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## (54) A process of treating fabrics with a laundry detergent additive tablet

(57) A process of treating fabrics which comprises the steps of forming an aqueous bath comprising water, a conventional laundry detergent dissolved or dispersed therein and a laundry detergent additive tablet comprising clay and subsequently contacting said fabrics with said aqueous bath.

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## Description

### Field of the Invention

**[0001]** This invention relates to a laundry additive tablet and in particular to a process of treating fabrics with a laundry detergent additive tablet comprising softening clay.

### Background of the Invention

**[0002]** It is known to provide laundry detergent compositions in the form of tablets made by compacting a particulate detergent composition. Usually a small amount of binder is included in the composition in order to promote the integrity of the tablets.

**[0003]** Although it is necessary that the tablets should have good integrity before use, it is necessary also that they should disintegrate rapidly during use, when contacted with wash water. It is known to include a disintegrant, which will promote disintegration of the tablet. Various classes of disintegrant are known, including the class in which disintegration is caused by swelling of the disintegrant. Various swelling disintegrants have been proposed in the literature, with the preference being directed predominantly towards starches, celluloses and water soluble organic polymers. Inorganic swelling disintegrants such as bentonite clay have also been mentioned, for instance in EP-A-0 466 484. In W098/40463 the disintegrant is a material such as starch or cellulose and is introduced substantially only in granular form. JP-A-9/87696 is concerned with tablets containing a non-ionic detergent composition with a non-ionic surfactant as the main component and in particular is concerned with preventing the non-ionic surfactant from oozing out of the tablets during storage, and it is also concerned with the fact that the non-ionic surfactant causes a loss in the softening effect that would be expected when a softening clay is included. It describes the formation of tablets containing finely divided clay mineral, together with a finely divided oil absorbing carrier, and a disintegrant.

**[0004]** The tablets known in the art are fully formulated laundry detergent tablets. However, it would be desirable to provide laundry detergent additive tablets, and bleach additive tablets in particular, that provide a softening and/or ease or ironing benefit to fabrics treated therewith. Laundry detergent additive tablets are less complex formulations compared to fully formulated laundry detergent tablets and are therefore easier to formulate for the manufacturer of said tablets. Furthermore, laundry detergent additive tablets are added to the laundry process only-if the specific softening and/or ease of ironing benefits provided by said tablets are desired.

**[0005]** It is thus an objective of the present invention to provide a laundry detergent additive tablet that gives a significant softening effect and/or ease or ironing benefits.

### Summary of the Invention

**[0006]** The present invention encompasses a process of treating fabrics which comprises the steps of forming an aqueous bath comprising water, a conventional laundry detergent dissolved or dispersed therein and a laundry detergent additive tablet comprising clay and subsequently contacting said fabrics with said aqueous bath.

**[0007]** In a preferred embodiment of the present invention, at least 50% by weight of the clay is present as granules which have a size of at least 0.1 mm. The clay is usually the major component in the granules and is usually present in an amount of at least 30%, and normally at least 50%, preferably at least 75%, by weight of the granules. The granules are preferably formed of at least 90% by weight of clay.

**[0008]** Preferably at least 60%, usually at least 75%, and most preferably at least 90% of the clay is present as granules of at least 0.1 mm but usually below 1.7 mm.

**[0009]** The tablet may comprise at least 5%, preferably at least 8%, and most preferably at least 10%, clay by weight of the tablet. The amount may be less than 25%, preferably less than 20% and preferably not more than 15% by weight of the tablet.

**[0010]** Preferably at least 70% and more preferably at least 90% by weight of the clay is present as granules having a particle size of between 0.15 mm and 0.85 mm. Preferably substantially all (e.g., at least 90% or 95% by weight) of the particles from which the tablets are formed have a size of at least 0.1 mm, more preferably from 0.1 to 1.7 mm.

**[0011]** In another preferred embodiment the tablet herein further comprises a flocculant.

### Detailed Description of the Invention

**[0012]** Generally, the tablet according to the present invention has a concentration of clay of greater than 1% by weight of the tablet, preferably greater than 3%, and most preferably greater than 5% by weight of the tablet. Generally, the upper limit of clay content is 60%, more preferably 45%, and most preferably 30% by weight of the tablet.

**[0013]** The tablet may be of uniform composition. Alternatively, the tablet may comprise one or more first regions

and one or more second regions (multi-phase tablets or multi-layer tablets), and the concentration of clay or other component in the or each first region may be different from the concentration in the or each second region. Preferably the concentration of clay in the or each first region is higher than in the or each second region. Thus, it may be at least 1.5 times, or as much as 2 to 5 times the concentration of clay in the or each second region. The first region will preferably have a concentration of at least 10% clay by weight of the or each first region. More than 50% of the total clay content of the tablet may be in the or each first region, preferably at least 60%, and more preferably at least 70% by weight of the tablet.

**[0014]** In a preferred embodiment of the present invention, said first region or regions comprise 100% of the total clay present in the tablet and said second region or regions are substantially free of clay. In another preferred embodiment of the present invention, said first region or regions are substantially free of clay and said second region or regions comprise 100% of the total clay present in the tablet.

**[0015]** The discrete first and second regions may be domains or other zones within the tablet, for instance created by forming the tablet from a particulate mixture containing large granules, typically above 1 mm, wherein some or all of the large granules have one content and the remainder of the large granules or the remainder of the particulate mixture have a different content, thereby forming the first and second regions in the compressed tablet. Preferably, however, the tablet is a multi-layer tablet and each region is a layer. If there are three layers, the tablet is typically a sandwich having similar layers on each outer surface and a different central layer.

**[0016]** In another preferred embodiment of the present invention, the tablets according to the present invention are multi-phase tablets, preferably multi-phase tablets having two separate phases. Multi-phase tablets are described in the Applicant's patent application PCT/US99/15492/WO 00/04129 (attorney's docket number CM1805M5).

**[0017]** Different layers or phases of the tablet may be coloured; this is particularly advisable for the first layer, or other layers containing clay, which may otherwise tend to impart an unattractive greyish tint on the tablet.

**[0018]** Typically the first regions makes up from 5% to 95%, preferably from 10% to 90% with the second regions containing the remainder.

**[0019]** Preferably at least 50%, preferably at least 75%, and most preferably at least 90% by weight of the clay is incorporated in the form of granules having a size above 0.1 mm, preferably from 0.1 mm to 1.18 mm, most preferably from 0.15 mm to 0.85 mm. This promotes disintegration. The granules usually contain clay in an amount of at least 50%, preferably at least 70% and most preferably at least 90% by weight.

**[0020]** As a result of introducing the clay as granules (instead of fines), it is possible to increase the amount of clay which can be included without causing gelling. Also, including the clay as granules instead of fines increases the disintegration effect of the clay.

**[0021]** In preferred embodiment of the present invention, the clay granules can be substantially uniformly distributed throughout the tablet whereby the high concentration will promote a softening effect and the concentration and the granular form will promote the disintegration effect throughout the tablet.

**[0022]** If desired, other materials can be incorporated as binder, for instance water soluble polyhydroxy compounds (such as glycerol) or other conventional clay binders, which are preferably freely water soluble. The total amount of binder is preferably less than 10% by weight, and more preferably less than 5%, by weight of the clay granules. If desired, other materials can be included in the granules, as a convenient way of introducing such materials into the tablet. The amount of clay is however usually at least 50%, and preferably at least 70% or 80% by weight of the granules.

**[0023]** In a preferred embodiment of the present invention, a clay flocculant may be included in the tablet in order to promote clay deposition on fabric. It has been observed by the Applicant that softening clay may tend to impede disintegration rather than promote it, particularly if the clay is present at high concentrations in the tablets described herein. This is because there may be a tendency, for the clay content of the tablet to gel upon contact with water so as to form a gel layer around the tablet which hinders penetration of water into the tablet, and thus inhibits tablet dispersion. Indeed, by adding a flocculant to the tablets as described herein, it is possible to incorporate the clay, preferably high concentrations of clay, in the tablet in such a way that the tendency for gelling at high clay concentrations in minimised, and the disintegration effect on the tablet of the clay is maximised.

**[0024]** A preferred design of tablet has discrete regions in which the flocculant, when present, is concentrated, and in which the concentration of clay is kept to a minimum. These regions may be granules or agglomerates, for example, or a layer or layers of a multi-layered tablet. Preferably at least 50%, preferably at least 75% and most preferably at least 90% by weight of the flocculant is incorporated in the form of granules having a size above 0.1 mm, preferably from 0.1 mm to 1.18 mm, most preferably from 0.15 mm to 0.85 mm. This promotes disintegration. The granules preferably comprise flocculant in an amount of at least 50%, preferably at least 70% and most preferably at least 90% by weight of the tablet.

