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(54) Title: ENZYME GRANULE WITH FLUORESCENT WHITENING AGENT

(57) Abstract: The invention provides enzyme granules, comprising a fluorescent whitening agent.



WO 2015/028567 A1

ENZYME GRANULE WITH FLUORESCENT WHITENING AGENT**FIELD OF THE INVENTION**

The present invention relates to enzyme containing granules comprising a fluorescent
5 whitening agent for use in detergents.

BACKGROUND

Titanium dioxide accounts for 70% of the total production volume of pigments worldwide. It is widely used to provide whiteness and opacity to products such as paints, plastics, papers,
10 inks, foods, and toothpastes. Titanium dioxide is also used as a pigment and a coating agent to improve the whiteness of enzyme containing granules used in granular (powder) detergents.

Pigments change the color of reflected or transmitted light as the result of selective absorption of certain wavelengths. This physical process differs fundamentally from fluorescence, in which a material emits light. Thus, pigments and fluorescent agents exhibit
15 quite different properties, and are used in different applications.

WO 97/23606 discloses enzyme containing coated granules. Several "pigments useful in the coating layers" are mentioned. As described above, pigments and fluorescent agents are dissimilar materials.

SUMMARY OF THE INVENTION

We have found that fluorescent whitening agents can be used very efficiently as substituents of pigments, like titanium dioxide, as a whitening agent in enzyme granules, in particular in the coating of enzyme granules. Thus, in a first aspect, the present invention provides an enzyme granule comprising an enzyme and a fluorescent whitening agent.

25 In an embodiment, the enzyme granule comprises a core and a coating, wherein the coating includes the fluorescent whitening agent.

The invention further provides a method of preparing the granules and a granular detergent composition comprising the enzyme granules.

Other aspects and embodiments of the invention are apparent from the description and
30 examples.

DETAILED DESCRIPTION

The enzyme concentrates used for preparing enzymes granules typically originate from a fermentation broth which is subsequently more or less purified. Even though some purification
35 of the enzyme from the fermentation broth is often used, the resulting enzyme concentrate is typically colored by various components from the fermentation broth, which often results in a brownish or yellowish color of the concentrate. When preparing enzyme granules, the resulting

granules will be visually affected by the color of the concentrate, giving a brownish or yellowish discoloration of the granule. Many consumers of, e.g., washing powders with enzyme granules do not like brownish/yellowish particles in the detergents, and therefore the enzyme granules are often whitened using whitening agents like titanium dioxide. The discoloration of the enzyme granule is proportional to the amount of enzyme concentrate used, *i.e.*, enzyme granules having a relatively high content of enzyme are more discolored than granules with a low content of enzyme.

The inventors of the present invention have found that titanium dioxide, which is commonly used as a whitening agent in enzyme granules, can be replaced with a fluorescent whitening agent. When titanium dioxide is replaced with a fluorescent whitening agent, according to the invention, the required amount of fluorescent whitening agent is more than a hundred-fold lower than the amount of titanium dioxide, in order to obtain the same whiteness appearance of the enzyme granule. Typical amounts of titanium dioxide is 1-10% wt of the granulate, whereas the amount of fluorescent whitening agent used to provide a similar whitening effect is only 0.01% wt of the granulate, according to Examples 1-8.

Titanium dioxide is a pigment dye, and it exerts its whitening effect in a different manner (simple reflection of light) compared to fluorescent agents (re-emission of light at a different wavelength). Thus, it was a surprise that titanium dioxide could actually be substituted with a fluorescent whitening agent, while obtaining a similar whiteness appearance.

Fluorescent whitening agents are well-known ingredients in commercial detergent. Adding a fluorescent whitening agent to the enzyme granules, could be considered a supplementary source of fluorescent whitening agent in the complete detergent formulation.

Enzyme granule

An enzyme granule of the invention is a small particle containing enzyme(s) and a fluorescent whitening agent. The granule may be (roughly) spherical.

The granule typically has a diameter of 20-2000 μm , particularly 50-1500 μm , 100-1500 μm or 250-1200 μm .

The granule is composed of a core, and optionally one or more coatings (outer layers) surrounding the core.

The fluorescent whitening agent may be contained in the core or in a coating. Preferably, the fluorescent whitening agent is contained in a coating. If the fluorescent whitening agent is contained in the core, any (optional) coating(s) must be sufficiently transparent to allow the fluorescent whitening agent to improve the whiteness of the enzyme granule, as compared to a granule containing no fluorescent whitening agent.

In an embodiment, the enzyme granule does not include a surfactant, a detergent builder, and/or a bleaching agent. In another embodiment, the enzyme granule includes less than 10%

w/w surfactant, or less than 5% w/w surfactant, or less than 2% w/w surfactant, or less than 1% w/w surfactant. Preferably, the surfactant is a laundry detergent surfactant.

In a preferred embodiment, the granule contains less than 3% w/w titanium dioxide, preferably less than 1% w/w titanium dioxide, more preferably less than 0.5% w/w titanium dioxide, more preferably less than 0.1% w/w titanium dioxide, even more preferably less than 0.05% w/w titanium dioxide, and most preferably less than 0.01% w/w titanium dioxide.

Core

The core comprises the enzyme.

The core may include additional materials such as fillers, fibre materials (cellulose or synthetic fibres), stabilizing agents, solubilising agents, suspension agents, viscosity regulating agents, light spheres, plasticizers, salts, lubricants and fragrances.

The core may include binders, such as synthetic polymer, wax, fat, or carbohydrate.

The core may comprise a salt of a multivalent cation, a reducing agent, an antioxidant, a peroxide decomposing catalyst and/or an acidic buffer component, typically as a homogenous blend.

The core may consist of an inert particle with the blend absorbed into it, or with the blend applied on to the surface, e.g., via fluid bed coating.

The core particle may have a diameter of 20-2000 µm, particularly 50-1500 µm, 100-1500 µm or 250-1200 µm.

Preparation of core

The core can be prepared by granulating a blend of the ingredients, e.g., by a method comprising granulation techniques such as crystallization, precipitation, pan-coating, fluid bed coating, fluid bed agglomeration, rotary atomization, extrusion, prilling, spheronization, size reduction methods, drum granulation, and/or high shear granulation.

Methods for preparing the core can be found in Handbook of Powder Technology; Particle size enlargement by C. E. Capes; Volume 1; 1980; Elsevier. Preparation methods include known feed and granule formulation technologies, e.g.:

a) Spray dried products, wherein a liquid enzyme-containing solution is atomized in a spray drying tower to form small droplets which during their way down the drying tower dry to form an enzyme-containing particulate material. Very small particles can be produced this way (Michael S. Showell (editor); *Powdered detergents*; Surfactant Science Series; 1998; vol. 71; page 140-142; Marcel Dekker).

b) Layered products, wherein the enzyme is coated as a layer around a pre-formed inert core particle, wherein an enzyme-containing solution is atomized, typically in a fluid bed apparatus wherein the pre-formed core particles are fluidized, and the enzyme-containing

solution adheres to the core particles and dries up to leave a layer of dry enzyme on the surface of the core particle. Particles of a desired size can be obtained this way if a useful core particle of the desired size can be found. This type of product is described in, e.g., WO 97/23606

5 c) Absorbed core particles, wherein rather than coating the enzyme as a layer around the core, the enzyme is absorbed onto and/or into the surface of the core. Such a process is described in WO 97/39116.

d) Extrusion or pelletized products, wherein an enzyme-containing paste is pressed to pellets or under pressure is extruded through a small opening and cut into particles which are
10 subsequently dried. Such particles usually have a considerable size because of the material in which the extrusion opening is made (usually a plate with bore holes) sets a limit on the allowable pressure drop over the extrusion opening. Also, very high extrusion pressures when using a small opening increase heat generation in the enzyme paste, which is harmful to the enzyme (see also Michael S. Showell (editor); *Powdered detergents*; Surfactant Science
15 Series; 1998; vol. 71; page 140-142; Marcel Dekker).

e) Prilled products, wherein an enzyme-containing powder is suspended in molten wax and the suspension is sprayed, e.g., through a rotating disk atomiser, into a cooling chamber where the droplets quickly solidify (Michael S. Showell (editor); *Powdered detergents*; Surfactant Science Series; 1998; vol. 71; page 140-142; Marcel Dekker). The product obtained
20 is one wherein the enzyme is uniformly distributed throughout an inert material instead of being concentrated on its surface. Also US 4,016,040 and US 4,713,245 are documents relating to this technique

f) Mixer granulation products, wherein a liquid is added to a dry powder composition of, e.g., conventional granulating components, the enzyme being introduced either via the liquid or
25 the powder or both. The liquid and the powder are mixed and as the moisture of the liquid is absorbed in the dry powder, the components of the dry powder will start to adhere and agglomerate and particles will build up, forming granulates comprising the enzyme. Such a process is described in US 4,106,991 and related documents EP 170360, EP 304332, EP 304331, WO 90/09440 and WO 90/09428. In a particular product of this process wherein
30 various high-shear mixers can be used as granulators, granulates consisting of enzyme as enzyme, fillers and binders etc. are mixed with cellulose fibres to reinforce the particles to give the so-called T-granulate. Reinforced particles, being more robust, release less enzymatic dust.

g) Size reduction, wherein the cores are produced by milling or crushing of larger particles, pellets, tablets, briquettes etc. containing the enzyme. The wanted core particle
35 fraction is obtained by sieving the milled or crushed product. Over and undersized particles can be recycled. Size reduction is described in (Martin Rhodes (editor); *Principles of Powder Technology*; 1990; Chapter 10; John Wiley & Sons).

h) Fluid bed granulation. Fluid bed granulation involves suspending particulates in an air stream and spraying a liquid onto the fluidized particles via nozzles. Particles hit by spray droplets get wetted and become tacky. The tacky particles collide with other particles and adhere to them and form a granule.

