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(54) GRANULAR ENZYMATIC DETERGENT COMPOSITIONS

GRANULARE ENZYMATISCHE REINIGUNGSZUSAMMENSETZUNGEN

COMPOSITIONS DÉTERGENTES ENZYMATIQUES GRANULAIRES

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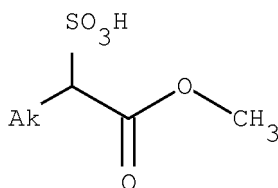
Description**TECHNICAL FIELD**

5 [0001] The present invention relates to granular detergent compositions, more in particular to granular detergent compositions comprising alkyl ester, in particular methyl ester fatty acid sulphonate surfactant and enzyme granules.

BACKGROUND OF THE INVENTION

10 [0002] Laundry detergent compositions have for many years contained anionic sulphonate or sulphate surfactant, for example, linear alkylbenzene sulphonate (LAS) or primary alkyl sulphate (PAS), together with ethoxylated alcohol non-ionic surfactants. Conventional ethoxylated alcohol nonionic surfactants used in laundry detergent compositions include typically ethoxylated C₁₀-C₁₆ alcohols having an average degree of ethoxylation of 3 to 9.

15 [0003] More recently, granular detergent compositions have been proposed wherein part or all of the linear alkylbenzene sulphonate has been replaced with methyl ester fatty acid sulphonate (MES), having the formula:



where Ak = predominantly linear C₁₄-C₁₆ alkyl chain.

25 [0004] The IUPAC name for e.g. a so-called C16 MES is Hexadecanoic acid, 2-sulfo-, 1-methylester, sodium salt (C₁₇H₃₃NaO₅S). Methyl ester sulphonate can be obtained by sulphonation of various renewable oleo-based methyl ester feedstocks derived from eg. coconut (C12-14), palm kernel (C8-18), palm stearin C16-18) or tallow (C16-18). Besides the renewable origin, MES is of special interest due to good biodegradability, detergency and calcium hardness tolerance.

30 [0005] EP-A-1 634 941 (Lion) or WO-A-01/90284 (Huish) disclose high bulk density granular detergents containing surfactants (including α-sulpho-fatty acid esters), (bi) carbonate, zeolite and a polymer containing of monoethylenic unsaturated mono- and di-carboxylic acid units.

35 [0006] US 4 194 986 discloses a detergent composition comprising on the basis of 100 parts by weight of total composition, at least 60 parts of soap and no more than 10 parts of a mixture of surfactants comprising 10 to 30% of at least one non-ionic polyalkoxylated surfactant and 90 to 70% of an anionic surfactant selected essentially from α-sulfonated fatty acid derivatives, the remainder of the composition comprising at least one ingredient selected from alkaline detergent additives, bleaching agents, optical brighteners, fragrances, antiredeposition agents and enzymes.

[0007] While the (partial) replacement of LAS by methyl ester fatty acid sulphonate (MES) might seem to be straightforward, the present inventors were unexpectedly confronted with a malodour problem which occurred upon storage.

40 [0008] It has now surprisingly been found that this malodour problem may be avoided by the granular detergent composition according to the invention comprising 1 to 30% by weight of an alkyl ester fatty acid sulphonate surfactant and enzyme granules, wherein said composition is substantially free of thiosulphate.

DEFINITION OF THE INVENTION

45 [0009] According to a first aspect of the invention, there is provided a granular detergent composition comprising 1 to 30% by weight of an alkyl ester fatty acid sulphonate surfactant and 0.1 to 10% by weight enzyme granules, wherein said composition is substantially free of thiosulphate, and wherein said detergent composition comprises methyl sulphate.

50 [0010] According to a second aspect of the invention, there is provided a detergent tablet obtained by compressing the granular detergent composition according to the invention.

[0011] According to a third aspect of the invention, there is provided a process for laundering textile fabrics by machine or hand, characterised in that it comprises the step of immersing the fabrics in a wash liquor comprising water in which a granular detergent composition or detergent tablet according to the invention is dissolved or dispersed.

DETAILED DESCRIPTION OF THE INVENTION

55 [0012] The granular detergent composition of the invention comprises 1 to 30% by weight of an alkyl ester fatty acid sulphonate surfactant, preferably methyl ester fatty acid sulphonate surfactant, and enzyme granules. Preferably, the

amount of α -sulpho-fatty acid esters is 1 to 15% by weight, more preferably 3 to 8% by weight.

