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(54) Fabric rejuvenating treatment

(57) The present invention is directed to a domestic process for rejuvenating an old fabric by contacting said fabric with a high dose of enzyme for an efficient period of time and subsequently contacting said fabric with an enzyme inhibitor. The present invention further relates to a rejuvenating composition for use in such process and is also directed to the manufacture of a rejuvenating composition for use in such process.

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Description

Technical Field of the invention

[0001] The present invention is directed to a domestic process for rejuvenating old fabrics by contacting said fabric with a high dose of enzyme for an efficient period of time and subsequently with an enzyme inhibitor. The present invention relates further to a rejuvenating composition for use in such process.

Background of the invention

[0002] Cleaning performance is one of the major objectives of all modern laundry detergent compositions. Therefore, detergent components such as bleaching agents, surfactants and enzymes, have been incorporated in laundry detergent compositions. However, some stains are highly difficult to remove by conventional detergents and it is known that fabrics can accumulate over time resistant stains and dinginess.

[0003] Furthermore, modern laundry detergent and/or fabric care compositions contain various detergent ingredients having one or more purposes in obtaining fabrics which are not only clean but also have retained appearance and integrity. Therefore, detergent components such as perfumes, soil release agents, fabric brightening agents, fabric softeners, chelants, dye fixatives and enzymes, have been incorporated in laundry detergent and/or fabric care compositions.

[0004] Indeed, the domestic treatment of fabric is a problem known in the art to the formulator of laundry compositions. Hence, it is well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles. Deterioration of fabric integrity and appearance can manifest itself in several ways. Short fibers are dislodged from woven and knit fabric/textile structures by the mechanical action of laundering. These dislodged fibers may form lint, fuzz or "pills" which are visible on the surface of fabrics and diminish the appearance of newness of the fabric. Such a problem of fabric abrasion is even more acute after multiwash cycles.

[0005] The object of the present invention is therefore to provide a single domestic fabric treatment to rejuvenate old, worn-out and/or pilled fabrics and/or fabrics with resistant stains and/or with a greying, dingy appearance. This objective has been met by providing a one-shot domestic process for rejuvenating such fabrics by contacting said fabric with a high dose of enzyme for an efficient period of time and subsequently with an enzyme inhibitor.

[0006] The use of enzymes such as proteases, lipases, amylases and/or cellulases are known in the detergency industry. Proteases are commonly used enzymes in cleaning applications. Proteases are known for their ability to hydrolyse other proteins. This ability has been taken advantage of through the incorporation of naturally occurring or engineered protease enzymes in laundry detergent compositions. The inclusion of lipolytic enzymes in detergent compositions for improved cleaning performance is known, e.g. enhancement of removal of triglycerides containing soils and stains from the fabrics. Amylase enzymes have long been recognised in detergent compositions to provide the removal of starchy food residues or starchy films from dishware or hard surfaces or to provide cleaning performance on starchy soils as well as other soils typically encountered in laundry applications. The activity of cellulase is one in which cellulosic fibres or substrates are attacked by the cellulase and is depending on the particular function of the cellulase, which can be endo- or exo- cellulase, and on the respective hemicellulases. The cellulose structures are depolymerized or cleaved into smaller and thereby more soluble or dispersible fractions. This activity in particular on fabrics provides a cleaning, rejuvenation, softening and generally improved handfeel characteristics to the fabric structure.

[0007] EP 495 258 describes detergent compositions comprising a high activity cellulase in combination with a softening clay to provide excellent colour rejuvenation and whiteness maintenance for fabrics. W098/17769 discloses detergent compositions comprising a cationic surfactant and a cellulolytic enzyme to provide enhance greasy stain removal, cleaning benefits, improved fabric feel and colour rejuvenation. W092/17572 is related to an improved method for treating cotton-containing fabrics with a cellulase solution containing a fungal cellulase composition which is substantially free of all CBH I type cellulase components for improved feel, appearance, softening, colour enhancement and/or stone wash appearance. WO98/17770 describes a method and an agent used in the retention of colour values on fabrics formed from cellulose. The method comprises treating a coloured fabric with a cellulase and a polymer selected from a polyalkylene oxide graft polymer, a polyamino acid polymer and/or a carboxylated polysaccharide polymer in an amount effective to preserve the colour of the fabric after at least one wash cycle. W097/30143 discloses detergent compositions comprising a cellulase termination composition and a cellulase in order to prevent potential tensile strength loss related to the hydrolytic activity of cellulase on cellulose substrates while maintaining the desired

benefits of cleaning, rejuvenation, softening and improved handfeel from the use of cellulase. EP 220 016 discloses clarification agents for coloured fabrics and methods of treatment of fabrics with a cellulase as the active component. EP 866 165 describes a method for depilling cotton goods with a *Trichoderma* cellulase enzyme preparation consisting of at least 80% of an endoglucanase II with minimum loos of fabric strength and for creating a smooth surface appearance. WO94/12578 is directed to an textile industry treatment of cellulosic fabrics to improve fabric quality with respect to handle and appearance without loss of fabric wettability by subjecting the fabric to two treatments of cellulase.

[0008] However, none of the above cited documents describes a domestic process whereby a fabric is contacted with a high dose of enzyme for an efficient period of time and subsequently with an enzyme inhibitor, to rejuvenate old, worn-out and/or pilled fabrics and/or fabrics with resistant stains and/or with a greying, dingy appearance.

Summary of the Invention

[0009] The present invention is directed to a one-shot domestic process for rejuvenating old, pilled, worn-out fabrics and/or fabrics with resistant stains and/or with a greying, dingy appearance. Said process comprises contacting said fabric with a high dose of enzyme for an efficient period of time, and subsequently contacting said fabric with an enzyme inhibitor. The enzyme will be comprised at a level of 0.01g/l to 1g/l expressed in grams of pure enzyme per litre of rejuvenating liquor, preferably at a level of from 0.25 to 0.3 g/l.

[0010] In a second embodiment, the present invention relates to a rejuvenating composition for use in such process. Preferably, such fabric treatment composition will be a multi-phase rejuvenating composition, more preferably for use in a washing machine, comprising a first region and one or more second discrete second regions, wherein the concentration of enzyme in said second discrete region(s) is at least 2 times the concentration of enzyme in said first region; and the total level of enzyme is greater than 2% by weight of pure enzyme of the total composition. The enzyme and/or further ingredient comprised in the second discrete regions of said rejuvenating compositions is released in a first stage. The rejuvenating compositions of the present invention will further comprise an enzyme inhibitor to be released in a second stage.

[0011] In a third embodiment, the present invention is directed to the manufacture of a rejuvenating composition for use in such rejuvenating process.

Detailed Description of the Invention

FABRIC TREATMENT PROCESS

[0012] The present invention is directed to a one-shot domestic process to be achieved in a conventional washing machine or conventional laundry appliance, for rejuvenating old, worn-out, pilled fabrics and/or fabrics with resistant stains and/or with a greying, dingy appearance. The rejuvenating process of the present invention can also be achieved within a domestic handwash process wherein the steps of the rejuvenating process of the present invention are carried out by hand in any suitable vessel as for example a tub, a sink or any plastic basin.

[0013] Clothes made of from cotton, synthetic fibres on cellulose basis such as rayon, flax, hemp, ramie or mixtures thereof often develop a greyish appearance after having being worn and washed repeatedly. This unwanted effect is particularly evident in case of dyed clothes, especially with dark colours. Without wishing to be bound by theory, it is believed that this greyish appearance is caused by disordered fibres which are broken or torn up by mechanical action. In addition, after conventional wash resistant stains might not have been removed and the clothes therefore look worn, dingy and fluffy. The rejuvenating process of the present invention re-establish the attractive look of the fabrics which have developed a greyish appearance, thereby offering the consumer a chance to avoid discarding clothes before it is actually needed. Such treated fabrics retrieve indeed their initial appearance and look like "new" again. They can be worn again and enter regular conventional laundering cycles.

[0014] The purpose of the present invention is to rejuvenate fabrics by a one-shot treatment of a high dose of enzyme. Without wishing to be bound by theory, it is believed that such process delivers a very effective enzyme activity at the beginning of the treatment resulting in a very effective enzyme performance. For example, such a high activity of cellulase will provide an excellent cleaning and excellent removal of damaged cellulosic fibers and removal of cellulosic-containing stains, resulting in removal of the pills from the fabric surface, darkening of the colours, overall improved fabric appearance and feel. Proteases will similarly provide excellent cleaning and excellent removal of damaged silk and wool fibers and removal of protein-containing stains, resulting in overall improved fabric appearance and feel. Similarly, the lipase and the other suitable enzymes of the present invention will provide excellent cleaning and overall improved fabric appearance and feel.

[0015] This one-shot rejuvenating domestic process comprises contacting said fabric within a handwash process or in a conventional washing machine with an enzyme for an efficient period of time, and contacting said fabric subsequently with an enzyme inhibitor. The enzyme will be comprised at a level of 0.01g/l to 1g/l expressed in g of pure

enzyme per litre of rejuvenating liquor, preferably at a level of from 0.25g/l to 0.3 g/l. Preferably, such efficient period of enzymatic contract will be from 5 minutes to 30 minutes, more preferably from 10 minutes to 15 minutes.

[0016] If the fabric is still damaged or is damaged again, i.e. old, worn-out, pilled and/or with resistant stains and/or with a greying, dingy appearance, those fabrics can undergo a second rejuvenating process of the present invention.

[0017] In a further step, after the second step of the rejuvenating process or when such rejuvenated fabrics enter again the conventional laundering, a fabric enhancement composition as described hereinafter is preferably used. Indeed, when further treated with such a composition, the rejuvenated fabrics of the present invention keep a better appearance. Indeed such compositions provide reduced fabric abrasion, dyes fixation and colour care over multiple wash cycles.

Without wishing to limit the scope of the present invention, a typical example of the rejuvenating process is given here below :

[0018] The process of the present invention can be carried out within a handwashing process or within a conventional laundry machine. Conventional machine laundry methods typically comprising treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition are used for the purpose of the present invention. By an effective amount of the detergent composition it is meant conventionally from 20g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 25 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods in Western Europe. This effective amount corresponds to 20g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres in typical US wash conditions and to 20g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 80 litres in typical Japanese wash conditions. A typical washload will be from 1 to 5 kg of fabrics for the Western European, North American and Japanese wash conditions.

[0019] The old, worn-out and/or pilled fabrics and/or fabrics with resistant stains and/or with a greying, dingy appearance to be rejuvenated are introduced into the drum/tub of such washing machine. This process can be achieved for one garment or for several garments together.

[0020] The process of the present invention encompasses several embodiments:

- The enzyme is added directly in the pre-wash compartment of the washing machine drawer. An enzyme inhibitor is added in the main compartment of the washing machine and hence will be released subsequently.
- In another embodiment, the enzyme is formulated within a composition comprising both the enzyme and an enzyme inhibitor. Such composition is formulated such as the enzyme is released in a first step and the inhibitor is released subsequently. This composition can be added to the washing machine directly into the drum or via any compartment of the drawer, for a pre-wash, short wash or full wash cycle(s). Examples of such compositions are given hereinafter.
- In a further embodiment, the enzymatic first step and the inhibitor second step can be achieved within two separate laundering treatments. The first step is the enzyme treatment achieved for example in a short wash or pre-wash cycle within a conventional washing machine. This treatment is followed by the inhibitor treatment which is achieved for example, by a separate pre-wash, wash cycle or rinse within a conventional washing machine.
- In a further embodiment, the rejuvenating processes described in the embodiments above can be followed by another short wash, wash or rinse cycle(s) with a fabric enhancer ingredient or composition as described hereinafter.
- As mentioned above, the steps of the rejuvenating process of the present invention can also be carried out by hand in any suitable washing basin.

[0021] A dispensing device can be employed in the rejuvenating method of the present invention. The dispensing device is charged with the enzyme component / composition and the inhibitor is added in the main compartment of the drawer. Alternatively the dispensing device might be charged with a rejuvenating composition comprising the enzyme and the inhibitor formulated in sequential releases, as described above, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Once the washing machine has been loaded with fabric to be rejuvenated, the dispensing device containing the product is placed inside the drum/tub. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water. To allow for release of the product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle. Preferred dispensing devices are

reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

[0022] The enzyme first step of the rejuvenating treatment is preferably achieved at a temperature of 20°C to 60°C, more preferably of from 30°C to 50°C. Preferably, the fabrics will be in contact with the enzyme for an efficient period of time of from 5 minutes to 30 minutes, more preferably from 10 minutes to 15 minutes.

[0023] This enzyme first step of the rejuvenating treatment allows the enzyme to perform at its best potential as the enzyme is not formulated with any ingredients known to be detrimental to the enzyme activity, as usually found in conventional laundry detergent compositions or conventional compositions used in the textile industry.

[0024] The rejuvenating process of the present invention comprises a second stage whereby the enzymatic activity released in the first stage is stopped by an enzyme inhibitor. When the process of the present invention is achieved within a conventional washing machine, said enzyme inhibitor can be added via the second or rinse compartment within the washing machine drawer, is already comprised in the second phase of the rejuvenase composition of the present invention (as described below) or is added within a separate laundering step. The inhibitor second step of the rejuvenating treatment is preferably achieved at a temperature above 30°C, more preferable at a temperature above 40°C for a period of time of from 5 minutes to 2 hours, more preferably from 20 minutes to 1 hour. The inhibitor second step is preferably carried out after a period of 10 minutes, more preferably 20 minutes, most preferably after 30 minutes.

[0025] As described above, the rejuvenated fabrics of the present invention can be further protected by a third fabric care step. Indeed, when further treated with fabric care ingredients or with a composition comprising such ingredients, as described hereinafter, the rejuvenated fabrics of the present invention keep a better appearance. Such fabric care ingredients or compositions provide reduced fabric abrasion, dyes fixation and colour care over multiple wash cycles. Such ingredients or composition can be added in the rinse compartment of the drawer of the washing machine, or can be formulated within or within a separate slow release phase of the rejuvenating composition of the present invention. The rejuvenated fabrics can also be soaked in a solution comprising such ingredients and or composition. This third fabric care step is preferably achieved after a period of 1h 15 minutes to 2 hours after the beginning of the rejuvenating process and last for 5 to 60 minutes, preferably for 40 to 60 minutes. Preferably, such treatment is achieved within the rinsing cycle(s) of conventional washing machine laundering process. Depending on the geographical areas, there are from 1 to 5 rinsing cycles of generally from 5-25, preferably 10-15 minutes. Such treatment is conventionally carried at a temperature of less than 30°C, preferably from 5°C to 25°C.