- 5 i) The cores may be subjected to drying, such as in a fluid bed drier. Other known methods for drying granules in the feed or detergent industry can be used by the skilled person. The drying preferably takes place at a product temperature of from 25 to 90°C. For some enzymes it is important the cores comprising the enzyme contain a low amount of water before coating. If water sensitive enzymes are coated before excessive water is removed, it will be
10 trapped within the core and it may affect the activity of the enzyme negatively. After drying, the cores preferably contain 0.1-10 % w/w water.

Coating

The core of the enzyme granule may optionally be surrounded by at least one coating, e.g., to improve the storage stability, to reduce dust formation during handling, or for coloring
15 the granule. The optional coating(s) may include a salt coating, or other suitable coating materials, such as polyethylene glycol (PEG), methyl hydroxy-propyl cellulose (MHPC) and polyvinyl alcohol (PVA). These coatings may include a fluorescent whitening agent. Examples of enzyme granules with multiple coatings are shown in WO 93/07263 and WO 97/23606.

20 Preferably, the core of the enzyme granule is surrounded by a coating comprising a fluorescent whitening agent.

The coating may be applied in an amount of at least 0.1% by weight of the core, e.g., at least 0.5%, 1% or 5%. The amount may be at most 100%, 70%, 50%, 40% or 30%.

The coating is preferably at least 0.1 µm thick, particularly at least 0.5 µm, at least 1 µm
25 or at least 5 µm. In a particular embodiment the thickness of the coating is below 100 µm. In a more particular embodiment the thickness of the coating is below 60 µm. In an even more particular embodiment the total thickness of the coating is below 40 µm.

The coating should encapsulate the core unit by forming a substantially continuous layer. A substantially continuous layer is to be understood as a coating having few or no holes, so
30 that the core unit it is encapsulating/enclosing has few or none uncoated areas. The layer or coating should in particular be homogeneous in thickness.

The coating can further contain other materials as known in the art, e.g., fillers, antisticking agents, pigments, dyes, plasticizers and/or binders, such as titanium dioxide, kaolin, calcium carbonate or talc.

35 A salt coating may comprise at least 60% by weight w/w of a salt, e.g., at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95% or at least 99% by weight w/w.

The salt may be added from a salt solution where the salt is completely dissolved or from a salt suspension wherein the fine particles is less than 50 μm , such as less than 10 μm or less than 5 μm .

The salt coating may comprise a single salt or a mixture of two or more salts. The salt may be water soluble, in particular having a solubility at least 0.1 grams in 100 g of water at 20°C, preferably at least 0.5 g per 100 g water, *e.g.*, at least 1 g per 100 g water, *e.g.*, at least 5 g per 100 g water.

The salt may be an inorganic salt, *e.g.*, salts of sulfate, sulfite, phosphate, phosphonate, nitrate, chloride or carbonate or salts of simple organic acids (less than 10 carbon atoms, *e.g.*, 6 or less carbon atoms) such as citrate, malonate or acetate. Examples of cations in these salts are alkali or earth alkali metal ions, the ammonium ion or metal ions of the first transition series, such as sodium, potassium, magnesium, calcium, zinc or aluminium. Examples of anions include chloride, bromide, iodide, sulfate, sulfite, bisulfite, thiosulfate, phosphate, monobasic phosphate, dibasic phosphate, hypophosphite, dihydrogen pyrophosphate, tetraborate, borate, carbonate, bicarbonate, metasilicate, citrate, malate, maleate, malonate, succinate, lactate, formate, acetate, butyrate, propionate, benzoate, tartrate, ascorbate or gluconate. In particular alkali- or earth alkali metal salts of sulfate, sulfite, phosphate, phosphonate, nitrate, chloride or carbonate or salts of simple organic acids such as citrate, malonate or acetate may be used.

The salt in the coating may have a constant humidity at 20°C above 60%, particularly above 70%, above 80% or above 85%, or it may be another hydrate form of such a salt (*e.g.*, anhydrate). The salt coating may be as described in WO 00/01793 or WO 2006/034710.

Specific examples of suitable salts are NaCl ($\text{CH}_{20^\circ\text{C}}=76\%$), Na_2CO_3 ($\text{CH}_{20^\circ\text{C}}=92\%$), NaNO_3 ($\text{CH}_{20^\circ\text{C}}=73\%$), Na_2HPO_4 ($\text{CH}_{20^\circ\text{C}}=95\%$), Na_3PO_4 ($\text{CH}_{25^\circ\text{C}}=92\%$), NH_4Cl ($\text{CH}_{20^\circ\text{C}}=79.5\%$), $(\text{NH}_4)_2\text{HPO}_4$ ($\text{CH}_{20^\circ\text{C}}=93.0\%$), $\text{NH}_4\text{H}_2\text{PO}_4$ ($\text{CH}_{20^\circ\text{C}}=93.1\%$), $(\text{NH}_4)_2\text{SO}_4$ ($\text{CH}_{20^\circ\text{C}}=81.1\%$), KCl ($\text{CH}_{20^\circ\text{C}}=85\%$), K_2HPO_4 ($\text{CH}_{20^\circ\text{C}}=92\%$), KH_2PO_4 ($\text{CH}_{20^\circ\text{C}}=96.5\%$), KNO_3 ($\text{CH}_{20^\circ\text{C}}=93.5\%$), Na_2SO_4 ($\text{CH}_{20^\circ\text{C}}=93\%$), K_2SO_4 ($\text{CH}_{20^\circ\text{C}}=98\%$), KHSO_4 ($\text{CH}_{20^\circ\text{C}}=86\%$), MgSO_4 ($\text{CH}_{20^\circ\text{C}}=90\%$), ZnSO_4 ($\text{CH}_{20^\circ\text{C}}=90\%$) and sodium citrate ($\text{CH}_{25^\circ\text{C}}=86\%$). Other examples include NaH_2PO_4 , $(\text{NH}_4)\text{H}_2\text{PO}_4$, CuSO_4 , $\text{Mg}(\text{NO}_3)_2$ and magnesium acetate.

The salt may be in anhydrous form, or it may be a hydrated salt, *i.e.* a crystalline salt hydrate with bound water(s) of crystallization, such as described in WO 99/32595. Specific examples include anhydrous sodium sulfate (Na_2SO_4), anhydrous magnesium sulfate (MgSO_4), magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), sodium phosphate dibasic heptahydrate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2(6\text{H}_2\text{O})$), sodium citrate dihydrate and magnesium acetate tetrahydrate.

Preferably the salt is applied as a solution of the salt, *e.g.*, using a fluid bed.

Enzyme

The enzyme included in the enzyme granule of the invention may be a hydrolase (Enzyme Nomenclature EC 3).

The enzyme granule as well as the detergent composition may comprise one or more enzymes such as a protease, lipase, cutinase, an amylase, carbohydrase, cellulase, pectinase, mannanase, arabinase, galactanase, xylanase, oxidase, e.g., a laccase, and/or peroxidase.

The enzyme may be a naturally occurring enzyme of bacterial or fungal origin, or it may be a variant derived from one or more naturally occurring enzymes by gene shuffling and/or by substituting, deleting or inserting one or more amino acids. Chemically modified or protein engineered mutants are included.

Preferably, the enzyme granule contains at least one enzyme in an amount of more than 0.5% w/w and less than 50% w/w active enzyme protein; more preferably in an amount of more than 0.6% w/w and less than 40% w/w active enzyme protein; more preferably in an amount of more than 0.75% w/w and less than 30% w/w active enzyme protein; and most preferably in an amount of more than 1% w/w and less than 25% w/w active enzyme protein.

Cellulases: Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, e.g., the fungal cellulases produced from *Humicola insolens*, *Myceliophthora thermophila* and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757 and WO 89/09259.

Especially suitable cellulases are the alkaline or neutral cellulases having colour care benefits. Examples of such cellulases are cellulases described in EP 0 495 257, EP 0 531 372, WO 96/11262, WO 96/29397, WO 98/08940. Other examples are cellulase variants such as those described in WO 94/07998, EP 0 531 315, US 5,457,046, US 5,686,593, US 5,763,254, WO 95/24471, WO 98/12307 and PCT/DK98/00299.

Commercially available cellulases include Celluzyme™, Carezyme™, and Celluclean™ (Novozymes A/S), Clazinase™, and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).

Proteases: Suitable proteases include those of bacterial, fungal, plant, viral or animal origin, e.g., vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. It may be an alkaline protease, such as a serine protease or a metalloprotease. A serine protease may for example be of the S1 family, such as trypsin, or the S8 family such as subtilisin. A metalloproteases protease may for example be a thermolysin from, e.g., family M4 or other metalloprotease, such as those from M5, M7 or M8 families.