[0013] Methods of preparing α -sulfofatty acid esters are known to skilled artisan. (See, e.g., US-A-5 587 500; US-A-5 384 422; US-A-5 382 677; US-A-5 329 030; US-A-4 816 188; and US-A- 4 671 900; and The Journal of American Oil Chemists Society 52:323-29 (1975) the disclosures of which are incorporated herein by reference). α -Sulfofatty acid esters can be prepared from a variety of sources, including beef tallow, oil, coco butter, palm oil, white grease, cottonseed oil, corn oil, rape seed oil, soybean oil, yellow grease, mixtures thereof or fractions thereof. Suitable fatty acids to make α -sulfofatty acid esters include, but are not limited to, caprylic (C₈), capric (C₁₀), lauric (C₁₂), myristic (C₁₄), myristoleic (C₁₄), palmitic (C₁₆), palmitoleic (C₁₆), stearic (C₁₈), oleic (C₁₈), linoleic (C₁₈), linolenic (C₁₈), ricinoleic (C₁₈), arachidic (C₂₀), gadolic (C₂₀), behenic (C₂₂), and erucic (C₂₂) fatty acids. α -Sulfofatty acid esters prepared from one or more of these sources are within the scope of the present invention.

[0014] Samples of alkyl ester fatty acid sulphonate surfactant prepared in dry powder form via above mentioned production processes typically contain about 75-85 % by weight of the desired surfactant. Amongst the other components in a typical production sample there is one of specific relevance for the present invention, which is sodium methylsulphate, typically present at (but not restricted to) a level of about 1-10 % based on the weight of the MES as such.

[0015] The composition may also comprise one or more other surfactants. The other surfactant is present in an amount of from 5 to 40 wt.%, preferably from 7 to 30 wt.%, based on the weight of the total composition.

[0016] Surfactants are well-known to those skilled in the art. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

[0017] Examples include alkylbenzene sulphonates, branched or linear alkyl benzene sulphonates, primary and secondary alcohol sulphates, particularly C₈-C₁₆ primary alcohol sulphates; alkyl ether sulphates, olefin sulphonates, including alpha olefin sulphonates, alkane sulphonates, alkyl xylene sulphonates, dialkyl sulphosuccinates, and alkyl carboxylates. These may be present as sodium, potassium, calcium or magnesium salts or mixtures of these. Sodium salts are generally preferred.

[0018] The other surfactant is preferably a sulphonate or sulphate anionic surfactant or a combination thereof. More preferably, the anionic surfactant is linear alkylbenzene sulphonate or primary alkyl sulphate. Most preferably the other surfactant is linear alkylbenzene sulphonate. The linear alkyl benzene sulphonate may be present as sodium, potassium, or alkaline earth metal salts, or mixtures of these salts. Sodium salts are generally preferred.

[0019] The other surfactant may also comprise a nonionic surfactant, preferably an ethoxylated alcohol nonionic surfactant with an average degree of ethoxylation ranging from about 3 to 9, preferably from about 3 to 7. The alcohol may be derived from natural or synthetic feedstock. Preferred alcohol feedstocks are coconut and palm kernel, predominantly C₁₂-C₁₄, and oxo C₁₂-C₁₅ alcohols.

[0020] The nonionic surfactant is suitably present in an amount of from 1 to 20 wt %, preferably from 1 to 10, more preferably from 2 to 6 wt %, most preferably from 3 to 5 wt %, based on the weight of the total composition.

[0021] Additional surfactants or detergent active compounds may comprise other nonionics such as alkylpolyglucosides, polyhydroxyamides (glucamide), methyl ester ethoxylates and glycerol monoethers. Also cationic, amphoteric surfactants and/or zwitterionic surfactants may be present. Preferred cationic surfactants are quaternary ammonium salts of the general formula R₁R₂R₃R₄N⁺ X⁻, for example where R₁ is a C₁₂-C₁₄ alkyl group, R₂ and R₃ are methyl groups, R₄ is a 2-hydroxyethyl group, and X⁻ is a chloride ion. This material is available commercially as Praepagen (Trade Mark) HY from Clariant GmbH, in the form of a 40 wt% aqueous solution.

[0022] Preferred amphoteric surfactants are amine oxides, for example coco dimethyl amine oxide. Preferred zwitterionic surfactants are betaines, and especially amidobetaines. Preferred betaines are C₈ to C₁₈ alkyl amidoalkyl betaines, for example coco amido betaine. These may be included as co-surfactants, preferably present in an amount of from 0 to 10 wt %, more preferably 1 to 5 wt %, based on the weight of the total composition.

Enzymes

[0023] The detergent compositions of the present invention comprise one or more other enzymes, which provide cleaning performance, fabric care and/or sanitation benefits.

[0024] Suitable enzymes for incorporation in detergent compositions preferably include protease, lipase, amylase, cellulase, mannanase and oxidase, peroxidase, oxidoreductase, beta-glucanase, pectinase and/or pectate lyase. Most preferably, the compositions contain a proteolytic enzyme or protease.