[0026] Such rejuvenated fabrics are then removed from the washing machine and can be line-dried or preferably are dried in any conventional dryer. It has been found that when such treated fabrics are dried within a dryer machine, it results in better fabric feel and appearance, and in better pills removal.

ENZYMES

[0027] An essential element of the rejuvenating process of the present invention is the first step of contacting fabric to be rejuvenated with a high dose of enzyme, for an efficient period of time. The enzyme will be comprised at a level of 0.01g/l to 1g/l expressed in grams of pure enzyme per litre of rejuvenating liquor, preferably at a level of from 0.25g/l to 0.3 g/l.

[0028] Suitable enzymes for the purpose of the present invention are selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

[0029] Preferred enzymes for the purpose of the present invention are cellulases, proteases, lipase and/or mixtures thereof, more preferably cellulases.

[0030] The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and W096/02653 which discloses fungal cellulase produced respectively from *Humicola insolens, Trichoderma, Thielavia* and *Sporotrichum.* EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and W095/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens,* DSM 1800, exhibiting cellulase activity sold under the tradename Carezyme by Novo Nordisk A/S; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having colour care benefits. Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and W091/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in W096/34092, WO96/17994 and WO95/24471.

Suitable commercially available cellulase enzymes are sold by Genencor under the tradenames: Indiage 2XL, Indiage Super L, Indiage RWF, Indiage MAXL, Indiage Super GX, Indiage Euro L, Indiage Euro G, Indiage TFC AC, Primafast 100, Primafast SGL, Puradax HA, Multifect CL, Multifect CSG, Multifect GC and Multifect GGC. Suitable commercially available cellulase enzymes are sold by Novo Nordisk A/S under the tradenames: Celluclast 1.5L, Cereflo, Cellusoft, Ultraflo, Denimax BT, Denimax Acid P, Denimax 302S, Denimax 402S, Denimax 502S, Novozym 476, Novozym 342, Novozym 613.

Preferred cellulases to be used in the rejuvenating process of the present invention are the liquid cellulase preparation from *Trichoderma reesei* sold by Novo Nordisk under the tradename Celluclast and ~43kD endoglucanase derived from *Humicola insolens,* DSM 1800, exhibiting cellulase activity sold under the tradename Carezyme by Novo Nordisk A/S. More preferred is the Carezyme cellulase.

[0031] Further preferred enzymes for the rejuvenating process and compositions of the present invention are proteases. Suitable are proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus,* having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine protealytic enzyme which is called "Protease A" herein. Suitable is what is called herein "Protease C", which is a variant of an alkaline serine protease from Bacillus in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in WO 91/06637. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in W095/10591 and WO95/10592. The "protease D" variants have preferably the amino acid substitution set 76/103/104, more preferably the substitution set N76D/S103A/V1041. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application published under W098/55634).

More preferred proteases are multiply-substituted protease variants. These protease variants comprise a substitution of an amino acid residue with another naturally occuring amino acid residue at an amino acid residue position corresponding to position 103 of *Bacillus amyloliquefaciens* subtilisin in combination with a substitution of an amino acid residue positions corresponding to positions 1, 3, 4, 8, 9, 10, 12, 13, 16, 17, 18, 19, 20, 21, 22, 24, 27, 33, 37, 38, 42,

43, 48, 55, 57, 58, 61, 62, 68, 72, 75, 76, 77, 78, 79, 86, 87, 89, 97, 98, 99, 101, 102, 104, 106, 107, 109, 111, 114, 116, 117, 119, 121, 123, 126, 128, 130, 131, 133, 134, 137, 140, 141, 142, 146, 147, 158, 159, 160, 166, 167, 170, 173, 174, 177, 181, 182, 183, 184, 185, 188, 192, 194, 198, 203, 204, 205, 206, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 222, 224, 227, 228, 230, 232, 236, 237, 238, 240, 242, 243, 244, 245, 246, 247, 248, 249, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 265, 268, 269, 270, 271, 272, 274 and 275 of *Bacillus amyloliquefaciens* subtilisin; wherein when said protease variant includes a substitution of amino acid residues at positions corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one or more amino acid residue positions other than amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens* subtilisin and/or multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occuring amino acid residue at one or more amino acid residue positions corresponding to positions 62, 212, 230, 232, 252 and 257 of *Bacillus amyloliquefaciens* subtilisin as described in PCT application Nos. PCT/US98/22588, PCT/US98/22482 and PCT/US98/22486 all filed on October 23, 1998 from The Procter & Gamble Company. Preferred multiply substituted protease variants have the amino acid substitution set 101/103/104/159/232/236/245/248/252, more preferably 101G/103A/104I/159D/232V/236H/245R/248D/252K according to the numbering of *Bacillus amyloliquiefaciens subtilisin.*

[0032] Other preferred enzymes that can be included in the rejuvenating process and compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum,* e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli.* Especially suitable lipases are lipases such as M1 Lipase^{R} and Lipomax^{R} (Gist-Brocades) and Lipolase^{R} and Lipolase Ultra^{R}(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitables are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

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

[0033] Also suitable are the amylases (α and/or β). W094/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Examples of commercial α-amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban ® ,Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. W095/26397 describes other suitable amylases: α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Suitable are variants of the above enzymes, described in W096/23873 (Novo Nordisk). Preferred variants are those demonstrating improved thermal stability, wherein at least one amino acid residue equivalent to F180, R181, G182, T183, G184, or K185 has been deleted from the parent α-amylase. Preferably said variants having improved thermal stability comprise the amino acid deletions R181* + G182*, or T183* + G184*.

Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in W095/35382. Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and W096/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, W095/26397 and W096/23873 (all by Novo Nordisk). Cleaning compositions which incorporate mutant amylases are described in W094/02597, Novo Nordisk A/S published February 03, 1994. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995.

[0034] Also suitable enzymes for the purpose of the present invention are the following enzymes as described in the following patent applications filed by the Procter & Gamble Company: the xylan degrading enzymes as described in the co-pending application published under EP 709 452 A; the cholesterol esterase EC 3.1.1.13 as described in WO93/10224 and in W094/23052 by Novo Nordisk A/S; Keratanase EC 3.2.1.103 as described in the published application EP 747 470 A; the chondroitinase EC 4.2.2.4, EC 4.2.2.5 and EC 4.2.2 as described in the published application EP 747 469 A; the bleaching enzymes including the peroxidase as described in WO89/099813, W089/09813,

EP 540 784 A and WO 97/30143, the laccase EC 1.10.3.2 as described in the published patent application W097/43384, the catechol oxidase EC 1.10.3.10, the bilirubin oxidase EC 1.3.3.5, the monophenol monooxygenase EC 1.14.99.1; the cytochrome EC 1.14.13, EC 1.14.14, EC 1.14.15 and EC 1.14.99. as described in co-pending patent application WO 99/02641 and in the co-pending patent application US serial No. US97/12445; the specific oxygenases described in the co-pending patent applications WO 99/02639, WO 99/2632 and WO99/02638: polyphenol / heterocyclic substrate based oxygenase enzyme as described WO99/02639; the proteinic substrate based oxygenase as described in WO99/02632; the oxygenase directed to body soils as described in WO99/02638; the endo-dextranase as described in the copending EP 883 673 A; the mycodextranase as described in the co-pending application EP 929 635 A; the hyaluronidase EC 3.2.1.35, EC 3.2.1.36 and EC 4.2.2.1. as described in the published patent application WO 97/24426; the hexosaminidase as described in the co-pending patent application WO98/50512.

[0035] The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. The enzymes can be used as separate single ingredients in prills, granulates, stabilised liquids, etc. forms containing one enzyme or as mixtures of two or more enzymes (e.g. cogranulates). Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

[0036] Although the useful enzyme may be used as such in the method of the present invention, it is preferred that it is formulated into a suitable composition. Thus the useful enzyme may be used in the form of a granulate, preferably a non-dusting granulate, a liquid, in particular a stabilised liquid, a slurry, or in a protected from. Dust-free granulates may be produced, e.g. as disclosed in US 4,106,991 and US 4,661,452 (both to Novo Nordisk A/S) and may optionally be coated by methods known in the art. Liquid enzyme preparations may, for instance, be stabilised by adding a polyol such as propylene glycol, a sugar or sugar alcohol or acetic acid, according to the established methods. Other enzyme stabilisers are well-known in the art. The enzyme can be also encompassed in a bag of material which disintegrates at the temperature of at least 25°C, preferably 40°C or is soluble in the rejuvenating liquor. This embodiment makes the dosage extremely easy for the consumer.

[0037] The enzyme component of the rejuvenating treatment or composition of the present invention can further comprise a buffer. The term "buffer" refers to the art recognised acid/base reagents which stabilise the enzyme solution against undesired pH shifts during the rejuvenating treatment. Preferably, the buffer employed is the one which is compatible with the specific enzyme composition and which will maintain the pH of the enzyme solution within the pH range required for optimal enzyme activity. Suitable buffers include phosphate, borate, citrate, acetate, adipate, triethanolamine, monoethanolamine, carbonate (especially alkali metal or alkaline earth metal, in particular, sodium or potassium carbonate, or ammonium and HCL salts), diamine, especially diaminoethane, imidazole, amino acid and or any other known in the art buffers. When a buffer is employed in the enzyme solution, the concentration of the buffer is that which is sufficient maintain the pH of the enzyme solution within the pH range wherein the enzyme exhibits activity which in turn, depends on the nature of each enzyme. The exact concentration of buffer employed will depend on several factors which the person skilled in the art can take into account. For example, in a preferred embodiment, the buffer nature as well as the concentration are selected as to maintain the pH of the cellulase solution within the pH range required for optimum cellulase activity. In general buffers concentration in the enzyme solution is about 0.005N and greater, preferably 0.01-0.5, more preferably 0.05-0.15N.

INHIBITORS

[0038] The second step of the rejuvenating process of the present invention will comprise in a second delayed phase, an enzyme inhibitor. This step is preferably achieved directly after the enzymatic step of the rejuvenating process of the present invention.

[0039] Suitable enzyme inhibitors for the purpose of the present invention are :

- anionic surfactants as described below, like linear alkyl benzene sulfonate, isostearyl alcohol sulfate, Sodium Dodecyl Sulfate and preferably linear alkyl benzene sulfonate;
- bleaching enzyme as described below, like the combination of a peroxidase, enhancer and hydrogen peroxide source;
- bleaching agents like the bleach activators, photobleach agents and metal catalyst described below, preferably the bleach activators and more preferably the tetraacethylene diamine (TAED), (6-nonamidocaproyl) oxybenzene sulfonate (NACA-OBS), nonanoyloxybenzene sulfonate (NOBS);
- proteases like papaine, chymotrypsine, Tyronidase, peptidase like tripeptidyl-peptidase II and those described hereinabove;

- metal ions like Cu^{2+} and Zn^{2+} added in their salt forms such as sulfate or preferably comprised within a detergent ingredient formulated within the rejuvenating composition.

Also suitable are fully formulated detergent compositions. Preferably, the enzyme inhibitors of the present invention are anionic surfactants, bleaching agents and/or metal ions or is, or is comprised within, a fully-formulated detergent composition.

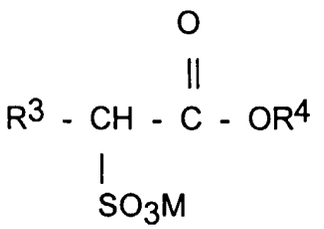
Further suitable enzyme inhibitors are described in the "Handbook of Enzymes Inhibitors" Part A and Part B, Helmward Zollner, VCH, Weinherm, Germany.

[0040] Suitable enzyme inhibitors specific for the cellulase enzymes are the phenols derivatives and polyphenol derivatives like chloroxyphenol and tannic acid; and the sugar based inhibitors, derivatives of oligosaccharides like: a) transition states analogues such as β-adiposine; b) thioderivatives like methyl-4-S-cellobiosyl-4-thio-β-cellobioside and c) suicidal inhibitors being epoxy-derivatives of oligosaccharides such as γ-epoxybutyl-1-β-cellotetraoside. Specific inhibitors for the protease enzymes is: indole; for the amylase enzymes are: the sugar based derivatives and transition state analogues such as Acarbose, 1-deoxynojirimycin, D-maltobionolactone and nojirimycin; and for the lipase enzymes are: propanol and N-ethylemaleimide.

[0041] Such inhibitors are typically comprised at a level of at least 0.3 g/l - expressed in grams of inhibitor per litre of rejuvenating liquor, preferably at least 0.5g/l. When encompassed in the rejuvenating composition, the inhibitor will generally be comprised at a level of at least 20%, preferably from 30 to 90% by weight of the rejuvenating composition. The level of inhibitors in the process and composition of the present invention should preferably be such that the remaining level of enzyme activity is less than 20%, preferably less than 10% of the maximum enzyme activity at the end of the inhibitor step. Such activity is easily measurable by persons skilled in the field of enzyme.

[0042] Anionic surfactants : Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

[0043] The preferred alkyl ester sulfonate surfactant comprise alkyl ester sulfonate surfactants of the structural formula:



wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10}-C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10}-C_{16} alkyl.

[0044] Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C_{12}-C_{16} are preferred for lower wash temperatures (e.g. below about 50°C) and C_{16-18} alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

[0045] Other anionic surfactants can also used as enzyme inhibitors. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_8-C_{22} primary of secondary alkanesulfonates, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C_{12}-C_{18} monoesters) and diesters

of sulfosuccinates (especially saturated and unsaturated C_6-C_{12} diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k$-CH_2COO-M+ wherein R is a C_8-C_{22} alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

[0046] Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

[0047] Further anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12}-$C_{18}E(1.0)M$), C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12}-$C_{18}E(2.25)M$), C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12}-$C_{18}E(3.0)M$), and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12}-$C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

[0048] Preferred anionic surfactants to be used as enzyme inhibitors in the rejuvenating process and composition of the present invention are C11-C18 alkyl benzene sulfonate and/or C10-C20 alkyl sulfate. These are usually present in the rejuvenating compositions of the present invention at a level of from 20% to 90%, preferably from 60-80% by weight of the first region.

[0049] Peroxidase, enhancer and hydrogen peroxide source: As described in the co-pending patent application WO97/30143 by the Procter & Gamble Company, a suitable cellulase terminator composition comprises a peroxidase, an enhancer and a hydrogen peroxide source which in combination act to irreversibly terminate the activity of the enzyme after a certain time. Suitable peroxidases, enhancers and hydrogen peroxide sources are described in WO97/30143.