The term "subtilases" refers to a sub-group of serine protease according to Siezen *et al.*, Protein Engng. 4 (1991) 719-737 and Siezen *et al.* Protein Science 6 (1997) 501-523. Serine proteases are a subgroup of proteases characterized by having a serine in the active site, which forms a covalent adduct with the substrate. The subtilases may be divided into 6 sub-

5 divisions, *i.e.*, the Subtilisin family, the Thermitase family, the Proteinase K family, the Lantibiotic peptidase family, the Kexin family and the Pyrolysin family.

Examples of subtilases are those derived from *Bacillus* such as *Bacillus lentus*, *B. alkalophilus*, *B. subtilis*, *B. amyloliquefaciens*, *Bacillus pumilus* and *Bacillus gibsonii* described in; US7262042 and WO09/021867, and subtilisin lentus, subtilisin Novo, subtilisin Carlsberg,

10 *Bacillus licheniformis*, subtilisin BPN', subtilisin 309, subtilisin 147 and subtilisin 168 described in WO89/06279 and protease PD138 described in WO93/18140. Other useful proteases may be those described in WO92/175177, WO01/016285, WO02/026024 and WO02/016547. Examples of trypsin-like proteases are trypsin (*e.g.*, of porcine or bovine origin) and the *Fusarium* protease described in WO89/06270, WO94/25583 and WO05/040372, and the

15 chymotrypsin proteases derived from *Cellulomonas* described in WO05/052161 and WO05/052146.

A further preferred protease is the alkaline protease from *Bacillus lentus* DSM 5483, as described for example in WO95/23221, and variants thereof which are described in WO92/21760, WO95/23221, EP1921147 and EP1921148.

20 Examples of metalloproteases are the neutral metalloprotease as described in WO07/044993 (Genencor Int.) such as those derived from *Bacillus amyloliquefaciens*.

Examples of useful proteases are the variants described in: WO92/19729, WO96/034946, WO98/20115, WO98/20116, WO99/011768, WO01/44452, WO03/006602, WO04/03186, WO04/041979, WO07/006305, WO11/036263, WO11/036264, especially the variants with

25 substitutions in one or more of the following positions: 3, 4, 9, 15, 27, 36, 57, 68, 76, 87, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 106, 118, 120, 123, 128, 129, 130, 160, 167, 170, 194, 195, 199, 205, 206, 217, 218, 222, 224, 232, 235, 236, 245, 248, 252 and 274 using the BPN' numbering. More preferred the subtilase variants may comprise the mutations: S3T, V4I, S9R, A15T, K27R, *36D, V68A, N76D, N87S,R, *97E, A98S, S99G,D,A, S99AD, S101G,M,R S103A,

30 V104I,Y,N, S106A, G118V,R, H120D,N, N123S, S128L, P129Q, S130A, G160D, Y167A, R170S, A194P, G195E, V199M, V205I, L217D, N218D, M222S, A232V, K235L, Q236H, Q245R, N252K, T274A (using BPN' numbering).

Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Duralase™, Durazym™, Relase®, Relase® Ultra, Savinase®, Savinase®

35 Ultra, Primase®, Polarzyme®, Kannase®, Liquanase®, Liquanase® Ultra, Ovozyme®, Coronase®, Coronase® Ultra, Neutrase®, Everlase® and Esperase® (Novozymes A/S), those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Purafect®, Purafect Prime®,

PreferenzTM, Purafect MA®, Purafect Ox®, Purafect OxP®, Puramax®, Properase®, EffectenzTM, FN2®, FN3®, FN4®, Excellase®, Opticlean®, Optimase®, and Excellenz P1000 (Danisco/DuPont), AxapemTM (Gist-Brocades N.V.), BLAP (sequence shown in Figure 29 of US5352604) and variants hereof (Henkel AG) and KAP (*Bacillus alkalophilus* subtilisin) from

5 Kao.

Lipases and Cutinases: Suitable lipases and cutinases include those of bacterial or fungal origin. Chemically modified or protein engineered mutant enzymes are included. Examples include lipase from *Thermomyces*, e.g., from *T. lanuginosus* (previously named *Humicola lanuginosa*) as described in EP258068 and EP305216, cutinase from *Humicola*, e.g., *H. insolens* (WO96/13580), lipase from strains of *Pseudomonas* (some of these now renamed to *Burkholderia*), e.g., *P. alcaligenes* or *P. pseudoalcaligenes* (EP218272), *P. cepacia* (EP331376), *P. sp.* strain SD705 (WO95/06720 & WO96/27002), *P. wisconsinensis* (WO96/12012), GDSL-type *Streptomyces* lipases (WO10/065455), cutinase from *Magnaporthe grisea* (WO10/107560), cutinase from *Pseudomonas mendocina* (US5,389,536), lipase from

10 *Thermobifida fusca* (WO11/084412), *Geobacillus stearothermophilus* lipase (WO11/084417), lipase from *Bacillus subtilis* (WO11/084599), and lipase from *Streptomyces griseus* (WO11/150157) and *S. pristinaespiralis* (WO12/137147).

Other examples are lipase variants such as those described in EP407225, WO92/05249, WO94/01541, WO94/25578, WO95/14783, WO95/30744, WO95/35381, WO95/22615,

20 WO96/00292, WO97/04079, WO97/07202, WO00/34450, WO00/60063, WO01/92502, WO07/87508 and WO09/109500.

Preferred commercial lipase products include include LipolaseTM, LipexTM; LipolexTM and LipocleanTM (Novozymes A/S), Lumafast (originally from Genencor) and Lipomax (originally from Gist-Brocades).

25 Still other examples are lipases sometimes referred to as acyltransferases or perhydrolases, e.g., acyltransferases with homology to *Candida antarctica* lipase A (WO10/111143), acyltransferase from *Mycobacterium smegmatis* (WO05/56782), perhydrolases from the CE 7 family (WO09/67279), and variants of the *M. smegmatis* perhydrolase in particular the S54V variant used in the commercial product Gentle Power

30 Bleach from Huntsman Textile Effects Pte Ltd (WO10/100028).

Amylases: Suitable amylases are alpha-amylases or glucoamylases and may be of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus*, e.g., a special strain of *Bacillus licheniformis*, described in more detail in GB 1,296,839.

35 Suitable amylases include amylases having SEQ ID NO: 3 in WO 95/10603 or variants having 90% sequence identity to SEQ ID NO: 3 thereof. Preferred variants are described in WO 94/02597, WO 94/18314, WO 97/43424 and SEQ ID NO: 4 of WO 99/019467, such as variants

with substitutions in one or more of the following positions: 15, 23, 105, 106, 124, 128, 133, 154, 156, 178, 179, 181, 188, 190, 197, 201, 202, 207, 208, 209, 211, 243, 264, 304, 305, 391, 408, and 444.

Different suitable amylases include amylases having SEQ ID NO: 6 in WO 02/010355 or
 5 variants thereof having 90% sequence identity to SEQ ID NO: 6. Preferred variants of SEQ ID NO: 6 are those having a deletion in positions 181 and 182 and a substitution in position 193. Other amylases which are suitable are hybrid alpha-amylase comprising residues 1-33 of the alpha-amylase derived from *B. amyloliquefaciens* shown in SEQ ID NO: 6 of WO 2006/066594 and residues 36-483 of the *B. licheniformis* alpha-amylase shown in SEQ ID NO: 4 of WO
 10 2006/066594 or variants having 90% sequence identity thereof. Preferred variants of this hybrid alpha-amylase are those having a substitution, a deletion or an insertion in one of more of the following positions: G48, T49, G107, H156, A181, N190, M197, I201, A209 and Q264. Most preferred variants of the hybrid alpha-amylase comprising residues 1-33 of the alpha-amylase derived from *B. amyloliquefaciens* shown in SEQ ID NO: 6 of WO 2006/066594 and residues
 15 36-483 of SEQ ID NO: 4 are those having the substitutions:
 M197T;
 H156Y+A181T+N190F+A209V+Q264S; or
 G48A+T49I+G107A+H156Y+A181T+N190F+I201F+A209V+Q264S.

Further amylases which are suitable are amylases having SEQ ID NO: 6 in WO
 20 99/019467 or variants thereof having 90% sequence identity to SEQ ID NO: 6. Preferred variants of SEQ ID NO: 6 are those having a substitution, a deletion or an insertion in one or more of the following positions: R181, G182, H183, G184, N195, I206, E212, E216 and K269. Particularly preferred amylases are those having deletion in positions R181 and G182, or positions H183 and G184.

Additional amylases which can be used are those having SEQ ID NO: 1, SEQ ID NO: 3, SEQ ID NO: 2 or SEQ ID NO: 7 of WO 96/023873 or variants thereof having 90% sequence identity to SEQ ID NO: 1, SEQ ID NO: 2, SEQ ID NO: 3 or SEQ ID NO: 7. Preferred variants of SEQ ID NO: 1, SEQ ID NO: 2, SEQ ID NO: 3 or SEQ ID NO: 7 are those having a substitution, a deletion or an insertion in one or more of the following positions: 140, 181, 182, 183, 184,
 30 195, 206, 212, 243, 260, 269, 304 and 476. More preferred variants are those having a deletion in positions 181 and 182 or positions 183 and 184. Most preferred amylase variants of SEQ ID NO: 1, SEQ ID NO: 2 or SEQ ID NO: 7 are those having a deletion in positions 183 and 184 and a substitution in one or more of positions 140, 195, 206, 243, 260, 304 and 476.