[0025] Suitable members of these enzyme classes are described in Enzyme nomenclature 1992: recommendations of the Nomenclature Committee of the International Union of Biochemistry and Molecular Biology on the nomenclature and classification of enzymes, 1992, ISBN 0-12-227165-3, Academic Press. The most recent information on the nomenclature of enzymes is available on the Internet through the ExPaSy Molecular Biology Server (<http://us.expasy.org/>)

[0026] The composition may contain additional enzymes as found in WO-A-01/007681 page 15, line 25 to page 19, line 29 as well as those found in WO-A-02/02726 page 16 line 21 to page 19 line 16 and those found in WO-A-02/02726

page 33 line 28 to page 39 line 34, the contents of which are herein incorporated by reference. It also may contain maltogenic α -amylases as described in WO-A-02/02726 page 5, line 14 to page 11 line 29. Commercially available maltogenic α -amylases are Novamyl™ and Maltogenase™ from Novozymes.

[0027] The composition may also contain a lipase variant of the Humicola lanuginosa lipase with substitutions T231R + N233R, commercially available as Lipex™ from Novozymes or another variant as described in WO-A-00/60063.

[0028] The composition may also contain other commercial enzymes not described in any of the previous specifications such as the new enzymes from Novozymes: Mannaway™, Natalase™, Renozyme™, Ovozyme™, CelluClean™, Polarzyme™, Stainzyme™, Coronase™, Pectaaway™, Pectawash™, Termamyl Ultra™. And the new enzymes from Genencor: FN-3, FN-4, Purafect Prime™, Properase™.

[0029] In the granular or particulate detergent compositions, detergency enzymes are employed in granular form in amounts of from about 0.1 to about 10.0 wt %, preferably from about 0.2 to about 3% by weight, more preferably from about 0.2 to about 1% by weight.

[0030] It was found to be important that the detergent compositions are substantially free of thiosulphate. Since enzyme granules sometimes contain thiosulphate, it was found to be important to use thiosulphate free enzyme granules. The amount of thiosulphate in the compositions can be determined using standard analytical techniques. Thiosulphate in the context of this invention means any salt thereof, such as alkalimetal, especially sodium, but also ammonium, Monoethanolamine or Triethanolamine salts.

The detergency builder

[0031] The compositions of the invention may contain a detergency builder. Preferably the builder is present in an amount of from 1 to less than 80 wt % based on the weight of the total composition. More preferably the amount of builder is from 1 to 60 wt %. Builders are well-known to those skilled in the art. Many suitable builder compounds are available. Examples are zeolites, sodium tripolyphosphate, layered silicate, sodium carbonate, sodium bicarbonate, burkeite, sodium silicate and mixtures thereof.

Other optional detergent ingredients

[0032] As well as the surfactants, builders and enzymes discussed above, the compositions may optionally contain other active ingredients to enhance performance and properties.

[0033] The compositions of the invention may contain from 0 to 85 wt % of an inorganic non-builder salt, such as sodium sulphate, sodium sesquicarbonate, sodium chloride, calcium chloride, magnesium chloride and calcite, preferably from 0 to 60 wt %, preferably from 0 to 40 wt %, based on the weight of the total composition.

[0034] The compositions of the invention may contain a polycarboxylate polymer. These include homopolymers and copolymers of acrylic acid, maleic acid and acrylic/maleic acids. The publication 'Polymeric Dispersing Agents, Sokalan', a printed publication of BASF Aktiengesellschaft, D-6700 Ludwigshaven, Germany describes organic polymers which are useful. Preferably, the polycarboxylate polymer is selected from the group consisting of sodium polyacrylate, sodium acrylate maleate and mixtures thereof.

Examples of suitable polymers include Sokalan CP5, ex BASF polyacrylate, namely maleic acid-acrylic acid copolymer, with a sodium salt.

[0035] The detergent compositions of the invention may comprise one or more optional ingredients selected from soap, peroxyacid and persalt bleaches, bleach activators, air bleach catalysts, sequestrants, cellulose ethers and esters, cellulosic polymers, other antiredeposition agents, sodium bicarbonate, other inorganic salts, fluorescers, photobleaches, polyvinyl pyrrolidone, other dye transfer inhibiting polymers, foam controllers, foam boosters, citric acid, soil release polymers, silicone, fabric conditioning compounds, coloured speckles such as blue speckles, and perfume. This list is not intended to be exhaustive.

Form of the composition

[0036] The compositions of the invention are granular detergent compositions, preferably in powder form, having a mean particle size between 200 and 800 micrometer. Alternatively, the compositions may be in tablet form. The compositions can be formulated for use as hand wash or machine wash detergents.

Preparation of the compositions

[0037] The granular compositions of the invention may be prepared by any suitable process. Powders of low to moderate bulk density may be prepared by spray-drying a slurry, and optionally postdosing (dry-mixing) further ingredients. "Concentrated" or "compact" powders may be prepared by mixing and granulating processes, for example, using

a highspeed mixer/granulator, or other non-tower processes.