REJUVENATING COMPOSITION

[0050] In a second embodiment, the present invention relates to a rejuvenating composition for use in the above described rejuvenating process. Such composition comprise an enzyme that will be released in a first stage and an enzyme inhibitor that will be released subsequently. Preferably, such rejuvenating composition will be a multi-phase rejuvenating composition for use in a washing machine, comprising a first region and one or more second discrete regions, wherein the concentration of enzyme in said second discrete region(s) is at least 2 times the concentration of enzyme in said first region; and the total level of enzyme is greater than 2% by weight of pure enzyme of the total composition.

[0051] Such compositions are preferably capable of delivering the enzyme in the rejuvenating liquor within 10, 5, 4 or even 3 minutes from the start of the rejuvenating process. It is also preferred that the rejuvenating composition of the present invention comprises the enzyme of the present invention predominantly concentrated in the second discrete phase(s), for example, at least about 50%, preferably at least about 60%, especially about 80% by weight of the active (based on the total weight of the active in tablet) is in the second discrete phase(s) of the rejuvenating composition.

[0052] The enzyme and/or further ingredient comprised in the second discrete regions of said rejuvenating compositions is released in a first stage. The rejuvenating compositions of the present invention will further comprise an enzyme inhibitor to be released in a second subsequent stage. The delayed release system of the rejuvenating composition of the present invention will achieve differential delivery of ingredients such as that the second discrete regions will deliver its enzyme(s) significantly before the first region and preferably will even deliver essentially completely before the first region has delivered its enzyme inhibitor. The rejuvenating compositions of the present invention may comprise several further regions which may be released sequentially at different stages of the rejuvenating process.

[0053] The multi-phase tablet is the preferred execution for the rejuvenating compositions of the present invention. However, sequential release achieved within multiple emulsions, Shell & Cage, sachets and pouches, compartimentated dosing devices technologies are also contemplated.

[0054] Examples of suitable multiples emulsion systems suitable as delayed release systems of the present invention are the stable multiple emulsion X/O/Y type - in which X is a component not miscible with Oil, O an oil phase and Y an aqueous phase - containing at least one emulsifying agent with an HLB value ≤ 6 and/or is a W/O-emulsifying agent

as described in WO 95/15143. W095/28467 discloses a detergent composition comprising an enzyme and an organic peroxyacid bleaching system wherein a coating is provided for delaying the release to a wash solution of said peroxide bleach relative to the release of said enzyme. Also suitable are the multicompartment sachet product comprising a first compartment capable of releasing its content solid or liquid within 3 minutes from the start of the treatment process and a second compartment of water-permeable material provided with a pore-occluding coating and/or in the form of a sachet so that release of its content is delayed for at least 5 minutes, advantageously from 10-15minutes, from the start of the fabric treatment and/or retarded as described in EP 236 136 and the multicompartment sachet formed of or comprising a thermoplastic film of water-soluble poly(ethylene oxide) having an outer covering of a flexible, apertured, water-insoluble but water-permeable non-woven, textile or paper sheet-like material as described in EP 253 566.

[0055] Preferably, the rejuvenating composition of the present invention is in the form of a multi-phase tablet wherein a second discrete region comprising the enzyme dissolves faster than a first region comprising an enzyme inhibitor. Such phases can be in any suitable shape such as layer, coatings or moulds and in any number: one ore more first and/or one or more second phases. The enzyme used in the rejuvenating process of the present invention can be comprised in substantially one second discrete region or in several second discrete regions. Such second discrete regions can comprise one or more different enzymes and can be released simultaneously or sequentially as long as released before the sequential release of the enzyme inhibitor.

[0056] Protease enzymes can be used in the present invention as an enzyme suitable for the enzymatic rejuvenating step as well as an enzyme inhibitor. Therefore, if the protease is to be used as an enzyme suitable for the enzymatic rejuvenating step together with a second non-proteolytic enzyme suitable for the enzymatic rejuvenating step, they will preferably be released sequentially, one after the other in either sequence, with preferably the proteolytic release in a second stage. In such instance, full enzyme activity of the non-proteolytic enzyme(s), is obtained. Such steps will be followed according to the present invention, by an inhibition step.

[0057] The rejuvenating tablet can be coloured, transparent, opaque or any possible shade in between these two extremes. The first region and the second discrete region can have the same or different degree of transparency, i.e. ranging from totally transparent to opaque. However, it is preferred that they be different. When there are more than one second discrete region present in the detergent tablet it is possible for each of the second discrete to have the same or different degree of transparency, i.e. ranging from totally transparent to opaque. However, it is preferred that they be different.

[0058] The rejuvenating tablets are preferably between 15g and 100g in weight, more preferably between 18g and 80g in weight, even more preferably between 20g and 60g in weight. In a preferred aspect of the present invention, the first region weighs greater than 3g, preferably greater than 4g, more preferably greater than 5g. More preferably the first region weights from 10g to 50g, even more preferably from 15g to 40g. The second discrete region(s) (as defined herebelow) weigh less than 15g. More preferably the second discrete region and/or optionally subsequent phases weigh between 1g and 12g, preferably between 5g and 10g. The weight ratio of first region to second discrete region(s) is generally greater than 1:1, preferably greater than 2:1, more preferably greater than 3:1 or even 4:1, most preferably at least 5:1.

[0059] The first region(s) of the rejuvenating tablet have Child Bite Strength (CBS) which is generally at least 6kg, preferably greater than 8kg, greater than 10kg, more preferably greater than 12kg, most preferably greater than 14kg. CBS is measured as per the U.S. Consumer Product Safety Commission Test Specification. Child Bite Strength Test Method: According to this method the tablet is placed horizontally between two strips/plates of metal. The upper and lower plates are hinged on one side, such that the plates resemble a human jaw. An increasing downward force is applied to the upper plate, mimicking the closing action of the jaw, until the tablet breaks. The CBS of the tablet is a measure of the force in Kilograms, required to break the tablet.

[0060] The dissolution rate of the second discrete region is greater than the dissolution rate of the first region as determined by the following method : A tablet or tablet phase with known weight (initial tablet or tablet phase weight) is put into the drum of a washing machine of the type Baucknet with 0.5kg of fabric. The short cycle or pre-wash cycle is used at a temperature of 40°C. The cycle is stopped after 3, 10 and after further intervals of 5 minutes. The remains of the tablet or tablet phase are recovered from the drum and weighted (tablet or tablet phase weight after a certain period of time). The percentage of dissolution is calculated as follows :

$$\% \text{ dissolution} = \frac{(TWi - TW)}{TWi} \times 100$$

Wherein TW is the tablet or tablet phase weight after a certain period of time and TWs is the initial tablet or tablet phase weight. Such percentage of dissolution is calculated for each period of time until complete dissolution of the tablet or tablet phase and result in a range dissolution.

Compressed Rejuvenating Tablet

[0061] Most preferred tablet composition to be used for the rejuvenating composition of the present invention, is the following multi-phase tablet as described in the co-pending European patent application EP 99 305 384.2 filed by The Procter & Gamble Company on July 7, 1999.

[0062] Such multi-phase tablet for use in a washing machine, comprises :

a) a first phase in the form of a shaped body having at least one mould therein (hereinafter referred to as the First region); and

b) a second phase in the form of a particulate solid compressed within said mould (hereinafter referred to as Second discrete region).

[0063] In preferred embodiments, the first region is a compressed shaped body prepared at an applied compression pressure of at least 4 kN/cm^2, preferably at least 5 kN/ cm^2, more preferably at least 10 kN/cm^2, even more preferably from 20 to 100, and especially from 50 to 75 kN/cm^2 (compression pressure herein is the applied force divided by the cross-sectional area of the tablet in a plane transverse to the applied force - in effect, the transverse cross-sectional area of the die of the rotary press). It is also preferred that the particulate solid of the second discrete region (which terminology is intended to include the possibility of multiple second discrete regions, sometimes referred to herein as 'optional subsequent phases') be compressed into said mould at an applied compression pressure less than that applied to the first region and preferably at a compression pressure of less than 20 kN/cm^2, preferably in the range from 2 kN/cm^2 to 10 kN/cm^2 and more preferably from 4-5 kN/cm^2, such tablets being preferred herein from the viewpoint of providing optimum tablet integrity and strength (measured for example by the Child Bite Strength [CBS] test as defined above) and product dissolution characteristics. Also, the compression pressures applied to the first and second discrete regions will generally be in a ratio of at least 2:1, preferably at least 5:1, more preferably at least 10:1.

Thus, there is provided a multi-phase rejuvenating tablet for use in a washing machine, the tablet comprising:

a) a first region in the form of a compressed shaped body having at least one mould therein, the shaped body being prepared at a compression pressure of at least 4 kN/cm^2; and

b) a second discrete region in the form of a particulate solid compressed within said mould, the second discrete region being compressed at a pressure of less than 20 kN/cm^2.

[0064] Preferably, the second discrete region is in the form of a compressed or shaped body adhesively contained, for example by physical or chemical adhesion, within the at least one mould of the first region.

[0065] The multi-phase rejuvenating tablets of the present invention are capable of dissolving in the rejuvenating liquor so as to deliver at least 50%, preferably at least 60%, and more preferably at least 80% by weight of the enzyme component to the wash liquor within 10, 5, 4 or even 3 minutes of the start of the wash process.

[0066] Preferably the delayed release system of the multi-phase rejuvenating tablet of the present invention will be achieved with a coating of the first region. It can be achieved with a coating of poorly water-soluble material or with a coating of sufficient thickness allowing the delayed release of at least 50%, preferably 60%, more preferably 80% of the enzyme inhibitor after 10 minutes, preferably 20 minutes, more preferably 30 minutes from the start of the rejuvenating process.

[0067] For the first region of the multi-phase rejuvenating tablet of the present invention, the coating is present generally at a level of from 1 to 20%, preferably from 5-10% of the composition. The amount of coating to be applied to said granulates will depend to a considerable extent on the nature and composition of the desired coating, and to the kind of protection said coating should offer to said granulates. Indeed, the thickness of said coating or a multilayered coating applied onto any of the above granulates may determine the period in which the content of said granulates is released.

[0068] Such tablet coating are preferably very hard and provide additional strength to the tablet. The coating may be used to affix the second discrete region(s) to the first region.

[0069] The coating layer preferably comprises a material that becomes solid on contacting the compressed and/or the non-compressed layers within preferably less than 15 minutes, more preferably less than 10 minutes, even more preferably less than 5 minutes, most preferably less than 60 seconds. The coating layer may be water-soluble or substantially water-insoluble. As defined herein "substantially insoluble" means having a very low solubility in water. This should be understood to mean having a solubility in water at 25°C of less than 20 g/L, preferably less than 5 g/l, and more preferably less than 1 g/l. Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

[0070] Preferred coating layers comprise materials selected from the group consisting of fatty acids, alcohols, diols, esters and ethers, carboxylic acid, dicarboxylic acid, polyvinyl acetate (PVA), polyvinyl pyrrolidone (PVP), polyacetic

acid (PLA), polyethylene glycol (PEG) and mixtures thereof. Preferred carboxylic or dicarboxylic acids preferably comprise an even number of carbon atoms. Preferably carboxylic or dicarboxylic acids comprise at least 4, more preferably at least 6, even more preferably at least 8 carbon atoms, most preferably between 8 and 13 carbon atoms. Preferred dicarboxylic acids include suberic acid, azelaic acid, subacic acid, undecanedioic acid, dodecandioic acid, tridecanedioic and mixtures thereof. Preferred fatty acids are those having a carbon chain length of from C12 to C22 and most preferably from C18 to C22. Preferred dicarboxylic acids are adipic acid (C6), suberic acid (C8), azelaic acid (C9), sebacic acid (C10), undecanedioic acid (C11), dodecanedioic acid (C12) and tridecanedioic acid (C13). Preferred fatty alcohols are those having a carbon chain length of from C12 to C22 and most preferably from C14 to C18. Preferred diols are 1,2-octadecanediol and 1,2-hexadecanediol. Preferred esters are tristearin, tripalmitin, methylbehenate, ethylstearate. Preferred ethers are diethyleneglycol mono hexadecylether, diethyleneglycol mono octadecylether, diethyleneglycol mono tetradecylether, phenylether, ethyl naphtyl ether, 2 methoxynaphtalene, beta naphtyl methyl ether and glycerol monooctadecylether. Other preferred coating materials include dimethyl 2,2 propanol, 2 hexadecanol, 2 octadecanone, 2 hexadecanone, 2, 15 hexadecanedione and 2 hydroxybenzyl alcohol. Melt-coating agents are a preferred class of fast or slow release coating agents which can be used without dilution with water. Reference may be made to Controlled Release Systems : Fabrication Technology, Vol. I, CRC Press, 1988, for further information on slow release coating.

[0071] The first region of the rejuvenating tablets are prepared and in whatever form they are, they are then preferably coated according to the present invention with a coating material having preferably a melting point of from 40°C to 200°C.

[0072] The coating can be applied in a number of ways. One method for applying the coating material involves agglomeration. Preferred agglomeration processes include the use of any of the conventional organic binder materials. Any conventional agglomerator/mixer may be used including, but not limited to pan, rotary drum and vertical blender types. Two other coating methods are a) coating with a molten material and b) coating with a solution of the material. In a), the coating material is applied at a temperature above its melting point, and solidifies on the tablet. In b), the coating is applied as a solution, the solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. Clearly substantially insoluble materials having a melting point below 40 °C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 180 °C are not practicable to use. Preferably, the materials melt in the range from 60 °C to 160 °C, more preferably from 70 °C to 120 °C. By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

[0073] More preferred coating materials for the purpose of the present invention are the fatty acids such as stearic acid and the C16-22 hydrogenated fatty acid sold under the tradename Radiacid by Fina.

[0074] The components of the rejuvenating composition are mixed together by, for example admixing dry components or spraying-on liquid components. The components are then formed into a first region using any suitable equipment, but preferably by compression, for example in a tablet press. Alternatively, the first region can be prepared by extrusion, casting, etc. The first region can take a variety of geometric shapes such as spheres, cubes, etc but preferred embodiments have a generally axially-symmetric form with a generally round, square or rectangular cross-section.

