.5 mm are typical.

The Rinse Composition

Use of a rinse composition is essential to the first aspect of the present invention and preferably for the second aspect of the invention.

The rinse composition contains at least one agent which exerts a beneficial action upon a textile in the rinse. Suitable examples of such agents include fabric softening
agents, especially cationic softening compounds, antistatic agents, ease of ironing agents, anti-wrinkling/crease protection agents, perfume and optical brighteners. Alternatively, delayed release by means of the invention is also beneficial for e.g. oxygen bleach, bleach activators, soil release agent, enzymes, suds suppressors, disinfectants, anti-redeposition aids, dye transfer inhibitors.

[0110] A discussion of materials which are known as fabric softening agents and which may be used in the tablets of the present invention is found in published International Patent Application WO-A-94/24999.

[0111] Some suitable softeners are cationic softening components, optionally used together with other materials such as oily sugar derivatives, formulation and dispersing aids, anti-oxygenation/reduction stabilisers and co-active softening surfactants; cellulosics; clays; and polysiloxanes and their derivatives. Mixtures of any of the foregoing can also be used.

[0112] (a) Cationic Fabric Softening Compounds

[0113] Suitable cationic fabric softening compounds may be selected from those typically included in rinse-added fabric softening compositions.

[0114] It is especially preferred if the cationic softening agent is a water insoluble quaternary ammonium material which comprises a compound having two C12-18 alkyl or alkenyl groups connected to the nitrogen head group via at least one ester link. It is more preferred if the quaternary ammonium material has two ester links.

[0115] A first preferred type of ester-linked quaternary ammonium material is represented by formula (I):

\[
(R')_nN^-(CH_2)_mCH_2\overset{O-O}{\longrightarrow}R^1
\]

wherein \( T \) is \(-O-C-\) or \(-C-O\).

[0118] A second type of ester-linked quaternary ammonium material is represented by the formula (II):

\[
R^1-N^-(CH_2)_mCH_2\overset{O-O}{\longrightarrow}R^2
\]

wherein \( T, R^1, R^2, n, \) and \( X^- \) are as defined above.

[0119] Especially preferred materials within this formula are di-alkenyl esters of triethanol ammonium methyl sulphate and \( N-N-di(tallowoxyloxy ethyl) \) \( N,N \)-dimethyl ammonium chloride. Commercial examples of compounds within this formula are Tetranyl® AOT-1 (di-oleic ester of triethanol ammonium methyl sulphate 80% active), AO-1 (di-oleic ester of triethanol ammonium methyl sulphate 90% active), and AHT-1 (di-hardened oleic ester of triethanol ammonium methyl sulphate 90% active), L1/90 (partially hardened tallow ester of triethanol ammonium methyl sulphate 90% active), L5/90 (palm ester of triethanol ammonium methyl sulphate 90% active) (supplied by Kao Corporation) and Rewoquat WE15 (C10,C20, and C16,C18 unsaturated fatty acid reaction products with triethanolamine dimethyl sulphate quarternised 90% active), ex Wilco Corporation.

[0121] A third preferred type of quaternary ammonium material is represented by formula (III):

\[
\begin{array}{c}
\text{(III)}
\end{array}
\]

where \( R_1, R_2 \) are C1-28 alkyl or alkenyl groups; \( R_3 \) and \( R_4 \) are C1-4 alkyl or C2-4 alkyl groups and \( X^- \) is as defined above.

[0122] Examples of compounds within this formula include di(tallow alkyl)dimethyl ammonium chloride, di(tallow alkyl) dimethyl ammonium methyl sulphate, dihexadecyl dimethyl ammonium chloride, di(hardened tallow alkyl) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride and di(coconut alkyl) dimethyl ammonium chloride.

[0123] It is advantageous for environmental reasons if the quaternary ammonium material is biologically degradable.

[0125] Preferably, the compositions are provided as super-concentrates comprising from 25-97% by weight of cationic surfactant (active ingredient) based on the total weight of the composition, more preferably from 35-95% by weight, most preferably from 45-90% by weight, e.g. 55-85% by weight.

[0126] If the quaternary ammonium softening agent comprises hydrocarbyl chains formed from fatty acids or fatty acyl compounds which are unsaturated or at least partially unsaturated (e.g. having an iodine value of from 5 to 140, preferably from 5 to 100, more preferably from 5 to 60, most preferably
5 to 40, e.g. 5 to 25), then the cis:trans isomer weight ratio in the fatty acid/fatty acyl compound is greater than 20:80, preferably greater than 30:70, more preferably greater than 40:60, most preferably greater than 50:50, e.g. 70:30 or greater. It is believed that higher cis:trans isomer weight ratios afford the compositions comprising the compound better low temperature stability and minimal odour formation. Suitable fatty acids include Radiacid 406, ex Fina. Saturated and unsaturated fatty acids/acyl compounds may be mixed together in varying amounts to provide a compound having the desired iodine value.

[0127] Fatty acids/acyl compounds may also be, at least partially hydrogenated to achieve lower iodine values.

[0128] Of course, the cis:trans isomer weight ratios can be controlled during hydrogenation by methods known in the art such as by optimal mixing, using specific catalysts and providing high H₂ availability.

[0129] For improved rapid dispersion and/or dissolution of the composition after its release from the water soluble package, it is preferred that the fatty acyl compounds or fatty acids from which the softening compound is formed have an iodine value of from 5 to 140, more preferably 10 to 100, most preferably 15 to 80, e.g. 25 to 60.

[0130] Iodine Value of the Parent Fatty Acid

[0131] In the context of the present invention, iodine value of the parent fatty acid of the cationic surfactant is defined as the number of grams of iodine which react with 100 grams of compound.

[0132] To calculate the iodine value of a parent fatty acid of a cationic surfactant, a prescribed amount (from 0.1-3 g) of the fatty acid was dissolved into about 15 ml chloroform. The dissolved parent fatty acid was then reacted with 25 ml of iodine monochloride in acetic acid solution (0.1M). To this, 20 ml of 10% potassium iodide solution and about 150 ml deionised water was added. After addition of the halogen to the parent fatty acid had taken place, the excess of iodine monochloride was determined by titration with sodium thiosulphate solution (0.1M) in the presence of a blue starch indicator powder. At the same time a blank was determined with the same quantity of reagents and under the same conditions. The difference between the volume of sodium thiosulphate used in the blank and that used in the reaction with the parent fatty acid enabled the iodine value to be calculated.

[0133] Oily Sugar Derivatives

[0134] The rinse conditioner may comprise an oily sugar derivative.

[0135] The oily sugar derivative is a liquid or soft solid derivative of a cyclic polyol or of a reduced saccharide, said derivative resulting from 35 to 100% of the hydroxyl groups in said polyol or in said saccharide being esterified or etherified. The derivative has two or more ester or ether groups independently attached to a C₈-C₂₂ alkyl or alkyl chain.

[0136] The oily sugar derivatives of the invention is also referred herein as “derivative-CP” and “derivative-RS” dependant upon whether the derivative is the product derived from a cyclic polyol or from a reduced saccharide starting material respectively.

[0137] Preferably the derivative-CP and derivative-RS contain 35% by weight tri or higher esters, e.g. at least 40%.

[0138] Preferably 35 to 85% most preferably 40 to 80%, even more preferably 45 to 75%, such as 45 to 70% of the hydroxyl groups in said cyclic polyol or in said reduced saccharide are esterified or etherified to produce the derivative-CPE and derivative-RSE respectively.

[0139] For the derivative-CP and derivative-RS, the tetra, penta etc prefixes only indicate the average degrees of esterification or etherification. The compounds exist as a mixture of materials ranging from the monooester to the fully esterified ester. It is the average degree of esterification as determined by weight that is referred to herein.

[0140] The derivative-CP and derivative-RS used do not have any substantial crystalline character at 20°C. Instead they are preferably in a liquid or soft solid state, as hereinbelow defined, at 20°C.

[0141] The starting cyclic polyol or reduced saccharide material is esterified or etherified with C₈-C₂₂ alkyl or alkylol chains to the appropriate extent of esterification or etherification so that the derivatives are in the requisite liquid or soft solid state. These chains may contain unsaturation, branching or mixed chain lengths.