**[0025]** The tablets of the invention are of a size which is convenient for dosing in a washing machine. The preferred size is from 3 g to 45 g, preferably from 15 g to 35 g, and the size can be selected in accordance with the intended wash load and the design of the washing machine which is to be used.

**[0026]** In a highly preferred embodiment of the present invention the tablet may additionally comprise a bleaching

agent. If the clay is more highly concentrated in one or more first regions than second regions, the concentration of said bleaching agent is preferably higher in the second regions than the first regions. Preferably the concentration of the bleaching agent in the or each second region is at least 1.5 times the concentration in the or each first region and preferably substantially all the bleaching agent is in the or each second region.

**[0027]** The tablet may further comprise an enzyme. When the clay is present in a higher concentration in one or more first regions, it is preferred for more enzyme to be in these regions than in the other regions, for instance the amount in the first regions should be normally at least 1.5 times and often at least 2 or at least 5 times the amount in the other regions, in order that the enzyme is dispersed as rapidly as possible with the fast dispersing first regions into the wash water.

**[0028]** The tablet may further comprise a laundry detergent, preferably the tablet further comprises at least 5% by weight of the tablet of laundry detergents, more preferably including non-ionic and/or anionic surfactants. If desired, the surfactant also may be present in a higher concentration in some regions than other regions (e.g., at least 1.5 times and usually 2-5 times). Generally at least 5% by weight non-ionic and/or anionic surfactant is present in any first regions of the tablet which have a higher clay concentration than remaining regions of the tablet.

Process of treating fabrics

**[0029]** The process of treating fabrics according to the present invention, comprises the steps of forming an aqueous bath comprising water, a conventional laundry detergent dissolved or dispersed therein and a, preferably an effective amount of, laundry detergent additive tablet dissolved or dispersed therein and subsequently contacting said fabrics with said aqueous bath. By an effective amount of the detergent tablet composition it is meant from 1 g to 60 g, preferably from 3 g to 45 g, more preferably from 15 g to 35 g, of product dissolved or dispersed in a wash solution of volume from 5 liters to 65 liters, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

**[0030]** The tablet and the conventional detergent composition may be delivered into the washing machine either by charging the dispenser drawer of the washing machine with one or both of the tablet or the conventional detergent or by directly charging the drum of the washing machine with one or both of tablet or the conventional detergent. More preferably the tablet is directly placed into the drum of the washing machine. Even more preferably the tablet and the convention detergent composition are both placed into the drum of the washing machine. The tablet may be delivered to the main wash cycle of the washing machine before, but more preferably at the same time as the conventional detergent composition.

**[0031]** In such a process the fabrics to be treated are contacted with a tablet, as defined herein. This is done in a "through the wash mode", where the dissolved or dispersed tablets, as defined herein, are used in addition to a wash liquor formed by dissolution or dispersion of a conventional laundry detergent in water, i.e., the tablets is used as a so-called "laundry additive tablet". The fabrics are then contacted with the aqueous bath comprising the tablets dissolved or dispersed therein and the conventional laundry detergent. Preferably, the fabrics are finally rinsed.

**[0032]** By "conventional laundry detergent" it is meant herein, a laundry detergent composition currently available on the market. Said laundry detergent compositions may be formulated as powders, as liquids or as tablets. Suitable laundry detergent compositions are for example DASH futur®, DASH liquid®, ARIEL tablets® and other products sold under the trade names ARIEL® or TIDE®.

**[0033]** In a preferred embodiment, the conventional laundry detergent as described herein comprises at least one surface active agent.

**[0034]** The contacting of the fabrics with the aqueous bath as described herein may be achieved by means of a washing machine or simply by hand.

Clays

**[0035]** The clay minerals used to provide the softening properties of the instant compositions can be described as expandable, three-layer clays, i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100g. of clay. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

**[0036]** There are two distinct classes of smectite-type clays; in the first, aluminum oxide is present in the silicate crystal lattice; in the second class of smectites, magnesium oxide is present in the silicate crystal lattice. The general formulas of these smectites are $Al_2(Si_2O_5)_2(OH)_2$ and $Mg_3(Si_2O_5)(OH)_2$ for the aluminum and magnesium oxide type clay, respectively. It is to be recognised that the range of the water of hydration in the above formulas can vary with the processing to which the clay has been subjected. This is immaterial to the use of the smectite clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure. Fur-

thermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as Na+, Ca++, as well as H+, can be co-present in the water of hydration to provide electrical neutrality. Except as noted hereinafter, such cation substitutions are immaterial to the use of the clays herein since the desirable physical properties of the clays are not substantially altered thereby.

**[0037]** The three-layer, expandable alumino-silicates useful herein are further characterised by a dioctahedral crystal lattice, while the expandable three-layer magnesium silicates have a trioctahedral crystal lattice.

**[0038]** As noted herein above, the clays employed in the compositions of the instant invention contain cationic counterions such as protons, sodium ions, potassium ions, calcium ion, magnesium ion, and the like. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation:

$$\text{smectite clay (Na)} + NH_4OH \rightarrow \text{smectite clay } (NH_4) + NaOH.$$

**[0039]** Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq./100 g.). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which, in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. for kaolinites to about 150 meq/100 g., and greater, for certain clays of the montmorillonite variety. Illite clays have an ion exchange capacity somewhere in the lower portion of the range, i.e., around 26 meq/100 g. for an average illite clay.

**[0040]** Illite and kaolinite clays, with their relatively low ion exchange capacities, are preferably not used as the clay in the instant compositions. Indeed, such illite and kaolinite clays constitute a major component of clay soils and, as noted above, are removed from fabric surfaces by means of the instant compositions. However, smectites, such as nontonite, having an ion exchange capacity of around 70 meq/100 g., and montmorillonite, which has an ion exchange capacity greater than 70 meq/100 g., have been found to be useful in the instant compositions in that they are deposited on the fabrics to provide the desired softening benefits. Accordingly, clay minerals useful herein can be characterised as expandable, three-layer smectite-type clays having an ion exchange capacity of at least about 50 meq/100 g.

**[0041]** While not intending to be limited by theory, it appears that advantageous softening (and potentially dye scavenging, etc.) benefits of the instant compositions are obtainable and are ascribable to the physical characteristics and ion exchange properties of the clays used therein. That is to say, experiments have shown that non-expandable clays such as the kaolinites and the illites, which are both classes of clays having an ion exchange capacities below 50 meq/100 g., do not provide the beneficial aspects of the clays employed in the instant compositions.

**[0042]** The smectite clays used in the compositions herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under various tradenames, for example, Thixogel #1® and Gelwhite GP® from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC® and Volclay #325®, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH450®, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R.T. Vanderbilt. It is to be recognised that such smectite-type minerals obtained under the foregoing tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

**[0043]** While any of the smectite-type clays having a cation exchange capacity of at least about 50 meq/100 g. are useful herein, certain clays are preferred. For example, Gelwhite GP® is an extremely white form of smectite clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC®, which is a smectite-type clay mineral containing at least 3% of iron (expressed as $Fe_2O_3$) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in laundry compositions and is preferred from the standpoint of product performance.

**[0044]** Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14Å x-ray diffraction pattern. This characteristic pattern, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type minerals for use in the granular detergent compositions disclosed herein.

**[0045]** The clay is preferably mainly in the form of granules, with at least 50%, preferably at least 75%, and more preferable at least 90% being in the form of granules having a size of at least 0.1 mm up to 1.8 mm, preferably up to 1.18 mm, preferably from 0.15 mm to 0.85 mm. Preferably the amount of clay in the granules is at least 50%, more

preferably at least 70% and most preferably at least 90% by weight of the granules.

**[0046]** In addition to the softening benefits provided by the clay to the fabrics treated with the tablets according to the present invention, the clay also provides an ironing ease benefit to laundry detergent tablets and in particular to laundry detergent additive tablets, preferably laundry bleach additive tablets, as described herein. Indeed, by "ironing ease benefit" it is meant herein that fabrics washed in a wash liquor wherein a tablet according to the present invention has been dissolved are easier to iron as compared to fabrics washed in a wash liquor wherein no tablets according to the present invention has been dissolved. Indeed, it has been observed that such an ease of ironing benefit may be provided by softening ingredients in general and is not limited to clay. Therefore, the present invention also relates to the use of a softening ingredient, preferably clay, in a laundry tablet or laundry detergent additive tablet, preferably laundry bleach additive tablet, whereby an ironing ease benefit is provided to fabrics treated with said tablet.