[0075] The first region is prepared such that it comprises at least one mould in the surface of the shaped body. The mould or moulds can also vary in size and shape and in their location, orientation and topology relative to the first region. For example, the mould or moulds can be generally circular, square or oval in cross-section; they can form an internally-closed cavity or recess in the surface of the shaped body, or they can extend between unconnected regions of the body surface (for example axially-opposed facing surfaces) to form one or more topological 'holes' in the shaped body; and they can be axially or otherwise symmetrically-disposed relative to the first region or they can be asymmetrically disposed. In a preferred embodiment the mould is created using a specially designed tablet press wherein the surface of the punch that contacts the rejuvenating composition is shaped such that when it contacts and presses the rejuvenating composition it presses a mould, or multiple moulds into the first region of the multi-phase rejuvenating tablet. Preferably, the mould will have an inwardly concave or generally concave surface to provide improved adhesion to the second discrete region. Alternatively, the mould can be created by compressing a preformed body of rejuvenating composition disposed annularly around a central dye, thereby forming a shaped body having a mould in the form of a cavity extending axially between opposing surfaces of the body.

[0076] At least one phase (herein referred to as a second discrete region) preferably takes the form of a particulate solid (which term encompasses powders, granules, agglomerates, and other particulate solids including mixtures thereof with liquid binders, meltable solids, spray-ons, etc) compressed into/within the one or more moulds of the first region of the rejuvenating tablet such that the second discrete region itself takes the form of a shaped body. Optional further phases include one or more compositions in the form a separate layer(s) our mould(s).

[0077] The second discrete region(s) comprises preferably a disrupting agent that may be selected from either a

disintegrating agent or an effervescent agent. Suitable disintegrating agents include agents that swell on contact with water or facilitate water influx and/or efflux by forming channels in the detergent tablet. Any known disintegrating or effervescing agent suitable for use in laundry or dishwashing applications is envisaged for use herein. Suitable disintegrating agent include starches (such as natural, modified, and pregelatinized starches, eg those derived from corn, rice and potato starch), starch derivatives such as U-Sperse (tradename), Primojel (tradename) and Explotab (tradename), celluloses, microcrystalline celluloses and cellulose derivatives such as Arbocel (tradename) and Vivapur (tradename) both available from Rettenmaier, Nymcel (tradename) available from Metsa-serla , Avicel (tradename), Lattice NT (tradename) and Hanfloc (tradename), alginates, acetate trihydrate, burkeite, monohydrated carbonate formula $Na_2CO_3.H_2O$, hydrated STPP with a phase I content of at least about 40%, carboxymethylcellulose (CMC), CMC-based polymers, sodium acetate, aluminium oxide. Suitable effervescing agents are those that produce a gas on contact with water. Suitable effervescing agents may be oxygen, nitrogen dioxide or carbon dioxide evolving species. Examples of preferred effervescent agents may be selected from the group consisting of perborate, percarbonate, carbonate, bicarbonate in combination with carboxylic or other acids such as citric, sulphamic, malic or maleic acid. Disrupting agents are typically included in the second discrete region(s) at levels of from 5% to 60%, and more preferably from 20% to 50%, by weight.

[0078] The components of the first region are mixed together by for example admixing dry components and admixing or spraying-on liquid components. The components of the second discrete region and optionally subsequent phases are then fed into and retained within the mould provided by the first phase.

[0079] Preferably, the multi-phase rejuvenating tablet of the present invention comprises two phases; a first region and a second discrete region. The first region comprising the enzyme inhibitor will normally comprise one mould and the second discrete region comprises the enzyme of the present invention. However, it is envisaged that the first region may comprise more than one mould and the second discrete region may further comprise ingredients not detrimental to the enzyme activity. It is also envisaged that several enzymes are contained in separate moulds. For example, a protease enzyme could be in this way separated from other enzyme(s) (see above).

[0080] The first and second discrete regions and/or optionally subsequent phases may comprise a binder. Where present the binder is selected from the group consisting of organic polymers, for example polyethylene and/or polypropylene glycols, especially those of molecular weight 4000, 6000 and 9000, paraffins, polyvinyl pyrolindone (PVP), especially PVP of molecular weight 90 000, polyacrylates, sugars and sugar derivatives, starch and starch derivatives, for example hydroxy propyl methyl cellulose (HPMC) and carboxy methyl cellulose (CMC); and inorganic polymers, such as hexametaphosphate. The binder is valuable both for tablet integrity and to help achieve differential dissolution of the first and second discrete regions as described below.

Suitable binders include the C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole of alcohol and more preferably the C_{15}-C_{20} primary alcohol ethoxylates containing from 20 - 100 moles of ethylene oxide per mole of alcohol. Other preferred binders include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols (PEG) with an average molecular weight of from 600 to 5 x 10^6 preferably 1000 to 400,000 most preferably 1000 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole. Further examples of binders include the C_{10}-C_{20} mono- and diglycerol ethers and also the C_{10}-C_{20} fatty acids. Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts are other examples of binders suitable for use herein.

[0081] In another embodiment of the present invention, a barrier layer comprising a barrier layer composition is located between the first and second discrete region and/or optionally subsequent regions or indeed between the second discrete region and optionally subsequent phases. The barrier layer composition comprises at least one binder selected from the group as described above. The advantage of the presence of a barrier layer is to prevent or reduce migration of components from one phase to another phase, for example from the first region into the second discrete region and/or optionally subsequent phases and vice versa.

[0082] The components of the second discrete region and optionally subsequent phases are preferably compressed at a very low compression force relative to compression force normally used to prepare tablets. The first region can be compressed at higher compression force than the second discrete region in order to achieve differential dissolution of the phases as described above.

Process

[0083] The multi-phase rejuvenating tablets are prepared using any suitable tabletting equipment, e.g., a Courtoy R253. Preferably the tablets are prepared by compression in a tablet press capable of preparing a tablet comprising

a mould. In an embodiment of the present invention, the first region is prepared using a specially designed tablet press following the procedure described below. The punch(es) of this tablet press are modified so that the surface of the punch that contacts the rejuvenating composition has a convex surface.

[0084] A first region composition is delivered into the die of the tablet press and the punch is lowered to contact and then compress the detergent composition to form a first phase. The first region composition is compressed using an applied pressure generally of at least 4 kN/cm^2, preferably between 5 and 100 kN/cm^2, more preferably 20 to 80 kN/cm^2, most preferably 50 to 75 kN/cm^2. The punch is then elevated, exposing the first region containing a mould. A second discrete region and optionally subsequent enzyme composition(s) is then delivered into the mould. The specially designed tablet press punch is then lowered a second time to lightly compress the second discrete region and optionally subsequent detergent composition(s) to form the second discrete region and optionally subsequent phase(s). In another embodiment of the present invention where an optionally subsequent phase is present the optionally subsequent phase is prepared in an optionally subsequent compression step substantially similar to the second compression step described above. The second and optionally subsequent rejuvenating composition(s) is compressed at a pressure of preferably less than 20 kN/cm^2, more preferably from 2 to 10 kN/cm^2, most preferably from 4 to 5 kN/cm^2. After compression of the second rejuvenating composition, the punch is elevated a second time and the multi-phase rejuvenating tablet is ejected from the tablet press.

[0085] More preferably, the rejuvenating multi-phase tablets of the present invention will be prepared by preparing separate tablet phases that will be adhesively attached to each other. The second discrete region composition is delivered into the die of the tablet press and the punch is lowered to contact and then compress the enzyme composition to form the second discrete phase. This second discrete region composition is compressed using an applied pressure of preferably less than 20KN/cm2, more preferably from 2 to 10 KN/cm2, most preferably from 4-5 kN/cm2. After compression, the second discrete region is extracted from the punch as a tablet phase. The second discrete region(s) phase are then adhesively attached to the first region phase (prepared as described above), preferably with a adhesive component such as PEG polymer.

Compressed / Non-compressed Rejuvenating Tablet

[0086] Suitable tablets to be used for the rejuvenating tablets of the present invention, are described in the co-pending patent application WO99/27063 by The Procter & Gamble Company, internationally filed on November 5, 1998. This application describes a suitable tablet comprising : i) a compressed solid first region having therein at least one mould; and ii) at least one non-compressed second discrete region mounted in the at least one mould of the compressed solid first region, wherein the non-compressed, non-encapsulating second discrete region(s) can be formulated so that at least 90% of the enzyme is delivered to the wash within the first 3 minutes of the rejuvenating process, and more preferably at least 95% of the enzyme is delivered to the wash within the first 2 minutes of the rejuvenating process.

[0087] As described in WO99/27063, enzyme inhibitor and optionally further detergent active component(s) present in the compressed first region may optionally be prepared in combination with a carrier and/or a binder for example polymer (e.g. PEG), liquid silicate and preferably prepared in particulate form. The compressed solid first region may also be provided with a coating of a water-soluble material to protect the first region.

[0088] As described in WO99/27063, the non-compressed, non-encapsulating second discrete region of the present invention comprises at least one enzyme. The enzyme component(s) may be in any form for example particulate (i.e. powder or granular), gel or liquid form. The second discrete region may also optionally comprise a carrier component. The enzyme component may be present in the form of a solid, gel or liquid, prior to combination with a carrier component and is delivered to the compressed first region. It may comprise one or more binding agents, disruptive agent, and/or drying agent and may be coated with a coating layer. The second discrete region may comprise particulates, of different particule sizes or density. The second second discrete region can comprise a solidified melt, may be in a form comprising a dissolved or suspended enzyme component, may be an extrudate or a gel mounted or formed onto the compressed solid first region of the tablet. Such gel form can comprise a thickening system and solid ingredients which are dispersed or suspended within the gel.

[0089] In more details, the first region can be a "Compressed region" as referred to hereinunder and second discrete region can indeed be a "Non-Compressed, Non-Encapsulating Portion" as referred hereinunder:

[0090] The non-compressed, non-encapsulating portion of the tablet may be in solid, gel, liquid or powder form wherein the non-compressed, non-encapsulating portion is delivered to the compressed portion such that the compressed portion and non-compressed, non-encapsulating portion contact each other. The non-compressed, non-encapsulating portion may be delivered to the compressed portion in solid or flowable form. Where the non-compressed, non-encapsulating portion is in solid form, it is pre-prepared, optionally shaped and then delivered to the compressed portion. The non-compressed, non-encapsulating portion is then affixed to a pre-formed compressed portion, for example by adhesion or by insertion of the non-compressed, non-encapsulating portion to a co-operating surface of the compressed portion. The compressed portion comprises at least one mould into which the non-compressed, non-

encapsulating portion/s is/are delivered. The non-compressed, non-encapsulating portion is preferably delivered to the compressed portion in flowable form. The non-compressed, non-encapsulating portion is then affixed to the compressed portion for example by adhesion, by forming a coating over the non-compressed, non-encapsulating layer to secure it to the compressed portion, or by hardening, for example (i) by cooling to below the melting point where the flowable composition becomes a solidified melt; (ii) by evaporation of a solvent; (iii) by crystallization; (iv) by polymerization of a polymeric component of the flowable non-compressed, non-encapsulating portion; (v) through pseudoplastic properties where the flowable non-compressed, non-encapsulating portion comprises a polymer and shear forces are applied to the non-compressed, non-encapsulating portion; (vi) combining a binding agent with the flowable non-compressed, non-encapsulating portion. In an alternative embodiment the flowable non-compressed, non-encapsulating portion may be an extrudate that is affixed to the compressed portion by for example any of the mechanism described above or by expansion of the extrudate to the parameters of a mould provided by the compressed portion.

[0091] The compressed portion comprises at least one mould into which the non-compressed non-encapsulated portion/s is/are delivered. In an alternative embodiment the surface of the compressed portion comprises more than one mould into which the non-compressed, non-encapsulating portion may be delivered. The mould(s) preferably at least partially accommodates one or more non-compressed, non-encapsulating portions. The non-compressed, non-encapsulating portion(s) is then delivered into the mould(s) and affixed to the compressed portion as described above. Alternatively, the detergent tablet contains one mould in which there are two non-compressed, non-encapsulating portions. The first non-compressed, non-encapsulating portion could be added as a liquid, which is allowed to set or harden, or as a pre formed gel. These two different non-compressed, non-encapsulating portion could have different rates of dissolution.

[0092] The non-compressed, non-encapsulating portion may comprise particulates, such as powders or granules. The particulates may be prepared by any known method, for example conventional spray drying, granulation, encapsulation or agglomeration. Particulates may be affixed to the compressed portion by incorporating a binding agent or by forming a coating layer over the non-compressed, non-encapsulating portion.

Where the tablet comprises more than one non-compressed, non-encapsulating portion, the subsequent non-compressed, non-encapsulating portion may comprise particulates having substantially different average particle size and/or can have substantially different density. Tablets in which one or more of the non-compressed, non-encapsulating portion comprise particulates and the average particle size and/or density of the first and the subsequent non-compressed, non-encapsulating portions are substantially different are preferred. Indeed multiple non-compressed, non-encapsulating portions provide different rates of dissolution.

[0093] Where the non-compressed, non-encapsulating portion comprises a solidified melt, the melt is prepared by heating a composition comprising a detergent active component and optional carrier component(s) to above its melting point to form a flowable melt. The flowable melt is then poured into a mould in the surface of the compressed portion and allowed to cool. As the melt cools it becomes solid, taking the shape of the mould at ambient temperature. Where the composition comprises one or more carrier components, the carrier component(s) may be heated to above their melting point, and then an detergent active component may be added. Carrier components suitable for preparing a solidified melt are typically non-active components that can be heated to above melting point to form a liquid and cooled to form an intermolecular matrix that can effectively trap active components. A preferred non-active carrier component is an organic polymer that is solid at ambient temperature. Preferably the non-active detergent component is polyethylene glycol (PEG). The compressed portion of the detergent tablet provides at least one mould to accommodate the melt.

[0094] The flowable non-compressed, non-encapsulating portion may be in a form comprising a dissolved or suspended enzyme component. The flowable non-compressed, non-encapsulating portion may harden over time to form a solid, semi-solid or highly viscous liquid non-compressed, non-encapsulating portion by any of the methods described above. In particular, the flowable non-compressed, non-encapsulating portion may harden by evaporation of a solvent. Solvents suitable for use herein may include any known solvent in which a binding agent is soluble. Preferred solvents may be polar or non-polar and may include water, alcohol, (for example ethanol, acetone) and alcohol derivatives. In an alternative embodiment more than one solvent may be used.