[0142] Typically the derivative-CP and derivative-RS has 3 or more, preferably 4 or more, for example 3 to 8, eg 3 to 5, ester or ether groups or mixtures thereof. It is preferred if two or more of the ester or ether groups of the derivative-CP and derivative-RS are independently of one another attached to a C₈ to C₂₂ alkyl or alkylol chain. The alkyl or alkylol groups may be branched or linear carbon chains.

[0143] The derivative-CPs are preferred for use as the oily sugar derivative. Inositol is preferred cyclic polyol, and Inositol derivatives are especially preferred.

[0144] In the context of the present invention the terms derivative-CP and derivative-RS encompass all ether or ester derivatives of all forms of saccharides which fall into the above definition, which are especially preferred for use. Examples of preferred saccharides for the derivative-CP and derivative-RS to be derived from are monosaccharides and disaccharides.

[0145] Examples of monosaccharides include xylose, arabinose, galactose, fructose, sorbose and glucose. Glucose is especially preferred. An example of a reduced saccharide is sorbitan. Examples of disaccharides include maltose, lactose, cellobiase and sucrose. Sucrose is especially preferred.

[0146] If the derivative-CP is based on a disaccharide it is preferred if the disaccharide has 3 or more ester or ether groups attached to it. Examples include sucrose tri, tetra and penta esters.

[0147] Where the cyclic polyol is a reducing sugar it is advantageous if each ring of the derivative-CP has one ether group, preferably at the C₁ position. Suitable examples of such compounds include methyl glucose derivatives.

[0148] Examples of suitable derivative-CPs include esters of alkyl(poly)glycosides, in particular alkyl glucoside esters having a degree of polymerisation from 1 to 2.

[0149] The ILB of the derivative-CP and derivative-RS is typically between 1 and 3.

[0150] The derivative-CP and derivative-RS may have branched or linear alkyl or alkylol chains (of varying
degrees of branching), mixed chain lengths and/or unsaturation. Those having unsaturated and/or mixed alkyl chain lengths are preferred.

[0151] One or more of the alkyl or alkenyl chains (independently attached to the ester or ether groups) may contain at least one unsaturated bond.

[0152] For example, predominantly unsaturated fatty chains may be attached to the ester/ether groups, e.g. those attached may be derived from natural oils such as rapeseed oil, cotton seed oil and soybean oil, or natural fatty acids such as oleic acid, tallow fatty acid, palmitoleic acid, linoleic acid, erucic acid or other sources of unsaturated vegetable fatty acids.

[0153] The alkyl or alkenyl chains of the derivative-CP and derivative-RS are preferably predominantly unsaturated, for example sucrose tetraethylate, sucrose tetraoleate, sucrose tetraesters of soybean oil or cotton seed oil, celebiotlose tetraoleate, sucrose trioleate, sucrose triapate, sucrose pentaoleate, sucrose pentaesters of soybean oil or cotton seed oil, glucose trioleate, glucose tetraoleate, xylose trioleate, or sucrose tetra- , nera- or hexa-esters with any mixture of predominantly unsaturated fatty acid chains.

[0154] However some derivative-CPs and derivative-Rss can be based on polyunsaturated fatty acid derived alkyl or alkenyl chains, e.g. sucrose tetraoleinate. However, it is preferred that most, if not all of the polyunsaturation has been removed by partial hydrogenation if such polyunsaturated fatty acids are used.

[0155] The most highly preferred liquid derivative-CP and derivative-RS are any of those mentioned in the above three paragraphs but where the polyunsaturation has been removed through partial hydrogenation.

[0156] Preferably 40% or more of the chains contain an unsaturated bond, more preferably 50% or more, most preferably 60% or more e.g. 65% 95% by number of the chains are unsaturated.

[0157] Oily sugar derivatives particularly suitable for use in the compositions include sucrose pentaoleate, sucrose pentaesters of soybean oil, or cotton seed oil, glucose trioleate, glucose tetraoleate, xylose trioleate, and sucrose pentaoleate. Suitable materials include some of the Kyoto series available from Mitsubishi Kagaku Foods Corporation.

[0158] The liquid or soft solid derivative-CP and derivative-RS are characterised as materials having a solid:liquid ratio of between 50:50 and 0:100 at 20°C as determined by T<sub>g</sub> relaxation time NMR, preferably between 43:57 and 0:100, most preferably between 40:60 and 0:100, such as, 20:80 and 0:100. The T<sub>g</sub> NMR relaxation time is commonly used for characterising solid:liquid ratios in soft solid products such as fats and margarines. For the purpose of the present invention, any component of the NMR signal with a T<sub>g</sub> of less than 100 microsecond is considered to be a solid component and any component with T<sub>g</sub> greater than 100 microseconds is considered to be a liquid component.

[0159] The liquid or soft solid derivative-CPE and derivative-RSE can be prepared by a variety of methods well known to those skilled in the art. These methods include acylation of the cyclic polyol or of a reduced saccharide with an acid chloride; trans-esterification of the cyclic polyol or of a reduced saccharide material with short chain fatty acid esters in the presence of a basic catalyst (e.g. KOH); acylation of the cyclic polyol or of a reduced saccharide with an acid anhydride, and, acylation of the cyclic polyol or of a reduced saccharide with a fatty acid. Typical preparations of these materials are disclosed in U.S. Pat. No. 4,386,213 and AU 14416/88 (Procter and Gamble).

[0160] The rinse compositions may comprise from 0.5%-90 wt % of the oily sugar derivatives, more preferably 5-80 wt %, most preferably 10-60 wt %, based on the total weight of the composition.

[0161] Formulation and Dispersion Aids

[0162] Rinse compositions may contain one or more formulation aids and/or dispersing aids.

[0163] A typical formulation aid is substantially non-aqueous and comprises one or more of the following components:

[0164] (a) nonionic stabilising agents;
[0165] (b) polymeric compounds having;
[0166] (c) single long hydrocarbyl chain cationic surfactants;
[0167] (d) long chain fatty alcohols or acids;
[0168] (e) short chain alcohols or oils; or
[0169] (f) inorganic and/or organic electrolytes

[0170] Nonionic Stabilising Agents

[0171] The nonionic stabilising agents suitable for use in the rinse conditioner compositions include any of the alkoxylated materials of the particular type described hereinafter can be used as the nonionic surfactant.

[0172] Substance water soluble surfactants of the general formula:

\[ R-Y=\text{C}_3\text{H}_6\text{O}_2 \text{C}_n\text{H}_{2n} \text{OH} \]

[0173] where R is selected from the group consisting of primary, secondary and branched chain alkyl and/or acyl hydrocarbyl groups; primary, secondary and branched chain alkyl hydrocarbyl groups; and primary, secondary and branched chain alkyl-substituted phenolic hydrocarbyl groups; the hydrocarbyl groups having a chain length of from 8 to about 25, preferably 10 to 20, e.g. 14 to 18 carbon atoms.

[0174] In the general formula for the ethoxylated nonionic surfactant, Y is typically:

\[ \text{O}--\text{C}=\text{O}--\text{O}--\text{C}(\text{O})\text{N}--\text{O}--\text{C}(\text{O})\text{N}--\text{R}--\]

[0175] where \( R \) is defined as a fatty acid; and \( Z \) is at least about 8, preferably at least about 10 or 11.

[0176] Preferably the nonionic surfactant has an HLB of from about 7 to about 20, more preferably from 10 to 18, e.g. 12 to 16.

[0177] Examples of nonionic surfactants follow. In the examples, the integer defines the number of ethoxy (EO) groups in the molecule.
A. Straight-Chain, Primary Alcohol Alkoxylates

The deca-, undeca-, dodeca-, tetradeca-, and pentadecaethoxylates of n-hexadecanol, and n-octadecanol having an HLB within the range recited herein are useful viscosity/dispersibility modifiers in the context of this invention. Exemplary ethoxylated primary alcohols useful herein as the viscosity/dispersibility modifiers of the compositions are C_{16} EO(10); and C_{18} EO(11). The ethoxylates of mixed natural or synthetic alcohols in the "tallow" chain length range are also useful herein. Specific examples of such materials include tallow alcohol EO(11), tallow alcohol EO(18), and tallow alcohol EO(25).

