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(54) CATALASE INHIBITION DURING A LAUNDERING PROCESS

(57) The present invention relates to the use of methylglycine diacetic acid or salt thereof (MGDA) to inhibit the enzymatic activity of catalase during a laundering process.

EP 3 546 557 A1

Description

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FIELD OF THE INVENTION

⁵ **[0001]** The present invention relates to the use of methylglycine diacetic acid or salt thereof (MGDA) to inhibit the enzymatic activity of catalase during a laundering process.

BACKGROUND OF THE INVENTION

[0002] Catalase is an enzyme present in nearly all aerobic organisms. Catalase protects these aerobic organisms from oxidative damage by catalyzing the decomposition of hydrogen peroxide to water and oxgen.

[0003] Hydrogen peroxide is a potentially harmful by-product of metabolic processes of aerobic organisms. The presence of catalase in aerobic organisms protects the organisms from unwanted oxidative damage by converting the highly reactive hydrogen peroxide to less reactive oxygen and water.

[0004] Hydrogen peroxide is an important bleach used in laundry detergent compositions, especially solid laundry detergent powder. Catalase is typically introduced into the laundry process due to its presence in biological soils. The presence of catalase in the laundry process can lead to poor cleaning performance, especially poor bleaching performance.

[0005] One of the challenges of a laundry detergent formulator is to ensure that good cleaning activity, and especially good bleaching activity, occurs quickly in the laundering process, and occurs before the catalase activity reduces this cleaning activity, especially the bleaching activity.

[0006] The inventors overcome this problem by providing a use of a specific chelant, namely methylglycine diacetic acid or salt thereof (MGDA), which inhibits the enzymatic activity of catalase during the laundering process. This is especially useful when the laundry detergent is a solid laundry detergent powder, and especially when the laundry detergent comprises a bleach, especially a sodium percarbonate bleach.

[0007] In addition, the inventors have found that MGDA can also be used to inhibit the enzymatic activity of catalase during a laundering process when the laundry detergent composition is a solid laundry detergent powder having a low pH profile, such as upon dissolution in de-ionized water at a temperature of 20°C and at a concentration of 1g/l, the equilibrium pH is from 4.0 to 9.0, or from 6.0 to 8.5. The pH of the solid laundry detergent powder affects the kinetics and efficacy of the bleach, and especially sodium percarbonate bleach. The pH also affects the binding metal ion constants of chelants such as MGDA. The inventors have found that even at this low pH profile, MGDA can still be used to inhibit the enzymatic activity of catalase during the laundering process.

SUMMARY OF THE INVENTION

[0008] The present invention relates to the use of methylglycine diacetic acid or salt thereof (MGDA) to inhibit the enzymatic activity of catalase during a laundering process.

DETAILED DESCRIPTION OF THE INVENTION

[0009] <u>Use:</u> Methylglycine diacetic acid or salt thereof (MGDA) is used to inhibit the enzymatic activity of catalase during a laundering process.

[0010] Typically, the laundering process comprises the step of contacting a laundry detergent composition to water to form a wash bath, and contacting soil laundry to the wash bath.

[0011] The laundry detergent can be a liquid, solid or unit dose form such a pouch. Preferably, the laundry detergent is a solid laundry detergent powder.

[0012] The solid laundry detergent powder, upon dissolution in de-ionized water at 20°C at a concentration of 1g/l, may have an equilibrium pH of from 4.0 to 9.0.

[0013] Typically, the laundry detergent comprises detersive surfactant. Typically, the laundry detergent comprises bleach. A preferred bleach is a sodium percarbonate bleach.

[0014] Preferably, the methylglycine diacetic acid or salt thereof (MGDA) is the tri-sodium salt of methylglycine diacetic acid.

[0015] The use preferably provides strain removal benefits to the fabric, preferably tea stain removal benefits to the fabric. The fabric typically comprises cotton, although other fabrics include polyester.

[0016] <u>Laundry detergent composition:</u> Typically, the laundry detergent composition is a solid free-flowing particulate laundry detergent composition, typically a fully formulated laundry detergent composition, not a portion thereof such as a spray-dried, extruded or agglomerate particle that only forms part of the laundry detergent composition. Typically, the solid composition comprises a plurality of chemically different particles, such as spray-dried base detergent particles

and/or agglomerated base detergent particles and/or extruded base detergent particles, in combination with one or more, typically two or more, or five or more, or even ten or more particles selected from: surfactant particles, including surfactant agglomerates, surfactant extrudates, surfactant needles, surfactant noodles, surfactant flakes; phosphate particles; zeolite particles; silicate salt particles, especially sodium silicate particles; carbonate salt particles, especially sodium carbonate particles; polymer particles such as carboxylate polymer particles, cellulosic polymer particles, starch particles, polyester particles, polyamine particles, terephthalate polymer particles, polyethylene glycol particles; aesthetic particles such as coloured noodles, needles, lamellae particles and ring particles; enzyme particles such as protease granulates, amylase granulates, lipase granulates, cellulase granulates, mannanase granulates, pectate lyase granulates, xyloglucanase granulates, bleaching enzyme granulates and co-granulates of any of these enzymes, preferably these enzyme granulates comprise sodium sulphate; bleach particles, such as percarbonate particles, especially coated percarbonate particles, such as percarbonate coated with carbonate salt, sulphate salt, silicate salt, borosilicate salt, or any combination thereof, perborate particles, bleach activator particles such as tetra acetyl ethylene diamine particles and/or alkyl oxybenzene sulphonate particles, bleach catalyst particles such as transition metal catalyst particles, and/or isoquinolinium bleach catalyst particles, pre-formed peracid particles, especially coated pre-formed peracid particles; filler particles such as sulphate salt particles and chloride particles; clay particles such as montmorillonite particles and particles of clay and silicone; flocculant particles such as polyethylene oxide particles; wax particles such as wax agglomerates; silicone particles, brightener particles; dye transfer inhibition particles; dye fixative particles; perfume particles such as perfume microcapsules and starch encapsulated perfume accord particles, or pro-perfume particles such as Schiff base reaction product particles; hueing dye particles; chelant particles such as chelant agglomerates; and any combination thereof.