[0038] Tablets may be prepared by compacting powders, especially "concentrated" powders. The choice of processing route may be in part dictated by the stability or heat-sensitivity of the surfactants involved, and the form in which they are available. In all cases, all ingredients may be added separately.

[0039] The invention will now be further illustrated by the following, non-limiting Examples, in which parts and percentages are by weight, unless indicated otherwise. In the examples, the following abbreviations are used and the compounds have the indicated functions:

Sodium LAS: sodium C₁₀-C₁₃ alkylbenzene sulphonate (anionic surfactant)

Nonionic 7EO: C₁₃-C₁₅ fatty alcohol ethoxylated with an average of 7 ethyleneoxide units per mole (nonionic surfactant)

MES: sodium C₁₆-C₁₈ methyl ester sulphonate (ca. 80-90% pure, having an average molecular weight of sodium salt = 370 - 390 g/mol) (anionic surfactant)

STP: Sodium Tri Polyphosphate (complexing builder)

Zeolite 4A: sodium alumino silicate with Si:Al ratio 1 (ionexchange builder)

Sodium carbonate (precipitating builder and buffer)

Calcite (filler)

Sodium disilicate (builder and buffer; alkaline silicate)

Polymer: acrylic acid/maleic acid type of polymer (anti-redeposition, anti-ashing or co-builder)

SCMC: sodium carboxy methyl cellulose (anti-redeposition polymer)

Fluorescer (optical brightener)

Sodium sulphate (filler salt)

Sodium chloride (filler salt)

Speckles: visual cue.

Sodium perborate mono hydrate; (hydrogen peroxide) bleach.

MS: Sodium methyl sulphate, chemical from Aldrich.

Sodium thiosulphate: chemical from BDH Prolabo.

Polarzyme 12.0 T: protease enzyme granule from Novozymes; granule contains sodium thiosulphate as stabilizer.

Savinase 24.0 GTT (12.0 or 24.0 T): protease enzyme granule from Novozymes; granule contains sodium thiosulphate as stabilizer.

Stainzyme 12.0 T: amylase enzyme granule from Novozymes; granule contains sodium thiosulphate as stabilizer.

Termamyl 60 T: amylase enzyme granule from Novozymes; granule contains sodium thiosulphate as stabilizer.

Properase 1000M: protease enzyme granule from Genencor; granule is free of sodium thiosulphate.

Purafect 3450M: protease enzyme granule from Genencor; granule is free of sodium thiosulphate.

Lipex 100 T: lipase enzyme granule from Novozymes; granule is free of sodium thiosulphate.

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Savinase pure: pure protease enzyme powder from Novozymes; without coating and sodium thiosulphate.

Dummy granule: granule from Novozymes without enzymes and sodium thiosulphate.

BSA: Bovine Serum Albumin; model protein.

Example 1

[0040] The following tables show the composition of the formulations used in examples 3-5:

Zeolite-based powder				
Ingredients	Control (no MES)	3.2% MES (= 20% LAS-replacement) with various levels Polarzyme		
	1A %	1B %	1C %	1D %
Sodium LAS	12.8	12.8	12.8	12.8
Sodium sulphate	41.0	37.6	37.4	36.6
Polymer	1.0	1.0	1.0	1.0
SCMC	0.7	0.7	0.7	0.7
Nonionic 7EO	1.3	1.3	1.3	1.3
Fluorescer	0.1	0.1	0.1	0.1
Zeolite 4A	17.2	17.2	17.2	17.2
Sodium carbonate	20.1	20.1	20.1	20.1
Sodium disilicate	3.0	3.0	3.0	3.0
Moisture, salt, NDOM	2.6	2.6	2.6	2.6
Polarzyme 12T	0.2	0.0	0.2	1.0
MES (as such)	0.0	3.6	3.6	3.6
	100.0	100.0	100.0	100.0

Zeolite-based powder							
Ingredients	10% MES with various types of enzymes				1% methyl sulphate with various types of enzymes		
	1E %	1F %	1G %	1H %	1I %	1J %	1K %
Sodium LAS	12.8	12.8	12.8	12.8	12.8	12.8	12.8
Sodium sulphate	30.0	29.0	29.0	29.0	39.2	39.2	39.2
Polymer	1.0	1.0	1.0	1.0	1.0	1.0	1.0
SCMC	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Nonionic 7EO	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Fluorescer	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Zeolite 4A	17.2	17.2	17.2	17.2	17.2	17.2	17.2
Sodium carbonate	20.1	20.1	20.1	20.1	20.1	20.1	20.1
Sodium disilicate	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Moisture, salt, NDOM	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Polarzyme 12T	0.0	1.0	0.0	0.0	1.0	0.0	0.0
Savinase 24GTT	0.0	0.0	1.0	0.0	0.0	1.0	0.0
Stainzyme 12T	0.0	0.0	0.0	1.0	0.0	0.0	1.0
MES (as such)	11.2	11.2	11.2	11.2	0.0	0.0	0.0
Methyl sulphate	0.0	0.0	0.0	0.0	1.0	1.0	1.0