Other amylases which can be used are amylases having SEQ ID NO: 2 of WO
 35 08/153815, SEQ ID NO: 10 in WO 01/66712 or variants thereof having 90% sequence identity to SEQ ID NO: 2 of WO 08/153815 or 90% sequence identity to SEQ ID NO: 10 in WO 01/66712. Preferred variants of SEQ ID NO: 10 in WO 01/66712 are those having a

substitution, a deletion or an insertion in one of more of the following positions: 176, 177, 178, 179, 190, 201, 207, 211 and 264.

Further suitable amylases are amylases having SEQ ID NO: 2 of WO 09/061380 or variants having 90% sequence identity to SEQ ID NO: 2 thereof. Preferred variants of SEQ ID NO: 2 are those having a truncation of the C-terminus and/or a substitution, a deletion or an insertion in one of more of the following positions: Q87, Q98, S125, N128, T131, T165, K178, R180, S181, T182, G183, M201, F202, N225, S243, N272, N282, Y305, R309, D319, Q320, Q359, K444 and G475. More preferred variants of SEQ ID NO: 2 are those having the substitution in one of more of the following positions: Q87E,R, Q98R, S125A, N128C, T131I, T165I, K178L, T182G, M201L, F202Y, N225E,R, N272E,R, S243Q,A,E,D, Y305R, R309A, Q320R, Q359E, K444E and G475K and/or deletion in position R180 and/or S181 or of T182 and/or G183. Most preferred amylase variants of SEQ ID NO: 2 are those having the substitutions:

N128C+K178L+T182G+Y305R+G475K;

N128C+K178L+T182G+F202Y+Y305R+D319T+G475K;

S125A+N128C+K178L+T182G+Y305R+G475K; or

S125A+N128C+T131I+T165I+K178L+T182G+Y305R+G475K wherein the variants are C-terminally truncated and optionally further comprises a substitution at position 243 and/or a deletion at position 180 and/or position 181.

Other suitable amylases are the alpha-amylase having SEQ ID NO: 12 in WO01/66712 or a variant having at least 90% sequence identity to SEQ ID NO: 12. Preferred amylase variants are those having a substitution, a deletion or an insertion in one of more of the following positions of SEQ ID NO: 12 in WO01/66712: R28, R118, N174; R181, G182, D183, G184, G186, W189, N195, M202, Y298, N299, K302, S303, N306, R310, N314; R320, H324, E345, Y396, R400, W439, R444, N445, K446, Q449, R458, N471, N484. Particular preferred amylases include variants having a deletion of D183 and G184 and having the substitutions R118K, N195F, R320K and R458K, and a variant additionally having substitutions in one or more position selected from the group: M9, G149, G182, G186, M202, T257, Y295, N299, M323, E345 and A339, most preferred a variant that additionally has substitutions in all these positions.

Other examples are amylase variants such as those described in WO2011/098531, WO2013/001078 and WO2013/001087.

Commercially available amylases are DuramylTM, TermamylTM, FungamylTM, StainzymeTM, Stainzyme PlusTM, NatalaseTM, Liquozyme X and BANTM (from Novozymes A/S), and RapidaseTM, PurastarTM/EffectenzTM, Powerase and Preferenz S100 (from Genencor International Inc./DuPont).

Lyase: The lyase may be a pectate lyase of bacterial or fungal origin. Chemically or genetically modified mutants are included. In a preferred embodiment the pectate lyase is derived from *Bacillus*, particularly *Bacillus subtilis*, *B. licheniformis* or *B. agaradhaerens*, or a variant derived of any of these, e.g. as described in US 6,124,127, WO 1999/027083, WO 1999/027084, WO 2002/006442, WO 2002/092741, WO 2003/095638, Commercially available pectate lyases include XPect; Pectawash and Pectaway (Novozymes A/S).

Mannanase: Suitable mannanases include those of bacterial or fungal origin. Chemically or genetically modified mutants are included. The mannanase may be an alkaline mannanase of Family 5 or 26. It may be a wild-type from *Bacillus* or *Humicola*, particularly *B.*

agaradhaerens, *B. licheniformis*, *B. halodurans*, *B. clausii*, or *H. insolens*. Suitable mannanases are described in WO 1999/064619. A commercially available mannanase is Mannaway (Novozymes A/S).

Peroxidases/Oxidases: Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from *Coprinus*, e.g., from *C. cinereus*, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257.

Other peroxidases include Guardzyme™ (Novozymes A/S).

Fluorescent whitening agent

The enzyme granule of the invention includes a fluorescent whitening agent.

Fluorescent whitening agents, also referred to as optical brighteners, optical brightening agents, or fluorescent brightening agents, are dyes that absorb light in the ultraviolet and violet region (usually 340-370 nm) of the electromagnetic spectrum, and re-emit light in the blue region (typically 420-470 nm). These agents are often used to enhance the appearance of color of fabric and paper, causing a whitening effect, making materials look less yellow by increasing the overall amount of blue light reflected.

Fluorescent whitening agents are well known in the art, and many such fluorescent agents are available commercially. Usually, fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the enzyme granule is generally from 0.001% w/w to 5% w/w, preferably 0.001% w/w to 2% w/w, more preferably 0.005% w/w to 1% w/w. However, if the majority of the fluorescent agent used in a detergent composition (see below under the heading "Detergent composition", "Adjunct materials") is added to, and thus becomes part of, the enzyme granule, the content of fluorescent agent in the enzyme granule is up to 80% w/w, preferably up to 50% w/w.

Preferred fluorescent agents are selected from the classes, distyrylbiphenyls, triazinylaminostilbenes, bis(1,2,3-triazol-2-yl)stilbenes, bis(benzo[b]furan-2-yl)biphenyls, 1,3-

diphenyl-2-pyrazolines, thiophenediyl benzoxazole, and coumarins. The fluorescent agent is preferably sulfonated.

Preferred classes of fluorescent agent are: di-styryl biphenyl compounds, e.g., Tinopal™ CBS-X; di-amine stilbene di-sulphonic acid compounds, e.g., Tinopal DMS-X and Blankophor™ HRH; pyrazoline compounds, e.g., Blankophor SN; and thiophenediyl benzoxazole compounds, e.g., Tinopal OB.

Any fluorescent whitening agent suitable for use in a laundry detergent composition is particularly useful in the enzyme granule of the invention. The most commonly used fluorescent whitening agents are those belonging to the classes of diaminostilbene-sulfonic acid derivatives, diarylpyrazoline derivatives and bisphenyl-distyryl derivatives. Examples of the diaminostilbene-sulfonic acid derivative type of fluorescent whitening agents include the sodium salts of: 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino) stilbene-2,2'-disulfonate, 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino) stilbene-2,2'-disulfonate, 4,4'-bis-(2-anilino-4-(*N*-methyl-*N*-2-hydroxy-ethylamino)-s-triazin-6-ylamino) stilbene-2,2'-disulfonate, 4,4'-bis-(4-phenyl-1,2,3-triazol-2-yl)stilbene-2,2'-disulfonate and sodium 5-(2*H*-naphtho[1,2-*d*][1,2,3]triazol-2-yl)-2-[(*E*)-2-phenylvinyl]benzenesulfonate. Preferred fluorescent whitening agents are Tinopal DMS and Tinopal CBS and Tinopal OB, available from BASF. Tinopal DMS is the disodium salt of 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene-2,2'-disulfonate. Tinopal CBS is the disodium salt of 2,2'-bis-(phenyl-styryl)-disulfonate. Tinopal OB is 2,5-thiophenediylbis(5-tert-butyl-1,3-benzoxazole). Another preferred fluorescent whitening agent is the commercially available Parawhite KX, supplied by Paramount Minerals and Chemicals, Mumbai, India. Other fluorescers suitable for use in the invention include the 1-3-diaryl pyrazolines and the 7-alkylaminocoumarins.

Suitable fluorescent agents for use in the invention are also described in McElhone, H.J. (2009), "Fluorescent Whitening Agents", Kirk-Othmer Encyclopedia of Chemical Technology, 1-16, DOI: 10.1002/0471238961.0612211513030512.a01.pub2.

Detergent composition

The enzyme granule of the invention may be added to and thus become a component of a detergent composition.

The detergent composition of the present invention may be formulated, for example, as a hand or machine laundry detergent composition including a laundry additive composition suitable for pre-treatment of stained fabrics and a rinse added fabric softener composition, or be formulated as a detergent composition for use in general household hard surface cleaning operations, or be formulated for hand or machine dishwashing operations.

In a specific aspect, the present invention provides a detergent additive comprising a granule of the present invention, as described herein.

In one embodiment, the invention is directed to detergent compositions comprising an enzyme granule of the present invention in combination with one or more additional cleaning composition components. The choice of additional components is within the skill of the artisan and includes conventional ingredients, including the exemplary non-limiting components set forth below.

The choice of components may include, for textile care, the consideration of the type of textile to be cleaned, the type and/or degree of soiling, the temperature at which cleaning is to take place, and the formulation of the detergent product. Although components mentioned below are categorized by general header according to a particular functionality, this is not to be construed as a limitation, as a component may comprise additional functionalities as will be appreciated by the skilled artisan.