**[0047]** A suitable test method for evaluating the ironing ease benefit as provided by the present invention is the following: A laundry detergent additive tablet according to the present invention is added into a standard washing machine in combination with a conventional laundry detergent (e.g., DASH futur®, DASH liquid® or ARIEL tablets®). A first fabric is treated in said washing machine according to the standard procedure of the washing machine and afterwards ironed by a group of expert panelists. After the ironing of said first fabric the ease of ironing is compared to the ease of ironing of a similar second fabric treated (washed and ironed) as described above but whiteout the addition of a laundry detergent additive tablet as described herein during said washing step.

**[0048]** A grading may be used by the expert panel to assign difference of the ease of ironing in panel units (psu) in a range from 0 to 4, wherein 0 means no noticeable difference in ease of ironing performance between said first and said second fabric can be observed and 4 means a noticeable difference in ease of ironing performance between the first and the second fabric.

**[0049]** A suitable test method for evaluating the softening benefit as provided by the present invention is the following: A laundry detergent additive tablet according to the present invention is added into a standard washing machine in combination with a conventional laundry detergent (e.g., DASH futur®, DASH liquid® or ARIEL tablets®). A first fabric is treated in said washing machine according to the standard procedure of the washing machine. After the washing of said first fabric the softness of said first fabric is compared to the softness of a similar second fabric treated (washed) as described above but whiteout the addition of a laundry detergent additive tablet as described herein.

**[0050]** A grading may be used by the expert panel to assign difference of softness in panel units (psu) in a range from 0 to 4, wherein 0 means no noticeable difference in softness between said first and said second fabric can be observed and 4 means a noticeable difference in softness between the first and the second fabric.

**[0051]** It should be noted that when a clay material is compressed prior to incorporation into a tablet or in a cleaning composition, improved disintegration or dispensing is achieved. For example, tablets comprising clay which is compressed prior to incorporation into a tablet, disintegrate more rapidly than tablets comprising the same clay material which has not been compressed prior to incorporation into a tablet. In particular the amount of pressure used for the compression of the clay is of importance to obtain clay particles which aid disintegration or dispensing.

**[0052]** Further, when softening clays are compressed and then incorporated in cleaning compositions or tablets, not only improved disintegration or dispensing is obtained, but also further improved softening of the fabrics is provided.

**[0053]** Preferably, the clay component is obtained by compression of a clay material.

**[0054]** A preferred process comprises the steps of submitting the clay material to a pressure of at least 10MPa, or even at least 20MPa or even 40MPa. This can for example be done by tabletting or roller compaction of a clay material, optionally together with one or more other ingredients, to form a clay tablet or sheet, preferably followed by size reduction, such as grinding, of the compressed clay sheet or tablet, to form compressed clay particles. The particles can then be incorporated in a tablet or cleaning composition.

**[0055]** Tabletting methods and roller compaction methods are known in the art. For example, the compression of the clay can be done in a Lloyd 50K tablet press or with a Chilsonator roller compaction equipment, available form Fitzpatrick Company.

Flocculants

**[0056]** Most clay flocculating polymers are fairly long chained polymers and copolymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone and ethylene imine. Gums, like guar gum, are suitable as well.

**[0057]** Preferred are polymers of ethylene oxide, acrylamide or acrylic acid. These polymers dramatically enhance the deposition of a fabric softening clay if their molecular weights are in the range of from 100 000 to 10 million. Preferred are such polymers having a weight average molecular weight of from 150000 to 5 million.

**[0058]** The most preferred polymer is poly (ethylene oxide). Molecular weight distributions can be readily determined using gel permeation chromatography, against standards of poly (ethylene oxide) of narrow molecular weight distributions.

**[0059]** The amount of flocculant, when present, is preferably from 0.01% to10%, most preferably from 0.1 % to 5% by weight of the tablet.

**[0060]** The flocculant is preferably mainly in the form of granules, with at least 50% by weighty, preferably at least 75%, and most preferably at least 90% being in the form of granules having a size of at least 0.1 mm up to 1.8 mm, preferably up to 1.18 mm and most preferably from 0.15 mm to 0.85 mm Preferably the amount of flocculant in the granules is at least 50%, more preferably at least 70% and most preferably at least 90%, of the weight of the granules.

**[0061]** Other components which are commonly used in detergent compositions and which may be incorporated into the detergent tablets of the present invention include chelating agents, soil release agents, soil antiredeposition agents, dispersing agents, brighteners, suds suppressors, fabric softeners, dye transfer inhibition agents and perfumes.

Bleaching agent

**[0062]** A highly preferred component of the laundry detergent additive tablets as described herein is a bleaching agent. Suitable bleaching agents include chlorine and oxygen-releasing bleaching agents.

**[0063]** Indeed, the highly preferred but optional presence of a bleaching agent in the tablets as described herein provides excellent bleaching performance to the laundry detergent additive tablets. In the preferred embodiment wherein the laundry detergent additive tablets additionally comprises a bleaching agent, the tablets are used as bleaching laundry detergent additive tablets providing a softening and/or ease of ironing benefit to the fabrics treated therewith.

**[0064]** The bleaching performance may be evaluated by the following test methods on various types of stains.

**[0065]** A suitable test method for evaluating the bleaching performance on a soiled fabric is the following: A laundry detergent additive tablets additionally comprising a bleaching agent according to the present invention is added into a standard washing machine in combination with a conventional laundry detergent (e.g., DASH futur® or DASH liquid®). A stained fabric (e.g., a fabric stained with a bleachable stains like coffee, tea and the like) is treated in said washing machine according to the standard procedure of the washing machine. After the treatment said fabric is compared to a similarly stained fabric treated as described above but with a laundry detergent additive tablets comprising no bleaching agent.

**[0066]** A visual grading may be used to assign difference in panel units (psu) in a range from 0 to 4, wherein 0 means no noticeable difference in bleaching performance between a tablet additionally comprising a bleaching agent and a tablet as described herein comprising no bleaching agent and 4 means a noticeable difference in bleaching performance between a tablet additionally comprising a bleaching agent and a tablet as described herein comprising no bleaching agent.

**[0067]** In one preferred aspect the oxygen-releasing bleaching agent contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred aspect a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Inorganic perhydrate bleaches

**[0068]** The laundry detergent additive tablets as described herein preferably include a hydrogen peroxide source, as an oxygen-releasing bleach. Suitable hydrogen peroxide sources include the inorganic perhydrate salts.

**[0069]** The inorganic perhydrate salts are normally incorporated in the form of the sodium salt at a level of from 1 % to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the tablets.

**[0070]** Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

**[0071]** Sodium perborate can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

**[0072]** Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates for inclusion in compositions in accordance with the invention. Sodium percarbonate is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid. Sodium percarbonate, being a hydrogen peroxide addition compound tends on dissolution to release the hydrogen peroxide quite rapidly which can increase the tendency for localised high bleach concentrations to arise. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in-product stability.

**[0073]** A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $Na_2SO_4.n.Na_2CO_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

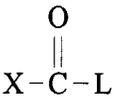
**[0074]** Another suitable coating material providing in product stability, comprises sodium silicate of $SiO_2 : Na_2O$ ratio from 1.8 : 1 to 3.0 : 1, preferably 1.8:1 to 2.4:1, and/or sodium metasilicate, preferably applied at a level of from 2% to 10%, (normally from 3% to 5%) of $SiO_2$ by weight of the inorganic perhydrate salt. Magnesium silicate can also be included in the coating. Coatings that contain silicate and borate salts or boric acids or other inorganics are also suitable.

**[0075]** Other coatings which contain waxes, oils, fatty soaps can also be used advantageously within the present invention.

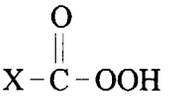
**[0076]** Potassium peroxymonopersulfate is another inorganic perhydrate salt of utility in the compositions herein.

Peroxyacid bleach precursor

**[0077]** Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



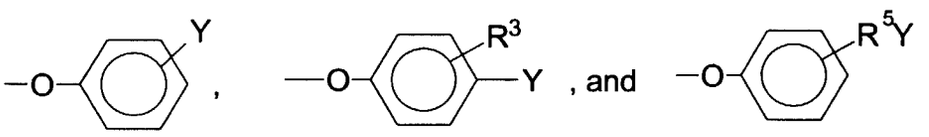
**[0078]** Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 10% by weight, most preferably from 1.5% to 5% by weight of the tablets.