B. Straight-Chain, Secondary Alcohol Alkoxylates

The deca-, undeca-, dodeca-, tetradeca-, pentadeca-, octadeca-, and nonadeca-ethoxylates of 3-hexadecanol, 2-octadecanol, 4-eicosanol, and 5-eicosanol having an HLB within the range recited herein are useful viscosity and/or dispersibility modifiers in the context of this invention. Exemplary ethoxylated secondary alcohols useful herein as the viscosity and/or dispersibility modifiers of the compositions are: C_{16} EO(11); C_{25} EO(11); and C_{18} EO(14).

C. Alkyl Phenol Alkoxylates

As in the case of the alcohol alkoxylates, the hexa- to octadeca-ethoxylates of alkylated phenols, particularly monohydric alkylphenols, having an HLB within the range recited herein are useful as the viscosity and/or dispersibility modifiers of the instant compositions. The hexa- to octadeca-ethoxylates of p-tridecylphenol, m-pentadecylphenol, and the like, are useful herein. Exemplary ethoxylated alkylphenols useful as the viscosity and/or dispersibility modifiers of the mixtures herein are: p-tridecylphenol EO(11) and p-pentadecylphenol EO(18).

As herein and as generally recognized in the art, a phenylene group in the nonionic formula is the equivalent of an alkylene group containing from 2 to 4 carbon atoms. For present purposes, nonionics containing a phenylene group are considered to contain an equivalent number of carbon atoms calculated as the sum of the carbon atoms in the alkyl group plus about 3.3 carbon atoms for each phenylene group.

D. Olefinic Alkoxylates

The alkyl aryl alcohols, both primary and secondary, and alkyl phenols corresponding to those disclosed immediately hereinafter can be ethoxylated to an HLB within the range recited herein and used as the viscosity and/or dispersibility modifiers of the instant compositions.

E. Branched Chain Alkoxylates

Branched chain primary and secondary alcohols which are available from the well-known "OXY" process can be ethoxylated and employed as the viscosity and/or dispersibility modifiers of compositions herein.

The above ethoxylated nonionic surfactants are useful in the present compositions alone or in combination, and the term "nonionic surfactant" encompasses mixed nonionic surface active agents.

The nonionic surfactant is present in an amount from 0.01 to 10%, more preferably 0.5 to 5%, most preferably 0.75 to 3.5%, e.g., 1 to 2% by weight, based on the total weight of the composition.

Single long hydrocarbyl chain cationic surfactants

The compositions of the invention optionally contain a single long hydrocarbyl chain cationic surfactant.

The single long hydrocarbyl chain cationic surfactant are particularly suitable for use in emulsions since they can be employed in the formulation to aid the dispersion characteristics of the emulsion and/or to emulsify the composition, in order to form a macroemulsion having oil droplets which are smaller than those in macroemulsion compositions comprising the cationic fabric softening agent alone.

The single long chain cationic surfactant is preferably a quaternary ammonium compound comprising a hydrocarbyl chain having 8 to 40 carbon atom, more preferably 8 to 30, most preferably 12 to 25 carbon atoms (e.g. quaternary ammonium compounds comprising a C10-18 hydrocarbyl chain are especially preferred).

Examples of commercially available single long hydrocarbyl chain cationic surfactants which may be used in the compositions of the invention include:

ETHOQUAD (RTM) 0/12 (oleylbis(2-hydroxyethyl)methylammonium chloride);

ETHOQUAD (RTM) C12 (cocoibis(2-hydroxyethyl)amino amonium chloride) and

ETHOQUAD (RTM) C25 (polyoxyethylene(15)cocohexammonium chloride), all ex

Alko Nobel; SERVAMINE KAC (RTM), (coconuttrimethylammonium methosulfate);

ex Condea; REWOQUAT (RTM) CPEM, (coconutalkylpentaoxyethylethylammonium methosulfate), ex Witco; cetlytrimethylammonium chloride (25% solution supplied by Aldrich); RADIQUAT (RTM) 6460, (coconut oil trimethylammonium chloride), ex Fina Chemicals; NORANIUM (RTM) MCS5, (oleyltrimethylammonium chloride), ex Eil Atochem.

The single long hydrocarbyl chain cationic surfactant is preferably present in an amount from 0 to 5% by weight, more preferably 0.01 to 3% by weight, most preferably 0.5 to 2.5% by weight, based on the total weight of the composition.

Long Chain Fatty Alcohols, Acids or Oils:

The formulation aid may further be selected from fatty alcohols, acids or oils, for example C8 to C24 alkyl or alkyl monocarboxylic acids, alcohols or polymers thereof and C16 to C35 oils. Preferably saturated fatty acids or alcohols are used, in particular, hardened tallow C16 to C18 fatty acids.

Preferably the fatty acid is non-saponified, more preferably the fatty acid is free, for example oleic acid, lauric acid or tallow fatty acid. The level of fatty acid material is preferably more than 0.1% by weight, more preferably more than 0.2% by weight. Concentrated and superfocused compositions may comprise from 0.5 to 20% by weight of fatty acid, more preferably 1% to 10% by weight.
Suitable fatty acids include stearic acid (PRIFAC 2980), myristic acid (PRIFAC 2940), lauric acid (PRIFAC 2920), palmitic acid (PRIFAC 2960), erucic acid (PRIFAC 2990), sunflower fatty acid (PRIFAC 7960), tallow acid (PRIFAC 7920), soybean fatty acid (PRIFAC 7951) all ex Unichema; azelaic acid (EMEROX 1110) ex Henkel.

The fatty acid may also act as a co-softerner in the rinse conditioner composition.

The formulation aid may comprise a long chain oil. The oil may be a mineral oil, an ester oil, a silicone oil and/or natural oils such as vegetable or essential oils. However, ester oils or mineral oils are preferred.

The ester oils are preferably hydrophobic in nature. They include fatty esters of mono or polyhydric alcohols having from 1 to 24 carbon atoms in the hydrocarbon chain, and mono or polycarboxylic acids having from 1 to 24 carbon atoms in the hydrocarbon chain, provided that the total number of carbon atoms in the ester oil is equal to or greater than 8, and that at least one of the hydrocarbon chains has 12 or more carbon atoms.

Suitable ester oils include saturated ester oils, such as the PRIOLUBES (ex Unichema), 2-ethyl hexyl stearate (PRIOLUBE 1545), neopentyl glycol monomethacrylate (PRIOLUBE 2045) and methyl laurate (PRIOLUBE 1415) are particularly preferred although oleic monoglyceride (PRIOLUBE 1407) and neopentyl glycol diolacate (PRIOLUBE 1446) are also suitable.

It is preferred that the viscosity of the ester oil is from 0.002 to 0.4 Pa.S (2 to 400 cps) at a temperature of 25° C. at 108 sec⁻¹, measured using a Haake rotoviscimeter NV1, and that the density of the mineral oil is from 0.8 to 0.9 g.cm⁻³ at 25° C.

Suitable mineral oils include branched or straight chain hydrocarbons (e.g. paraffins) having 8 to 35, more preferably 9 to 20 carbon atoms in the hydrocarbon chain.

Preferred mineral oils include the Marcol technical range of oils (ex Esso) although particularly preferred is the Sirius range (ex Sillkone) or Sontrel (ex Witco Corp.). The molecular weight of the mineral oil is typically within the range 100 to 400.

One or more oils of any of the above mentioned types may be used.

It is believed that the oil provides excellent perfume delivery to the cloth and also increases perfume longevity upon storage of the composition.

The oil may be present in an amount from 0.1 to 40% by weight, more preferably 0.2-20%, by weight, most preferably 0.5-15% by weight based on the total weight of the composition.

Short Chain Alcohols

The formulation aid may comprise a short chain alcohol. Preferred are low molecular weight alcohols having a molecular weight of preferably 180 or less. The alcohol may be mono or polyhydric.

The presence of the lower molecular weight alcohol helps improve physical stability upon storage by lowering the viscosity to a more desired level and also assists the formation of the micro-emulsion. Examples of suitable alcohols include ethanol, isopropanol, n-propanol, dipropylene glycol, t-butyl alcohol, hexylene glycol, and glycerol.