In one embodiment of the present invention, the enzyme granule of the present invention may be added to a detergent composition in an amount corresponding to 0.001-200 mg of enzyme protein, such as 0.005-100 mg of enzyme protein, preferably 0.01-50 mg of enzyme protein, more preferably 0.05-20 mg of enzyme protein, even more preferably 0.1-10 mg of enzyme protein per liter of wash liquor.

Surfactants

The detergent composition may comprise one or more surfactants, which may be anionic and/or cationic and/or non-ionic and/or semi-polar and/or zwitterionic, or a mixture thereof. In a particular embodiment, the detergent composition includes a mixture of one or more nonionic surfactants and one or more anionic surfactants. The surfactant(s) is typically present at a level of from about 0.1% to 60% by weight, such as about 1% to about 40%, or about 3% to about 20%, or about 3% to about 10%. The surfactant(s) is chosen based on the desired cleaning application, and includes any conventional surfactant(s) known in the art. Any surfactant known in the art for use in detergents may be utilized.

When included therein the detergent will usually contain from about 1% to about 40% by weight, such as from about 5% to about 30%, including from about 5% to about 15%, or from about 20% to about 25% of an anionic surfactant. Non-limiting examples of anionic surfactants include sulfates and sulfonates, in particular, linear alkylbenzenesulfonates (LAS), isomers of LAS, branched alkylbenzenesulfonates (BABS), phenylalkanesulfonates, alpha-olefinsulfonates (AOS), olefin sulfonates, alkene sulfonates, alkane-2,3-diylbis(sulfates), hydroxyalkanesulfonates and disulfonates, alkyl sulfates (AS) such as sodium dodecyl sulfate (SDS), fatty alcohol sulfates (FAS), primary alcohol sulfates (PAS), alcohol ethersulfates (AES or AEOS or FES, also known as alcohol ethoxysulfates or fatty alcohol ether sulfates), secondary alkanesulfonates (SAS), paraffin sulfonates (PS), ester sulfonates, sulfonated fatty acid glycerol esters, alpha-sulfo fatty acid methyl esters (alpha-SFMe or SES) including methyl

ester sulfonate (MES), alkyl- or alkenylsuccinic acid, dodecenyl/tetradecenyl succinic acid (DTSA), fatty acid derivatives of amino acids, diesters and monoesters of sulfo-succinic acid or soap, and combinations thereof.

When included therein the detergent will usually contain from about 0.1% to about 10% by weight of a cationic surfactant. Non-limiting examples of cationic surfactants include alkyltrimethylammonium bromide (CTAB), dimethyldistearylammonium chloride (DSDMAC), and alkylbenzyltrimethylammonium, alkyl quaternary ammonium compounds, alkoxyated quaternary ammonium (AQA) compounds, and combinations thereof.

When included therein the detergent will usually contain from about 0.2% to about 40% by weight of a non-ionic surfactant, for example from about 0.5% to about 30%, in particular from about 1% to about 20%, from about 3% to about 10%, such as from about 3% to about 5%, or from about 8% to about 12%. Non-limiting examples of non-ionic surfactants include alcohol ethoxylates (AE or AEO), alcohol propoxylates, propoxylated fatty alcohols (PFA), alkoxyated fatty acid alkyl esters, such as ethoxylated and/or propoxylated fatty acid alkyl esters, alkylphenol ethoxylates (APE), nonylphenol ethoxylates (NPE), alkylpolyglycosides (APG), alkoxyated amines, fatty acid monoethanolamides (FAM), fatty acid diethanolamides (FADA), ethoxylated fatty acid monoethanolamides (EFAM), propoxylated fatty acid monoethanolamides (PFAM), polyhydroxy alkyl fatty acid amides, or *N*-acyl *N*-alkyl derivatives of glucosamine (glucamides, GA, or fatty acid glucamide, FAGA), as well as products available under the trade names SPAN and TWEEN, and combinations thereof.

When included therein the detergent will usually contain from about 0.1% to about 20% by weight of a semipolar surfactant. Non-limiting examples of semipolar surfactants include amine oxides (AO) such as alkyltrimethylamineoxide, *N*-(coco alkyl)-*N,N*-dimethylamine oxide and *N*-(tallow-alkyl)-*N,N*-bis(2-hydroxyethyl)amine oxide, fatty acid alkanolamides and ethoxylated fatty acid alkanolamides, and combinations thereof.

When included therein the detergent will usually contain from about 0.1% to about 10% by weight of a zwitterionic surfactant. Non-limiting examples of zwitterionic surfactants include betaine, alkyltrimethylbetaine, sulfobetaine, and combinations thereof.

Hydrotropes

A hydrotrope is a compound that solubilises hydrophobic compounds in aqueous solutions (or oppositely, polar substances in a non-polar environment). Typically, hydrotropes have both hydrophilic and a hydrophobic character (so-called amphiphilic properties as known from surfactants); however the molecular structure of hydrotropes generally do not favor spontaneous self-aggregation, see for example review by Hodgdon and Kaler (2007), Current Opinion in Colloid & Interface Science 12: 121-128. Hydrotropes do not display a critical

concentration above which self-aggregation occurs as found for surfactants and lipids forming micellar, lamellar or other well defined meso-phases. Instead, many hydrotropes show a continuous-type aggregation process where the sizes of aggregates grow as concentration increases. However, many hydrotropes alter the phase behavior, stability, and colloidal properties of systems containing substances of polar and non-polar character, including mixtures of water, oil, surfactants, and polymers. Hydrotropes are classically used across industries from pharma, personal care, food, to technical applications. Use of hydrotropes in detergent compositions allow for example more concentrated formulations of surfactants (as in the process of compacting liquid detergents by removing water) without inducing undesired phenomena such as phase separation or high viscosity.

The detergent may contain 0-5% by weight, such as about 0.5 to about 5%, or about 3% to about 5%, of a hydrotrope. Any hydrotrope known in the art for use in detergents may be utilized. Non-limiting examples of hydrotropes include sodium benzene sulfonate, sodium p-toluene sulfonate (STS), sodium xylene sulfonate (SXS), sodium cumene sulfonate (SCS), sodium cymene sulfonate, amine oxides, alcohols and polyglycolethers, sodium hydroxynaphthoate, sodium hydroxynaphthalene sulfonate, sodium ethylhexyl sulfate, and combinations thereof.

Builders and Co-Builders

The detergent composition may contain about 0-65% by weight, such as about 5% to about 50% of a detergent builder or co-builder, or a mixture thereof. In a dish wash detergent, the level of builder is typically 40-65%, particularly 50-65%. The builder and/or co-builder may particularly be a chelating agent that forms water-soluble complexes with calcium and magnesium ions. Any builder and/or co-builder known in the art for use in laundry detergents may be utilized. Non-limiting examples of builders include citrates, zeolites, diphosphates (pyrophosphates), triphosphates such as sodium triphosphate (STP or STPP), carbonates such as sodium carbonate, soluble silicates such as sodium metasilicate, layered silicates (e.g., SKS-6 from Hoechst), ethanolamines such as 2-aminoethan-1-ol (MEA), diethanolamine (DEA, also known as iminodiethanol), triethanolamine (TEA, also known as 2,2',2"-nitrilotriethanol), and carboxymethyl inulin (CMI), and combinations thereof.

The detergent composition may also contain 0-50% by weight, such as about 5% to about 30%, of a detergent co-builder, or a mixture thereof. The detergent composition may include a co-builder alone, or in combination with a builder, for example a zeolite builder. Non-limiting examples of co-builders include homopolymers of polyacrylates or copolymers thereof, such as poly(acrylic acid) (PAA) or copoly(acrylic acid/maleic acid) (PAA/PMA). Further non-limiting examples include citrate, chelators such as aminocarboxylates, aminopolycarboxylates and phosphonates, and alkyl- or alkenylsuccinic acid. Additional specific examples include 2,2',2"-

nitritotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), iminodisuccinic acid (IDS), ethylenediamine-*N,N'*-disuccinic acid (EDDS), methylglycinediacetic acid (MGDA), glutamic acid-*N,N*-diacetic acid (GLDA), 1-hydroxyethane-1,1-diphosphonic acid (HEDP),

5 ethylenediaminetetra(methylenephosphonic acid) (EDTMPA), diethylenetriaminepentakis(methylenephosphonic acid) (DTMPA or DTPMPA), *N*-(2-hydroxyethyl)iminodiacetic acid (EDG), aspartic acid-*N*-monoacetic acid (ASMA), aspartic acid-*N,N*-diacetic acid (ASDA), aspartic acid-*N*-monopropionic acid (ASMP), iminodisuccinic acid (IDA), *N*-(2-sulfomethyl)-aspartic acid (SMAS), *N*-(2-sulfoethyl)-aspartic acid (SEAS), *N*-(2-

10 sulfomethyl)-glutamic acid (SMGL), *N*-(2-sulfoethyl)-glutamic acid (SEGL), *N*-methyliminodiacetic acid (MIDA), α -alanine-*N,N*-diacetic acid (α -ALDA), serine-*N,N*-diacetic acid (SEDA), isoserine-*N,N*-diacetic acid (ISDA), phenylalanine-*N,N*-diacetic acid (PHDA), anthranilic acid-*N,N*-diacetic acid (ANDA), sulfanilic acid-*N,N*-diacetic acid (SLDA), taurine-*N,N*-diacetic acid (TUDA) and sulfomethyl-*N,N*-diacetic acid (SMDA), *N*-(2-hydroxyethyl)-

15 ethylenediamine-*N,N',N'*-triacetate (HEDTA), diethanolglycine (DEG), diethylenetriamine penta(methylenephosphonic acid) (DTPMP), aminotris(methylenephosphonic acid) (ATMP), and combinations and salts thereof. Further exemplary builders and/or co-builders are described in, *e.g.*, WO 2009/102854, US 5,977,053.