[0095] The flowable non-compressed, non-encapsulating portion may comprise one or more binding agents. Any binding agent that has the effect of causing the composition to become solid, semi-solid or highly viscous over time is envisaged for use herein. Preferred binding agents include a sugar/gelatine combination, starch, glycerol and organic polymers. The sugar may be any monosaccharide (e.g. glucose), disaccharide (e.g. sucrose or maltose) or polysaccharide. The most preferred sugar is commonly available sucrose. For the purposes of the present invention type A or B gelatine may be used, available from for example Sigma. Type A gelatine is preferred since it has greater stability in alkaline conditions in comparison to type B. Preferred gelatine also has a bloom strength of between 65 and 300, most preferably between 75 and 100. Preferred organic polymers include polyethylene glycol (PEG) of molecular weight from 500 to 10,000, preferably from 750 to 8000, most preferably from 1000 to 6000 available from for example from Hoechst.

[0096] Where the non-compressed, non-encapsulating portion is an extrudate, the extrudate is prepared by premixing the enzyme components with optional carrier components to form a viscous paste. The viscous paste is then extruded using any suitable commonly available extrusion equipment such as for example a single or twin screw extruder available from for example APV Baker, Peterborough, U.K. The extrudate is then cut to size either after delivery to the compressed portion, or prior to delivery to the compressed portion of the detergent tablet. The compressed portion of the tablet comprises at least one mould into which the extruded non-compressed, non-encapsulating portion is be delivered.

[0097] In a preferred embodiment the non-compressed, non-encapsulating portion is coated with a coating layer. The coating may be used to affix a non-compressed, non-encapsulating portion to the compressed portion. This may be particularly advantageous where the non-compressed, non-encapsulating portion comprises flowable particulates, gels or liquids. The coating layer preferably comprises a material that becomes solid on contacting the compressed and/or the non-compressed, non-encapsulating portions within preferably less than 15 minutes, more preferably less than 10 minutes, even more preferably less than 5 minutes, most preferably less than 60 seconds. Preferably the coating layer is water-soluble and suitabel materials are described above. The coating layer may also preferably comprise a disrupting agent.

[0098] In a preferred embodiment the compressed and/or non-compressed, non-encapsulating portions and/or coating layer additionally comprise a disrupting agent. The disrupting agent may be a disintegrating or effervescing agent as described above.

[0099] The non-compressed, non-encapsulating portion may additionally contain a drying agent. Any, conventional drying agent can be used. See Vogels Text book of Practical Organic Chemistry, 5th Edition (1989) Longman Scientific & Technical, pp. 165-168, incorporated herein by reference. For example, suitable drying agents are anhydrous $CaSO_4$, anhydrous Na_2SO_4, calcium chloride, sodium sulfite and $MgSO_4$. The selection of suitable drying agents may depend on the end use of the tablet. A drying agent for a detergent tablet for an automatic dishwashing composition for low temperatures preferably is sodium sulfite or calcium chloride, but anhydrous CaSO4, may be used for higher use temperatures. When present, drying agents are included in an amount of about 0.1% to about 15%, more preferably from about 0.1% to about 10%, even more preferably from about 0.5% to about 7%, by weight.

[0100] When the non-compressed, non-encapsulating portion is a gel mounted or formed onto the compressed solid body portion of the detergent tablet into a mould formed on the compressed solid body portion, the non-compressed, non-encapsulating portion may additionally contain a thickening system in addition to the enzyme component. It may further include solid ingredients which are dispersed or suspended within the gel. The solid ingredients aid in the control of the viscosity of the gel formulation in conjunction with the thickening system. When included, the non-compressed, non-encapsulating portion typically comprises at least about 15% solid ingredients, more preferably at least about 30% solid ingredients and most preferably at least about 40% solid ingredients. However, due to pumpability and other processing concerns, the non-compressed, non-encapsulating portion of the present invention typically do not include more than about 90% solid ingredients, when in the form of a gel.

Thickening System

[0101] As noted earlier, such tablet comprises thickening system in the non-compressed, non-encapsulating portion when it is a gel, to provide the proper viscosity or thickness of the gel portion. The thickening system typically comprises a non-aqueous liquid diluent and an organic or polymeric gelling additive.

a) Liquid Diluent

[0102] The term "diluent" is used herein to connote the liquid portion of the thickening system. While some of the essential and/or optional components of the compositions herein may actually dissolve in the "diluent"-containing phase, other components will be present as particulate material dispersed within the "diluent"-containing phase. Thus the term "diluent" is not meant to require that the solvent material be capable of actually dissolving all of the detergent composition components added thereto. Suitable types of diluent useful in the non-aqueous thickening systems herein include alkylene glycol mono lower alkyl ethers, propylene glycols, ethoxylated or propoxylated ethylene or propylene, glycerol esters, glycerol triacetate, lower molecular weight polyethylene glycols, lower molecular weight methyl esters and amides, and the like.

[0103] A preferred type of non-aqueous diluent for use herein comprises the mono-, di-, tri-, or tetra- C_2-C_3 alkylene glycol mono C_2-C_6 alkyl ethers. The specific examples of such compounds include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monoethyl ether, and dipropylene glycol monobutyl ether. Diethylene glycol monobutyl ether and dipropylene glycol monobutyl ether are especially preferred. Compounds of the type have been commercially marketed under the tradenames Dowanol, Carbitol, and Cellosolve.

[0104] Another preferred type of non-aqueous diluent useful herein comprises the lower molecular weight polyeth-

ylene glycols (PEGs). Such materials are those having molecular weights of at least about 150. PEGs of molecular weight ranging from about 200 to 600 are most preferred.

[0105] Yet another preferred type of non-aqueous diluent comprises lower molecular weight methyl esters. Such materials are those of the general formula: R^1-C(O)-OCH_3 wherein R^1 ranges from 1 to about 18. Examples of suitable lower molecular weight methyl esters include methyl acetate, methyl propionate, methyl octanoate, and methyl dodecanoate.

[0106] The non-aqueous organic diluent(s) employed should, of course, be compatible and non-reactive with other composition components, such as the enzymes, used in the tablets herein. Such a diluent component will generally be utilized in an amount of from about 10% to about 60% by weight of the composition. More preferably, the non-aqueous, low-polarity organic diluent will comprise from about 20% to about 50% by weight of the composition, most preferably from about 30% to about 50% by weight of the composition.

b) Gelling Additive

[0107] As noted earlier, a gelling agent or additive is added to the non aqueous diluent of the present invention to complete the thickening system. To form the gel required for suitable phase stability and acceptable rheology of the non-compressed, non-encapsulating portion, the organic gelling agent is generally present to the extent of a ratio of diluent to gelling agent in thickening system typically ranging from about 99:1 to about 1:1 More preferably, the ratios range from about 19:1 to about 4:1.

[0108] The preferred gelling agents of the present invention are selected from castor oil derivatives, propylene glycol, polyethylene glycol, sorbitols and related organic thixatropes, organoclays, cellulose and cellulose derivatives, pluronics, stearates and stearate derivatives, sugar/gelatin combination, starches, glycerol, organic acid amides such as N-lauryl-L-glutamic acid di-n-butyl amide and mixtures thereof.

[0109] The preferred gelling agents are castor oil derivatives. Castor oil is a naturally occurring triglyceride obtained from the seeds of Ricinus Communis, a plant which grows in most tropical or subtropical areas. The primary fatty acid moiety in the castor oil triglyceride is ricinoleic acid (12-hydroxy oleic acid). It accounts for about 90% of the fatty acid moieties. The balance consists of dihydroxystearic, palmitic, stearic, oleic, linoleic, linolenic and eicosanoic moieties. Hydrogenation of the oil (e.g., by hydrogen under pressure) converts the double bonds in the fatty acid moieties to single bonds, thus "hardening" the oil. The hydroxyl groups are unaffected by this reaction.

[0110] The resulting hydrogenated castor oil, therefore, has an average of about three hydroxyl groups per molecule. It is believed that the presence of these hydroxyl groups accounts in large part for the outstanding structuring properties which are imparted to the non-compressed, non-encapsulating portion compared to similar liquid detergent compositions which do not contain castor oil with hydroxyl groups in their fatty acid chains. For use in the compositions of the present invention the castor oil should be hydrogenated to an iodine value of less than about 20, and preferably less than about 10. Iodine value is a measure of the degree of unsaturation of the oil and is measured by the "Wijis Method, " which is well-known in the art. Unhydrogenated castor oil has an iodine value of from about 80 to 90.

[0111] Hydrogenated castor oil is a commercially available commodity being sold, for example, in various grades under the trademark CASTORWAX.RTM. by NL Industries, Inc., Highstown, New Jersey. Other Suitable hydrogenated castor oil derivatives are Thixcin R, Thixcin E, Thixatrol ST, Perchem R and Perchem ST, made by Rheox, Laporte. Especially preferred is Thixatrol ST.

[0112] Polyethylene glycols when employed as gelling agents, rather than solvents, have a molecular weight range of from about 2000 to about 30000, preferably about 4000 to about 12000, more preferably about 6000 to about 10000.

[0113] Cellulose and cellulose derivatives when employed in the present invention preferably include: i) Cellulose acetate and Cellulose acetate phthalate (CAP); ii) Hydroxypropyl Methyl Cellulose (HPMC); iii)Carboxymethylcellulose (CMC); and mixtures thereof. The hydroxypropyl methylcellulose polymer preferably has a number average molecular weight of about 50,000 to 125,000 and a viscosity of a 2 wt. % aqueous solution at 25°C (ADTMD2363) of about 50,000 to about 100,000 cps. An especially preferred hydroxypropyl cellulose polymer is Methocel® J75MS-N wherein a 2.0 wt. % aqueous solution at 25°C. has a viscosity of about 75,000 cps.

[0114] The sugar may be any monosaccharide (e.g. glucose), disaccharide (e.g. sucrose or maltose) or polysaccharide. The most preferred sugar is commonly available sucrose. Type A or B gelatin may be used, available from for example Sigma. Type A gelatin is preferred since it has greater stability in alkaline conditions in comparison to type B. Preferred gelatin also has a bloom strength of between 65 and 300, most preferably between 75 and 100.

[0115] The non-compressed, non-encapsulating portion may include a variety of other ingredients in addition to the thickening agent as herein before described and the enzyme component disclosed in more detail above. Ingredients such as perfumes and dyes may be included as well as swelling/adsorbing agents such as carboxymethylcelluloses and starches to aid in adsorption of excess diluent or aid in the dissolution or breakup of the non-compressed, non-encapsulating portion in the wash. In addition, hardness modifying agents may incorporated into the thickening system to adjust the hardness of the gel if desired. These hardness control agents are typically selected from various polymers

and polyethylene glycol's and when included are typically employed in levels of less than about 20% and more preferably less than about 10% by weight of the solvent in the thickening system. For example, hardening agents, such as high molecular weight PEG, preferably of a molecular weight from 10,000 to 20,000 or possibly even higher molecular weight, can be added to decrease the hardening time of the non-compressed, non-encapsulating portion. Alternatively, water soluble polymeric materials such as of low molecular weight polyethylene glycols may be added to the mould to form an intermediate barrier layer prior to addition of the non-compressed, non-encapsulating portion when it is a gel. This speeds cooling and hardening of the gel by the melting/mixing of the water soluble polymeric material when the gel is added to the at least one mould. In addition, the intermediate layer may act as a barrier to prevent ingredients from the gel mixing or bleeding into the compressed portion. Addition of an alkaline material, such as sodium or potassium hydroxide can also speed in hardening of the non-compressed, non-encapsulating portion when it is a gel. Preferably, these alkaline materials would be added to the mould before the addition of the gel. However, in alternative systems, the alkaline material may be added to the gel composition. These alkaline materials also have the advantage of acting as an additional alkalinity source that is discrete and would be slower dissolving and hence have a minimal impact on any effervescence system present in the non-compressed, non-encapsulating portion yet provide an alkalinity boost in the wash.

[0116] When it is a gel the non-compressed, non-encapsulating portion is formulated so that the gel is a pumpable, flowable gel at slightly elevated temperatures of around 30°C or greater to allow increased flexibility in producing the detergent tablet, but becomes highly viscous or hardens at ambient temperatures so that the gel in maintained in position in the at least one mould in the compressed solid body portion of the detergent tablet through shipping and handling of the detergent tablet. Such hardening of the non-compressed, non-encapsulating portion may achieved, for example, by (i) by cooling to below the flowable temperature of the gel; (ii) by evaporation of the diluent; or by (iii) by polymerization of the gelling agent. Preferably, the gel portion is formulated such that the gel hardens to sufficiently so that the maximum force needed to push a probe into the dimple preferably ranges from about 0.5N to about 40N. This force may be characterized by measuring the maximum force needed to push a probe, fitted with a strain gauge, a set distance into the gel. The set distance may be between 40 and 80% of the total gel depth. This force can be measured on a QTS 25 tester, using a probe of 5mm diameter. Typical forces measured are in the range of 1N to 25N.

[0117] Additionally, it is preferred that when a 48 hour old tablet is inverted, at ambient conditions, for 10 minutes, more preferably 30 minutes, even more preferably 2 hours, the non-compressed, non-encapsulating portion does not drip or separate from the compressed solid body.

Other suitable Rejuvenating Tablets

[0118] Other suitable tablets forms that can be used for the rejuvenating tablets of the present invention are described in the following co-pending patent applications :

[0119] The co-pending patent application US99/15490 internationally filed by The Procter & Gamble Company on September 7, 1999, provides another suitable for the rejuvenating tablet of the present invention. It describes a multi-phase detergent tablet for use in a washing machine, the tablet comprising a first phase in adhesive contact with one or more second phases, at least one second phase being in the form of a compressed particulate solid incorporating liquid adhesive and having an average porosity of less than about 0.15 ml/g, preferably less than about 0.13 ml/g and more preferably less than about 0.11 ml/g.

[0120] The co-pending patent application WO99/24547 internationally filed on November 5, 1998 by The Procter & Gamble Company, describes a further tablet form that could be used for the rejuvenating tablet of the present invention. WO99/24547 describes a tablet comprising one or more ingredients and wherein at least one detergent composition is compressed and dissolves in a dishwashing machine in less than 3 minutes, preferably in less than 2.5 minutes, most preferably less than 2 minutes or even less than 1 minute, determined according to DIN 44990 using a dishwashing machine available from Bosch on the normal 65°C washing programme with water hardness at 18°d. Such tablets can comprise an explosive detergent-release component. Such tablet may be a multi-layer tablet wherein each layer comprises a one or more ingredient(s). Optional additional layers may be formed by compression or may be non-compressed layers.