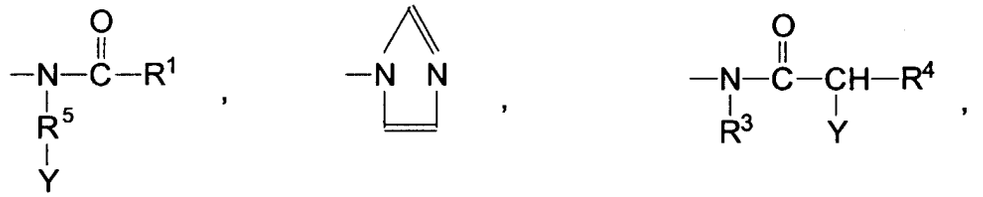
**[0079]** Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

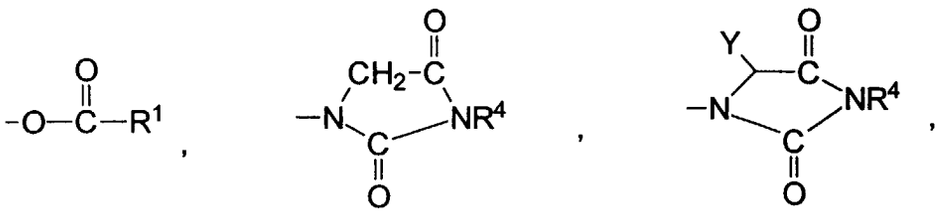
Leaving groups

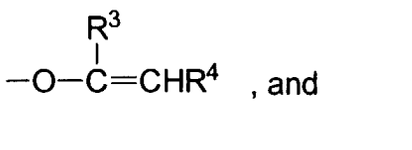
**[0080]** The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilise for use in a bleaching composition.

**[0081]** Preferred L groups are selected from the group consisting of:









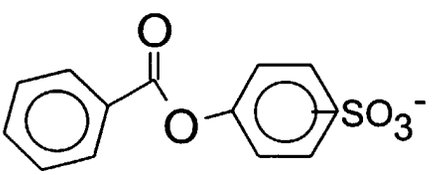
and mixtures thereof, wherein $R^1$ is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, $R^3$ is an alkyl chain containing from 1 to 8 carbon atoms, $R^4$ is H or $R^3$, $R^5$ is an alkenyl chain containing from 1 to 8 carbon atoms and Y is H or a solubilizing group. Any of $R^1$, $R^3$ and $R^4$ may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

**[0082]** The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and O<--$N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein $R^3$ is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

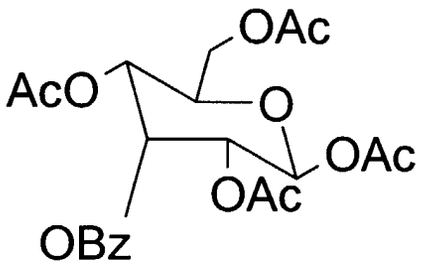
Perbenzoic acid precursor

**[0083]** Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis.

**[0084]** Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, including for example benzoyl oxybenzene sulfonate:



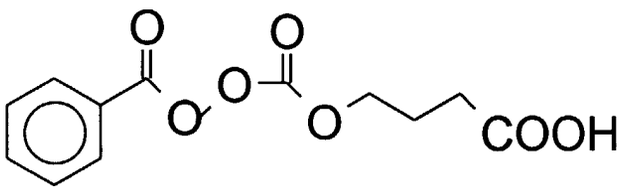
**[0085]** Also suitable are the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, including for example:



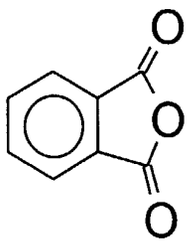

Ac = COCH3; Bz = Benzoyl

**[0086]** Perbenzoic acid precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

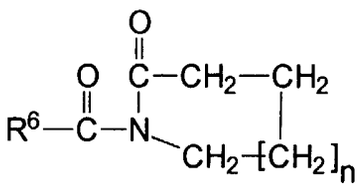
**[0087]** Other perbenzoic acid precursors include the benzoyl diacyl peroxides, the benzoyl tetraacyl peroxides, and the compound having the formula:




**[0088]** Phthalic anhydride is another suitable perbenzoic acid precursor compound herein:




**[0089]** Suitable N-acylated lactam perbenzoic acid precursors have the formula:



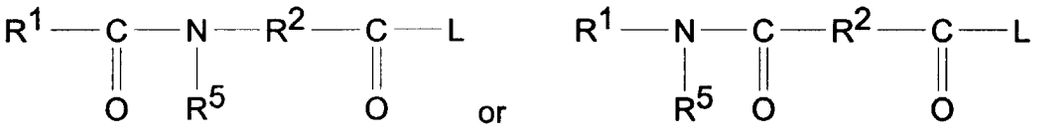

wherein n is from 0 to 8, preferably from 0 to 2, and $R^6$ is a benzoyl group.

Perbenzoic acid derivative precursors

**[0090]** Perbenzoic acid derivative precursors provide substituted perbenzoic acids on perhydrolysis.

**[0091]** Suitable substituted perbenzoic acid derivative precursors include any of the herein disclosed perbenzoic precursors in which the benzoyl group is substituted by essentially any non-positively charged (i.e.; non-cationic) functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl and amide groups.

**[0092]** A preferred class of substituted perbenzoic acid precursor compounds are the amide substituted compounds of the following general formulae:



wherein $R^1$ is an aryl or alkaryl group with from 1 to 14 carbon atoms, $R^2$ is an arylene, or alkarylene group containing from 1 to 14 carbon atoms, and $R^5$ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. $R^1$ preferably contains from 6 to 12 carbon atoms. $R^2$ preferably contains from 4 to 8 carbon atoms. $R^1$ may be aryl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for $R^2$. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. $R^5$ is preferably H or methyl. $R^1$ and $R^5$ should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Cationic peroxyacid precursors

**[0093]** Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

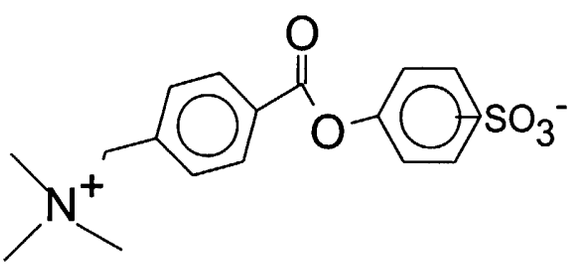
**[0094]** Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the compositions as a salt with a suitable anion, such as for example a halide ion or a methylsulfate ion.

**[0095]** The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter

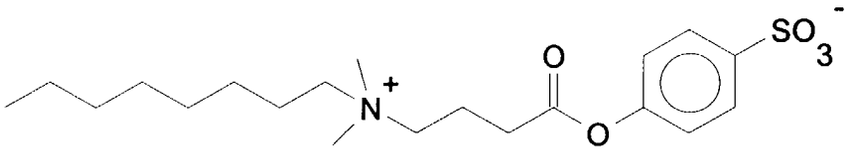
**[0096]** Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

**[0097]** Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

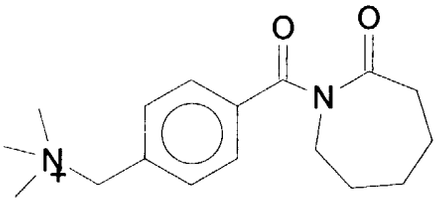
**[0098]** A preferred cationically substituted benzoyl oxybenzene sulfonate is the 4-(trimethyl ammonium) methyl derivative of benzoyl oxybenzene sulfonate:



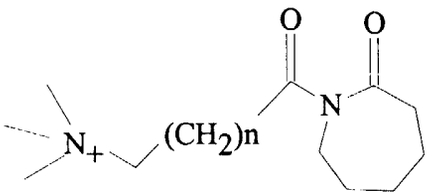
**[0099]** A preferred cationically substituted alkyl oxybenzene sulfonate has the formula:



**[0100]** Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams, particularly trimethyl ammonium methylene benzoyl caprolactam:



**[0101]** Other preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene alkyl caprolactams:



where n is from 0 to 12, particularly from 1 to 5.

**[0102]** Another preferred cationic peroxyacid precursor is 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride.

Alkyl percarboxylic acid bleach precursors

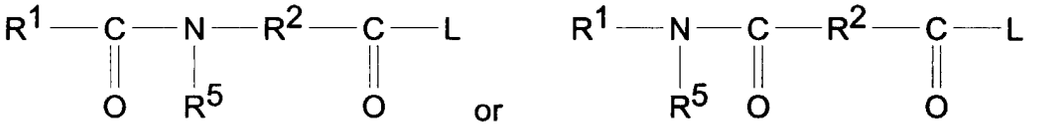
**[0103]** Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

**[0104]** Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,$N^1N^1$ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

**[0105]** Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-trimethyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and penta acetyl glucose.