[0017] Suitable laundry detergent compositions comprise a detergent ingredient selected from: detersive surfactant, such as anionic detersive surfactants, non-ionic detersive surfactants, cationic detersive surfactants, zwitterionic detersive surfactants and amphoteric detersive surfactants; polymers, such as carboxylate polymers, soil release polymer, anti-redeposition polymers, cellulosic polymers and care polymers; bleach, such as sources of hydrogen peroxide, bleach activators, bleach catalysts and pre-formed peracids; photobleach, such as such as zinc and/or aluminium sulphonated phthalocyanine; enzymes, such as proteases, amylases, cellulases, lipases; zeolite builder; phosphate builder; cobuilders, such as citric acid and citrate; carbonate, such as sodium carbonate and sodium bicarbonate; sulphate salt, such as sodium sulphate; silicate salt such as sodium silicate; chloride salt, such as sodium chloride; brighteners; chelants; hueing agents; dye transfer inhibitors; dye fixative agents; perfume; silicone; fabric softening agents, such as clay; flocculants, such as polyethyleneoxide; suds supressors; and any combination thereof.

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[0018] Suitable laundry detergent compositions may have a low buffering capacity. Such laundry detergent compositions typically have a reserve alkalinity to pH 9.5 of less than 5.0gNaOH/100g. These low buffered laundry detergent compositions typically comprise low levels of carbonate salt.

[0019] Detersive Surfactant: Suitable detersive surfactants include anionic detersive surfactants, non-ionic detersive surfactant, cationic detersive surfactants, zwitterionic detersive surfactants and amphoteric detersive surfactants. Suitable detersive surfactants may be linear or branched, substituted or un-substituted, and may be derived from petrochemical material or biomaterial.

[0020] Anionic detersive surfactant: Suitable anionic detersive surfactants include sulphonate and sulphate detersive surfactants.

[0021] Suitable sulphonate detersive surfactants include methyl ester sulphonates, alpha olefin sulphonates, alkyl benzene sulphonates, especially alkyl benzene sulphonates, preferably C₁₀₋₁₃ alkyl benzene sulphonate. Suitable alkyl benzene sulphonate (LAS) is obtainable, preferably obtained, by sulphonating commercially available linear alkyl benzene (LAB); suitable LAB includes low 2-phenyl LAB, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®.

45 [0022] Suitable sulphate detersive surfactants include alkyl sulphate, preferably C₈₋₁₈ alkyl sulphate, or predominantly C₁₂ alkyl sulphate.

[0023] A preferred sulphate detersive surfactant is alkyl alkoxylated sulphate, preferably alkyl ethoxylated sulphate, preferably a C_{8-18} alkyl alkoxylated sulphate, preferably a C_{8-18} alkyl ethoxylated sulphate, preferably the alkyl alkoxylated sulphate has an average degree of alkoxylation of from 0.5 to 20, preferably from 0.5 to 10, preferably the alkyl alkoxylated sulphate is a C_{8-18} alkyl ethoxylated sulphate having an average degree of ethoxylation of from 0.5 to 10, preferably from 0.5 to 5, more preferably from 0.5 to 3 and most preferably from 0.5 to 1.5.

[0024] The alkyl sulphate, alkyl alkoxylated sulphate and alkyl benzene sulphonates may be linear or branched, substituted or un-substituted, and may be derived from petrochemical material or biomaterial.

[0025] Other suitable anionic detersive surfactants include alkyl ether carboxylates.

⁵⁵ **[0026]** Suitable anionic detersive surfactants may be in salt form, suitable counter-ions include sodium, calcium, magnesium, amino alcohols, and any combination thereof. A preferred counterion is sodium.

[0027] Non-ionic detersive surfactant: Suitable non-ionic detersive surfactants are selected from the group consisting of: C_8 - C_{18} alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C_6 - C_{12} alkyl phenol alkoxylates

wherein preferably the alkoxylate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C_{12} - C_{18} alcohol and C_6 - C_{12} alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; alkylpolysaccharides, preferably alkylpolyglycosides; methyl ester ethoxylates; polyhydroxy fatty acid amides; ether capped poly(oxyalkylated) alcohol surfactants; and mixtures thereof.

[0028] Suitable non-ionic detersive surfactants are alkylpolyglucoside and/or an alkyl alkoxylated alcohol.

[0029] Suitable non-ionic detersive surfactants include alkyl alkoxylated alcohols, preferably C_{8-18} alkyl alkoxylated alcohol, preferably a C_{8-18} alkyl ethoxylated alcohol, preferably the alkyl alkoxylated alcohol has an average degree of alkoxylation of from 1 to 50, preferably from 1 to 30, or from 1 to 20, or from 1 to 10, preferably the alkyl alkoxylated alcohol is a C_{8-18} alkyl ethoxylated alcohol having an average degree of ethoxylation of from 1 to 10, preferably from 1 to 7, more preferably from 1 to 5 and most preferably from 3 to 7. The alkyl alkoxylated alcohol can be linear or branched, and substituted or un-substituted.