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(continued)

Zeolite-based powder							
Ingredients	10% MES with various types of enzymes				1% methyl sulphate with various types of enzymes		
	1E %	1F %	1G %	1H %	1I %	1J %	1K %
	100.0	100.0	100.0	100.0	100.0	100.0	100.0

STP-based powder								
Ingredients	Control (no MES)	19% MES (= 80% LAS-replacement level) with various types and levels of enzymes						
	2A %	2B %	2C %	2D %	2E %	2F %	2G %	2H %
Sodium LAS	23.9	4.8	4.8	4.8	4.8	4.8	4.8	4.8
STP	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1
Sodium disilicate	8.0	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Sodium sulphate	15.6	27.5	27.4	26.5	27.4	26.5	26.5	26.5
Sodium carbonate	20.1	20.1	20.1	20.1	20.1	20.1	20.1	20.1
Sodium chloride	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
SCMC	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Fluorescer	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Calcite	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Speckles	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Moisture, salt, NDOM	9.7	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Polarzyme 12T	0.1	0.0	0.1	1.0	0.0	0.0	0.0	0.0
Savinase 24.0GTT	0.0	0.0	0.0	0.0	0.1	1.0	0.0	0.0
Properase 1000M	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0
Purafect 3450M	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0
MES (as such)	0.0	21.5	21.5	21.5	21.5	21.5	21.5	21.5
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Carbonate-based powder		
Ingredients	Control (no enzyme)	with 1% enzyme
	3A %	3B %
Sodium LAS	3.2	3.2
Sodium disilicate	6.3	6.3
Polymer	1.0	1.0
Sodium sulphate	28.9	27.9
Sodium carbonate	39.9	39.9
Fluorescer	0.1	0.1
Sodium perborate	1.0	1.0
Speckles	0.5	0.5
MES	15.0	15.0
Moisture, salt, NDOM	4.1	4.1

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Carbonate-based powder		
Ingredients	Control (no enzyme)	with 1% enzyme
	3A %	3B %
Polarzyme 12T	0.0	1.0
	100.0	100.0

Example 2

[0041] The malodour molecule generated during storage has been identified via GC/MS headspace analyses to be a dimethylsulfide (abbr. DMS), predominantly dimethyl-disulfide, dimethyl-trisulfide and dimethyl-tetrasulfide. The severity of malodour due to dimethylsulfides can be best assessed olfactively using following intensity scale:

intensity scale of DMTS-like malodour	
0	no
1	moderate
2	strong
3	severe

[0042] Samples of various products have been stored for 8 weeks in closed glass jars at Room Temperature, 37°C/70%RH, and 45°C.

[0043] At 37°C/70%RH the products are also stored in closed carton packs.

Example 3

[0044] MES in combination with thiosulphate-containing proteases in various products.

Zeolite-based powder				
	product no.	malodour after 8 weeks storage at		
		37°C/70% RH		45°C (glass)
		(carton)	(glass)	
no MES (Control)	1A	0	0	0
20% LAS repl. by MES; 0% Polarzyme 12T	1B	0	0	0
20% LAS repl. by MES; 0.2% Polarzyme 12T	1C	0	0	1
20% LAS repl. by MES; 1% Polarzyme 12T	1D	0	1	2
STP-based powder				
	product no.	malodour after 8 weeks storage at		
		37°C/70% RH		45°C (glass)
		(carton)	(glass)	
no MES (Control)	2A	0	0	0
80% LAS repl. by MES; 0% protease	2B	0	0	0
80% LAS repl. by MES; 0.1% Polarzyme 12T	2C	0	0	0
80% LAS repl. by MES; 1% Polarzyme 12T	2D	1	0	1

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STP-based powder				
	product no.	malodour after 8 weeks storage at		
		37°C/70% RH		45°C (glass)
		(carton)	(glass)	
80% LAS repl. by MES; 0.1% Savinase 24GTT	2E	0	0	0
80% LAS repl. by MES; 1% Savinase 24GTT	2F	2	0	1
Carbonate-based powder				
	product no.	malodour after 8 weeks storage at		
		37°C/70% RH		45°C (glass)
		(carton)	(glass)	
no enzymes (Control)	3A	0	0	0
1% Polarzyme 12T	3B	0	0	1

[0045] It can be concluded that malodour development increases with increasing level of enzymes for all formulations with the various builder types.

Example 4

[0046] MES or sodium methylsulphate in combination with thiosulphate-containing enzymes.