Amide substituted alkyl peroxyacid precursors

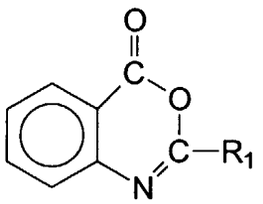
**[0106]** Amide substituted alkyl peroxyacid precursor compounds are also suitable, including those of the following general formulae:



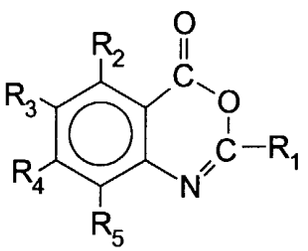
wherein $R^1$ is an alkyl group with from 1 to 14 carbon atoms, $R^2$ is an alkylene group containing from 1 to 14 carbon atoms, and $R^5$ is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. $R^1$ preferably contains from 6 to 12 carbon atoms. $R^2$ preferably contains from 4 to 8 carbon atoms. $R^1$ may be straight chain or branched alkyl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for $R^2$. The substitution can include alkyl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. $R^5$ is preferably H or methyl. $R^1$ and $R^5$ should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Benzoxazin organic peroxyacid precursors

**[0107]** Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

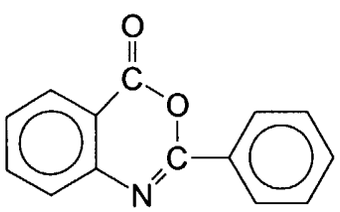


including the substituted benzoxazins of the type



wherein $R_1$ is H, alkyl, alkaryl, aryl, arylalkyl, and wherein $R_2$, $R_3$, $R_4$, and $R_5$ may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxyl, amino, alkyl amino, $COOR_6$ (wherein $R_6$ is H or an alkyl group) and carbonyl functions.

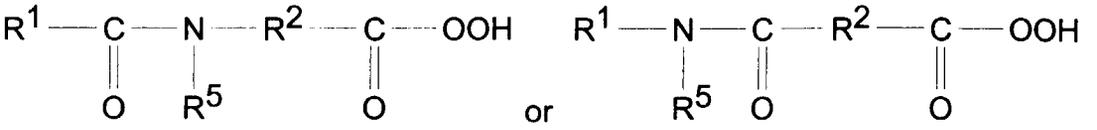
**[0108]** An especially preferred precursor of the benzoxazin-type is:



Preformed organic peroxyacid

**[0109]** The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid , typically at a level of from 0.5% to 25% by weight, more preferably from 1% to 10% by weight of the composition.

**[0110]** A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein $R^1$ is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, $R^2$ is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and $R^5$ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. $R^1$ preferably contains from 6 to 12 carbon atoms. $R^2$ preferably contains from 4 to 8 carbon atoms. $R^1$ may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for $R^2$. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. $R^5$ is preferably H or methyl. $R^1$ and $R^5$ should not contain more than 18 carbon atoms in total. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

**[0111]** Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid, and diperoxyhexadecanedioc acid. Dibenzoyl peroxide is a preferred organic peroxyacid herein. Mono- and diperazelaic acid, mono- and diperbrassylic acid, and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Metal-containing bleach catalyst

**[0112]** The tablet described herein which contain bleach as an optional component may additionally contain as a preferred component, a metal containing bleach catalyst. Preferably the metal containing bleach catalyst is a transition metal containing bleach catalyst, more preferably a manganese or cobalt-containing bleach catalyst.

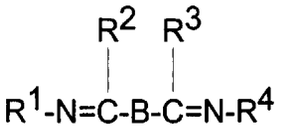
**[0113]** A suitable type of bleach catalyst is a catalyst comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminium cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

**[0114]** Preferred types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. 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)$_4$-$(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

**[0115]** The bleach catalysts useful in the compositions herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)$(OCH_3)_3$-$(PF_6)$.

**[0116]** Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulsitol, mannitol, xylithol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

**[0117]** U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with an non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein $R^1$, $R^2$, $R^3$, and $R^4$ can each be selected from H, substituted alkyl and aryl groups such that each $R^1$-N=C-$R^2$ and $R^3$-C=N-$R^4$ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S. $CR^5R^6$, $NR^7$ and C=O, wherein $R^5$, $R^6$, and $R^7$ can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe,-bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include Co(2,2'-bispyridylamine)$Cl_2$, Di(isothiocyanato)bispyridylamine-cobalt (II), trisdipyridylamine-cobalt(II) perchlorate, Co(2,2-bispyridylamine)$_2O_2ClO_4$, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

**[0118]** Preferred examples include binuclear Mn complexes with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$and $[Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}bipy_2]$-$(ClO_4)_3$.

**[0119]** While the structures of the bleach-catalyzing manganese complexes of the present invention have not been elucidated, it may be speculated that they comprise chelates or other hydrated coordination complexes which result from the interaction of the carboxyl and nitrogen atoms of the ligand with the manganese cation. Likewise, the oxidation state of the manganese cation during the catalytic process is not known with certainty, and may be the (+II), (+III), (+IV) or (+V) valence state. Due to the ligands' possible six points of attachment to the manganese cation, it may be reasonably speculated that multi-nuclear species and/or "cage" structures may exist in the aqueous bleaching media. Whatever the form of the active Mn·ligand species which actually exists, it functions in an apparently catalytic manner to provide improved bleaching performances on stubborn stains such as tea, ketchup, coffee, wine, juice, and the like.

**[0120]** Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

**[0121]** Other preferred examples include cobalt (III) catalysts having the formula:

$$Co[(NH_3)_nM'_mB'_bT'_tQ_qP_p]Y_y$$

wherein cobalt is in the +3 oxidation state; n is an integer from 0 to 5 (preferably 4 or 5; most preferably 5); M' represents a monodentate ligand; m is an integer from 0 to 5 (preferably 1 or 2; most preferably 1); B' represents a bidentate ligand; b is an integer from 0 to 2; T' represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is a pentadentate ligand; p is 0 or 1; and n + m + 2b + 3t + 4q + 5p = 6; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt, preferred Y are selected from the group consisting of chloride, nitrate, nitrite, sulfate, citrate, acetate, carbonate, and combinations thereof; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining coordination sites stabilise the cobalt under automatic dishwashing conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than 0.4 volts (preferably less than 0.2 volts) versus a normal hydrogen electrode.

**[0122]** Preferred cobalt catalysts of this type have the formula:

$$[Co(NH_3)_n(M')_m]Y_y$$

wherein n is an integer from 3 to 5 (preferably 4 or 5; most preferably 5); M' is a labile coordinating moiety, preferably selected from the group consisting of chlorine, bromine, hydroxide, water, and (when m is greater than 1) combinations thereof; m is an integer from 1 to 3 (preferably 1 or 2; most preferably 1); m+n = 6; and Y is an appropriately selected

counteranion present in a number y, which is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt.

**[0123]** The preferred cobalt catalyst of this type useful herein are cobalt pentaamine chloride salts having the formula $[Co(NH_3)_5Cl]\ Y_y$, and especially $[Co(NH_3)_5Cl]Cl_2$.

**[0124]** More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:

$$[Co(NH_3)_n(M)_m(B)_b]\ T_y$$

wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand co-ordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than 0.23 $M^{-1}\ s^{-1}$ (25°C).

**[0125]** Preferred T are selected from the group consisting of chloride, iodide, $I_3^-$, formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, $PF_6^-$, $BF_4^-$, $B(Ph)_4^-$, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof. Optionally, T can be protonated if more than one anionic group exists in T, e.g., $HPO_4^{2-}$, $HCO_3^-$, $H_2PO_4^-$, etc.

**[0126]** Further, T may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants (e.g., linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc.) and/or anionic polymers (e.g., polyacrylates, polymethacrylates, etc.).