[0030] Suitable nonionic detersive surfactants include secondary alcohol-based detersive surfactants.

[0031] <u>Cationic detersive surfactant</u>: Suitable cationic detersive surfactants include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof.

[0032] Preferred cationic detersive surfactants are quaternary ammonium compounds having the general formula:

$$(R)(R_1)(R_2)(R_3)N^+X^-$$

wherein, R is a linear or branched, substituted or unsubstituted C₆₋₁₈ alkyl or alkenyl moiety, R₁ and R₂ are independently selected from methyl or ethyl moieties, R₃ is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, preferred anions include: halides, preferably chloride; sulphate; and sulphonate.

[0033] Zwitterionic detersive surfactant: Suitable zwitterionic detersive surfactants include amine oxides and/or betaines.

[0034] Polymer: Suitable polymers include carboxylate polymers, soil release polymers, anti-redeposition polymers, cellulosic polymers, care polymers and any combination thereof.

[0035] Carboxylate polymer: The composition may comprise a carboxylate polymer, such as a maleate/acrylate random copolymer or polyacrylate homopolymer. Suitable carboxylate polymers include: polyacrylate homopolymers having a molecular weight of from 4,000 Da to 9,000 Da; maleate/acrylate random copolymers having a molecular weight of from 50,000 Da to 100,000 Da, or from 60,000 Da to 80,000 Da.

[0036] Another suitable carboxylate polymer is a co-polymer that comprises: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; and (iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

formula (I):

H₂C=C H₂C=C R Q CH

wherein in formula (I), R₀ represents a hydrogen atom or CH₃ group, R represents a CH₂ group, CH₂CH₂ group or single bond, X represents a number 0-5 provided X represents a number 1-5 when R is a single bond, and R₁ is a hydrogen atom or C₁ to C₂₀ organic group;

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formula (II)

 H_2C

 $\begin{array}{c} R_{0} \\ H_{2}C = C \\ I \\ R \\ I \\ O \\ CH_{2} \\ HC - OH \\ I \\ H_{2}C - O - CH_{2}CH_{2} \\ X - O - R_{1} \end{array}$

wherein in formula (II), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, R_1 represents a number 0-5, and R_1 is a hydrogen atom or R_1 to R_2 0 organic group.

It may be preferred that the polymer has a weight average molecular weight in the range of from 20kDa to 70kDa.

[0037] Soil release polymer: The composition may comprise a soil release polymer. A suitable soil release polymer has a structure as defined by one of the following structures (I), (II) or (III):

(I) $-[(OCHR^1-CHR^2)_a-O-OC-Ar-CO-]_d$

(II) $-[(OCHR^3-CHR^4)_b-O-OC-sAr-CO-]_e$

(III) $-[(OCHR^5-CHR^6)_c-OR^7]_f$

wherein:

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a, b and c are from 1 to 200;

d, e and f are from 1 to 50;

Ar is a 1,4-substituted phenylene;

sAr is 1,3-substituted phenylene substituted in position 5 with SO₃Me;

Me is Li, K, Mg/2, Ca/2, Al/3, ammonium, mono-, di-, tri-, or tetraalkylammonium wherein the alkyl groups are C_1 - C_{18} alkyl or C_2 - C_{10} hydroxyalkyl, or mixtures thereof;

 R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are independently selected from H or C_1 - C_{18} n- or iso-alkyl; and

 R^7 is a linear or branched C_1 - C_{18} alkyl, or a linear or branched C_2 - C_{30} alkenyl, or a cycloalkyl group with 5 to 9 carbon atoms, or a C_8 - C_{30} aryl group, or a C_6 - C_{30} arylalkyl group.

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Suitable soil release polymers are sold by Clariant under the TexCare® series of polymers, e.g. TexCare® SRN240 and TexCare® SRA300. Other suitable soil release polymers are sold by Solvay under the Repel-o-Tex® series of polymers, e.g. Repel-o-Tex® SF2 and Repel-o-Tex® Crystal.

[0038] <u>Anti-redeposition polymers</u> Suitable anti-redeposition polymers include polyethylene glycol polymers and/or polyethyleneimine polymers.

[0039] Suitable polyethylene glycol polymers include random graft co-polymers comprising: (i) hydrophilic backbone comprising polyethylene glycol; and (ii) hydrophobic side chain(s) selected from the group consisting of: C_4 - C_{25} alkyl group, polypropylene, polybutylene, vinyl ester of a saturated C_1 - C_6 mono-carboxylic acid, C_1 - C_6 alkyl ester of acrylic or methacrylic acid, and mixtures thereof. Suitable polyethylene glycol polymers have a polyethylene glycol backbone with random grafted polyvinyl acetate side chains. The average molecular weight of the polyethylene glycol backbone can be in the range of from 2,000 Da to 20,000 Da, or from 4,000 Da to 8,000 Da. The molecular weight ratio of the polyethylene glycol backbone to the polyvinyl acetate side chains can be in the range of from 1:1 to 1:5, or from 1:1.2 to 1:2. The average number of graft sites per ethylene oxide unit can be less than 0.02, or less than 0.016, the average number of graft sites per ethylene oxide unit can be in the range of from 0.010 to 0.018, or the average number of graft sites per ethylene oxide unit can be less than 0.020.