[0121] Co-pending European patent application EP 99 305386.7 filed by The Procter & Gamble Company on July 7, 1999, describes further suitable tablets to be used for the purpose of the present invention, allowing to achieve further differential dissolution of the phases, such that one phase of the tablet will dissolve significantly before another phase, and may even dissolve essentially completely before the other phase has dissolved. Co-pending patent European application EP 99 305386.7 (See above) provides for a multi-phase tablet for use in a washing machine, said tablet comprising: a) a first phase in the form of a shaped body having at least one mould therein; and b) a second phase in the form of a particulate solid compressed within said mould, and wherein the second phase additionally comprises a binder. Said binder will provide for the slow release of the binder-containing phase allowing the slow release of a further ingredient.

[0122] Indeed, the rejuvenating tablet of the present invention can further comprise a third subsequent step, i.e. after the enzyme treatment or after the enzyme and inhibitor treatments, whereby a fabric care and/or detergent ingredient is released. Suitable tablets to be used for such purpose are described in the co-pending European patent application EP 99 305386.7 (see above).

DETERGENT COMPONENTS

[0123] As indicated above, the first region of the rejuvenating tablet of the present invention comprises an enzyme inhibitor and can be a fully-formulated laundry detergent composition.

[0124] Suitable detergent ingredients to be included in the first region of the rejuvenating tablet of the present invention, in addition of the above cited inhibitors are described in the co-pending patent application WO99/07819 internationally filed on August 4, 1998 by The Procter & Gamble Company. The levels herebelow are expressed in % by weight of the first region.

[0125] Detersive surfactants : as described above in the description of suitable enzyme inhibitors, Nonlimiting examples of surfactants useful herein, include the conventional C_{11}-C_{18} alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C_{10}-C_{20} alkyl sulfates ("AS"), the C_{10}-C_{18} secondary (2,3) alkyl sulfates of the formula $CH_3(CH_2)_x(CHOSO_3^-M^+)$ CH_3 and CH_3 $(CH_2)_y(CHOSO_3^-M^+)$ CH_2CH_3 where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C_{10}-C_{18} alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C_{10}-C_{18} alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C_{10-18} glycerol ethers, the C_{10}-C_{18} alkyl polyglycosides and their corresponding sulfated polyglycosides, and C_{12}-C_{18} alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C_{12}-C_{18} alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C_6-C_{12} alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C_{12}-C_{18} betaines and sulfobetaines ("sultaines"), C_{10}-C_{18} amine oxides, and the like, can also be included in the overall compositions. The C_{10}-C_{18} N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C_{12}-C_{18} N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C_{10}-C_{18} N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C_{12}-C_{18} glucamides can be used for low sudsing. C_{10}-C_{20} conventional soaps may also be used. If high sudsing is desired, the branched-chain C_{10}-C_{16} soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

[0126] Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils. The level of builder can vary widely depending upon the end use of the composition.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders. Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1}\cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$M_z(zAlO_2)_y]\cdot xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264. Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxy-disuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C_{12}-C_{18} monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

[0127] Bleach : The rejuvenating composition herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from 1-30%, more typically from 5-20%, of the detergent composition. If present, the amount of bleach activators will typically be from 0.1-60%, more typically from 0.5-40% of the bleaching composition comprising the

bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetrahydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

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

Mixtures of bleaching agents can also be used.

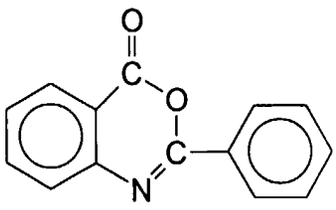
Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Highly preferred amido-derived bleach activators are those of the formulae:

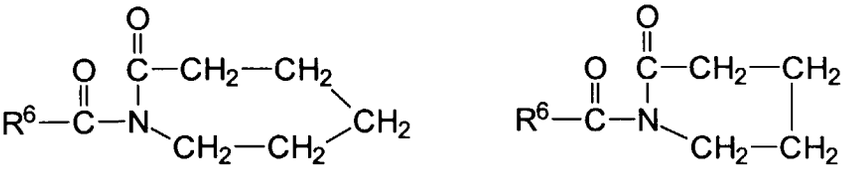
$$R^1N(R^5)C(O)R^2C(O)L \text{ or } R^1C(O)N(R^5)R^2C(O)L$$

wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate. Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

[0128] Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U. S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



[0129] Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U. S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6$(1,4,7-triazacyclononane)$_4(ClO_4)_4$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2(ClO_4)_3$, Mn^{IV}(1,4,7-trimethyl-1,4,7-triazacyclononane)- $(OCH_3)_3(PF_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

[0130] Other components which are commonly used in detergent compositions and which may be incorporated into the rejuvenating compositions of the present invention include chelating agents, soil release agents, soil antiredeposition agents, dispersing agents, brighteners, suds suppressors, fabric softeners, dye transfer inhibition agents, enzyme at a lower level as described above and perfumes.

FURTHER FABRIC TREATMENT COMPONENTS

[0131] As described above, the rejuvenating process of the present invention can be further coupled with a fabric care process. Similarly, the rejuvenating compositions of the present invention may further comprise in the first region or in any subsequently released phase, a fabric care ingredient. Suitable fabric care ingredients are described below. These fabric care ingredients are preferably released after the enzyme treatment step and more preferably after the enzyme and inhibitor treatment steps.

[0132] Such fabric care ingredients can be incorporated into the thirdly released phase of the rejuvenating composition of the present invention or can be used within a separate fabric care composition (Levels are expressed in % by weight of the first region):

a) Optionally from 0.01-60%, preferably from 10-50% by weight of a modified cellulosic material:

b) Optionally from 0.01%, preferably from 0.1% to 20%, preferably to 10% by weight, of a fabric abrasion reducing polymer, said fabric abrasion polymer comprising:

i) at least one monomeric unit comprising an amide moiety;

ii) at least one monomeric unit comprising an N-oxide moiety;

iii) and mixtures thereof;

c) Optionally from 1%, preferably from 10%, more preferably from 20% to 80%, preferably to 60%, more preferably to 45% by weight, of a fabric softening active;
d) Optionally less than 15% by weight, of a principal solvent, preferably said principal solvent has a ClogP of from 0.15 to 1;
e) Optionally from 0.001 % to 90% by weight, of one or more dye fixing agents;
f) Optionally from 0.01% to 50% by weight, of one or more cellulose reactive dye fixing agents;
g) Optionally from 0.01% to 15% by weight, of a chlorine scavenger;
h) Optionally 0.005% to 1 % by weight, of one or more crystal growth inhibitors;
j) Optionally from 0.01% to 8% by weight, of a polyolefin emulsion or suspension;
k) Optionally from 0.01 % to 0.2% by weight, of a stabilizer;
l) Optionally from 1 % to 80% by weight, of a fabric softening active; and
m) Optionally from 0.01% by weight, of one or more linear or cyclic polyamines which provide bleach protection;

[0133] Such ingredients and/or composition formulated therewith as described in the co-pending US patent application US60/106759 and US60/110310 respectively filed on November 2, 1998 and November 30, 1998 by The Procter & Gamble Company, will provide in particular a fabric anti-abrasion benefit, i.e. when applied to fabric provide a reduction in the amount of damage which is incurred by the fabric, and a dye transfer inhibition benefit.

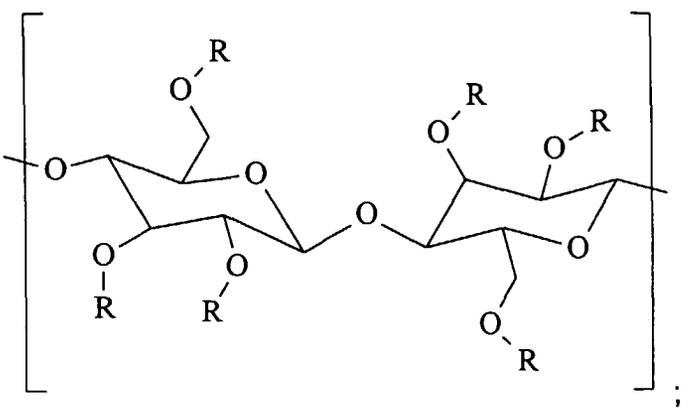
Hydrophobically Modified Cellulosic Based Polymers or Oligomers

[0134] Most preferred additional fabric care ingredient to be used in the rejuvenating process and composition of the present invention are the hydrophobically modified cellulosic based materials. Such materials have been found to impart a number of appearance benefits to fabrics and textiles. Such fabric appearance benefits can include, for example, improved overall appearance of the laundered fabrics, reduction of the formation of pills and fuzz, protection against colour fading, improved abrasion resistance, etc. Indeed, it is believed that such materials reduce the rate of pills formation and increase the strength of the cellulosic fibres.

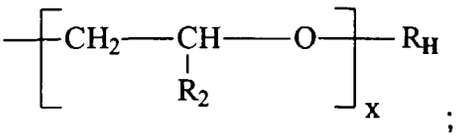
[0135] Preferably the cellulosic materials are released after 90 to 120 minutes from the beginning of the rejuvenating treatment and even preferred during the rinse cycles. When encompassed in the rejuvenating tablets of the present invention, the cellulosic materials are comprised at a level of from 0.01-60%, preferably from 10-50% by weight of the total composition.

[0136] As will be apparent to those skilled in the art, an oligomer is a molecule consisting of only a few monomer units while polymers comprise considerably more monomer units. For the present invention, oligomers are defined as molecules having an average molecular weight below about 1,000 and polymers are molecules having an average molecular weight of greater than about 1,000. One suitable type of cellulosic based polymer or oligomer fabric treatment material for use herein has an average molecular weight of from about 5,000 to about 2,000,000, preferably from about 50,000 to about 1,000,000.

[0137] One suitable group of cellulosic based polymer or oligomer materials for use herein is characterized by the following formula:

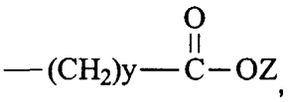


wherein each R is selected from the group consisting of R_2, R_c, and



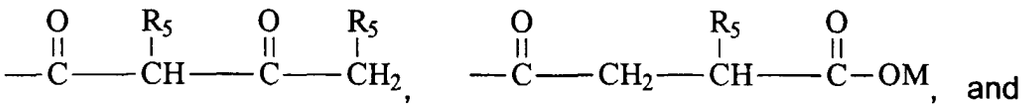
wherein:

- each R_2 is independently selected from the group consisting of H and C_1-C_4 alkyl;
- each R_c is

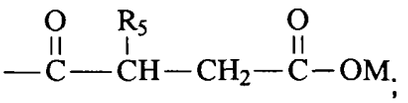


wherein each Z is independently selected from the group consisting of M, R_2, R_c, and R_H;

- each R_H is independently selected from the group consisting of C_5 -C_{20} alkyl, C_5-C_7 cycloalkyl, C_7-C_{20} alkylaryl, C_7-C_{20} arylalkyl, substituted alkyl, hydroxyalkyl, C_1-C_{20} alkoxy-2-hydroxyalkyl, C_7-C_{20} alkylaryloxy-2-hydroxyalkyl, $(R_4)_2$N-alkyl, $(R_4)_2$N-2-hydroxyalkyl, $(R_4)_3$ N-alkyl, $(R_4)_3$ N-2-hydroxyalkyl, C_6-C_{12} aryloxy-2-hydroxyalkyl,



and



- each R_4 is independently selected from the group consisting of H, C_1-C_{20} alkyl, C_5-C_7 cycloalkyl, C_7-C_{20} alkylaryl, C_7-C_{20} arylalkyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, piperidinoalkyl, morpholinoalkyl, cycloalkylaminoalkyl and hydroxyalkyl;
- each R_5 is independently selected from the group consisting of H, C_1-C_{20} alkyl, C_5-C_7 cycloalkyl, C_7-C_{20} alkylaryl, C_7-C_{20} arylalkyl, substituted alkyl, hydroxyalkyl, $(R_4)_2$N-alkyl, and $(R_4)_3$N-alkyl;

wherein:

M is a suitable cation selected from the group consisting of Na, K, 1/2Ca, and 1/2Mg;
each x is from 0 to about 5;
each y is from about 1 to about 5; and

provided that:

- the Degree of Substitution for group R_H is between about 0.001 and 0.1, more preferably between about 0.005 and 0.05, and most preferably between about 0.01 and 0.05;
- the Degree of Substitution for group R_c wherein Z is H or M is between about 0.2 and 2.0, more preferably between about 0.3 and 1.0, and most preferably between about 0.4 and 0.7;
- if any R_H bears a positive charge, it is balanced by a suitable anion; and
- two R_4's on the same nitrogen can together form a ring structure selected from the group consisting of piperidine and morpholine.

[0138] The "Degree of Substitution" for group R_H, which is sometimes abbreviated herein "DS_{RH}", means the number of moles of group R_H components that are substituted per anhydrous glucose unit, wherein an anhydrous glucose unit is a six membered ring as shown in the repeating unit of the general structure above.

[0139] The "Degree of Substitution" for group R_c, which is sometimes abbreviated herein "DS_{RC}", means the number

of moles of group R_c components, wherein Z is H or M, that are substituted per anhydrous glucose unit, wherein an anhydrous glucose unit is a six membered ring as shown in the repeating unit of the general structure above. The requirement that Z be H or M is necessary to insure that there are a sufficient number of carboxy methyl groups such that the resulting polymer is soluble. It is understood that in addition to the required number of R_c components wherein Z is H or M, there can be, and most preferably are, additional R_c components wherein Z is a group other than H or M.

[0140] Suitable hydrophobically modified carboxyl methyl cellulose for use in the present invention are those available from Metsa Speciality Chemicals such as the preferred material sold under the tradename Finofix.

Fabric Abrasion Reducing Polymers

[0141] Suitable fabric abrasion reducing polymers are described in the co-pending US patent application US60/110310 on pages 4 to 9 of the version as filed (See above). The molecular weight of these fabric abrasion reducing polymers are from 500, preferably from 1,000, more preferably from 100,000 most preferably from 160,000 to 6,000,000, preferably to 2,000,000, more preferably to 1,000,000, yet more preferably to 500,000, most preferably to 360,000 daltons. Theses polymers are polymers comprising amide units, polymers comprising N-oxide units and/or polymers comprising amide and N-oxide units.