**[0127]** The M moieties include, but are not limited to, for example, F-, $SO_4^{-2}$, $NCS^-$, SCN-, $S_2O_3^{-2}$, $NH_3$, $PO_4^{3-}$, and carboxylates (which preferably are monocarboxylates, but more than one carboxylate may be present in the moiety as long as the binding to the cobalt is by only one carboxylate per moiety, in which case the other carboxylate in the M moiety may be protonated or in its salt form). Optionally, M can be protonated if more than one anionic group exists in M (e.g., $HPO_4^{2-}$, $HCO_3^-$, $H_2PO_4^-$, $HOC(O)CH_2C(O)O$-, etc.) Preferred M moieties are substituted and unsubstituted $C_1$-$C_{30}$ carboxylic acids having the formulas:

$$RC(O)O\text{-}$$

wherein R is preferably selected from the group consisting of hydrogen and $C_1$-$C_{30}$ (preferably $C_1$-$C_{18}$) unsubstituted and substituted alkyl, $C_6$-$C_{30}$ (preferably $C_6$-$C_{18}$) unsubstituted and substituted aryl, and $C_3$-$C_{30}$ (preferably $C_5$-$C_{18}$) unsubstituted and substituted heteroaryl, wherein substituents are selected from the group consisting of $-NR'_3$, $-NR'_4^+$, -C(O)OR', -OR',$-C(O)NR'_2$, wherein R' is selected from the group consisting of hydrogen and $C_1$-$C_6$ moieties. Such substituted R therefore include the moieties $-(CH_2)_nOH$ and $-(CH_2)_nNR'_4^+$, wherein n is an integer from 1 to 16, preferably from 2 to 10, and most preferably from 2 to 5.

**[0128]** Most preferred M are carboxylic acids having the formula above wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, straight or branched $C_4$-$C_{12}$ alkyl, and benzyl. Most preferred R is methyl. Preferred carboxylic acid M moieties include formic, benzoic, octanoic, nonanoic, decanoic, dodecanoic, malonic, maleic, succinic, adipic, phthalic, 2-ethylhexanoic, naphthenoic, oleic, palmitic, triflate, tartrate, stearic, butyric, citric, acrylic, aspartic, fumaric, lauric, linoleic, lactic, malic, and especially acetic acid.

**[0129]** The B moieties include carbonate, di- and higher carboxylates (e.g., oxalate, malonate, malic, succinate, maleate), picolinic acid, and alpha and beta amino acids (e.g., glycine, alanine, beta-alanine, phenylalanine).

**[0130]** Cobalt bleach catalysts useful herein are known, being described for example along with their base hydrolysis rates, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. For example, Table 1 at page 17, provides the base hydrolysis rates (designated therein as $k_{OH}$) for cobalt pentaamine catalysts complexed with oxalate ($k_{OH}$= 2.5 x $10^{-4}$ $M^{-1}\ s^{-1}$ (25°C)), NCS- ($k_{OH}$= 5.0 x $10^{-4}$ $M^{-1}\ s^{-1}$ (25° C)), formate ($k_{OH}$= 5.8 x $10^{-4}$ $M^{-1}\ s^{-1}$ (25°C)), and acetate ($k_{OH}$= 9.6 x $10^{-4}$ $M^{-1}\ s^{-1}$ (25°C)). The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[Co(NH_3)_50Ac]\ T_y$, wherein OAc represents an acetate moiety, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$ (herein "PAC").

**[0131]** These cobalt catalysts are readily prepared by known procedures, such as taught for example in the Tobe article hereinbefore and the references cited therein, in U.S. Patent 4,810,410, to Diakun et al, issued March 7,1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Pren-

tice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952); as well as the synthesis examples provided hereinafter.

**[0132]** Cobalt catalysts suitable for incorporation into the detergent tablets of the present invention may be produced according to the synthetic routes disclosed in U.S. Patent Nos. 5,559,261, 5,581,005, and 5,597,936, the disclosures of which are herein incorporated by reference.

**[0133]** These catalysts may be co-processed with adjunct materials so as to reduce the colour impact if desired for the aesthetics of the product, or to be included in enzyme-containing particles as exemplified hereinafter, or the tablets may be manufactured to contain catalyst "speckles".

Enzymes

**[0134]** Enzymes are preferred components of the tablets as disclosed herein. Where present said enzymes are selected from the group consisting of 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.

**[0135]** Preferred enzymes include protease, amylase, lipase, peroxidases, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

**[0136]** The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 12 and an activity above 50 CEVU (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and W096/02653 which disclose fungal cellulases 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.

**[0137]** Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800. Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in 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 color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme® and Celluzyme® (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in W096/34092, WO96/17994 and WO95/24471.

**[0138]** Said cellulases are normally incorporated in the tablets at levels from 0.0001% to 2% of active enzyme by weight of the tablets.

**[0139]** Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

**[0140]** Preferred enhancers are substitued phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substitued syringates (C3-C5 substitued alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

**[0141]** Said cellulases and/or peroxidases are normally incorporated in the tablets at levels from 0.0001% to 2% of active enzyme by weight of the tablets.

**[0142]** Other preferred enzymes that can be included in the tablets 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.

**[0143]** Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism Pseudomonas fluorescent IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter

viscosum var. lipolyticum NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; Chromobacter viscosum lipases from U. S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. Especially suitable lipases are lipases such as M1 Lipase® and Lipomax® (Gist-Brocades) and Lipolase® and Lipolase Ultra® (Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitables are the lipolytic enzymes described in EP 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.

**[0144]** 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).

**[0145]** The lipases and/or cutinases are normally incorporated in the tablets at levels from 0.0001% to 2% of active enzyme by weight of the tablets.

**[0146]** Suitable proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in 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 EP 90915958:4, corresponding to WO 91/06637, Published Mayl6, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

**[0147]** 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 WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994.

**[0148]** 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.

**[0149]** 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.

**[0150]** Other preferred protease enzymes include protease enzymes which are a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived by replacement of a plurality of amino acid residues of a precursor carbonyl hydrolase with different amino acids, wherein said plurality of amino acid residues replaced in the precursor enzyme correspond to position +210 in combination with one or more of the following residues: +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218 and +222, where the numbered positions correspond to naturally-occurring subtilisin from Bacillus amyloliquefaciens or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins (such as Bacillus lentus subtilisin). Preferred enzymes of this type include those having position changes +210, +76, +103, +104, +156, and +166.

**[0151]** The proteolytic enzymes are incorporated in the tablets of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the tablet.

**[0152]** Amylases ($\alpha$ and/or $\beta$) can be included for removal of carbohydrate-based stains. 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 $\alpha$- and $\beta$-amylases. $\alpha$-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). 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).

**[0153]** Examples of commercial α-amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban® , Fungamyl® and Duramyl®, Natalase ® all available from Novo Nordisk A/S Denmark. 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). 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.

**[0154]** Preferred amylase enzymes include those described in W095/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056.

**[0155]** The amylolytic enzymes are incorporated in the tablets of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the tablet

**[0156]** In a particularly preferred embodiment, detergent tablets of the present invention comprise amylase enzymes, particularly those described in W095/26397 and co-pending application by Novo Nordisk PCT/DK96/00056 in combination with a complementary amylase.

**[0157]** By "complementary" it is meant the addition of one or more amylase suitable for detergency purposes. Examples of complementary amylases (a and/or β) are described below. W094/02597 and WO95/10603, Novo Nordisk A/S describe cleaning compositions which incorporate mutant amylases. Other amylases known for use in cleaning compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US 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). Other suitable amylases are stability-enhanced amylases described in WO94/18314, and W096/05295, Genencor and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603. Also suitable are amylases described in EP 277 216 (Novo Nordisk). 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). 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. Preferred complementary amylases for the present invention are the amylases sold under the tradename Purafect Ox Am$^{R}$ described in WO 94/18314, W096/05295 sold by Genencor; Termamyl®, Fungamyl®, Ban® Natalase® and Duramyl®, all available from Novo Nordisk A/S and Maxamyl® by Gist-Brocades.

**[0158]** Said complementary amylase is generally incorporated in the tablets of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the tablet. Preferably a weight of pure enzyme ratio of specific amylase to the complementary amylase is comprised between 9:1 to 1:9, more preferably between 4:1 to 1:4, and most preferably between 2:1 and 1:2.

**[0159]** The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

**[0160]** Said enzymes are normally incorporated in the tablets herein at levels from 0.0001% to 2% of active enzyme by weight of the tablets. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc. containing one enzyme ) or as mixtures of two or more enzymes ( e.g. cogranulates).

**[0161]** Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

**[0162]** A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xy-

lanases and cellulases, is described in WO 9401532 A to Novo.

Effervescent

**[0163]** In another preferred embodiment of the present invention the tablets further comprises an effervescent.

**[0164]** Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,

$$\text{i.e. } C_6H_8O_7 + 3NaHCO_3 \rightarrow Na_3C_6H_5O_7 + 3CO_2 + 3H_2O$$

**[0165]** Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291).

**[0166]** An effervescent may be added to the tablet as described herein. The addition of this effervescent to the detergent tablet improves the disintegration time of the tablet. The amount will preferably be between 5% and 20 % and most preferably between 10% and 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separated particles.