20 Bleaching Systems

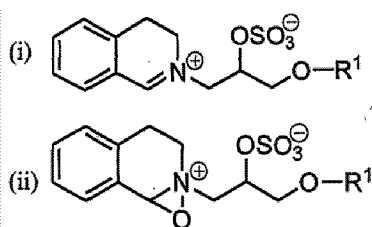
The detergent may contain 0-50% by weight of a bleaching system. Any bleaching system known in the art for use in laundry detergents may be utilized. Suitable bleaching system components include bleaching catalysts, photobleaches, bleach activators, sources of hydrogen peroxide such as sodium percarbonate and sodium perborates, preformed peracids

25 and mixtures thereof. Suitable preformed peracids include, but are not limited to, peroxydicarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, for example, Oxone (R), and mixtures thereof. Non-limiting examples of bleaching systems include peroxide-based bleaching systems, which may comprise, for example, an inorganic salt, including alkali metal salts such as sodium salts of

30 perborate (usually mono- or tetra-hydrate), percarbonate, persulfate, perphosphate, persilicate salts, in combination with a peracid-forming bleach activator. The term bleach activator is meant herein as a compound which reacts with peroxygen bleach like hydrogen peroxide to form a peracid. The peracid thus formed constitutes the activated bleach. Suitable bleach activators to be used herein include those belonging to the class of esters amides, imides or

35 anhydrides. Suitable examples are tetracetylene diamine (TAED), sodium 4-[(3,5,5-trimethylhexanoyl)oxy]benzene sulfonate (ISONOBS), diperoxy dodecanoic acid, 4-(dodecanoyloxy)benzenesulfonate (LOBS), 4-(decanoyloxy)benzenesulfonate, 4-

(decanoyloxy)benzoate (DOBS), 4-(nonanoyloxy)-benzenesulfonate (NOBS), and/or those disclosed in WO 98/17767. A particular family of bleach activators of interest was disclosed in EP624154 and particularly preferred in that family is acetyl triethyl citrate (ATC). ATC or a short chain triglyceride like triacetin has the advantage that it is environmental friendly as it eventually
 5 degrades into citric acid and alcohol. Furthermore acetyl triethyl citrate and triacetin has a good hydrolytical stability in the product upon storage and it is an efficient bleach activator. Finally ATC provides a good building capacity to the laundry additive. Alternatively, the bleaching system may comprise peroxyacids of, for example, the amide, imide, or sulfone type. The bleaching system may also comprise peracids such as 6-(phthalimido)peroxyhexanoic acid
 10 (PAP). The bleaching system may also include a bleach catalyst. In some embodiments the bleach component may be an organic catalyst selected from the group consisting of organic catalysts having the following formulae:



and mixtures thereof; wherein each R¹ is independently a branched alkyl group containing from
 15 9 to 24 carbons or linear alkyl group containing from 11 to 24 carbons, preferably each R¹ is independently a branched alkyl group containing from 9 to 18 carbons or linear alkyl group containing from 11 to 18 carbons, more preferably each R¹ is independently selected from the group consisting of 2-propylheptyl, 2-butyloctyl, 2-pentylnonyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl. Other
 20 exemplary bleaching systems are described, e.g., in WO 2007/087258, WO 2007/087244, WO 2007/087259 and WO 2007/087242. Suitable photobleaches may for example be sulfonated zinc phthalocyanine.

Polymers

25 The detergent may contain 0-10% by weight, such as 0.5-5%, 2-5%, 0.5-2% or 0.2-1% of a polymer. Any polymer known in the art for use in detergents may be utilized. The polymer may function as a co-builder as mentioned above, or may provide antiredeposition, fiber protection, soil release, dye transfer inhibition, grease cleaning and/or anti-foaming properties. Some polymers may have more than one of the above-mentioned properties and/or more than
 30 one of the below-mentioned motifs. Exemplary polymers include (carboxymethyl)cellulose (CMC), poly(vinyl alcohol) (PVA), poly(vinylpyrrolidone) (PVP), poly(ethyleneglycol) or poly(ethylene oxide) (PEG), ethoxylated poly(ethyleneimine), carboxymethyl inulin (CMI), and polycarboxylates such as PAA, PAA/PMA, poly-aspartic acid, and lauryl methacrylate/acrylic

acid copolymers, hydrophobically modified CMC (HM-CMC) and silicones, copolymers of terephthalic acid and oligomeric glycols, copolymers of poly(ethylene terephthalate) and poly(oxyethene terephthalate) (PET-POET), PVP, poly(vinylimidazole) (PVI), poly(vinylpyridine-N-oxide) (PVPO or PVPNO) and polyvinylpyrrolidone-vinylimidazole (PVPVI). Further
5 exemplary polymers include sulfonated polycarboxylates, polyethylene oxide and polypropylene oxide (PEO-PPO) and diquatonium ethoxy sulfate. Other exemplary polymers are disclosed in, e.g., WO 2006/130575 and US 5,955,415. Salts of the above-mentioned polymers are also contemplated.

10 Fabric hueing agents

The detergent compositions of the present invention may also include fabric hueing agents such as dyes or pigments, which when formulated in detergent compositions can deposit onto a fabric when said fabric is contacted with a wash liquor comprising said detergent compositions and thus altering the tint of said fabric through absorption/reflection of visible light.
15 Fluorescent whitening agents emit at least some visible light. In contrast, fabric hueing agents alter the tint of a surface as they absorb at least a portion of the visible light spectrum. Suitable fabric hueing agents include dyes and dye-clay conjugates, and may also include pigments. Suitable dyes include small molecule dyes and polymeric dyes. Suitable small molecule dyes include small molecule dyes selected from the group consisting of dyes falling into the Colour
20 Index (C.I.) classifications of Direct Blue, Direct Red, Direct Violet, Acid Blue, Acid Red, Acid Violet, Basic Blue, Basic Violet and Basic Red, or mixtures thereof, for example as described in WO 2005/03274, WO 2005/03275, WO 2005/03276 and EP 1876226 (hereby incorporated by reference). The detergent composition preferably comprises from about 0.00003 wt% to about 0.2 wt%, from about 0.00008 wt% to about 0.05 wt%, or even from about 0.0001 wt% to about
25 0.04 wt% fabric hueing agent. The composition may comprise from 0.0001 wt% to 0.2 wt% fabric hueing agent, this may be especially preferred when the composition is in the form of a unit dose pouch. Suitable hueing agents are also disclosed in, e.g., WO 2007/087257 and WO 2007/087243.

30 Detergent enzyme(s)

The detergent additive as well as the detergent composition may comprise one or more (additional) enzymes, such as those mentioned above under the heading "Enzyme".

In general the properties of the selected enzyme(s) should be compatible with the selected detergent, (i.e., pH-optimum, compatibility with other enzymatic and non-enzymatic
35 ingredients, etc.), and the enzyme(s) should be present in effective amounts.

The detergent enzyme(s) may be included in a detergent composition by adding separate additives containing one or more enzymes, or by adding a combined additive comprising all of

these enzymes. A detergent additive of the invention, *i.e.*, a separate additive or a combined additive, can be formulated, for example, as a granulate, liquid, slurry, etc. Preferred detergent additive formulations are granulates, in particular non-dusting granulates, liquids, in particular stabilized liquids, or slurries.

5 The detergent enzyme(s) may be included in a detergent composition by adding separate additives containing one or more enzymes, or by adding a combined additive comprising all of these enzymes. A detergent additive of the invention, *i.e.*, a separate additive or a combined additive is formulated as a granule of the invention.

10 Adjunct materials

Any detergent components known in the art for use in laundry detergents may also be utilized. Other optional detergent components include anti-corrosion agents, anti-shrink agents, anti-soil redeposition agents, anti-wrinkling agents, bactericides, binders, corrosion inhibitors, disintegrants/disintegration agents, dyes, enzyme stabilizers (including boric acid, borates, 15 CMC, and/or polyols such as propylene glycol), fabric conditioners including clays, fillers/processing aids, fluorescent whitening agents/optical brighteners, foam boosters, foam (suds) regulators, perfumes, soil-suspending agents, softeners, suds suppressors, tarnish inhibitors, and wicking agents, either alone or in combination. Any ingredient known in the art for use in laundry detergents may be utilized. The choice of such ingredients is well within the 20 skill of the artisan.

Dispersants - The detergent compositions of the present invention can also contain dispersants. In particular powdered detergents may comprise dispersants. Suitable water-soluble organic materials include the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not 25 more than two carbon atoms. Suitable dispersants are for example described in Powdered Detergents, Surfactant science series volume 71, Marcel Dekker, Inc.