[0142] Polymers comprising amide units are polyvinyl-pyrrolidones, polyvinyloxazolidones, N,N-disubstituted polyacrylamides, and N,N-disubstituted polymethacrylamides. A preferred polymeric compound is polyvinylpyrrolidone (PVP). This polymer has an amphiphilic character with a highly polar amide group conferring hydrophilic and polar-attracting properties, and also has non-polar methylene and methine groups, in the backbone and/or the ring, conferring hydrophobic properties. The rings may also provide planar alignment with the aromatic rings in the dye molecules. PVP is readily soluble in aqueous and organic solvent systems. PVP is available ex ISP, Wayne, New Jersey, and BASF Corp., Parsippany, New Jersey, as a powder or aqueous solutions in several viscosity grades, designated as, e.g., K-12, K-15, K-25, and K-30. These K-values indicate the viscosity average molecular weight, as shown below:

PVP viscosity average molecular weight (in thousands of daltons)	K-12	K-15	K-25	K-30	K-60	K-90
	2.5	10	24	40	160	360

PVP K-12, K-15, and K-30 are also available ex Polysciences, Inc. Warrington, Pennsylvania, PVP K-15, K-25, and K-30 and poly(2-ethyl-2-oxazoline) are available ex Aldrich Chemical Co., Inc., Milwaukee, Wisconsin. PVP K30 (40,000) through to K90 (360,000) are also commercially available ex BASF under the tradename Luviskol or commercially available ex ISP. Still higher molecular PVP like PVP 1.3MM, commercially available ex Aldrich is also suitable for use herein. Yet further PVP-type of material suitable for use in the present invention are polyvinylpyrrolidone-co-dimethylaminoethylmethacrylate, commercially available commercially ex ISP in a quaternised form under the tradename Gafquat® or commercially available ex Aldrich Chemical Co. having a molecular weight of approximately 1.0MM; polyvinylpyrrolidone-co-vinyl acetate, available ex BASF under the tradename Luviskol®, available in vinylpyrrolidone: vinylacetate ratios of from 3:7 to 7:3.

[0143] A preferred polymer comprising N-oxide units is poly(4-vinylpyriding N-oxide, PVNO. The average molecular weight of the N-oxide comprising polymers which provide a dye transfer inhibitor benefit to reduced fabric abrasion polymers is from about 500 daltons, preferably from about 100,000 daltons, more preferably from about 160,000 daltons to about 6,000,000 daltons, preferably to about 2,000,000 daltons, more preferably to about 360,000 daltons.

Dye Fixing Agents

[0144] The compositions of the present invention optionally comprise from 0.001%, preferably from 0.5% to 90%, preferably to 50%, more preferably to 10%, most preferably to 5% by weight, of one or more dye fixing agents. Dye fixing agents, or "fixatives", are well-known, commercially available materials which are designed to improve the appearance of dyed fabrics by minimizing the loss of dye from fabrics due to washing. Not included within this definition are components which can in some embodiments serve as fabric softener actives. Suitable fixatives compounds are described in the co-pending US patent application US60/110310 on pages 12-15 of the version as filed (See above). A preferred dye fixing agent for use in the compositions of the present invention is CARTAFIX CB® ex Clariant.

[0145] Another dye fixing agent suitable for use in the present invention are cellulose reactive dye fixing agents as described in the co-pending US patent application US60/110310 on pages 13-15 of the version as filed (See above).

The compositions of the present invention optionally comprise from 0.01%, preferably from 0.05%, more preferably from 0.5% to 50%, preferably to 25%, more preferably to 10% by weight, most preferably to 5% by weight, of one or more cellulose reactive dye fixing agents. The cellulose reactive dye fixatives may be suitably combined with one or more dye fixatives described herein above in order to comprise a "dye fixative system". The term "cellulose reactive dye fixing agent" is defined herein as "a dye fixative agent which reacts with the cellulose fibers upon application of heat or upon a heat treatment either *in situ* or by the formulator" and can be defined by the Cellulose Reactivity Test (CRT) as described in in the co-pending US patent application US60/110310 on pages 13-15 of the version as filed (See above). Preferred cellulose reactive dye fixing agents are hydroxyethylene urea derivatives including dimethyloldihydroxyethylene, urea, and dimethyl urea glyoxal. Preferred formaldehyde condensation products include the condensation products derived from formaldehyde and a group selected from an amino-group, an imino-group, a phenol group, an urea group, a cyanamide group and an aromatic group. Most preferred cellulosic reactive dye fixing agents are commercialized under the tradename Rewin DWR and Rewin WBS ex CHT R. Beitlich.

Chlorine Scavengers

[0146] The compositions of the present invention optionally comprise from 0.01%, preferably from 0.02%, more preferably from 0.25% to 15%, preferably to 10%, more preferably to 5% by weight, of a chlorine scavenger. In cases wherein the cation portion and the anion portion of the non-polymeric scavenger each react with chlorine, the amount of scavenger can be adjusted to fit the needs of the formulator.
Suitable chlorine scavengers include ammonium salts having the formula:

$$[(R)_3R^1N]^+ X^-$$

wherein each R is independently hydrogen, C_1-C_4 alkyl, C_1-C_4 substituted alkyl, and mixtures thereof, preferably R is hydrogen or methyl, more preferably hydrogen. R^1 is hydrogen C_1-C_9 alkyl, C_1-C_9 substituted alkyl, and mixtures thereof, preferably R is hydrogen. X is a compatible anion, non-limiting examples include chloride, bromide, citrate, sulfate; preferably X is chloride. Non-limiting examples of preferred chlorine scavengers includ ammonium chloride, ammonium sulfate, and mixtures thereof; preferably ammonium chloride.

Crystal Growth Inhibitor

[0147] The compositions of the present invention optionally comprise from 0.005%, preferably from 0.5%, more preferably from 0.1% to 1%, preferably to 0.5%, more preferably to 0.25%, most preferably to 0.2% by weight, of one or more crystal growth inhibitors. The "Crystal Growth Inhibition Test" is used to determine the suitability of a material for use as a crystal growth inhibitor as described in the co-pending US patent application US60/110310 on pages 15-17 of the version as filed (See above).
[0148] The preferred crystal growth inhibitors are selected from the group consisting of carboxylic compounds, organic diphosphonic acids, and mixtures thereof.

- Non-limiting examples of carboxylic compounds include glycolic acid, phytic acid, polycarboxylic acids, polymers and co-polymers of carboxylic acids and polycarboxylic acids, and mixtures thereof. Examples of commercially available materials include, polyacrylate polymers Good-Rite® ex BF Goodrich, Acrysol® ex Rohm & Haas, Sokalan® ex BASF, and Norasol® ex Norso Haas. Preferred are the Norasol® polyacrylate polymers, more preferred are Norasol ® 410N (MW 10,000) and Norasol® 440N (MW 4000) which is an amino phosphonic acid modified polyacrylate polymer, and also more preferred is the acid form of this modified polymer sold as Norasol® QR 784 (MW 4000) ex Norso-Haas.
- Organic diphosphonic acid are also suitable for use as crystal growth inhibitors. For the purposes of the present invention the term "organic diphosphonic acid" is defined as "an organo-diphosphonic acid or salt which does not comprise a nitrogen atom". Preferred organic diphosphonic acids include C_1-C_4 diphosphonic acid, preferably C_2 diphosphonic acid selected from the group consisting of ethylene diphosphonic acid, α-hydroxy-2 phenyl ethyl diphosphonic acid, methylene diphosphonic acid, vinylidene-1,1-diphosphonic acid, 1,2-dihydroxyethane-1,1-diphosphonic acid, hydroxy-ethane 1,1 diphosphonic acid, the salts thereof, and mixtures thereof. More preferred is hydroxyethane-1,1-diphosphonic acid (HEDP).
- Still useful herein as crystal growth inhibitor are the organic monophosphonic acid. Organo monophosphonic acid or one of its salts or complexes is also suitable for use herein as a crystal growth inhibitor. By organo monophosphonic acid it is meant herein an organo monophosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be

included in compositions of the invention as heavy metal ion sequestrants. The organo monophosphonic acid component may be present in its acid form or in the form of one of its salts or complexes with a suitable counter cation. Preferably any salts/complexes are water soluble, with the alkali metal and alkaline earth metal salts/complexes being especially preferred. A prefered organo monophosphonic acid is 2-phosphonobutane-1,2,4-tricarboxylic acid commercially available from Bayer under the tradename of Bayhibit.

Fabric Softening Actives

[0149] The compositions of the present invention optionally comprise at least 1%, preferably from 10%, more preferably from 20% to 80%, more preferably to 60%, most preferably to 45% by weight, of the composition of one or more fabric softener actives. Suitable fabric softening actives are described in the co-pending US patent application US60/110310 on pages 18-23 of the version as filed (See above).
. The following are examples of preferred softener actives according to the present invention.

N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(canolyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
N,N-di(canolyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
N,N-di(tallowylamidoethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
N,N-di(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(2-canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(2-tallowyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
N,N-di(2-canolyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
N-(2-tallowoyloxy-2-ethyl)-N-(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N-(2-canolyloxy-2-ethyl)-N-(2-canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
N,N,N-tri(canolyl-oxy-ethyl)-N-methyl ammonium chloride;
N-(2-tallowyloxy-2-oxoethyl)-N-(tallowyl)-N,N-dimethyl ammonium chloride;
N-(2-canolyloxy-2-oxoethyl)-N-(canolyl)-N,N-dimethyl ammonium chloride;
1,2-ditallowyloxy-3-N,N,N-trimethylammoniopropane chloride; and
1,2-dicanolyloxy-3-N,N,N-trimethylammoniopropane chloride;

and mixtures of the above actives.
Particularly preferred is N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium chloride, where the tallow chains are at least partially unsaturated and N,N-di(canoloyl-oxy-ethyl)-N,N-dimethyl ammonium chloride, N,N-di(tallowyl-oxyethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate; N,N-di(canolyloxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate; and mixtures thereof.

Hydrophobic Dispersant

[0150] As described in the co-pending US patent application US60/110310 on pages 25-27 of the version as filed (See above), the composition of the present invention can further comprise from 0.1%, preferably from 5%, more preferably form 10% to 80%, preferably to 50%, more preferably to 25% by weight, of a color care hydrophobic polyamine dispersant having the formula:

$$[(R^1)_2N-R]_w[N-R]_x[N-R]_yN(R^1)_2$$

wherein R, R^1 and B are suitably described in U.S. 5,565,145 Watson et al., issued October 15, 1996 incorporated herein by reference, and w, x, and y have values which provide for a backbone prior to substitution of preferably at least about 1200 daltons, more preferably 1800 daltons.
[0151] R^1 units are preferably alkyleneoxy units having the formula:

$$-(CH_2CHR'O)_m(CH_2CH_2O)_nH$$

wherein R' is methyl or ethyl, m and n are preferably from about 0 to about 50, provided the average value of alkoxylation provided by m + n is at least about 0.5.

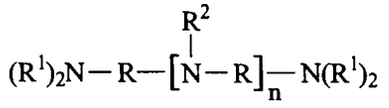
[0152] A further description of polyamine dispersants suitable for use in the present invention is found in U.S. 4,891,160 Vander Meer, issued January 2, 1990; U.S.4,597,898, Vander Meer, issued July 1, 1986; European Patent Application 111,965, Oh and Gosselink, published June 27, 1984; European Patent Application 111,984, Gosselink, published June 27, 1984; European Patent Application 112,592, Gosselink, published July 4, 1984; U.S. 4,548,744, Connor, issued October 22, 1985; and U.S. 5,565,145 Watson et al., issued October 15, 1996; all of which are included herein by reference. However, any suitable clay/soil dispersent or anti-redepostion agent can be used in the laundry compositions of the present invention.

Bleach Protection Polyamines

[0153] As described in the co-pending US patent application US60/110310 on pages 32-33 of the version as filed (See above), the compositions of the present invention optionally comprise from 0.01%, preferably from 0.75%, more preferably from 10%, most preferably from 15% to 50%, preferably to 35%, more preferably to 30%, most preferably to 5% by weight, of one or more linear or cyclic polyamines which provide bleach protection.

Linear Polyamines

[0154] The bleach protection polyamines are of the formula:



wherein R is 1,2-propylene, 1,3-propylene, and mixtures thereof; preferably 1,3-propylene. R^1 is hydrogen or an alkyleneoxy unit having the formula:

$$-(R^3O)-R^4$$

wherein R^3 is ethylene, 1,2-propylene, 1,2-butylene, or mixtures thereof; preferably R^3 is ethylene or 1,2-propylene, more preferably 1,2-propylene. R^4 is hydrogen, C_1-C_4 alkyl, and mixtures thereof; preferably hydrogen. R^1 may comprise any mixture of alkyleneoxy units. R^2 is hydrogen, R^1, $-RN(R^1)_2$, and mixtures thereof; preferably at least one R^2 is hydrogen when n is equal to 2. The integer n is 1 or 2.

A prefered bleach protection linear polyamine has a backbone wherein R is 1,3-propylene, R^2 is hydrogen, or alkoxy, and n is equal to 2 is N,N'-bis(3-aminopropyl)-1,3-propylenediamine (TPTA).

Cyclic Amines

[0155] The bleach protection cyclic polyamines comprise polyamine backbones having the formula:

$$R\text{-}L\text{-}R$$

wherein L is a linking unit, said linking unit comprising a ring having at least 2 nitrogen atoms; R is hydrogen, $-(CH_2)_kN(R^1)_2$, and mixtures thereof; wherein each index k independently has the value from 2 to 4, preferably 3. Preferably the backbone of the cyclic amines including R units is 200 daltons or less. R^1 is hydrogen or an alkyleneoxy unit having the formula:

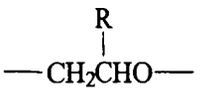
$$-(R^3O)-R^4$$

wherein R^3 is ethylene, 1,2-propylene, 1,2-butylene, or mixtures thereof; preferably R^3 is ethylene or 1,2-propylene, more preferably 1,2-propylene. R^4 is hydrogen, C_1-C_4 alkyl, and mixtures thereof; preferably hydrogen. R^1 may comprise any mixture of alkyleneoxy units.

Examples of preferred optional polyamines have the formula:

$$(R^1)_2N\text{-}(CH_2)_k\text{—}L\text{—}(CH_2)_k\text{-}N(R^1)_2$$

wherein the indices k each have the same value and each R^1 is the same unit. It has been found that bleach protection is enhanced when the backbone nitrogens are substituted with one or more modifications which comprise an alkyleneoxy unit having the general formula:



wherein said unit is R^3 as defined herein above.

[0156] The rejuvenating compositions of the present invention can further comprise a perfume, a properfume, a stabiliser, dispersing olefins such as Velustrol®, sun protecting agent, a bacteriocide, a preservative, and the following ingredients described in the co-pending US patent applications US60/106759 and US60/110310 (See above): a solvent, an electrolyte, a cationic charge booster, a dispersibility aid, a soil release agent and mixtures thereof.