**[0167]** Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

**[0168]** Further dispersion aid could be provided by using compounds such as sodium acetate or urea. A list of suitable dispersion aid may also be found in Pharmaceutical Dosage Forms: Tablets, Volume 1, Second edition, Edited by H. A. Lieberman et all, ISBN 0-8247-8044-2.

Binders

**[0169]** Non gelling binders may be integrated to the particles forming the tablet in order to further facilitate dispersion.

**[0170]** If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e. ethoxylated hexamethylene diamine quaternary compounds, bishexamethylene triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

**[0171]** Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

**[0172]** Non-gelling binder materials are preferably used in an amount within the range from 0.1% to 15% by weight of the tablet, more preferably below 5% and especially if it is a non laundry active material below 2% by weight of the tablet.

**[0173]** It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials, and not as liquids.

Detersive surfactants

**[0174]** Non-limiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, anionics such as sulphonates, sulphates and ether sulphates. These include the conventional C11-C18 alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C10-C20 alkyl sulfates ("AS"), the C10-C18 secondary (2,3) alkyl sulfates of the formula $CH_3(CH_2)_x(CHOSO_3\text{-}M^+)\ CH_3$ and $CH_3\ (CH_2)_y(CHOSO_3\text{-}M+)\ CH_2CH_3$ 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 C10-C18 alkyl alkoxy sulfates ("AExS"; especially EO 1-7 ethoxy sulfates), C10-C18 alkyl alkoxy carboxylates (especially the $EO_{1\text{-}5}$ ethoxycarboxylates), the C10-18 glycerol ethers, the C10-C18 alkyl polyglycosides and their corresponding sulfated polyglycosides, and C12-C18 alpha-sulfonated fatty

acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C12-C18 alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C6-C12 alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C12-C18 betaines and sulfobetaines ("sultaines"), C10-C18 amine oxides, and the like, can also be included in the overall compositions. The C10-C18 N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C12-C18 N-methylglucamides. See WO 92/06154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C10-C18 N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C12-C18 glucamides can be used for low sudsing. C10-C20 conventional soaps may also be used. If high sudsing is desired, the branched-chain C10-C16 soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful anionic, amphoteric, nonionic or cationic surfactants are listed in standard texts.

In preferred embodiments, the tablet comprises at least 5% by weight of surfactant, more preferably at least 15% by weight, even more preferably at least 25% by weight, and most preferably between 35% and 55% by weight of surfactant. The amount of anionic is preferably at least 1.5 times, generally at least 2 or 3 times, the total amount of other surfactants.

Builders

**[0175]** Detergent builders can optionally be included in the tablets 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.

**[0176]** The level of builder can vary widely depending upon the end use of the composition.

**[0177]** 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 meta-phosphates), 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.

**[0178]** 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 $NaMSixO_2x+1.yH_2O$ 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) 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.

**[0179]** Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

**[0180]** 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:

$$Mz(zAlO_2)y].xH_2O$$

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.

**[0181]** 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:

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

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.

**[0182]** 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.

**[0183]** 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.

**[0184]** 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, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

**[0185]** 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.

**[0186]** 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 C5-C20 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.

**[0187]** 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.

**[0188]** Fatty acids, e.g., C12-C18 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.

**[0189]** 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.

Coating

**[0190]** Solidity of the tablet according to the invention may be further improved by making a coated tablet, the coating covering a non-coated tablet according to the invention, thereby further improving the mechanical characteristics of the tablet while maintaining or further improving dispersion.

**[0191]** In one embodiment of the present invention, the tablets may then be coated so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dispersed under alkaline conditions, or is readily emulsified by surfactants. This contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also avoids deposition of particles or lumps of coating material on the laundry load.

**[0192]** Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

**[0193]** Suitable coating materials are dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof. The coating material has a melting point preferably of from 40°C to 200°C.

**[0194]** The coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material.

**[0195]** 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 200°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.

**[0196]** By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

**[0197]** A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

**[0198]** The tablet coatings are preferably very hard and provide extra strength to the tablet.

**[0199]** In a preferred embodiment of the present invention the fracture of the coating in the wash is improved by adding a disintegrant in the coating. This disintegrant will swell once in contact with water and break the coating in small pieces. This will improve the dispersion of the coating in the wash solution. The disintegrant is suspended in the coating melt at a level of up to 30%, preferably between 5% and 20%, most preferably between 5 and 10% by weight. Possible disintegrants are described in Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch: natural, modified or pregelatinized starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum; croscarmylose Sodium, crospovidone, cellulose, carboxymethyl cellulose, algenic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysacharides, ion exchange resins and mixtures thereof.

Tablet Manufacture

**[0200]** Laundry detergent additive tablets of the present invention can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients, in particular gelling surfactants, when present, are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.

**[0201]** The ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 5000N and most preferably of less than 3000 N. Indeed, the most preferred embodiment is a tablet compressed using a force of less than 2500N.

**[0202]** The particulate material used for making the tablet of this invention can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige® CB and/or Lodige® KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sentering, etc. Individual particles can also be any other particle, granule, sphere or grain.

**[0203]** The components of the particulate material may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components of the particulate material. Other liquid ingredients may also be sprayed on to the mix of components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

**[0204]** The tablets may be manufactured by using any compacting process, such as tabletting, briquetting, or extrusion, preferably tabletting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy®, Korch®, Manesty®, or Bonals®). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m2, preferably not exceed 30000 kN/m2, more preferably not exceed 5000 kN/m2, even more preferably not exceed 3000kN/m2 and most preferably not exceed 1000kN/m2. In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least 1.0 g/cc, and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25 g/cc and most preferably of less than 1.1 g/cc.

**[0205]** Multi-phase can be made as described in the Applicant's patent application PCT/US99/15492 / WO 00/04129 (attorney's docket number CM1805M5).

**[0206]** Multi-layer tablets can be made by known techniques.

Tensile Strength

**[0207]** Depending on the composition of the starting material, and the shape of the tablets, the used compacting force may be adjusted to not affect the tensile strength, and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape.

**[0208]** For a cylindrical tablet, the tensile strength corresponds to the diametrical fracture stress (DFS) which is a way to express the strength of a tablet, and is determined by the following equation :

$$= \frac{2\,F}{\pi\,Dt}$$

**[0209]** Where F is the maximum force (Newton) to cause tensile failure (fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet, and t the thickness of the tablet (Method Pharmaceutical Dosage Forms : Tablets Volume 2 Page 213 to 217).

**[0210]** A tablet having a diametral fracture stress of less than 20 kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A diametral fracture stress of at least 25 kPa is preferred.

**[0211]** This applies similarly to non cylindrical tablets, to define the tensile strength, whereby the cross section normal to the height of the tablet is non round, and whereby the force is applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non round cross section.

Examples

**[0212]** The following examples will further illustrate the present invention. The compositions are made by combining the listed ingredients in the listed proportions (weight % unless otherwise specified). The following Examples are meant to exemplify compositions used in a process according to the present invention but are not necessarily used to limit or otherwise define the scope of the present invention.

Abbreviations used in Examples

**[0213]** In the detergent compositions, the abbreviated component identifications have the following meanings:

| | |
|---|---|
| STPP : | Sodium tripolyphosphate |
| Bicarbonate : | Sodium hydrogen carbonate |
| Citric Acid : | Anhydrous Citric acid |
| Carbonate : | Anhydrous sodium carbonate |
| Silicate : | Amorphous Sodium Silicate ($SiO_2$:$Na_2O$ ratio = 2.0) |
| SKS-6 : | Crystalline layered silicate of formula δ-$Na_2Si_2O_5$ |
| PB1 : | Anhydrous sodium perborate monohydrate |
| Nonionic : | $C_{13}$-$C_{15}$ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5, sold under the tradename Plurafac by BASF |
| TAED : | Tetraacetyl ethylene diamine |
| HEDP : | Ethane 1-hydroxy-1,1-diphosphonic acid |
| DTPMP : | Diethylene triamine penta methylene phosphonic acid |
| ATMP : | Amino trimethylene phosphonic acid |

| | |
|---|---|
| PAAC : | Pentaamine acetate cobalt (III) salt |
| Paraffin : | Paraffin oil sold under the tradename Winog 70 by Wintershall. |
| Protease : | Proteolytic enzyme |
| Amylase : | Amylolytic enzyme. |
| BTA : | Benzotriazole |
| Sulphate : | Anhydrous sodium sulphate. |
| PEG 3000 : | Polyethylene Glycol molecular weight approximately 3000 available from Hoechst |
| PEG 6000 : | Polyethylene Glycol molecular weight approximately 6000 available from Hoechst |
| pH : | Measured as a 1% solution in distilled water at 20°C |
| Flocculant | Polyethylene oxide with an average molecular weight of 300,000 commercially available from SUMITOMO |
| Clay | Bentonite clay commercially available from CSM (UK), Voclay (UK), Laviosa (Italy). |

**[0214]** Examples I to VI illustrate multi-phase laundry detergent additive tablets of the present invention suitable for use as a laundry additive in a laundry washing machine.