Zeolite-based powder		
	product no.	malodour 8w at 45°C (glass)
no MES (Control)	1A	0
10% MES; 0% enzyme	1E	0
10% MES; 1% Polarzyme 12T	1F	1
10% MES; 1% Savinase 24GTT	1G	2
10% MES; 1% Stainzyme 12T	1H	2
1% methyl sulphate; 1% Polarzyme 12T	2I	2
1% methyl sulphate; 1% Savinase 24GTT	1J	2
1% methyl sulphate; 1% Stainzyme 12T	1K	2

[0047] Malodour formation seems to be triggered by an interaction between enzymes and methylsulphate rather than MES itself (note: methylsulphate is one of the main by-products formed during MES production).

Example 5

[0048] Comparison of protease enzymes with and without thiosulphate.

STP-based powder				
		product no.	malodour after 8w at	
			37°C/70% RH (carton)	45°C (glass)
references	no MES (Control)	2A	0	0
	80% LAS repl. by MES; 0% protease	2B	0	0
with thiosulfate (from Novozymes)	80% LAS repl. by MES; 1% Polarzyme 12T	2D	1	1
	80% LAS repl. by MES; 1% Savinase 24GTT	2F	2	1
without thiosulfate (from Genencor)	80% LAS repl. by MES; 1% Properase 1000M	2G	0	0
	80% LAS repl. by MES; 1% Purafect 3450M	2H	0	0

[0049] Malodour is due to an interaction of MES/MS and thiosulphate (which is present within enzyme-granules of Novozymes), since no malodour develops in the presence of thiosulphate-free enzymes from Genencor.

Example 6

[0050] Mixtures of MES or methylsulphate with various enzymes (1:1 mixtures of single ingredients).

Controls (i.e. single ingredients)	
	malodour 4w storage
	45°C glass
MES	0
Methyl sulphate	0
Polarzyme 12T	0
Savinase 24GTT	0
Stainzyme 12T	0
Termamyl 60T	0
Lipex 100T	0
Properase 1000M	0
Purafect 3450M	0
Savinase pure	0
BSA (model proteine)	0
Dummy granule (coating only)	0
Sodium thiosulphate (chemical)	0

1:1 mixtures with thiosulphate-containing enzymes	
	malodour 4w storage
	45°C glass
MES/Polarzyme	1
MES/Savinase	1
MES/Stainzyme	1
MES/Termamyl	2
1:1 mixtures with thiosulphate-free enzymes	
MES/Lipex	0
MES/Properase	0
MES/Purafect	0
MES/Savinase pure	0
MES/BSA	0
MES/Dummy	0

1:1 mixtures with thiosulphate (chemical)	
	malodour 4w storage
	45°C glass
MES/thiosulphate	3
Methyl sulphate/thiosulphate	3

[0051] The 1:1 mixtures show again that malodour is due to an interaction of MES/MS and thiosulphate (which is present within enzyme-granules of Novozyme), since no malodour develops in the presence of thiosulphate-free enzymes from Genencor, pure Savinase, BSA, and the thiosulphate-free coating of Novozyme-granules. In addition, very severe malodour generates during storage of MES/MS with thiosulphate as such. Malodour is identified via GC/MS headspace analyses to be DMS.

Claims

- Granular detergent composition comprising 1 to 30% by weight of an alkyl ester fatty acid sulphonate surfactant and 0.1 to 10% by weight enzyme granules, wherein said composition is substantially free of thiosulphate, and wherein said detergent composition comprises methyl sulphate.
- A detergent composition according to claim 1, wherein the alkyl ester fatty acid sulphonate surfactant is methyl ester fatty acid sulphonate surfactant.
- A detergent composition according to claim 1, containing 0.5 to 10% methyl sulphate, based on the amount of methyl ester fatty acid sulphonate.
- A detergent composition according to any one of the preceding claims, wherein the enzyme is selected from the group consisting of protease, lipase, amylase, cellulase, mannanase and oxidoreductase.
- A detergent composition according to any one of the preceding claims, further comprising linear alkyl benzene sulphonate.