The alcohol is preferably present in an amount from 0.1% to 4% by weight, more preferably from 0.2% to 3%, most preferably 0.5 to 2% by weight based on the total weight of the composition.

Inorganic and/or organic electrolytes

The fabric softening composition optionally comprises an electrolyte.

The electrolyte may be an inorganic or organic electrolyte.

Preferably the electrolyte is present in an amount from 0.001 to 1.5%, more preferably 0.01 to 1%, most preferably 0.02 to 0.7% by weight based on the total weight of the composition.

Suitable inorganic electrolytes include sodium sulphate, sodium chloride, calcium(II) chloride, magnesium(II) chloride, potassium sulphate and potassium chloride.

The electrolyte improves viscosity control (especially viscosity reduction) of the compositions and assists dispersion of the composition.

Anti-Oxidation/Reduction Stabilisers

Rinse compositions of the invention may, optionally, also comprise one or more additional stabilisers which stabilise against oxidation and/or reduction.

If the stabilisers are present as anti-oxidants, they may be added at a level of from 0.005 to 2% by weight based on the total weight of the composition, more preferably from 0.01 to 0.2% by weight, most preferably from 0.035% to 0.1% by weight.

If present as an anti-reduction agent, then the stabiliser is preferably used in an amount from 0.001% to 0.2% by weight based on the total weight of the composition.

The stabilisers assist by ensuring good odour stability upon storage particularly when the composition is prepared using a surfactant having substantial unsaturated character (i.e. type (a) surfactants as herein defined).

Typically, such additional stabilisers include mixtures of ascorbic acid, ascorbic palmitate and propyl gallate (under the trademarks Tenox® PG and Tenox® S-1); mixtures of butylated hydroxytoluene, butylated hydroxyanisole, propyl gallate and citric acid (under the tradename Tenox® 6); tertiary butylhydroquinone (under the tradename Tenox® TBHQ); natural tocopherols (under the trademarks Tenox® GT-1 and GT-2); long chain esters of gallic acid (under the tradenames Irganox® 1010, Irganox® 1035, Irganox® B 117 and Irganox® 1425) and mixtures thereof. Tenox products are supplied by Eastman Chemical Products Inc. Irganox products are supplied by Eastman Chemical Products Inc. The above stabilisers can also be mixed with chelating agents such as citric acid; 1-hydroxyethylidene-1,1-diphosphonic acid (Dquest® 2010, ex Monsanto); 4,5-dihydroxy-m-benzenesulphonic acid/sodium salt (under the tradename Tiron®, ex Kodak) and diethylene-triaminepentaacetic acid (under the tradename DTPA®, ex Aldrich).
Co-Active Softening Surfactants

Co-active softening surfactants for cationic surfactants may also be incorporated in an amount from 0.01 to 20% by weight, more preferably 0.05 to 10%, based on the total weight of the composition. Preferred co-active softening surfactants are fatty amines and fatty N-oxides.

Cellulases

Cellulase British Patent Specification GB 1 368 599 (Unilever) discloses the use of cellulolytic enzymes, i.e. cellulases, as harshness reducing agents. It is thought that cellulase achieves its anti-harshening effect on, e.g. cotton, by cleaving the cellulose fibrils which form on the cotton fibres during the normal washing process.

This cleavage prevents the fibrils from bonding together and thereby introducing a degree of rigidity into the fabric.

It is preferred to use cellulases which have an optimum activity at alkaline pH values, such as those described in British Patent Specifications GB 2 075 028 A (Novo Industries A/S), GB 2 095 275 A (Kao Soap Co Ltd) and 2 094 826 A (Kao Soap Co Ltd).

Examples of such alkaline cellulases are cellulases produced by a strain of *Humicola insolens* (Humicola grisea var. the-romioidea) particularly the Humicola strain DSM 1800, cellulases produced by a fungus of Bacillus N or a cellulase 212-producing fungus belonging to the genus *Aeronomas*, and cellulase extracted from the hepatopancreas of a marine mollusc (Dolabella Auricularia Solander).

The amount of cellulase in a tablet of the invention will, in general, be from 0.1 to 10% by weight. In terms of cellulase activity the use of cellulase in an amount corresponding to from 0.25 to 150 or higher regular CX units/gram of the detergent composition.

Clays

Certain clays with ion exchange properties are effective as fabric softeners. It is believed that clay materials achieve their softening benefit, on e.g. cotton, by coating the cotton fibrils with a layer of lubricating material. This coating lowers the friction between the fibrils and reduced their tendency to bond together.

Suitable clay materials are phyllosilicate clays with a 2:1 layer structure, which definition includes smectite clays such as pyrophyllite, montmorillonite, hectorite, saponite and vermiculite, and includes micas. Particularly suitable clay materials are the smectite clays described in United States patent specification U.S. Pat. No. 4,062,647 (Storm et al assigned to the Procter & Gamble Company). Other disclosures of suitable clay materials for fabric softening purposes include European patent specification EP 26526-a (Procter & Gamble Limited). United States Patent Specification U.S. Pat. No. 3,959,155 (Montgomery et al assigned to The Procter & Gamble Company) and United States Patent Specification U.S. Pat. No. 3,936,537.

EP 177 165 disclosures that clays can be used in combination with cellulose. Also suitable for use in the tablets of the present invention are the combinations of clays and tertiary amines which are disclosed in EP 011340 (The Procter & Gamble Company).

Particularly preferred clays have an ion exchange capacity of at least 50 meq/100 g of clay. The ion exchange capacity relates to the expandable properties of the clay and to the charge of the clay, and is conventionally measured by electrodialysis or by exchange with ammonium ion followed by titration.

Polysiloxanes and Their Derivatives

Silicone oils (polysiloxanes) have been proposed as fabric conditioning agents, and more specifically polysiloxanes with amino alkyl side chains have been proposed. Discussions of these materials can be found in GB-A-1549180 where they are included in fabric softener formulations to assist ironing of the fabric and to inhibit wrinkling.

EP-A-150867 discloses the incorporation of amino alkyl polysiloxanes into particulate detergent compositions to enhance the softeners and handling of washed fabrics. Their use in particulate compositions is also disclosed in FR-A-2713237 which utilises them as fabric softeners.

These materials may be mixed into nonionic detergent before that is incorporated into a particulate composition, as taught by EP-A-150867, or absorbed directly into a particulate carrier, as taught by FR-A-2713237, and mixed with the remainder of a particulate composition. The particulate composition can thereafter be compacted to form a zone of a tablet in accordance with the present invention. The amino alkyl polysiloxanes function as fibre lubricants. They are desirably incorporated into the more rapidly disintegrating first zone(s) of a tablet of this invention, so as to deposit on fabric at an early stage of the washing cycle.

Another fabric conditioning agent which may be utilised is a curable amine functional silicone (amino alkyl polysiloxane) disclosed in U.S. Pat. No. 4,911,852 (Procter Gamble) as an anti-wrinkle agent.

Wash Compositions

Wash compositions contain one or more components useful for the washing of textile fabrics, for example, surfactants, detergent builders, bleaches, enzymes and other minor ingredients.

Surfactants

Compositions according to the invention comprises one or more surfactants at least one of which is a branched anionic surfactant suitable for use in laundry wash products.

Suitable amendments may be chosen from one or more of anionic, cationic, nonionic amphoteric and zwitterionic surface-active compounds and mixtures thereof. Many suitable surface-active compounds are available and are fully disclosed in the literature, for example, in “Surface-Active Agents and Detergents”, Volumes I and II, by Schwartz, Perry and Berch.

The total level of all surfactant(s) in the composition as a whole may for example be from 0.1% to 70% by weight the total composition but is preferably from 5% to 40%.
Anionic Surfactants

Preferably least one of the surfactants in any wash composition is anionic surfactant.

As all or part (e.g. at least 50%, 60%, 70%, 80%, 90% or 95% by weight) of the total anionic surfactant component, most preferred are the linear alkylbenzene sulphonate anionic surfactants having an average alkyl component of C₈-C₁₅.

Yet other suitable branched anionic surfactants include secondary alkylsulphonates, secondary alcohol sulphates and secondary alkyl carboxylates.