Dye Transfer Inhibiting Agents - The detergent compositions of the present invention may also include one or more dye transfer inhibiting agents. Suitable polymeric dye transfer inhibiting agents include, but are not limited to, polyvinylpyrrolidone polymers, polyamine *N*-oxide polymers, copolymers of *N*-vinylpyrrolidone and *N*-vinylimidazole, polyvinylloxazolidones 30 and polyvinylimidazoles or mixtures thereof. When present in a subject composition, the dye transfer inhibiting agents may be present at levels from about 0.0001 % to about 10%, from about 0.01% to about 5% or even from about 0.1% to about 3% by weight of the composition.

Fluorescent whitening agent - The detergent compositions of the present invention will 35 preferably also contain additional components that may tint articles being cleaned, such as fluorescent whitening agent or optical brighteners. Where present the brightener is preferably at a level of about 0.01% to about 0.5%. Any fluorescent whitening agent suitable for use in a

laundry detergent composition may be used in the composition of the present invention.

Examples of the most commonly used fluorescent whitening agents are described above under the heading "Fluorescent whitening agent".

Suitable fluorescent brightener levels include lower levels of from about 0.01, from 0.05, 5 from about 0.1 or even from about 0.2 wt % to upper levels of 0.5 or even 0.75 wt%.

Soil release polymers - The detergent compositions of the present invention may also include one or more soil release polymers which aid the removal of soils from fabrics such as cotton and polyester based fabrics, in particular the removal of hydrophobic soils from polyester based fabrics. The soil release polymers may for example be nonionic or anionic terephthalate 10 based polymers, polyvinyl caprolactam and related copolymers, vinyl graft copolymers, polyester polyamides see for example Chapter 7 in Powdered Detergents, Surfactant science series volume 71, Marcel Dekker, Inc. Another type of soil release polymers are amphiphilic alkoxylated grease cleaning polymers comprising a core structure and a plurality of alkoxylate groups attached to that core structure. The core structure may comprise a polyalkylenimine 15 structure or a polyalkanolamine structure as described in detail in WO 2009/087523 (hereby incorporated by reference). Furthermore random graft co-polymers are suitable soil release polymers. Suitable graft co-polymers are described in more detail in WO 2007/138054, WO 2006/108856 and WO 2006/113314 (hereby incorporated by reference). Other soil release polymers are substituted polysaccharide structures especially substituted cellulosic structures 20 such as modified cellulose derivatives such as those described in EP 1867808 or WO 2003/040279 (both are hereby incorporated by reference). Suitable cellulosic polymers include cellulose, cellulose ethers, cellulose esters, cellulose amides and mixtures thereof. Suitable cellulosic polymers include anionically modified cellulose, nonionically modified cellulose, cationically modified cellulose, zwitterionically modified cellulose, and mixtures thereof. Suitable 25 cellulosic polymers include methyl cellulose, carboxy methyl cellulose, ethyl cellulose, hydroxyl ethyl cellulose, hydroxyl propyl methyl cellulose, ester carboxy methyl cellulose, and mixtures thereof.

Anti-redeposition agents - The detergent compositions of the present invention may also include one or more anti-redeposition agents such as carboxymethylcellulose (CMC), polyvinyl 30 alcohol (PVA), polyvinylpyrrolidone (PVP), polyoxyethylene and/or polyethyleneglycol (PEG), homopolymers of acrylic acid, copolymers of acrylic acid and maleic acid, and ethoxylated polyethyleneimines. The cellulose based polymers described under soil release polymers above may also function as anti-redeposition agents.

Other suitable adjunct materials include, but are not limited to, anti-shrink agents, anti- 35 wrinkling agents, bactericides, binders, carriers, dyes, enzyme stabilizers, fabric softeners, fillers, foam regulators, perfumes, pigments, sod suppressors, solvents, and structurants for liquid detergents and/or structure elasticizing agents.

Laundry soap bars

The granule of the invention may be added to laundry soap bars and used for hand washing laundry, fabrics and/or textiles. The term laundry soap bar includes laundry bars, soap bars, combo bars, syndet bars and detergent bars. The types of bar usually differ in the type of surfactant they contain, and the term laundry soap bar includes those containing soaps from fatty acids and/or synthetic soaps. The laundry soap bar has a physical form which is solid and not a liquid, gel or a powder at room temperature. The term solid is defined as a physical form which does not significantly change over time, *i.e.*, if a solid object (*e.g.*, laundry soap bar) is placed inside a container, the solid object does not change to fill the container it is placed in. The bar is a solid typically in bar form but can be in other solid shapes such as round or oval.

The laundry soap bar may contain one or more additional enzymes, protease inhibitors such as peptide aldehydes (or hydrosulfite adduct or hemiacetal adduct), boric acid, borate, borax and/or phenylboronic acid derivatives such as 4-formylphenylboronic acid, one or more soaps or synthetic surfactants, polyols such as glycerine, pH controlling compounds such as fatty acids, citric acid, acetic acid and/or formic acid, and/or a salt of a monovalent cation and an organic anion wherein the monovalent cation may be for example Na^+ , K^+ or NH_4^+ and the organic anion may be for example formate, acetate, citrate or lactate such that the salt of a monovalent cation and an organic anion may be, for example, sodium formate.

The laundry soap bar may also contain complexing agents like EDTA and HEDP, perfumes and/or different type of fillers, surfactants, *e.g.*, anionic synthetic surfactants, builders, polymeric soil release agents, detergent chelators, stabilizing agents, fillers, dyes, colorants, dye transfer inhibitors, alkoxyated polycarbonates, suds suppressers, structurants, binders, leaching agents, bleaching activators, clay soil removal agents, anti-redeposition agents, polymeric dispersing agents, brighteners, fabric softeners, perfumes and/or other compounds known in the art.

The laundry soap bar may be processed in conventional laundry soap bar making equipment such as but not limited to: mixers, plodders, *e.g.*, a two stage vacuum plodder, extruders, cutters, logo-stampers, cooling tunnels and wrappers. The invention is not limited to preparing the laundry soap bars by any single method. The premix of the invention may be added to the soap at different stages of the process. For example, the premix containing a soap, an enzyme granule of the invention, optionally one or more additional enzymes, a protease inhibitor, and a salt of a monovalent cation and an organic anion may be prepared and the mixture is then plodded. The enzyme and optional additional enzymes may be added at the same time as the protease inhibitor for example in liquid form. Besides the mixing step and the plodding step, the process may further comprise the steps of milling, extruding, cutting, stamping, cooling and/or wrapping.

Compositions, methods and uses

In a first aspect, the invention provides an enzyme granule comprising an enzyme and a fluorescent whitening agent. Preferably, the enzyme is a protease, a lipase, a cutinase, an amylase, a carbohydrase, a cellulase, a pectinase, a pectate lyase, a mannanase, an arabinase, a galactanase, a xylanase, an oxidase, a laccase, or a peroxidase.

In an embodiment, the enzyme granule comprises a core and a coating, and the coating includes the fluorescent whitening agent. Preferably, the core includes the enzyme. In an embodiment, the coating includes wax (a wax coating).

In an embodiment, the enzyme granule contains at least one enzyme in an amount of more than 0.5% w/w and less than 50% w/w active enzyme protein.

In an embodiment, the enzyme granule contains the fluorescent whitening agent in an amount of from 0.001% w/w to 5% w/w. Preferably, the fluorescent whitening agent is a diaminostilbene-sulfonate, such as the disodium salt of 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene-2,2'-disulfonate; bisphenyl-distyryl compound, such as the disodium salt of 2,2'-bis-(phenyl-styryl)-disulfonate; or thiophenediyl benzoxazole compound, such as 2,5-thiophenediylbis(5-tert-butyl-1,3-benzoxazole).

In an embodiment, the enzyme granule comprises a salt coating and/or a wax coating.

In an embodiment, the enzyme granule contains less than 3% w/w titanium dioxide and/or less than 10% w/w surfactant. Preferably, the enzyme granule contains less than 1% w/w titanium dioxide, more preferably less than 0.5% w/w titanium dioxide, more preferably less than 0.1% w/w titanium dioxide, even more preferably less than 0.05% w/w titanium dioxide, and most preferably less than 0.01% w/w titanium dioxide. Preferably, the enzyme granule contains less than 5% w/w surfactant; more preferably less than 1% w/w surfactant.

In a second aspect, the invention provides a method for preparing the enzyme granule of the invention, as described above, which comprises granulating a blend which comprises the enzyme, followed by applying a coating which comprises the fluorescent whitening agent.

In another aspect, the invention provides a detergent composition (e.g., a laundry or automatic dishwash detergent), comprising a surfactant and/or a detergent builder, and the enzyme granule of the invention, as described above. Preferably, the detergent composition contains a fluorescent whitening agent in an amount of from 0.01% w/w to 0.5% w/w of the total detergent composition, and the enzyme granule comprises up to 80% w/w, preferably up to 50% w/w, of the fluorescent whitening agent. The content of fluorescent whitening agent in the enzyme granule is used not only to provide the granule with a white appearance, but may also be used as a supply of fluorescent whitening agent in the overall detergent composition, to provide whitening benefits to laundry after wash.

In a further aspect, the invention provides a method for reducing the yellowness (Hunter b-value) of an enzyme granule, comprising applying a (wax) coating comprising a fluorescent whitening agent to the enzyme granule.