6. A detergent composition according to any one of the preceding claims, comprising an ethoxylated alcohol nonionic surfactant.
7. A detergent composition according to claim 6, wherein the ethoxylated alcohol nonionic surfactant has an average degree of ethoxylation n of from 3 to 7.
8. A detergent composition according to any one of the preceding claims, comprising a builder in an amount of from 1 to 60%, preferably from 1 to 40% by weight.
9. A detergent composition according to claim 8, wherein said builder is selected from the group consisting of zeolite, sodium tripolyphosphate, layered silicate, sodium carbonate, sodium bicarbonate, burkeite, sodium silicate and mixtures thereof.
10. A detergent composition according to any one of the preceding claims, comprising sodium sulphate in an amount of from 2 to 50%, preferably from 10 to 40% by weight.
11. A detergent composition according to claim 9, wherein the sodium silicate is present in an amount of from 1 to 20 % by weight.
12. A detergent composition according to any one of the preceding claims, further comprising a cationic surfactant in an amount of from 0.1 to 5% by weight.
13. A detergent composition according to any one of the preceding claims, further comprising a polycarboxylate polymer selected from the group consisting of sodium polyacrylate, sodium acrylate maleate and mixtures thereof.
14. A detergent composition according to any one of the preceding claims, **characterised in that** it further comprises one or more optional ingredients selected from soap, peroxyacid and persalt bleaches, bleach activators, air bleach catalyst, sequestrants, cellulose ethers and esters, cellulosic polymers, other antiredeposition agents, fluorescers, photobleaches, polyvinyl pyrrolidone, other dye transfer inhibiting polymers, foam controllers, foam boosters, colourants, citric acid, soil release polymers, fabric conditioning compounds, coloured speckles, and perfume.
15. A detergent tablet obtained by compressing the granular detergent composition according to any one of the preceding claims.
16. Process for laundering textile fabrics by machine or hand, **characterised in that** it comprises the step of immersing the fabrics in a wash liquor comprising water in which a granular detergent composition or detergent tablet as claimed in any preceding claim is dissolved or dispersed.

Patentansprüche

1. Granulare Reinigungszusammensetzung, umfassend 1 bis 30 Gewichts-% eines Fettsäurealkylester-Sulfonat-Tensids und 0,1 bis 10 Gewichts-% Enzymgranulate, wobei die Zusammensetzung im Wesentlichen frei von Thiosulfat ist und wobei die Reinigungszusammensetzung Methylsulfat umfasst.
2. Reinigungszusammensetzung nach Anspruch 1, wobei das Fettsäurealkylester-Sulfonat-Tensid Fettsäuremethylester-Sulfonat-Tensid ist.
3. Reinigungszusammensetzung nach Anspruch 1, die 0,5 bis 10% Methylsulfat, bezogen auf die Menge des Fettsäuremethylester-Sulfonats, enthält.
4. Reinigungszusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei das Enzym aus der aus Protease, Lipase, Amylase, Cellulase, Mannanase und Oxidoreduktase bestehenden Gruppe ausgewählt ist.
5. Reinigungszusammensetzung nach irgendeinem der vorhergehenden Ansprüche, die ferner lineares Alkylbenzolsulfonat umfasst.
6. Reinigungszusammensetzung nach irgendeinem der vorhergehenden Ansprüche, die ein nichtionisches Tensid in

Form eines ethoxylierten Alkohols umfasst.

7. Reinigungszusammensetzung nach Anspruch 6, wobei das nicht-ionische Tensid in Form des ethoxylierten Alkohols einen durchschnittlichen Ethoxylierungsgrad von 3 bis 7 aufweist.
8. Reinigungszusammensetzung nach irgendeinem der vorhergehenden Ansprüche, die einen Builder in einer Menge von 1 bis 60 Gewichts-%, vorzugsweise von 1 bis 40 Gewichts-%, umfasst.
9. Reinigungszusammensetzung nach Anspruch 8, wobei der Builder aus der aus Zeolith, Natriumtripolyphosphat, geschichtetem Silikat, Natriumcarbonat, Natriumbicarbonat, Burkeit, Natriumsilikat und Mischungen davon bestehenden Gruppe ausgewählt ist.
10. Reinigungszusammensetzung nach irgendeinem der vorhergehenden Ansprüche, die Natriumsulfat in einer Menge von 2 bis 50 Gewichts-%, vorzugsweise von 10 bis 40 Gewichts-%, umfasst.
11. Reinigungszusammensetzung nach Anspruch 9, wobei das Natriumsilikat in einer Menge von 1 bis 20 Gewichts-% vorliegt.
12. Reinigungszusammensetzung nach irgendeinem der vorhergehenden Ansprüche, die ferner ein kationisches Tensid in einer Menge von 0,1 bis 5 Gewichts-% umfasst.
13. Reinigungszusammensetzung nach irgendeinem der vorhergehenden Ansprüche, die ferner ein Polycarboxylat-Polymer umfasst, das aus der aus Natriumpolyacrylat, Natriumacrylat-Maleat und Mischungen davon bestehenden Gruppe ausgewählt ist.
14. Reinigungszusammensetzung nach irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** sie ferner ein oder mehrere optionale Bestandteile umfasst, die aus Seife, Peroxysäure- und Persalz-Bleichmitteln, Bleichaktivatoren, Luftbleichkatalysator, Komplexbildnern, Celluloseethern und -estern, cellulosischen Polymeren, anderen Antiwiederablagerungsmitteln, Fluoreszenzmitteln, Photobleichmitteln, Polyvinylpyrrolidon, anderen polymeren Farbstoffübertragungsinhibitoren, Schaumreglern, Schaumverstärkern, Bleichmitteln, Zitronensäure, Soil-Release-Polymeren, Textilkonditionierverbindungen, gefärbten Sprenkeln und Parfüm ausgewählt sind.
15. Reinigungstablette, erhalten durch Komprimieren der granularen Reinigungszusammensetzung nach irgendeinem der vorhergehenden Ansprüche.
16. Verfahren zum Waschen von textilen Erzeugnissen mit Maschine oder Hand, **dadurch gekennzeichnet, dass** es den Schritt des Eintauchens des Textils in eine Waschlauge umfasst, die Wasser umfasst, in der eine granuläre Reinigungszusammensetzung oder Reinigungstablette, wie in irgendeinem der vorhergehenden Ansprüche beansprucht, gelöst oder dispergiert wird.