Suitable laundry wash compositions may additionally or alternatively contain one or more other anionic surfactants in total amounts corresponding to percentages quoted above for branched anionic surfactants, provided that at least some branched anionic surfactant is present. Suitable anionic surfactants are well-known to those skilled in the art. These include primary alkyl sulphates, particularly C₈-C₁₅ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred. Such other anionic surfactants typically are used at from 5% to 70% by weight of the total anionic surfactant, preferably from 10% to 30%. Moreover, they typically represent from 1% to 15% by weight of the total composition.

Nonionic Surfactants

Wash compositions preferably also contain nonionic surfactant. Nonionic surfactants that may be used include fatty acid methyl ester ethoxylates (FAMEE's), e.g. as supplied by Lion Corp., Henkel KGA, Condea or Clairant, the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₈-C₁₂ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerc monoethers, and polyhydroxymides (glucamides).

It is preferred if the level of total non-ionic surfactant is from 0 wt % to 30 wt %, preferably from 1 wt % to 25 wt %, most preferably from 2 wt % to 15 wt % by weight of the total wash composition.

Other Surfactants

Another class of suitable surfactants comprises certain mono-long chain-alkyl cationic surfactants for use in main-wash laundry compositions according to the invention. Cationic surfactants of this type include quaternary ammonium salts of the general formula R₁R₂R₃R₄N³⁺X⁻ wherein the R groups are long or short hydrocarbon chains, typically alkyl, hydroxalkyl or ethoxylated alkyl groups, and X is a counter-ion (for example, compounds in which R₁ is a C₁₂-C₂₂ alkyl group, preferably a C₁₀-C₁₄ or C₁₂-C₁₄ alkyl group, R₂ is a methyl group, and R₃ and R₄ may be the same or different, are methyl or hydroxethyl groups); and cationic esters (for example, choline esters).

The choice of surface-active compound (surfactant), and the amount present in the laundry wash compositions according to the invention, will depend on the intended use of the detergent composition. In fabric washing compositions, different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine. The total amount of surfactant present will also depend on the intended end use and may be as high as 60 wt %, for example, in a composition for washing fabrics by hand. In compositions for machine washing of fabrics, an amount of from 5 to 40 wt % is generally appropriate. Typically the compositions will comprise at least 2 wt % surfactant e.g. 2-60%, preferably 15-40% most preferably 25-35%.

Surfactant Blends

Preferred blends comprise the anionic surfactant(s) and one or more nonionic surfactants. Compositions suitable for use in most automatic fabric washing machines will generally contain anionic non-soap surfactant, or non-ionic surfactant, or combinations of the two in any suitable ratio, optionally together with soap. Typical blends contain total anionic to total nonionic surfactant in a weight ratio of from 5:1 to 1:1, preferably from 4:1 to 2:1.

It is also generally preferred that the weight ratio of total anionic surfactant to total builder is from 1:5 to 10:1, more preferably from 2:1 to 10:1, especially from 3:1 to 7:1.

b) Detergency Builders

Laundry wash compositions, will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will typically range from 5 to 80 wt %, preferably from 10 to 60 wt % by weight of the total composition.

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB-A-1 437 950; crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB-A-1 473 201, amorphous aluminosilicates as disclosed in GB-A-1 473 202 and mixed crystalline/amorphous aluminosilicates as disclosed in GB-A-1 470 250; and layered silicates as disclosed in EP-A-164 514. Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

The compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt %.

When the aluminosilicate is zeolite, the maximum amount is 19% by weight.

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula: 0.8-1.5 Na₂O. Al₂O₃. 0.8-6 SiO₂.

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. Suitable
crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

[0278] The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP-A-384 070. Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

[0279] Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

[0280] Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphonates; monomeric polycarboxylates such as citrates, gluconates, oxysuccinates, glycerol mono-, di- and trisuccinates, carbomethylxoy succinates, carboxymethylxylxammonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylxlamonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

[0281] Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt %, preferably from 10 to 25 wt %; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt %, preferably from 1 to 10 wt %.

[0282] Builders, both inorganic and organic, are preferably present in alkaline metal salt, especially sodium salt, form.

[0283] c) Bleaches

[0284] Laundry wash compositions may also suitably contain a bleach system. Fabric washing compositions may desirably contain peroxo bleach compounds, for example, inorganic peroxides or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.

[0285] Suitable peroxo bleach compounds include organic peroxides such as urea peroxide, and inorganic peroxides such as the alkaline metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic peroxides are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

[0286] Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB-A-2 123 044.

[0287] The peroxo bleach compound is suitably present in an amount of from 0.1 to 35 wt %, preferably from 0.5 to 25 wt %. The peroxo bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 0.1 to 8 wt %, preferably from 0.5 to 5 wt %.


[0289] The bleach system can be either supplemented with or replaced by a peroxyacid. Examples of such peracids can be found in U.S. Pat. No. 4,686,063 and U.S. Pat. No. 5,397,501. A preferred example is the imido peroxycarboxylic class of peracids described in EP-A-325 288, EP-A-349 940, DE-A-382 3172 and EP-A-325 289. A particularly preferred example is phthalimido peroxy caprylic acid (PAP). Such peracids are suitably present at 0.1-12%, preferably 0.5-10%.

[0290] A bleach stabiliser (transition metal sequestant) may also be present. Suitable bleach stabilisers include ethylenediamine tetra-acetate (EDTA), the polyphosphates such as Dequest (Trade Mark) and non-phosphate stabilisers such as EDDS (ethylene diamine di-succinic acid). These bleach stabilisers are also useful for stain removal especially in products containing low levels of bleaching species or no bleaching species.


[0292] d) Enzymes

[0293] Laundry wash compositions according to the invention may also contain one or more enzyme(s). Suitable enzymes include the proteases, amylases, cellulases, oxida-ses, peroxidases and lipases usable for incorporation in detergent compositions. Preferred proteolytic enzymes (pro-teeses) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

[0294] Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of B. Subtilis B. lichenformis, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Gist Brocades N. V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

[0295] Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esp erase (Trade Mark) and Savinase (Trade-Mark). The prepa-
ration of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark obtainable from Showa-Denko of Japan), Optimase (Trade Mark from Miles Kali-Chemic, Hannover, West Germany), and Supersase (Trade Mark obtainable from Pfizer of U.S.A.).

[0296] Detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt %. However, any suitable physical form of enzyme may be used.

[0297] c) Other Optional Minor Ingredients

[0298] Laundry wash compositions may contain alkali metal, preferably sodium carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt %, preferably from 2 to 40 wt %. However, compositions containing little or no sodium carbonate are also within the scope of the invention.

[0299] Yet other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulose polymers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; dyes; coloured speckles; perfumes; foam controllers; fluorescers and decoupling polymers. This list is not intended to be exhaustive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0300] FIG. 1 shows a tablet for use in a first embodiment of the present invention;

[0301] FIG. 2 shows a water soluble sachet for use in a second embodiment of the present invention;

[0302] FIG. 3 shows a bag net receptacle for use in the first and second embodiments of the present invention;

[0303] FIG. 4 shows another tablet for use in a third embodiment of the present invention, in conjunction with the bag net receptacle of FIG. 3;

[0304] FIG. 5 shows a capsule for use in the fourth embodiment of the present invention;

[0305] FIGS. 6A-6C show layered tablet embodiments;

[0306] FIG. 7 shows a sachet in tablet embodiment; and

[0307] FIGS. 8A-8C show embodiments wherein the delayed release rinse composition is embedded in the tablet.

EXAMPLES AND DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0308] In the following examples, various embodiments of unit dose compositions are disclosed which in use, are dosed in the net described hereinbelow with respect to FIG. 3.

EXAMPLE 1

Polymer Matrix in Tablet

[0309] FIG. 1 shows a unit dose unit 1 for use according to the present invention. It comprises a tablet 3 of a granular detergent wash composition 5, having a composition in the range of formulation A. In all formulations herein, percentages are by weight unless specified to the contrary.