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| | | | | | | |
| Phase 1 | | | | | | |
| Percarbonate | 25.0 | 25.0 | 25.0 | 30.0 | 33.0 | 29.0 |
| TAED | 9.7 | 9.7 | 9.7 | 9.7 | 7.7 | 9.7 |
| Bleach Catalyst | 0.02 | 0.04 | - | - | - | - |
| Citric acid | 10.0 | 15.0 | 20.0 | 15.0 | 17.0 | 20.0 |
| STPP | - | - | - | - | - | 6.0 |
| Acrylic-Maleic copolymer | 6.0 | 6.0 | 1.0 | 5.0 | - | - |
| Silicates | - | - | - | - | 6.0 | - |
| Bicarbonate | 15.0 | 15.0 | 10.0 | 15.0 | 15.0 | 15.0 |
| Carbonate | 5.0 | - | - | - | - | - |
| HEDP | - | - | - | 0.1 | - | 0.1 |
| DTPMP | - | - | - | - | 0.1 | - |
| ATMP | - | - | - | - | - | 0.1 |
| Brightener 49® | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 |
| Perfume | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| C12-16 Fatty acid | - | - | - | 1.0 | - | - |
| Protease - FN3 | 0.60 | 0.60 | 0.60 | 0.60 | 0.94 | 0.60 |
| Protease - Savinase | 0.34 | 0.34 | 0.34 | 0.34 | - | 0.34 |
| Amylase - Termamyl | 1.21 | 1.21 | 1.21 | 1.11 | 1.11 | 1.11 |
| Clay | 20 | - | 15 | 5 | 10 | - |
| Flocculant | - | - | - | - | 1 | 1 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Phase 2 | | | | | | |
| Protease - FN3 | 1.24 | 1.24 | 1.24 | 1.24 | 1.24 | 1.24 |
| Amylase - JE1 | 1.34 | 1.34 | 1.34 | 1.34 | 1.34 | 1.34 |
| Blue PEG | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| PEG 4000 | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 |
| Citric acid | 1.06 | 1.06 | 1.06 | 1.06 | 1.06 | 1.06 |
| Bicarbonate | 2.87 | 2.87 | 2.87 | 2.87 | 2.87 | 2.87 |
| Clay | - | 20 | 5 | 10 | - | 10 |
| Flocculant | - | - | - | - | 1 | - |

Brightener 49® available from Ciba Specialty Chemicals
Acrylic-Maleic copolymer having average molecular weight approximately 7000 Bleach Catalyst is a stable complex of Cobalt with NH3 and Acetate

**[0215]** The multi-phase tablet compositions are prepared as follows. The detergent active composition of phase 1 is prepared by admixing the granular and liquid components and is then passed into the die of a conventional rotary press. The press includes a punch suitably shaped for forming the mould. The crosssection of the die is approximately 30x38 mm. The composition is then subjected to a compression force of 940 kg/cm$^2$ and the punch is then elevated exposing the first phase of the tablet containing the mould in its upper surface. The detergent active composition of phase 2 is prepared in similar manner and is passed into the die. The particulate active composition is then subjected to a compression force of 170 kg/cm$^2$, the punch is elevated, and the multi-phase tablet ejected from the tablet press.

**[0216]** Examples VII to XI illustrate single-phase laundry detergent additive tablets of the present invention suitable for use as a laundry additive in a laundry washing machine.

| | VII | VIII | IIX | IX | X | XI |
|---|---|---|---|---|---|---|
| | | | | | | |
| Percarbonate | 20.0 | 20.0 | 25.0 | 34.0 | 35.0 | 19.0 |
| TAED | 9.7 | 9.7 | 9.7 | 9.7 | 7.7 | 9.7 |
| Bleach Catalyst | 0.02 | 0.04 | - | - | - | - |

| | | | | | | |
|---|---|---|---|---|---|---|
| Citric acid | 10.0 | 15.0 | 20.0 | 15.0 | 17.0 | 20.0 |
| STPP | - | - | - | - | - | 6.0 |
| Acrylic-Maleic copolymer | 6.0 | 6.0 | 1.0 | 5.0 | - | - |
| Silicates | - | - | - | - | 6.0 | - |
| Bicarbonate | 15.0 | 15.0 | 10.0 | 15.0 | 15.0 | 15.0 |
| Carbonate | 5.0 | - | - | - | - | - |
| HEDP | - | - | - | 0.1 | - | 0.1 |
| DTPMP | - | - | - | - | 0.1 | - |
| ATMP | - | - | - | - | - | 0.1 |
| Brightener 49® | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 |
| Perfume | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| C12-16 Fatty acid | - | - | - | 1.0 | - | - |
| Protease - FN3 | 0.60 | 0.60 | 0.60 | 0.60 | 0.94 | 0.60 |
| Protease - Savinase | 0.34 | 0.34 | 0.34 | 0.34 | - | 0.34 |
| Amylase - Termamyl | 1.21 | 1.21 | 1.21 | 1.11 | 1.11 | 1.11 |
| Protease - FN3 | 1.24 | 1.24 | 1.24 | 1.24 | 1.24 | 1.24 |
| Amylase - JE1 | 1.34 | 1.34 | 1.34 | 1.34 | 1.34 | 1.34 |
| Blue PEG | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| PEG 4000 | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 |
| Citric acid | 1.06 | 1.06 | 1.06 | 1.06 | 1.06 | 1.06 |
| Bicarbonate | 2.87 | 2.87 | 2.87 | 2.87 | 2.87 | 2.87 |
| Clay | 20 | 25 | 15 | 10 | 10 | 20 |
| Flocculant | 5 | - | 5 | 1 | - | 1 |

Brightener 49® available from Ciba Specialty Chemicals
Acrylic-Maleic copolymer having average molecular weight approximately 7000 Bleach Catalyst is a stable complex of Cobalt with NH3 and Acetate

**Claims**

1. A process of treating fabrics which comprises the steps of forming an aqueous bath comprising water, a conventional laundry detergent dissolved or dispersed therein and a laundry detergent additive tablet comprising clay and subsequently contacting said fabrics with said aqueous bath.

2. A process according to claim 1 wherein the clay content of the tablet is at least 1 % by weight of the tablet.

3. A process according to any of the preceding claims, wherein the clay content of the tablet is at least 3%, preferably at least 5%, by weight of the tablet.

4. A process according to any of the preceding claims, wherein at least 75% by weight of the clay is present as granules having a size of from 0.1 mm to 1.18 mm, preferably from 0.15 mm to 0.85 mm.

5. A process according to any of the preceding claims, in which the clay granules contain at least 50% by weight of the clay.

6. A process according to any of the preceding claims, wherein the tablet further comprises a flocculant.

7. A process according to claim 6, wherein said tablet comprises from 0.01% to 10% by weight of the tablet of said flocculant.

8. A process according to any of the preceding claims, the tablet further comprises a bleaching agent.

9. A process according to claim 8, wherein said bleaching agent is an inorganic perhydrate bleach, preferably percarbonate.

10. A process according to any of claims 8 or 9, wherein the tablet further comprises an alkyl percarboxylic bleach precursor, preferably tetraacetyl ethylene diamine.

11. A process according to any of claims 8 to 10, wherein the tablet further comprises a metal containing bleach catalyst.

12. A process according to any of the preceding claims, wherein the tablet further comprises an enzyme.

13. A process according to any of the preceding claims, wherein said tablet is a multi-phase tablet, preferably multi-phase tablets having two separate phases.

14. The use of a softening ingredient in a laundry detergent tablet or a laundry detergent additive tablet, wherein an ease of ironing benefit is provided to a fabric treated with said tablet.

15. The use according to claim 14, wherein said softening ingredient is a clay.

16. The use according to any of claims 14 and 15, wherein said laundry detergent additive tablet is a laundry bleach additive tablet.

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# EUROPEAN SEARCH REPORT

Application Number
EP 00 87 0024

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