[0040] Suitable polyethylene glycol polymers are described in WO08/007320.

[0041] A suitable polyethylene glycol polymer is Sokalan HP22.

[0042] Cellulosic polymer: Suitable cellulosic polymers are selected from alkyl cellulose, alkyl alkoxyalkyl cellulose,

carboxyalkyl cellulose, alkyl carboxyalkyl cellulose, sulphoalkyl cellulose, more preferably selected from carboxymethyl cellulose, methyl cellulose, methyl

[0043] Suitable carboxymethyl celluloses have a degree of carboxymethyl substitution from 0.5 to 0.9 and a molecular weight from 100,000 Da to 300,000 Da.

[0044] Suitable carboxymethyl celluloses have a degree of substitution greater than 0.65 and a degree of blockiness greater than 0.45, e.g. as described in WO09/154933.

[0045] <u>Care polymers:</u> Suitable care polymers include cellulosic polymers that are cationically modified or hydrophobically modified. Such modified cellulosic polymers can provide anti-abrasion benefits and dye lock benefits to fabric during the laundering cycle. Suitable cellulosic polymers include cationically modified hydroxyethyl cellulose.

[0046] Other suitable care polymers include dye lock polymers, for example the condensation oligomer produced by the condensation of imidazole and epichlorhydrin, preferably in ratio of 1:4:1. A suitable commercially available dye lock polymer is Polyquart® FDI (Cognis).

[0047] Other suitable care polymers include amino-silicone, which can provide fabric feel benefits and fabric shape retention benefits.

[0048] <u>Bleach:</u> Suitable bleach includes sources of hydrogen peroxide, bleach activators, bleach catalysts, pre-formed peracids and any combination thereof. A particularly suitable bleach includes a combination of a source of hydrogen peroxide with a bleach activator and/or a bleach catalyst.

[0049] Source of hydrogen peroxide: Suitable sources of hydrogen peroxide include sodium perborate and/or sodium percarbonate.

[0050] Bleach activator: Suitable bleach activators include tetra acetyl ethylene diamine and/or alkyl oxybenzene sulphonate.

[0051] Bleach catalyst: The composition may comprise a bleach catalyst. Suitable bleach catalysts include oxazirid-inium bleach catalysts, transistion metal bleach catalysts, especially manganese and iron bleach catalysts. A suitable bleach catalyst has a structure corresponding to general formula below:

 OSO_3^{Θ} $O-R^1$

wherein R¹³ is selected from the group consisting of 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl, 2-pentylnonyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, isodecyl, iso-tridecyl and iso-pentadecyl.

[0052] Pre-formed peracid: Suitable pre-form peracids include phthalimido-peroxycaproic acid.

[0053] Enzymes: Suitable enzymes include lipases, proteases, cellulases, amylases and any combination thereof.

[0054] Protease: Suitable proteases include metalloproteases and/or serine proteases. Examples of suitable neutral or alkaline proteases include: subtilisins (EC 3.4.21.62); trypsin-type or chymotrypsin-type proteases; and metalloproteases. The suitable proteases include chemically or genetically modified mutants of the aforementioned suitable proteases.

[0055] Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzyme®, Kannase®, Liquanase®, Liquanase Ultra®, Savinase Ultra®, Ovozyme®, Neutrase®, Everlase® and Esperase® by Novozymes A/S (Denmark), those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Preferenz P® series of proteases including Preferenz® P280, Preferenz® P281, Preferenz® P2018-C, Preferenz® P2081-WE, Preferenz® P2082-EE and Preferenz® P2083-A/J, Properase®, Purafect®, Purafect Prime®, Purafect Ox®, FN3®, FN4®, Excellase® and Purafect OXP® by DuPont, those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes, those available from Henkel/ Kemira, namely BLAP (sequence shown in Figure 29 of US 5,352,604 with the folowing mutations S99D + S101 R + S103A + V104I + G159S, hereinafter referred to as BLAP), BLAP R (BLAP with S3T + V4I + V199M + V205I + L217D), BLAP X (BLAP with S3T + V4I + V205I) and BLAP F49 (BLAP with S3T + V4I + A194P + V199M + V205I + L217D) - all from Henkel/Kemira; and KAP (Bacillus alkalophilus subtilisin with mutations A230V + S256G + S259N) from Kao.

[0056] A suitable protease is described in WO11/140316 and WO11/072117.

[0057] Amylase: Suitable amylases are derived from AA560 alpha amylase endogenous to Bacillus sp. DSM 12649, preferably having the following mutations: R118K, D183*, G184*, N195F, R320K, and/or R458K. Suitable commercially available amylases include Stainzyme®, Stainzyme® Plus, Natalase, Termamyl®, Termamyl® Ultra, Liquezyme® SZ, Duramyl®, Everest® (all Novozymes) and Spezyme® AA, Preferenz S® series of amylases, Purastar® and Purastar® Ox Am, Optisize® HT Plus (all Du Pont).

A suitable amylase is described in WO06/002643.

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[0058] <u>Cellulase:</u> Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are also suitable. 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*.

[0059] Commercially available cellulases include Celluzyme®, Carezyme®, and Carezyme® Premium, Celluclean® and Whitezyme® (Novozymes A/S), Revitalenz® series of enzymes (Du Pont), and Biotouch® series of enzymes (AB Enzymes). Suitable commercially available cellulases include Carezyme® Premium, Celluclean® Classic. Suitable cellulases are described in WO07/144857 and WO10/056652.