<table>
<thead>
<tr>
<th>Formulation A</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaLAS</td>
<td>8.0-11.0%</td>
</tr>
<tr>
<td>Nonionic 7EO</td>
<td>4.0-5.0%</td>
</tr>
<tr>
<td>Soap</td>
<td>0.5-1.0%</td>
</tr>
<tr>
<td>Zeolite A24 (anhydrous)</td>
<td>20-25.0%</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>20-25%</td>
</tr>
<tr>
<td>Soda ash</td>
<td>3.0-4.0%</td>
</tr>
<tr>
<td>SCMC</td>
<td>0.3-0.4%</td>
</tr>
<tr>
<td>Minor</td>
<td>4.00%</td>
</tr>
<tr>
<td>Anion Carrier</td>
<td>1.5-2.5%</td>
</tr>
<tr>
<td>Fluorescer (10% ac.)</td>
<td>1.0-2.0%</td>
</tr>
<tr>
<td>Soil release polymer</td>
<td>0.3-0.5%</td>
</tr>
<tr>
<td>Na-di-silicate (granular)</td>
<td>2.0-3.0%</td>
</tr>
<tr>
<td>TAED</td>
<td>4.0-5.0%</td>
</tr>
<tr>
<td>Percarbonate (coated)</td>
<td>10.0-15.0%</td>
</tr>
<tr>
<td>Sequestrant</td>
<td>1-15%</td>
</tr>
<tr>
<td>Proteolytic and Lypolytic enzymes</td>
<td>1-5%</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

[0310] NaLAS—Sodium Docecyl Benzene Sulphonate

[0311] Nonionic 7EO—C8-C13 alcohol ethoxylated with an average of seven ethylene oxide units

[0312] SCMC—Sodium carboxy methyl cellulose

[0313] The tablet is formed by compression of the granular ingredient 5 but in a die such as to be formed with a central cavity 7.

[0314] The central cavity 7 is formed with a polymer 9 having the following composition:

Polymer (1)

[0315] Polymer (1) is a pH-sensitive polyacrylate-terpolymer, synthesized from a blend of the following weight composition 23% MMA (methylmethacrylate), 45% DMAEMA (N,N-dimethylamino ethyl methacrylate) and 32% DMAPMA (dimethylaminopropylmethacrylic acid amine)

[0316] A granular fabric softening composition 11 (Formation B) is, together with a dissolution aid like Na-acetate or Na-citrate, dispersed in the polymer composition 9. The fabric softener is mixed with the polymer and poured into the cavity 7, whereupon it sets to form a solid matrix of the composition 11 and solidified polymer 9.

Polymer (2)

[0317] Polymer (2) is an hydroxybutylmethyl cellulose (hydroxybutyl content of 3.5 mole %) having a number average molecular weight of ca. 115,000 g/mole.

[0318] The granular fabric softening composition 11 has the following formulation B:

<table>
<thead>
<tr>
<th>Formulation B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HEQ</td>
<td>34.5%</td>
</tr>
<tr>
<td>Urea</td>
<td>41.48%</td>
</tr>
<tr>
<td>Dobanol 91/6</td>
<td>6.14%</td>
</tr>
<tr>
<td>Water</td>
<td>5.77%</td>
</tr>
<tr>
<td>Perfume</td>
<td>2.88%</td>
</tr>
<tr>
<td>FFG</td>
<td>1.95%</td>
</tr>
</tbody>
</table>
Formulation B

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye</td>
<td>0.28</td>
</tr>
<tr>
<td>Microsil GP</td>
<td>7.00%</td>
</tr>
</tbody>
</table>

[0319] HEQ is a hardened tallowyl fatty acid quaternary fabric softener, ex Clairant.

[0320] Dobanol 91/6 is a C<sub>8-11</sub> average 6EO nonionic surfactant ex Shell.

[0321] PEG 1500 is polyethylene glycol MW=1500.

[0322] Microsil GP is a commercially available silica based flow aid.

[0323] Polymer (1) is such that it is substantially insoluble at the pH and ionic strength of the wash liquor (the granular wash composition 5 dissolves quite rapidly, at least sufficiently to achieve these conditions). However, the Polymer I is readily soluble at the pH and ionic strength of the rinse liquor).

[0324] A variant of this example, wherein the polymer is in the form of a melt, is described hereinbelow in Example 3.

EXAMPLE 2

Dual Sachet

[0325] FIG. 2 shows a water soluble sachet embodiment 21. This comprises an outer sachet 23, formed from a polyvinyl alcohol film by the VfSS technique. The film is Monosol T, ex Chris-Craft Industrial Products Inc., with polyhydroxy plasticisers. Located inside outer sachet 23 is an inner sachet 25, of smaller dimensions than the outer sachet 23, formed also by the VfSS technique made from Polymer (1). This means that it will not dissolve at the wash liquor pH but only at the rinse liquor pH, unlike the polymer of the outer sachet.

[0326] The top edge 31 and bottom edge 33 of the inner sachet 25 are sealed by conventional heat or ultrasonic sealing common in VfSS polymer sachet manufacture. Prior to final sealing, the inner sachet 25 is filled with the granular fabric softener composition of Formulation B recited above.

[0327] The space between the inner sachet 25 and the film of the outer sachet 23 is filled with the granular detergent wash composition of Formulation A defined in Example 1.

[0328] The top edge 35 and the bottom edge 37 of the outer sachet 23 are also sealed by heat or ultrasonic method.

[0329] In a variant of the embodiment of FIG. 2, instead of a granular detergent wash composition 30, in the outer sachet, there is located a substantially non-aqueous liquid laundry cleaning composition having the following composition:

Formulation C

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic (Neodol C11. SEO)</td>
<td>26%</td>
</tr>
<tr>
<td>LAS acid</td>
<td>20%</td>
</tr>
</tbody>
</table>

[0330] In the inner sachet 25, is located a substantially non-aqueous liquid fabric softening composition having the following formulation D:

Formulation D

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOT-1</td>
<td>19.6%</td>
</tr>
<tr>
<td>Nonionic SEO</td>
<td>38.6%</td>
</tr>
<tr>
<td>Estol 1545</td>
<td>38.4%</td>
</tr>
<tr>
<td>Dipropylene Glycol</td>
<td>4.9%</td>
</tr>
<tr>
<td>Perfume</td>
<td>1.5%</td>
</tr>
</tbody>
</table>

[0331] AOT-1 is a commercially available unsaturated triester amine quaternary ammonium fabric softener.

[0332] Nonionic SEO is a C<sub>8-11</sub> alcohol ethoxylated with an average of 5 ethylene oxide units.

[0333] Estol 1545 is a commercially available ester mineral oil.

[0334] The inner sachet is formed of polymer (2). In this case, the inner sachet will not dissolve at a wash liquor temperature of 40°C or higher but only at a rinse liquor temperature below 40°C.

[0335] FIG. 3 shows a net bag 41 for use with either the tablet 1 of FIG. 1 or the sachet 21 of FIG. 2, as well as other examples and embodiments described hereinbelow. It has an average mesh size of 5 mm. It comprises a substantially elongate bag member 43 of nylon mesh, open at a mouth 45. The mouth 45 can be closed at constricted neck region 51 by means of a drawstring 47. A plastics constriction member 49 can be slid along the drawstring 47 to keep the restricted neck region 51 closed.

[0336] In use, either the tablet 1 or sachet 21, is placed in the bag 41 and the bag is closed by use of the constrictions 47 as indicated above.

[0337] The net with sachet or tablet inside, is then placed in an automatic washing machine, directly into the drum. The fabrics to be cleaned are also loaded into the drum.

[0338] In the case of the tablet of FIG. 1, in the wash cycle, the detergent wash composition 5 is released into the wash liquor to clean the fabric. However, the pH of the wash liquor is around 10.5 and the conductivity is 4.5 mS/cm which is too alkaline and too high an ionic strength for the polymer matrix 9 to substantially dissolve. However, after the rinse cycle, the pH of the rinse liquor is only about 8.5 and the conductivity is 1.1 mS/cm.

[0339] As a result, at this lower pH, the polymer matrix 9 dissolves so as to release the granular rinse condition of composition 11 into the rinse liquor.
In the case of the sachet of FIG. 2, the composition of the film of the outer sachet 23 is such that it dissolves in the wash liquor, i.e. at the wash liquor pH. However, the composition of the polymer film of the inner sachet 25 is insoluble at the wash liquor pH. In a variant, the outer sachet 23 may be formed of a polymer which dissolves at the wash liquor temperature.