[0157] The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

Example 1

[0158] The following rejuvenating tablets were prepared in accordance with the present invention.

	I	II	III	IV	V	VI
First Region	g/tablet	g/tablet	g/tablet	g/tablet	g/tablet	g/tablet
LAS	-	11.0	22.0	21.0	11.0	17.0
AS	-	3.0	6.0	6.0	3.0	5.0
powder soap	-	1.5	3.0	3.0	1.5	3.0
HFA	-	4.0	4.0	4.0	4.0	10.0
EMC	-	-	-	-	-	20.0
Second second discrete region						
Cellulase	1.3	2.6	2.6	1.3	1.3	1.3
Citric acid	0.5	1.0	1.0	0.5	0.5	0.5
Bicarbonate	2.0	4.0	4.0	2.0	2.0	2.0
PEG 4000	1.3	2.5	2.5	1.3	1.3	1.3
Total	5.1	29.6	45.1	39.1	24.6	60.1

[0159] The second discrete region can further comprise 0.01g/tablet of a dye.

[0160] Wherein the abbreviations have the following meaning :

LAS	Sodium salt of linear dodecyl benzene sulphonate
AS	Sodium salt of alkyl (C14-C15) sulphate
Powder soap	Dried powdered sodium soap made from fully saponified blend of Tallow and Coconut or Palm Kernel glycerides
Cellulase	Carezyme (100000 cevu/g raw material from Novo Nordisk, 30% protein content + sodium sulphate and minors)
HFA	Hydrogenated fatty acid (C16-C22), such as sold by Fina under the tradename Radiacid, is used for the coating
EMC	Ethoxy modified cellulosic polymer sold under the tradename Finofix by the Metsa Speciality Chemicals
PEG x	Polyethylene glycol MW about x such as available from Hoechst

Example 2

[0161] The following rejuvenating tablets were prepared in accordance with the present invention. The second second discrete region of the tablet has the following composition wherein the abbreviations have the meaning as described above in example 1.

Second discrete region	g/tablet
Cellulase	1.3
Citric acid	0.5
Bicarbonate	2.0
PEG 4000	1.2
Total	5

[0162] About 15 grams of the below composition was used to formulate the first region.

	% First region
Dry add	
Anionic surfactant agglomerate A	9.8
Anionic surfactant agglomerate B	22.3
Nonionic surfactant agglomerate	9.1
Cationic surfactant agglomerate	4.7
Bleach activator agglomerate	6.1
Zinc Phthalocyanine sulfonate encapsulate	0.03
Suds suppressor	2.8
Layered silicate	9.7
Fluorescer	0.11
Sodium carbonate	8.1
Citric acid	4.7
Sodium percarbonate	12.3
Chelant particle	0.49
1,1-hydroxyethane diphosphonic acid.	0.8
Soil release polymer	0.4
Protease prill	1.0
Cellulase prill	0.2
Lipase prill	0.3
Amylase prill	1.1
Soap	1.4
Spray-on	
Perfume	0.6
Binder	4.0
TOTAL	100%

[0163] Anionic agglomerate A include 40% anionic surfactant, 29% Zeolite and 20% Sodium carbonate.
Anionic agglomerate B include 40% anionic surfactant, 27% Zeolite and 11% Sodium carbonate.
Nonionic agglomerate comprises 25% nonionic surfactant, 7% polyethoxylated hexamethylene diamine (quaternary salt), 36% anhydrous sodium acetate , 20% sodium carbonate and 12% Zeolite.
Cationic agglomerate include 20% cationic surfactant and 56% Zeolite.
Bleach activator agglomerate comprises 81% TAED, 17% acrylic/maleic copolymer and 2% water.
Zinc Phthalocyanine sulfonate encapsulates are 10% active.
Suds suppressor comprises 11.5% silicone oil and 88.5% starch.

Layered silicate comprises 95% SKS-6, 2.5% Sodium silicate-2.0R and 2.5% water.
Fluorescer contains Brightener 47 (70% active) and Brightener 49 (13% active).
Chelant particle contains ethylene diamine disuccinate and is 58% active.
Soil Release Polymer: Anionically end capped polyesters
Amylase prill : Amylolytic enzyme agglomerate (120 KNU/g) sold under the tradename Termamyl by Novo Nordisk A/S
Cellulase prill : Cellulolytic enzyme agglomerate sold under the tradename Carezyme by Novo Nordisk AS/S (1000 cevu/g)
Protease prill : Proteolytic enzyme granule as described in W095/10591 and WO95/10592 with the amino acid substitution set n set N76D/S103A/V1041 sold by Genencor FN3 protease (20 APU/g)
Lipase prill : Lipolytic granule of Lipolase ultra 50T sold by Novo Nordisk (KULU/g)
Soap : fully saponified blend of Tallow and Coconut or Palm Kernel glycerides
The binder is polyethoxylated hexamethylene diamine (quaternary salt)

Example 3

[0164] The following rejuvenating tablets were prepared in accordance with the present invention.

[0165] The composition of the first region is prepared by admixing the granular components and is then passed into the die of a INSTRON press. The composition of the first region is pressed in a punch suitably shaped for forming the mould. The cross section of the die is approximately 40×40 mm. For the tablets of example 1, compositions I to V and example 2, the composition is subjected to a compression force of 50kN/cm^2.

[0166] For example 1, composition VI, the tablet is a sandwich tablet in which the EMC material is placed in between two layers made with the rest of first region composition. Each layer is pressed separately at 100kN/cm^2 and then the three layers are glued with few drops of PEG 4000.

[0167] The first region of the tablets of examples 1, compositions II to VI and example 2, are coated with HFA. The coating is obtained by dipping the tablet body into melted HFA at a constant temperature of 60°C.

[0168] The composition of the second discrete region is prepared in similar manner. The raw enzyme material is for example, Carezyme from Novo Nordisk, with an activity of 100000 cevu/g and containing 30% active cellulases. The enzyme raw material is mixed with sodium bicarbonate, citric acid anhydrous and melted PEG 4000 (at 60°C) to form an agglomerate. Then it is pressed into a die. The shape of the die is such that the tablet could fit the mould. The cross-section of the die has a diameter of approximately 30 mm. The composition is subjected to a compression force of 4kN/cm^2.

[0169] Both regions of the tablet are glued together with a few drops of PEG 4000.

Example 4

[0170] The following rejuvenating processes were achieved in accordance with the present invention. The washing machine used in a Miele W715 machine and the dryer used is a Miele T454 tumble dryer..

Process 1:

[0171]

1. Tablets according to any of the compositions II to VI of example 1 or the composition of example 2, were put in the prewash compartment of the drawer or directly into the drum of the washing machine with the 480 grams of fabrics (one tablet/machine).
2. A prewash cycle was run for a 15 minutes with a water level of 71 and temperature 38°C; which was followed by a wash and rinse cycles for 1 hour and 30 minutes at 40°C.
3. After the wash, fabrics were dried in the tumble dryer for 1 hour.

Process 2:

[0172]

1. A tablet according to the composition I of example 1 was put in the prewash compartment of the drawer or preferably directly into the drum of the washing machine with the 480 grams of fabrics (one tablet/machine).
2. A prewash cycle was run for a 15 minutes with a water level of 71 and temperature 38°C.
3. After the prewash cycle, 75g of a laundry detergent composition such as sold by The Procter & Gamble Company under the tradename "Ariel Futur", were put in the main compartment of the drawer of the washing machine. The

fabrics followed a wash and rinse cycles for 1 hour and 30 minutes at 40°C. Steps 2 and 3 can be achieved separately or within a pre-wash / wash cycles sequence of a conventional washing machine.
4. After the second wash, fabrics were dried in the tumble dryer for 1hour.

Process 3:

[0173]

1) Tablets according to Example 1, compositions II to V were put in the main compartment or preferably directly into the drum of the washing machine with the 480 grams of fabrics (one tablet/machine).
2) A wash cycle was run for 1hour and 30 minutes with a main wash water intake of 11l and temperature 40°C.
3) After the wash, fabrics were dried in the tumble dryer for 1hour.

Process 4:

[0174]

1. Tablets according to any of the compositions II to V of example 1 or the composition of example 2, were put in the prewash compartment of the drawer or preferably directly into the drum of the washing machine with the 480 grams of fabrics (one tablet/machine).
2. A prewash cycle was run for a 15 minutes with a water level of 7L and temperature 38°C; which was followed by a wash with 75g of a laundry detergent composition such as "Ariel Futur" and rinse cycles for 1hour and 30 minutes at 40°C. Alternatively these pre-wash and wash cycles sequence can be replaced by 2 consecutive conventional wash cycles.
3. After the wash, the fabrics were rinsed with 50 ml of a fabric enhancement composition as described in example 5. Said composition was added in the beginning of the treatment within the rinse compartment of the drawer of the washing machine.
4. After the wash and the rinse cycles, fabrics were dried in the tumble dryer for 1hour.

Example 5

[0175] The rejuvenating treatment of the present invention can be followed by a fabric care step to be used in the rinse or in a soaking solution. These following are non-limiting examples of pre-soak fabric conditioning and/or fabric enhancement compositions.

	I	II	III	IV	V	VI
Polymer	3.5	3.5	3.5	3.5	3.5	3.5
Dye fixative	2.3	2.3	2.4	2.4	2.5	2.5
Polyamine	15.0	15.0	17.5	17.5	20.0	20.0
Bayhibit AM	1.0	1.0	1.0	1.0	1.0	1.0
C12-C14 dimethyl hydroxyethyl quaternary ammonium chloride	-	5.0	5.0	-	-	-
Fabric softener active	-	-	2.5	2.5	-	-
Genamin C100	0.33	-	0.33	0.33	0.33	-
Genapol V4463	0.2	-	0.2	0.2	0.2	-
PARP3(c)	15	30	1.5	7.5	0.75	1.0
Water & Minors	Balance to 100%					

[0176] Wherein the abbreviations have the following meanings :

Polymer	Polyvinylpyrrolidone K90 available from BASF under the tradename Luviskol K90
Dye fixative	Dye fixative commercially available from Clariant under the tradename Cartafix CB
Polyamine	1,4-Bis-(3-aminopropyl)piperazine
Bayhibit AM	2-Phosphonobutane-1,2,4-tricarboxylic acid commercially available from Bayer
Fabric softener active	Di-(canoloyl-oxy-ethyl)hydroxyethyl methyl ammonium methylsulfate
Genamin C100	Coco fatty amine ethoxylated with 10 moles ethylene oxide and commercially available

	from Clariant
Genapol V4463	Coco alcohol ethoxylated with 10 moles ethylene oxide and commercially available from Clariant

Claims

1. A process for rejuvenating fabrics comprising contacting fabrics with an enzyme at a level of 0.01 to 1 grams of pure enzyme per litre of rejuvenating liquor, preferably of from 0.25g/l to 0.3 g/l for an efficient period of time, and subsequently contacting said fabric with an enzyme inhibitor.

2. A process according to claim 1 wherein said enzyme inhibitor is used at a level of at least 0.3 grams per litre of rejuvenating liquor, preferably of at least 0.5g/l.

4. A process according to claims 1-3 wherein said efficient period of time is of from 5 to 30 minutes, preferably from 10 to 15 minutes,

5. A rejuvenating composition for use in a process according to claims 1-4.

6. A rejuvenating composition according to claim 5 wherein said composition is in the form of multi-phase composition, comprising a first region and one or more second discrete regions, wherein the concentration of enzyme in said second discrete region(s) is at least 2 times the concentration of enzyme in said first region; and the total level of enzyme is greater than 2% by weight of pure enzyme of the total composition; wherein the second discrete region(s) dissolves faster than the first region and wherein the first region comprises an enzyme inhibitor which is released subsequently.

7. A rejuvenating composition according to claims 5-6 in the form of a multi-phase tablet.

8. A rejuvenating composition according to claims 6-7 comprising:

a) a first region which is in the form of a shaped body having at least one mould therein; and
b) a second discrete region comprised within said mould.

9. A rejuvenating composition according to claim 8 wherein said second discrete region is in the form of a particulate solid compressed within said mould.

10. A rejuvenating composition according to claim 9 wherein said first region is prepared at a compression pressure of at least 4kN/cm^2 and said second discrete region being compressed at a pressure of less than 20kN/cm^2.

11. A rejuvenating composition according to claims 6-10 wherein said first region is coated.

12. A rejuvenating composition according to claims 6-11 wherein said second discrete region further comprises a binder, a disrupting agent and/or mixtures thereof.

13. A rejuvenating composition according to claims 6-12 wherein said second discrete region is adhesively attached to said first region.

14. A rejuvenating composition according to claims 6-13 wherein said enzyme is predominantly concentrated in the second discrete region(s) at a level of at least 50%, preferably at least 60%, especially 80% by weight in the second discrete region(s).

15. A rejuvenating process or rejuvenating composition according to any of the preceding claims wherein said enzyme is selected from the group consisting of cellulases, proteases, lipases, amylases or mixtures thereof.

16. A rejuvenating process or rejuvenating composition according to any of the preceding claims wherein said enzyme is a cellulase, preferably selected from a ~43kD endoglucanase derived from *Humicola insolens,* DSM 1800, exhibiting cellulase activity and/or liquid cellulase preparation from *Trichoderma reesei.,* more preferably is a "43kD endoglucanase derived from *Humicola insolens,* DSM 1800, exhibiting cellulase activity.

17. A rejuvenating process or rejuvenating composition according to any of the preceding claims wherein at least 50%, preferably at least 60% and more preferably at least 80% by weight of the enzyme is released in the rejuvenating liquor within 10, preferably 5, more preferably 4, most preferably 3 minutes from the start of the rejuvenating process.

18. A rejuvenating process or rejuvenating composition according to any of the preceding claims wherein the enzyme inhibitor is selected from anionic surfactants, bleaching agents, metal ions and/or mixtures thereof.

19. A rejuvenating process according to any of the preceding claims wherein a fabric care ingredient is released together with or after said enzyme inhibitor.

20. A rejuvenating composition according to claims 6-18 wherein said first region comprises a fabric care ingredient.

21. A rejuvenating composition according to claim 20 wherein said fabric care ingredient is comprised in a third phase that is released after said first region.

22. A rejuvenating process or rejuvenating composition according to claims 19-21 wherein said fabric care ingredient is a hydrophobically modified cellulosic base polymer.

23. The manufacture of a rejuvenating composition for use in a process according to any of the above claims.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 87 0205

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	25 February 2000	Pfannenstein, H

CATEGORY OF CITED DOCUMENTS

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