[0060] <u>Lipase:</u> Suitable lipases include those of bacterial, fungal or synthetic origin, and variants thereof. Chemically modified or protein engineered mutants are also suitable. Examples of suitable lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g., from *H. lanuginosa* (*T. lanuginosus*).

[0061] The lipase may be a "first cycle lipase", e.g. such as those described in WO06/090335 and WO13/116261. In one aspect, the lipase is a first-wash lipase, preferably a variant of the wild-type lipase from Thermomyces lanuginosus comprising T231R and/or N233R mutations. Preferred lipases include those sold under the tradenames Lipex®, Lipolex® and Lipoclean® by Novozymes, Bagsvaerd, Denmark.

[0062] Other suitable lipases include: Liprl 139, e.g. as described in WO2013/171241; and TfuLip2, e.g. as described in WO2011/084412 and WO2013/033318.

[0063] Other enzymes: Other suitable enzymes are bleaching enzymes, such as peroxidases/oxidases, which include those of plant, bacterial or fungal origin and variants thereof. Commercially available peroxidases include Guardzyme® (Novozymes A/S). Other suitable enzymes include choline oxidases and perhydrolases such as those used in Gentle Power Bleach™.

[0064] Other suitable enzymes include pectate lyases sold under the tradenames X-Pect®, Pectaway® (from Novozymes A/S, Bagsvaerd, Denmark) and PrimaGreen® (DuPont) and mannanases sold under the tradenames Mannaway® (Novozymes A/S, Bagsvaerd, Denmark), and Mannastar® (Du Pont).

[0065] Other suitable enzymes include nuclease enzymes, such as deoxyribonuclease enzymes.

[0066] Zeolite <u>builder</u>: The composition may comprise zeolite builder. The composition may comprise from 0wt% to 5wt% zeolite builder, or 3wt% zeolite builder. The composition may even be substantially free of zeolite builder; substantially free means "no deliberately added". Typical zeolite builders include zeolite A, zeolite P and zeolite MAP.

[0067] Phosphate builder: The composition may comprise phosphate builder. The composition may comprise from 0wt% to 5wt% phosphate builder, or to 3wt%, phosphate builder. The composition may even be substantially free of phosphate builder; substantially free means "no deliberately added". A typical phosphate builder is sodium tri-polyphosphate.

[0068] <u>Carbonate salt:</u> The composition may comprise carbonate salt. The composition may comprise from 0wt% to 10wt% carbonate salt, or to 5wt% carbonate salt. The composition may even be substantially free of carbonate salt; substantially free means "no deliberately added". Suitable carbonate salts include sodium carbonate and sodium bicarbonate

[0069] Silicate salt: The composition may comprise silicate salt. The composition may comprise from 0wt% to 10wt% silicate salt, or to 5wt% silicate salt. A preferred silicate salt is sodium silicate, especially preferred are sodium silicates having a Na₂O:SiO₂ ratio of from 1.0 to 2.8, preferably from 1.6 to 2.0.

[0070] Sulphate salt: A suitable sulphate salt is sodium sulphate.

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[0071] Brightener: Suitable fluorescent brighteners include: di-styryl biphenyl compounds, e.g. Tinopal® CBS-X, diamino stilbene di-sulfonic acid compounds, e.g. Tinopal® DMS pure Xtra and Blankophor® HRH, and Pyrazoline compounds, e.g. Blankophor® SN, and coumarin compounds, e.g. Tinopal® SWN.

Preferred brighteners are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2hydroxyethyl)amino 1,3,5-triazin-2-yl)];amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfostyryl)biphenyl. A suitable fluorescent brightener is C.I. Fluorescent Brightener 260, which may be used in its beta or alpha crystalline forms, or a mixture of these forms.

[0072] <u>Chelant:</u> The composition may also comprise a chelant selected from: diethylene triamine pentaacetate, diethylene triamine penta(methyl phosphonic acid), ethylene diamine-N'N'-disuccinic acid, ethylene diamine tetraacetate, ethylene diamine tetra(methylene phosphonic acid) and hydroxyethane di(methylene phosphonic acid). A preferred chelant is ethylene diamine-N'N'-disuccinic acid (EDDS) and/or hydroxyethane diphosphonic acid (HEDP). The composition preferably comprises ethylene diamine-N'N'- disuccinic acid or salt thereof. Preferably the ethylene diamine-N'N'-disuccinic acid is in S,S enantiomeric form. Preferably the composition comprises 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt. Preferred chelants may also function as calcium carbonate crystal growth inhibitors such as: 1-hydroxyethanediphosphonic acid (HEDP) and salt thereof; N,N-dicarboxymethyl-2-aminopentane-1,5-dioic acid and salt thereof; 2-phosphonobutane-1,2,4-tricarboxylic acid and salt thereof; and combination thereof.

[0073] Hueing agent: Suitable hueing agents include small molecule dyes, typically falling into the Colour Index (C.I.)

classifications of Acid, Direct, Basic, Reactive (including hydrolysed forms thereof) or Solvent or Disperse dyes, for example classified as Blue, Violet, Red, Green or Black, and provide the desired shade either alone or in combination. Preferred such hueing agents include Acid Violet 50, Direct Violet 9, 66 and 99, Solvent Violet 13 and any combination thereof.

Many hueing agents are known and described in the art which may be suitable for the present invention, such as hueing agents described in WO2014/089386.