The present invention also provides for use of a fluorescent whitening agent for improving the whiteness of an enzyme granule which comprises at least one enzyme in an amount of more than 0.5% w/w active enzyme protein. Preferably, the enzyme is a protease, a lipase, a cutinase, an amylase, a carbohydrase, a cellulase, a pectinase, a pectate lyase, a mannanase, an arabinase, a galactanase, a xylanase, an oxidase, a laccase, or a peroxidase. Preferably, the enzyme granule contains less than 10% w/w surfactant; more preferably less than 5% w/w surfactant; and most preferably less than 1% w/w surfactant.

In an embodiment, the enzyme granule comprises a core and a coating. Preferably, the core includes the enzyme and the coating includes the fluorescent whitening agent.

The present invention is further described by the following examples which should not be construed as limiting the scope of the invention.

EXAMPLES

A production scale uncoated lipase T-granulate with an approximate protein content of 2% was produced as described in US 4,106,991 (Example 1) with the following exceptions:

- finely grinded sodium sulfate was used instead of sodium chloride as filler material, and
- the enzyme concentrate (added as a liquid) contained also a carbohydrate binder (Stadex 79 dextrin).

The granules were sieved in the fraction 300 to 1100 microns and coated with the compositions given in the examples below (in a 5 liter Lödige mixer) as described in US 4,109,991 (Example 22).

Chemicals were commercial products of at least reagent grade. "Fluorescent whitening agent" is abbreviated "FWA". The percentages in the Examples are given relative to uncoated granules.

EXAMPLE 1

Reference without titanium dioxide or FWA

1500 gram uncoated lipase granulate was loaded in the mixer. The granules were coated with (in order of addition to the mixer):

75 g melted PEG-4000,
210 g Precipitated calcium carbonate,
30 g melted PEG-4000, and
22.5 g Kaolin.

EXAMPLE 2**3% titanium dioxide**

1500 gram uncoated lipase granulate was loaded in the mixer. The granules were coated
with (in order of addition to the mixer):
75 g melted PEG-4000,
165 g Precipitated calcium carbonate + 45 g Titanium dioxide (TiO₂),
30 g melted PEG-4000, and
22.5 g Kaolin.

EXAMPLE 3**0.01% FWA in wax 1**

Coated granules were produced as in Example 1 but with the addition of 0.15 g Tinopal
OB (BASF) mixed with the first PEG-4000.

EXAMPLE 4**0.01% FWA in wax 2**

Coated granules were produced as in Example 1 but with the addition of 0.15 g Tinopal
OB (BASF) mixed with the final PEG-4000.

EXAMPLE 5**0.01% FWA in kaolin**

Coated granules were produced as in Example 1 but with the addition of 0.15 g Tinopal
OB (BASF) mixed with the final kaolin.

EXAMPLE 6**0.1% FWA in wax 1**

Coated granules were produced as in Example 1 but with the addition of 1.5 g Tinopal OB
(BASF) mixed with the first PEG-4000.

EXAMPLE 7**0.1% FWA in wax 2**

Coated granules were produced as in Example 1 but with the addition of 1.5 g Tinopal
OB (BASF) mixed with the final PEG-4000.

Example 8**0.1% FWA in kaolin**

Coated granules were produced as in Example 1 but with the addition of 1.5 g Tinopal OB (BASF) mixed with the final kaolin.

EXAMPLE 9

5 Improvement in whiteness

The coated granules from Examples 1-8 were all sieved 300-1180 microns to remove eventual lumps from the coating, and the granulate color was measured on a HunterLab ColorFlex sensor (Model 45°/0°) using the Hunter L,a,b scale well known in the art:

- L is measured on a scale from 0 to 100, where 100 indicate perfect white and zero indicates black,
- a measures redness when positive and greenness when negative, and
- b measures yellowness when positive and blueness when negative.

Thus, to get a white granule the L value should be as close to 100 as possible and the a and b values as close to zero as possible.

15 The results below are given as delta values compared to the values from Example 1 (without titanium dioxide and FWA), where a positive delta value indicates an improvement towards increased whiteness such that for the a and b values it is the difference in the distance to value 0 (e.g., if the a value for the reference is -1.5 and for the sample is +1.0 the delta value is 0.5). This definition is chosen as the objective is to make as white a granule as possible.

20 A total whiteness improvement can be defined as $\Delta W = \Delta L + \Delta a + \Delta b$. It is our experience that a ΔW of approximately 1 gives a visible difference in color.

Table 1. Granule color measurement relative to the reference of Example 1.

Granulate	ΔL	Δa	Δb	ΔW
Example 1 (reference)	0.00	0.00	0.00	0.00
Example 2 (3% TiO ₂)	1.24	0.20	1.14	2.58
Example 3 (0.01% FWA)	1.76	0.55	1.82	4.13
Example 4 (0.01% FWA)	1.19	0.43	1.32	2.94
Example 5 (0.01% FWA)	1.13	0.21	1.92	3.26
Example 6 (0.1% FWA)	1.51	0.70	2.45	4.66

Example 7 (0.1% FWA)	1.13	1.04	2.26	4.43
Example 8 (0.1% FWA)	0.81	0.92	1.74	3.47

The results show that the addition of the FWA improves the whiteness of the granule, and that the addition of about 0.01% FWA can replace 3% titanium dioxide. Increasing the amount of the FWA results in a further improvement. The addition of the FWA in the final kaolin coating powder also yielded an improved whiteness.

EXAMPLE 10

Reduced yellowness

The Hunter b-color is a measure of yellowness (also described above). Fluorescent whitening agents (FWA) emit in the blue wavelengths and thereby reduce the measured yellowness, which can be seen in Table 2. The reduced yellowness contributes to an improved whiteness appearance. The data in Table 2 shows the impact of FWA on the color of an enzyme granule, when the FWA is applied in a wax coating of the enzyme granule.

Table 2. FWA applied in a wax coating of an enzyme granule.

% FWA in granule	Hunter b-color
0	9.3
0.0002	9.1
0.001	8.5
0.005	7.7
0.01	7.8
0.05	7.8

CLAIMS

1. An enzyme containing granule comprising a core and a coating, wherein the coating comprises a fluorescent whitening agent.

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2. The granule of claim 1, wherein the enzyme is a protease, a lipase, a cutinase, an amylase, a carbohydrase, a cellulase, a pectinase, a pectate lyase, a mannanase, an arabinase, a galactanase, a xylanase, an oxidase, a laccase, or a peroxidase.

10 3. The granule of claim 1 or 2, wherein the core comprises the enzyme.

4. The granule of any of claims 1-3, wherein the enzyme is present in an amount of more than 0.5% w/w and less than 50% w/w active enzyme protein.

15 5. The granule of any of claims 1-4, which further comprises less than 3% w/w titanium dioxide and/or less than 10% w/w surfactant.

6. The granule of any of claims 1-5, which further comprises a wax and/or a salt coating.

20 7. The granule of any of claims 1-6, wherein the fluorescent agent is selected from the group consisting of distyrylbiphenyls, triazinylaminostilbenes, bis(1,2,3-triazol-2-yl)stilbenes, bis(benzo[b]furan-2-yl)biphenyls, 1,3-diphenyl-2-pyrazolines, thiophenediyl benzoxazole, and coumarins.

25 8. The granule of any of claims 1-7, wherein the fluorescent whitening agent is a diaminostilbene-sulfonate, such as the disodium salt of 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene-2,2'-disulfonate; bisphenyl-distyryl compound, such as the disodium salt of 2,2'-bis-(phenyl-styryl)-disulfonate; or thiophenediyl benzoxazole compound, such as 2,5-thiophenediylbis(5-tert-butyl-1,3-benzoxazole).

30

9. The granule of any of claims 1-8, which contains the fluorescent whitening agent in an amount of from 0.001% w/w to 5% w/w.

35 10. A method for preparing the enzyme granule of any of claims 1-9, which comprises granulating a blend which comprises the enzyme, followed by applying a coating which comprises the fluorescent whitening agent.

11. A detergent composition, comprising a surfactant and/or a detergent builder, and the enzyme granule of any of claims 1-9.

5 12. A detergent composition, comprising a surfactant and/or a detergent builder, and the enzyme granule of any of claims 1-8, and a fluorescent whitening agent in an amount of from 0.01% w/w to 0.5% w/w of the total detergent composition.

10 13. The composition of claim 12, wherein the enzyme granule comprises up to 80% w/w fluorescent whitening agent.

14. Use of a fluorescent whitening agent for improving the whiteness of an enzyme granule which comprises at least one enzyme in an amount of more than 0.5% w/w active enzyme protein.

15 15. The use according to claim 14, wherein the enzyme granule contains less than 10% w/w surfactant.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/068296

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/386
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	Page 8 lines 30-33, Page 9 line 35; claim 5; figures 1,2	6-9, 12-15
Y	----- Suzan Biran: "STABILITY OF ENZYMES IN GRANULAR ENZYME PRODUCTS FOR LAUNDRY DETERGENTS", DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING, TECHNICAL UNIVERSITY OF DENMARK PhD thesis, 2010, pages 1, 38-41, XP055098920, Retrieved from the Internet: URL: http://wwwx.dtu.dk/upload/kt-chec/sbiran_phd_thesis.pdf [retrieved on 2014-01-28] page 38 - page 41; figures 2.9-a ----- -/-	6-9, 12-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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International application No

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