After the wash cycle, at the lower rinse cycle pH, (or lower rinse cycle temperature, in the case of the variant). The polymer of the inner sachet 25 is soluble and so the granular rinse composition can be released.

EXAMPLE 3

Gel in Tablet

FIG. 4 shows another tablet embodiment 61. The tablet comprises a granular wash composition 63 identical to the composition of detergent wash composition 5 in FIG. 1 (i.e. having Formulation A). As with the embodiment of FIG. 1, the tablet also includes a central cavity 65.

A granular fabric softening composition 67, identical to that having Formulation B recited above, is located in the cavity 67, dispersed in a water-soluble polyethylene glycol (PEG). The composition is mixed with the polymer melt before pouring into the cavity 67, by making use of the shear thinning behaviour of the gel of by using a cooling tunnel.

The upper surface 71 of the set gel matrix 69, including the softening composition 67, is covered with a polymer film 73 which extends in contiguous fashion to line the inside of the cavity 65 in the form of a lining 75. The polymer used to form the lining 75 and film 73 is identical to that of Polymer (1) recited above.

In use, the tablet of FIG. 4 dissolves in the wash liquor but the pH of the wash liquor is such that the “capsule” formed by the polymer film 73 and lining 75 does not dissolve. It survives until the rinse cycle, when the lower pH allows it to dissolve and the contents released. At that point, the gel 69 dissolves or disperses, releasing the rinse composition 67 into the rinse liquor.

It will be appreciated that the “capsule” of polymer is fragile. Therefore, it is especially advantageous in this embodiment for the tablet as a whole to be dosed by means of the net of FIG. 3.

EXAMPLE 4

Rinse Conditioner Capsule

FIG. 5 shows a capsule 81 according to a fourth embodiment of the present invention, when used in the net shown in FIG. 3.

A granule of 1.5 cm diameter is formed by granulating the composition of Formula B (fabric softening composition) with a dissolution aid such as sodium citrate or sodium acetate in a fluid bed granulator, operated such that large agglomerates can form. This produces a nearly-spherical granule 83. This granule is then dipped-coated in a melt of Polymer 1 as recited above. In this way, the granule 83 is coated with a polymer film 85. When coated in the bag of FIG. 3 into the wash liquor, it remains intact until the rinse cycle, whereupon, the lower pH allows the polymer to dissolve and the granular rinse conditioner to be dispersed into the rinse liquor. Preferably, a conventional main wash detergent tablet is also dosed in the same bag at the start of the wash process.

The filling of the core 83 of capsule 85 in FIG. 5 may also be a non-aqueous liquid rinse composition.

The composition can be used in combination with liquid detergents, powder detergent, conventional main wash tablets, main wash sachets and the like. Alternatively, it may be glued on top of the tablet with a cavity such as shown in FIG. 1 or 4, or can be used as an insert in a larger capsule containing a main wash composition.

The embodiments of FIGS. 6-8 (Examples 5-7) are also dosed in the net of FIG. 3.

EXAMPLES 5A -5D

Multi-Layer Tablets

Turning now to FIG. 6A, there is shown a tablet form 91 according to the present invention. It comprises a larger lower portion 93 comprising a tableted wash composition corresponding to composition 5 in the embodiment of FIG. 1. The upper layer 95 comprises the same rinse composition 11 of the embodiment of FIG. 1, in a delayed release matrix as before. The manufacture of bi-layer tablets is well known in the art.

In FIG. 6B, a bi-layer tablet 97 has a lower layer 99 corresponding to the lower layer 93 of the embodiment of FIG. 6A. However, the upper layer 101 comprises a rinse composition 103 corresponding to composition 67 in the embodiment of FIG. 4, encapsulated in a delayed release polymer shell 105 corresponding to shell 75 in the embodiment of FIG. 4.

FIG. 6C shows a variant of the embodiment of FIG. 6A but as a tri-layer tablet. This designated 107. The upper 109 and lower 111 layers correspond to the tableted wash composition 93 in the embodiment of FIG. 6A. The middle layer 113 has the same rinse composition embedded in a delayed release matrix as the layer 95 in the embodiment of FIG. 6A.

In the embodiment of FIG. 6D, the tri-layer tablet is analogous to the embodiment of FIG. 6B and is denoted by numeral 115. A central layer 117 has the same rinse composition as composition 103 in the embodiment of FIG. 6B and is denoted by numeral 119. It is surrounded by a delayed release polymer shell 121 of the same composition as that of shell 105 in FIG. 6B.

Thus in general, the softener composition may be co-granulated in a delayed release polymer melt as referred to in hereinbefore or coated with a polymer in a bi or tri layer tablet form.

In a variant of the embodiment of FIG. 6A, the upper layer consists of a matrix of capsules, like those of the embodiment of FIG. 5 (Example 4) except that they are formed with a diameter of 7.5 mm. They are embedded in a soft solid matrix comprising a surfactant mixture. In a further variation, a dissolution aid is admixed with this surfactant mixture. In still a further variation, the capsules are dispersed in polyethylene glycol (MW ca. 4,000). The latter is water soluble.
EXAMPLE 6

Sachet in Tablet

[0358] Turning now to FIG. 7, there is shown a tablet embodiment 125 containing a tablet form 127 of a wash composition corresponding to the composition of tablet form 63 in the embodiment of FIG. 4. It contains a cavity 129 extending into the centre from the outside thereof, in which is contained a water-soluble delayed release sachet 131. This is formed of Polymer (1). It is filled with a liquid or granular rinse composition 133.

EXAMPLES 7A-7C

Tablets with Embedded Rinse Compositions

[0359] Turning now to FIGS. 8A-8C, there are shown various embodied tablet forms, which may be made by methods known to those skilled in the art. In all cases, there is a cylindrical tablet 135 of wash composition in the middle of which is a cavity 137 which does not connect with the exterior surface of the tablet.

[0360] In the embodiment of FIG. 8A, a central rinse composition is co-granulated with a delayed release polymer matrix 139 of the same composition as the layer 95 in the embodiment of FIG. 6A.

[0361] In the embodiment of FIG. 8B, the rinse composition 141 is coated with delayed release polymer 145 and so the central insert has the same composition as the upper layer 101 in the embodiment of FIG. 6B.

[0362] In FIG. 8C, the central cavity contains a delayed release water-soluble sachet 147 filled with a granular or liquid rinse composition 149.

EXAMPLE 8

Unit Dose Rinse Conditioner

[0363] Composition and Method of Manufacture:

[0364] A tablet composition was prepared from the following ingredients

<table>
<thead>
<tr>
<th>Formulation E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite clay</td>
</tr>
<tr>
<td>Sodium acetate</td>
</tr>
<tr>
<td>Perfume</td>
</tr>
<tr>
<td>Dye</td>
</tr>
</tbody>
</table>

[0365] The method of manufacture consisted of mixing all ingredients in a Fukae high-shear mixer to form a powder. The powder was then compacted using a Korsch rotative tablet press with concave shaped upper and lower punch. The weight of the convex shaped unit dose was 10 grams having a diameter of 25 mm. The unit dose dispersed in water of 20°C within 5 minutes. The tablet was coated with polymer (2) by means of a Glatt GC300 drum coater. The polymer was applied from an aqueous solution using glycerol as a plasticizer.

[0366] Method of Dosing the Unit Dose Rinse Additive

[0367] The dispersion of the unit dose rinse additive was evaluated in a Zanussi FGS 1276 washing machine. Different methods of dosing the unit dose rinse additive to the washing machine were evaluated: (a) dosing via the drawer together with two laundry wash tablets of formulation A above; (b) dosing directly in the drum together with the two laundry wash tablets; and (c) dosing directly in the drum using the net of FIG. 3, together with the two laundry wash tablets.

[0368] By dosing via the drawer the rinse additive tablet could not be dispersed to the drum as a result of its dimension. Due to partial dissolution of the tablet coating a lump of residue was formed, which remained in the drawer for the remainder of the wash cycle.