[0075] Suitable hueing agents include phthalocyanine and azo dye conjugates, such as described in WO2009/069077. [0076] Suitable hueing agents may be alkoxylated. Such alkoxylated compounds may be produced by organic synthesis that may produce a mixture of molecules having different degrees of alkoxylation. Such mixtures may be used directly to provide the hueing agent, or may undergo a purification step to increase the proportion of the target molecule. Suitable hueing agents include alkoxylated bis-azo dyes, such as described in WO2012/054835, and/or alkoxylated thiophene azo dyes, such as described in WO2008/087497 and WO2012/166768.

[0077] The hueing agent may be incorporated into the detergent composition as part of a reaction mixture which is the result of the organic synthesis for a dye molecule, with optional purification step(s). Such reaction mixtures generally comprise the dye molecule itself and in addition may comprise un-reacted starting materials and/or by-products of the organic synthesis route. Suitable hueing agents can be incorporated into hueing dye particles, such as described in WO 2009/069077.

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[0078] <u>Dye transfer inhibitors:</u> Suitable dye transfer inhibitors include polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone, polyvinyloxazolidone, polyvinylimidazole and mixtures thereof. Preferred are poly(vinyl pyrrolidone), poly(vinylpyridine betaine), poly(vinylpyridine N-oxide), poly(vinyl pyrrolidone-vinyl imidazole) and mixtures thereof. Suitable commercially available dye transfer inhibitors include PVP-K15 and K30 (Ashland), Sokalan® HP165, HP50, HP53, HP59, HP56K, HP56, HP66 (BASF), Chromabond® S-400, S403E and S-100 (Ashland).

[0079] Perfume: Suitable perfumes comprise perfume materials selected from the group: (a) perfume materials having a ClogP of less than 3.0 and a boiling point of less than 250°C (quadrant 1 perfume materials); (b) perfume materials having a ClogP of less than 3.0 and a boiling point of 250°C or greater (quadrant 2 perfume materials); (c) perfume materials having a ClogP of 3.0 or greater and a boiling point of less than 250°C (quadrant 3 perfume materials); (d) perfume materials having a ClogP of 3.0 or greater and a boiling point of 250°C or greater (quadrant 4 perfume materials); and (e) mixtures thereof.

[0080] It may be preferred for the perfume to be in the form of a perfume delivery technology. Such delivery technologies further stabilize and enhance the deposition and release of perfume materials from the laundered fabric. Such perfume delivery technologies can also be used to further increase the longevity of perfume release from the laundered fabric. Suitable perfume delivery technologies include: perfume microcapsules, pro-perfumes, polymer assisted deliveries, molecule assisted deliveries, fiber assisted deliveries, amine assisted deliveries, cyclodextrin, starch encapsulated accord, zeolite and other inorganic carriers, and any mixture thereof. A suitable perfume microcapsule is described in WO2009/101593.

[0081] Silicone: Suitable silicones include polydimethylsiloxane and amino-silicones. Suitable silicones are described in WO05075616.

[0082] Process for making the solid composition: Typically, the particles of the composition can be prepared by any suitable method. For example: spray-drying, agglomeration, extrusion and any combination thereof.

[0083] Typically, a suitable spray-drying process comprises the step of forming an aqueous slurry mixture, transferring it through at least one pump, preferably two pumps, to a pressure nozzle. Atomizing the aqueous slurry mixture into a spray-drying tower and drying the aqueous slurry mixture to form spray-dried particles. Preferably, the spray-drying tower is a counter-current spray-drying tower, although a co-current spray-drying tower may also be suitable.

[0084] Typically, the spray-dried powder is subjected to cooling, for example an air lift. Typically, the spray-drying powder is subjected to particle size classification, for example a sieve, to obtain the desired particle size distribution. Preferably, the spray-dried powder has a particle size distribution such that weight average particle size is in the range of from 300 micrometers to 500 micrometers, and less than 10wt% of the spray-dried particles have a particle size greater than 2360 micrometers.

[0085] It may be preferred to heat the aqueous slurry mixture to elevated temperatures prior to atomization into the spray-drying tower, such as described in WO2009/158162.

[0086] It may be preferred for anionic surfactant, such as linear alkyl benzene sulphonate, to be introduced into the spray-drying process after the step of forming the aqueous slurry mixture: for example, introducing an acid precursor to the aqueous slurry mixture after the pump, such as described in WO 09/158449.

[0087] It may be preferred for a gas, such as air, to be introduced into the spray-drying process after the step of forming the aqueous slurry, such as described in WO2013/181205.

[0088] It may be preferred for any inorganic ingredients, such as sodium sulphate and sodium carbonate, if present in the aqueous slurry mixture, to be micronized to a small particle size such as described in WO2012/134969.

[0089] Typically, a suitable agglomeration process comprises the step of contacting a detersive ingredient, such as a detersive surfactant, e.g. linear alkyl benzene sulphonate (LAS) and/or alkyl alkoxylated sulphate, with an inorganic material, such as sodium carbonate and/or silica, in a mixer. The agglomeration process may also be an in-situ neutralization agglomeration process wherein an acid precursor of a detersive surfactant, such as LAS, is contacted with an alkaline material, such as carbonate and/or sodium hydroxide, in a mixer, and wherein the acid precursor of a detersive surfactant is neutralized by the alkaline material to form a detersive surfactant during the agglomeration process.

[0090] Other suitable detergent ingredients that may be agglomerated include polymers, chelants, bleach activators, silicones and any combination thereof.