Revendications

1. Composition de détergent granulaire comprenant de 1 à 30 % en masse d'un tensio-actif de sulfonate d'acide gras d'ester alkylique et de 0,1 à 10 % en masse de granulés d'enzyme, dans laquelle ladite composition est pratiquement exempte de thiosulfate, et dans laquelle ladite composition de détergent comprend du sulfate de méthyle.
2. Composition de détergent selon la revendication 1, dans laquelle le tensioactif de sulfonate d'acide gras d'ester alkylique est un tensioactif de sulfonate d'acide gras d'ester méthylique.
3. Composition de détergent selon la revendication 1, contenant de 0,5 à 10 % de sulfate de méthyle, sur la base de la quantité de sulfonate d'acide gras d'ester méthylique.
4. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle l'enzyme est choisie dans le groupe constitué de protéase, lipase, amylase, cellulase, mananase et oxydoréductase.
5. Composition de détergent selon l'une quelconque des revendications précédentes, comprenant de plus un benzène-sulfonate d'alkyle linéaire.

6. Composition de détergent selon l'une quelconque des revendications précédentes, comprenant un tensioactif non ionique d'alcool éthoxylé.
- 5 7. Composition de détergent selon la revendication 6, dans laquelle le tensioactif non ionique d'alcool éthoxylé présente un degré moyen d'éthoxylation n de 3 à 7.
8. Composition de détergent selon l'une quelconque des revendications précédentes, comprenant un adjuvant dans une quantité de 1 à 60 %, de préférence de 1 à 40 % en masse.
- 10 9. Composition de détergent selon la revendication 8, dans laquelle ledit adjuvant est choisi dans le groupe constitué de zéolite, tripolyphosphate de sodium, silicate lamellaire, carbonate de sodium, bicarbonate de sodium, burkéite, silicate de sodium et mélanges de ceux-ci.
- 15 10. Composition de détergent selon l'une quelconque des revendications précédentes, comprenant du sulfate de sodium dans une quantité de 2 à 50 %, de préférence de 10 à 40 % en masse.
11. Composition de détergent selon la revendication 9, dans laquelle le silicate de sodium est présent dans une quantité de 1 à 20 % en masse.
- 20 12. Composition de détergent selon l'une quelconque des revendications précédentes, comprenant de plus un tensioactif cationique dans une quantité de 0,1 à 5 % en masse.
- 25 13. Composition de détergent selon l'une quelconque des revendications précédentes, comprenant de plus un polymère de polycarboxylate choisi dans le groupe constitué de polyacrylate de sodium, acrylate maléate de sodium et mélanges de ceux-ci.
- 30 14. Composition de détergent selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'il** comprend de plus un ou plusieurs ingrédients facultatifs choisis parmi le savon, des blanchissants de peroxyacide et de persel, des activateurs de blanchiment, un catalyseur de blanchiment à l'air, des séquestrants, des éthers et esters de cellulose, des polymères cellulodiques, d'autres agents anti-redéposition, des azurants optiques, des photoblanchissants, de la polyvinylpyrrolidone, d'autres polymères inhibant le transfert de colorant, des agents de contrôle de mousse, des agents de promotion de mousse, des colorants, de l'acide citrique, des polymères libérant la saleté, des composés conditionnant les textiles, des billes colorées et du parfum.
- 35 15. Tablette de détergent obtenue par compression de la composition de détergent granulaire selon l'une quelconque des revendications précédentes.
- 40 16. Procédé de lessive de tissus textiles à la machine ou à la main, **caractérisé en ce qu'il** comprend l'étape d'immersion des tissus dans une liqueur de lavage comprenant de l'eau dans laquelle une composition de détergent granulaire ou une tablette de détergent selon l'une quelconque des revendications précédentes est dissoute ou dispersée.

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REFERENCES CITED IN THE DESCRIPTION

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