[0369] By dosing the rinse additive tablet directly in the drum, it was observed that, out of ten wash cycles, the tablet became entrapped in the rubber gasket of the machine three times. This resulted in significant residue at the end of the wash cycle, which is not acceptable for the consumer.

[0370] By dosing the rinse additive tablet using the net, entrapment of the tablet in the rubber gasket was prevented, and the tablet dispersed properly during the rinse portion of the wash cycle due to the triggered dissolution of the coating. Only by use of the net the unit dose rinse additive could be properly delivered in the rinse liquor.

[0371] Lubrication Benefit

[0372] In a Zanussi FGS 1276 washing machine, 1 kg load comprising 3:3:2:3 flat cotton, knitted cotton, P/C polyester (including 10 poplin monitors (40x40 cm)) was washed at 40°C, 27th F.H., using a normal wash cycle (with a spin speed of 1200 rpm). Two tablets of a composition corresponding to Formulation A were dosed together with the rinse conditioner tablet described above. The effect of the dosing method on the lubrication of poplin swatches after one wash is summarised below. Lubrication was measured by means of the Kawabata shear methodology.

<table>
<thead>
<tr>
<th>Method of dosing rinse additive</th>
<th>Triggered release coating</th>
<th>Kawabata shear (the lower the better)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drawer</td>
<td>Yes</td>
<td>8.06</td>
<td>0.14</td>
</tr>
<tr>
<td>Drum, In Net</td>
<td>No</td>
<td>7.59</td>
<td>0.34</td>
</tr>
<tr>
<td>Drum, Outside Net</td>
<td>Yes</td>
<td>8.15</td>
<td>0.25</td>
</tr>
<tr>
<td>Drum, In Net</td>
<td>Yes</td>
<td>7.22</td>
<td>0.15</td>
</tr>
</tbody>
</table>

[0373] The data show that the highest lubrication benefit is obtained by dosing the unit dose rinse additive with the polymer (2) coating in the net.

[0374] In the light of the described embodiments and examples, variations of those embodiments and examples, as well as other embodiments and examples, all within the spirit and scope of the present invention, for example as defined by the appended claims, will now become apparent to persons skilled in this art.

1. A method of washing and rinsing a textile fabric, the method comprising:
(a) placing in a water permeable receptacle, a wash composition and a rinse composition;

(b) a washing step comprising bringing the receptacle and the fabric into contact with a wash liquor; and

(c) subsequent to the washing step (b), a rinse step comprising contacting the receptacle and the fabric with a rinse liquor;

wherein the rinse composition is formulated such that release of at least some of the rinse composition is delayed until the rinse step.

2. The method of claim 1, wherein at least the rinse composition is provided in unit dose form.

3. The method of claim 1, wherein the water permeable receptacle comprises a bag formed of a net material.

4. The method of claim 3, wherein the bag is provided means for closure of the bag.

5. The method of claim 2, wherein the unit dose form of the rinse composition comprises a component which substantially retains its physical integrity until the rinse step and which is too large to pass through the mesh of the net bag.

6. The method of claim 1, wherein the rinse composition comprises one or more rinse agents selected from fabric softening agents, antistatic agents, ease of ironing agents, anti-wrinkling/crease protection agents, perfumes and optical brighteners.

7. The method of claim 6, wherein the rinse composition comprises a fabric softening agent selected from cationic fabric softening compounds, celluloses, clays and polyisloxanes and their derivatives, and mixtures thereof.

8. The method of claim 1, wherein the rinse composition is formulated with means for inhibiting a release of the rinse composition during the washing step.

9. The method of claim 8, wherein the release inhibit means comprises a polymer, the solubility of reaching an aqueous environment depends on the pH and/or ionic strength and/or temperature of that environment.

10. The method of claim 9, wherein the polymer comprises monomer units selected from one or more vinyl alcohol derivatives, acrylates and alkylacrylates, the acrylates and/or alkylacrylates optionally having basic functionality, said polymer optionally being in admixture with an alkylecellulose and/or a cross-linking agent.

11. The method of claim 9, wherein the polymer is an alkyl substituted cellulose ether.

12. A method of rinsing a textile fabric, the method comprising:

(a) placing in a water permeable receptacle, at least one unit dose unit comprising a rinse composition; and

(b) effecting a rinse step of contacting the water permeable receptacle and fabric with a rinse liquor;

wherein the rinse composition is formulated such that release of substantial amount of the rinse composition cannot occur during a prior wash step.

13. The method of claim 12, wherein a washing step is effected prior to the rinse step, the washing step comprising contacting the water permeable receptacle containing the unit dose unit comprising the rinse composition with a wash liquor.

14. The method of claim 13, wherein the washing step also comprises contacting the wash liquor with a wash composition.

15. The method of claim 14, wherein in step (a), the wash composition is also placed in the water permeable receptacle.

16. The method of claim 14, the wash composition is provided in unit dose form.

17. The method of claim 16, wherein the wash composition and the rinse composition are provided in a single combined unit dose form.

18. The method of claim 12, wherein the unit dose form(s) is or are independently selected from tablets, water soluble sachets and capsules.

19. The method of claim 13, wherein release of at least some of the rinse composition is delayed until the rinse step.

20. The method of claim 12, wherein the water permeable receptacle comprises a bag formed of a net material.

21. The method of claim 20, wherein the bag is provided means for closure of the bag.

22. The method of claim 20, wherein the unit dose form of the rinse composition comprises a component which substantially retains its physical integrity until the rinse step and which is too large to pass through the mesh of the net bag.

23. The method of claim 12, wherein the rinse composition comprises one or more rinse agents selected from fabric softening agents, antistatic agents, ease of ironing agents, anti-wrinkling/crease protection agents, perfumes and optical brighteners.

24. The method of claim 23, wherein the rinse composition comprises a fabric softening agent selected from cationic fabric softening compounds, celluloses, clays and polyisloxanes and their derivatives, and mixtures thereof.

25. The method of claim 12, wherein the rinse composition is formulated with means for inhibiting a release of the rinse composition during the washing step.

26. The method of claim 25, wherein the release inhibiting means comprises a polymer, the solubility of reaching an aqueous environment depends on the pH and/or ionic strength and/or temperature of that environment.

27. The method of claim 26, wherein the polymer comprises monomer units selected from one or more vinyl alcohol derivatives, acrylates and alkylacrylates, the acrylates and/or alkylacrylates optionally having basic functionality, said polymer optionally being in admixture with an alkylecellulose and/or a cross-linking agent.

28. The method of claim 27, wherein the polymer is an alkyl substituted cellulose ether.

29. A unit dose product for washing and rinsing of a textile fabric comprising a wash composition, a rinse composition and means for inhibiting release of the rinse composition during washing, until the rinse.

30. The unit dose product of claim 29, wherein the wash composition and the rinse composition are located in respective separate zones of the product.

31. The unit dose product of claim 30, wherein the zones comprise separate zones of a tablet.

32. The unit dose product of claim 31, wherein at least the wash composition and preferably also the rinse composition is in solid form.

33. The unit dose product of claim 31, wherein the rinse conditioner zone substantially retains its physical integrity until the rinse step and has at least one dimension greater than the average mesh size of a net or bag in which it is to be dosed.
34. The unit dose product of claim 31, wherein the rinse composition is encapsulated in at least one polymer capsule, sachet or gel matrix combined with the tablet.

35. The unit dose product of claim 30, wherein the zones comprise separate zones of the water soluble sachet, preferably formed of water soluble polymer.

36. The unit dose product of claim 35, wherein at least the wash composition and preferably also the rinse composition is in the form of a powder or tablet.

37. The unit dose product of claim 35, wherein the at least the wash composition and preferably also the rinse composition is in liquid form, especially in the form of a substantially non-aqueous liquid.

38. The unit dose product of claim 35, wherein the separate sachet zones comprise one sachet located inside another, the inner sachet containing the rinse composition and the wash composition being located between the inner and outer sachets.

39. The unit dose product of claim 34, wherein the rinse combination is incorporated in at least polymer capsule, sachet or gel matrix having at least one dimension, preferably a diameter, greater than the average mesh size of a net or bag in which it is to be dosed.

40. The unit dose product of claim 29, wherein the release inhibiting means is pH and/or ionic strength and/or temperature dependent.