[0091] The agglomeration process may be a high, medium or low shear agglomeration process, wherein a high shear, medium shear or low shear mixer is used accordingly. The agglomeration process may be a multi-step agglomeration process wherein two or more mixers are used, such as a high shear mixer in combination with a medium or low shear mixer. The agglomeration process can be a continuous process or a batch process.

[0092] It may be preferred for the agglomerates to be subjected to a drying step, for example to a fluid bed drying step. It may also be preferred for the agglomerates to be subjected to a cooling step, for example a fluid bed cooling step. [0093] Typically, the agglomerates are subjected to particle size classification, for example a fluid bed elutriation and/or a sieve, to obtain the desired particle size distribution. Preferably, the agglomerates have a particle size distribution such

that weight average particle size is in the range of from 300 micrometers to 800 micrometers, and less than 10wt% of the agglomerates have a particle size of less than 150 micrometers, and less than 10wt% of the agglomerates have a particle size greater than 1200 micrometers.

[0094] It may be preferred for fines and over-sized agglomerates to be recycled back into the agglomeration process. Typically, over-sized particles are subjected to a size reduction step, such as grinding, and recycled back into an appropriate place in the agglomeration process, such as the mixer. Typically, fines are recycled back into an appropriate place in the agglomeration process, such as the mixer.

[0095] It may be preferred for ingredients such as polymer and/or non-ionic detersive surfactant and/or perfume to be sprayed onto base detergent particles, such as spray-dried base detergent particles and/or agglomerated base detergent particles. Typically, this spray-on step is carried out in a tumbling drum mixer.

[0096] Method of laundering fabric: The method of laundering fabric comprises the step of contacting the composition to water to form a wash liquor, and laundering fabric in said wash liquor. Typically, the wash liquor has a temperature of above 0°C to 90°C, or to 60°C, or to 40°C, or to 30°C, or to 20°C. The fabric may be contacted to the water prior to, or after, or simultaneous with, contacting the composition with water. Typically, the wash liquor is formed by contacting the laundry detergent to water in such an amount so that the concentration of laundry detergent composition in the wash liquor is from 0.2g/l to 20g/l, or from 0.5g/l to 10g/l, or to 5.0g/l. The method of laundering fabric can be carried out in a front-loading automatic washing machine, top loading automatic washing machines, including high efficiency automatic washing machines, or suitable hand-wash vessels._Typically, the wash liquor comprises 90 litres or less, or 60 litres or less, or 15 litres or less, or 10 litres or less of water. Typically, 200g or less, or 150g or less, or 100g or less, or 50g or less of laundry detergent composition is contacted to water to form the wash liquor.

EXAMPLES

Illustrative solid free-flowing particulate laundry detergent composition examples:

[0097]

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(continued)

	Ingredient	Amount (in wt%)
5	$\frac{Other\ detersive\ surfactant}{mixtures\ thereof)} (such\ as\ zwiterionic\ detersive\ surfactants,\ amphoteric\ surfactants\ and\ mixtures\ thereof)$	from 0wt% to 4wt%
	Carboxylate polymer (such as co-polymers of maleic acid and acrylic acid and/or carboxylate polymers comprising ether moieties and sulfonate moieties)	from 0.1wt% to 4wt%
10	Polyethylene glycol polymer (such as a polyethylene glycol polymer comprising polyvinyl acetate side chains)	from 0wt% to 4wt%
	Polyester soil release polymer (such as Repel-o-tex and/or Texcare polymers)	from 0wt% to 2wt%
15	<u>Cellulosic</u> <u>polymer</u> (such as carboxymethyl cellulose, methyl cellulose and combinations thereof)	from 0.5wt% to 2wt%
	Other polymer (such as care polymers)	from 0wt% to 4wt%
20	Zeolite builder and phosphate builder (such as zeolite 4A and/or sodium tripolyphosphate)	from 0wt% to 4wt%
	Other co-builder (such as sodium citrate and/or citric acid)	from 0wt% to 3wt%
25	Carbonate salt (such as sodium carbonate and/or sodium bicarbonate)	from 0wt% to 20wt%
	Silicate salt (such as sodium silicate)	from 0wt% to 10wt%
30	Filler (such as sodium sulphate and/or bio-fillers)	from 10wt% to 70wt%
	Source of hydrogen peroxide (such as sodium percarbonate)	from 0wt% to 20wt%
35	Bleach activator (such as tetraacetylethylene diamine (TAED) and/or nonanoyloxybenzenesulphonate (NOBS))	from 0wt% to 8wt%
	Bleach catalyst (such as oxaziridinium-based bleach catalyst and/or transition metal bleach catalyst)	from 0wt% to 0.1wt%
40	Other bleach (such as reducing bleach and/or pre-formed peracid)	from 0wt% to 10wt%
	Photobleach (such as zinc and/or aluminium sulphonated phthalocyanine)	from 0wt% to 0.1wt%
45	Chelant (such as ethylenediamine-N'N'-disuccinic acid (EDDS) and/or hydroxyethane diphosphonic acid (HEDP))	from 0.2wt% to 1wt%
70	Hueing agent (such as direct violet 9, 66, 99, acid red 50, solvent violet 13 and any combination thereof)	from 0wt% to 1wt%
50	Brightener (C.I. fluorescent brightener 260 or C.I. fluorescent brightener 351)	from 0.1wt% to 0.4wt%
50	Protease (such as Savinase, Savinase Ultra, Purafect, FN3, FN4 and any combination thereof)	from 0.1wt% to 0.4wt%
	Amylase (such as Termamyl, Termamyl ultra, Natalase, Optisize, Stainzyme, Stainzyme Plus and any combination thereof)	from 0wt% to 0.2wt%
55	Cellulase (such as Carezyme and/or Celluclean)	from 0wt% to 0.2wt%

(continued)

	Ingredient	Amount (in wt%)
5	<u>Lipase</u> (such as Lipex, Lipoclean and any combination thereof)	from 0wt% to 1wt%
	Other enzyme (such as xyloglucanase, cutinase, pectate lyase, mannanase, bleaching enzyme)	from 0wt% to 2wt%
10	Fabric softener (such as montmorillonite clay and/or polydimethylsiloxane (PDMS))	from 0wt% to 15wt%
	Flocculant (such as polyethylene oxide)	from 0wt% to 1wt%
15	Suds suppressor (such as silicone and/or fatty acid)	from 0wt% to 4wt%
	Perfume (such as perfume microcapsule, spray-on perfume, starch encapsulated perfume accords, perfume loaded zeolite, and any combination thereof)	from 0.1wt% to 1wt%
20	Aesthetics (such as coloured soap rings and/or coloured speckles/noodles)	from 0wt% to 1wt%
	<u>Miscellaneous</u>	balance to 100wt%

Example 1: Effect of chelants on hydrogen peroxide recovery

[0098] A nil-chelant detergent base was prepared, as shown below.

Detergent Base

[0099]

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Ingredient	Total parts	Grams in 4L
Zeolite	4.0000	0.5
Lipase	0.5600	0.070
Carboxylate polymer	2.6667	0.33
Brightener 15	0.2825	0.036
Suds suppressor	0.5770	0.072
Sodium carbonate	2.0000	0.250
Sodium sulphate	32.7300	6.1
Protease	0.2470	0.03
Amylase	0.1833	0.025
Carboxymethyl Cellulose (CMC)	0.3000	0.038
Anionic detersive surfactant (LAS & AE1S) agglomerate	36.0000	5.5
Total	100.00	13

[0100] 13g of this detergent base was dissolved in 4 L of city water. Three samples of 800mL of the detergent solution was placed into a Pharmatest Dissolution Tester which was set to 40°C and 150rpm. The solutions were equilibrated to the set temperature. 1g of sodium percarbonate and 0.20 g of tetraacetyl ethylenediamine (TAED) was then added to each sample pot which were stirred until the contents were dissolved. The solution pH was adjusted to pH 8.5 using 10% citric acid solution.

[0101] 500 mg of each chelant sample was added to separate pots as follows.

pot - 1 = 500mg hydroxyethane 1,1-diphosphonic acid (HEDP)

pot - 2 = 500mg 1-Hydroxy-2-pyridone (HPNO)

pot - 3 = 500mg methylglycine diacetic acid (MGDA)

[0102] A catalase solution (representing soil load into the wash) was prepared by diluting 200 μ L bovine catalase (bovine liver catalase, 10,000-40,000 units/mg protein) in 20 mL of deionised water.

[0103] 2ml of 1% catalase solution was added to pot 1. This timepoint was set as t=0 for the removal of aliquots for available oxygen analysis.

[0104] At t = 1, 3, 5, 10, 15, 20 and 60 minutes, 20ml aliquots were taken and neutralised with 20 mL 20% acetic acid solution.

[0105] Samples were analyzed for available oxygen content by thiosulfate titration. The lower the AvO value the greater the enzymatic activity of catalase.

	AvO/mL thiosulfate					
Time (minutes)	500mg HEDP	500mg HPNO	500mg MGDA			
1	3.25	3.02	3.16			
3	2.41	2.28	2.98			
5	1.87	1.92	2.92			
10	1	1.15	2.85			
15	0.9	0.88	2.65			
20	0.71	0.75	2.57			
60	0.62	0.3	2.31			
MGDA inhibits the e	MGDA inhibits the enzymatic activity of catalase greater than HEDP and HPNO.					

[0106] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

Claims

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- 1. Use of methylglycine diacetic acid or salt thereof (MGDA) to inhibit the enzymatic activity of catalase during a laundering process.
- 2. Use according to claim 1, wherein the laundering process comprises the step of contacting a laundry detergent composition to water to form a wash bath, and contacting soil laundry to the wash bath.
- 3. Use according to claim 2, wherein the laundry detergent is a solid laundry detergent powder.
- **4.** Use according to any of claims 2-3, wherein the solid laundry detergent powder, upon dissolution in de-ionized water at 20°C at a concentration of 1g/l, has an equilibrium pH of from 4.0 to 9.0.
- 5. Use according to any of claims 2-4, wherein the laundry detergent comprises detersive surfactant.
- 6. Use according to any of claims 2-5, wherein the laundry detergent comprises bleach.
- 7. Use according to any of claim 6, wherein the bleach is a sodium percarbonate bleach.
- 8. Use according to any preceding claim, wherein the methylglycine diacetic acid or salt thereof (MGDA) is the trisodium salt of methylglycine diacetic acid.
 - 9. Use according to any preceding claim, to provide stain removal benefits to fabric.

	10.	Use according to claim 9, to provide tea stain removal benefits to fabric. $ \\$
	11.	Use according to claim 9 or 10, wherein the fabric comprises cotton.
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INV.

C11D3/33 C11D7/32

Relevant

to claim

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	Place of search
4C01)	Munich

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page 2 of 2

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