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(54) Detergent Compositions

(57) Detergent compositions containing high efficiency lipase enzymes and specific detergent formulations comprising a high reserve alkalinity, greater than 6.5, and a bleaching agent comprising hydrogen peroxide source and peracid or precursor thereof such that the Avox to peracid ratio is 1:1 to 35:1, enables control of diacyl peroxide formation. Preferred formulations comprise surfactants selected from alkyl benzene sulphonates in combination with alky ethoxylated sulfates or MES or non-ionic surfactants.

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Description

Technical field

[0001] The present invention relates to detergent compositions, particularly laundry detergents and in particular to detergents comprising lipolytic or lipase enzymes.

Background of the Invention and Prior Art

[0002] Many detergent compositions comprise bleaching systems for assisting in stain removal of articles being washed. These bleaching systems commonly comprise a source of hydrogen peroxide such as perborate or percarbonate. The performance of hydrogen peroxide bleaches is often enhanced by use of a peracid which may be preformed or a peracid precursor (often called a bleach activator) in addition to the hydrogen peroxide (or oxygen source). In use, the bleach activator reacts with an excess of hydrogen peroxide to form a peracid bleaching species. Typical laundry formulations use an excess of hydrogen peroxide source.

[0003] The most common bleach activator is TAED (tetra acetyl ethylene diamine), the active bleach species that is formed on reaction with hydrogen peroxide being peracetic acid. Other activators result in bleaching species that have a longer carbon chain and that are hydrophobic. These are desirable for producing effective bleaching, especially on oily stains.

[0004] One well-known example of such hydrophobic bleach activators is nonanoyl oxybenzene sulphonate (NOBS). This bleach activator reacts to form a reactive bleaching species pemonanoic acid. However, it has been found that this bleaching species will react with the bleach activator itself to form a di-C_9 acyl peroxide; other hydrophobic bleach activators react to form their corresponding diacyl peroxides in the same way. These species are strong bleaching species and are useful in the washing process, but they are insoluble. In some types of washing machines, there may be a tendency for these compounds to settle out in the sump of washing machines as the wash water drains out of the washing machine. Thus, strong bleaching agents may become artificially concentrated in these areas and it has been found that in some types of washing machines, over time, damage may be caused to washing machines in these areas where the material used in these areas is vulnerable to high levels of bleach, such as polymeric and/or rubber sumps.

[0005] The problem addressed by this invention is how to alleviate this problem such that the benefits of hydrophobic bleaches may be achieved whilst at the same time minimizing or preventing damage to washing equipment.

[0006] Lipase enzymes have been used in detergents since the late 1980s for removal of fatty soils by breakdown of fatty soils into tri-glycerides.

[0007] Until relatively recently, the main commercially available lipase enzymes, such as Lipolase (trade name, Novozymes) worked particularly effectively at the lower moisture levels of the drying phase of the wash process. These enzymes tended to produce significant cleaning only in the second wash step because the active site of the enzyme was occupied by water during the washing process, so that fat breakdown was significant only on soils remaining on laundered clothes during the drying stage, the broken down fats then being removed in the next washing step. However, more recently, higher efficiency lipases have been developed that also work effectively during the wash phase of the cleaning process, so that as well as cleaning in the second washing step, a significant improvement in cleaning effect due to lipase enzyme can be found in the first wash-cycle. Examples of such enzymes are as described in WO00/60063 and Research Disclsoure IP6553D. Such enzymes are referred to below as first wash lipases. Examples of such enzymes include certain variants of lipolase (wild-type Humicola lanuginosa) which should comprise one or more substitutions with positive amino acids near the N-terminal in the three-dimensional structure. The variants should further comprise a peptide addition at the C-terminal and/or should meet certain limitations on electrically charged amino acids at positions 90-101 and 210. The present inventors have found that using a combination of these first wash enzymes with a specific type of detergent formulation enables use of these hydrophobic bleach activators to achieve good stain removal, whilst reducing any of the disadvantages set out above.

Definition of the Invention

[0008] In accordance with the present invention there is provided a detergent composition comprising a hydrogen peroxide source, a hydrophobic peracid or precursor thereof having the formula R-(C=O)-L where R is an alkyl group having from 6 to 14, preferably from 8 to 12 carbon atoms, and L is a leaving group, and a lipase enzyme which is a polypeptide having an amino acid sequence which: (a) has at least 90% identity with the wild-type lipase derived from *Humicola lanuginosa* strain DSM 4109; (b) compared to said wild-type lipase, comprises a substitution of an electrically neutral or negatively charged amino acid at the surface of the three-dimensional structure within 15Å of E1 or Q249 with a positively charged amino acid; and (c) comprises a peptide addition at the C-terminal; and/or (d) comprises a peptide addition at the N-terminal and/or (e) meets the following limitations: i) comprises a negative amino acid in position E210 of said wild-type lipase; ii) comprises a negatively charged amino acid in the region corresponding to positions 90-101 of said wild-type lipase; and iii) comprises a neutral or negative amino acid at a position corresponding to N94 of said wild-type lipase and/or has a negative or neutral net electric charge in the region corresponding to positions 90-101 of said wild-type lipase; the detergent composition having a reserve alkalinity of greater than 6.5, the quantity of oxygen source and peracid being such as to provide the detergent composition with a molar ratio of Available oxygen (from the peroxide source): peracid of from 1:1 to 35:1.

[0009] In accordance with the present invention there is also provided a detergent composition comprising a hydrogen peroxide source, a hydrophobic bleach activator having the formula R-(C=O)-L where R is an alkyl group having from 6 to 14, preferably from 8 to 12 carbon atoms, and L is a leaving group, a lipase enzyme producing First Wash lard removal performance better than that produced by WT Lipolase (tradename from Novozymes) using the Lard First Wash Test described below, and the detergent composition having a reserve alkalinity of greater than 6.5, the quantity of oxygen source and peracid being such as to provide the detergent composition with a molar ratio of Available oxygen (from the peroxide source): peracid of from 1:1 to 35:1.

[0010] WT Lipolase from Novozymes is described in US 5 869 438, seq#2.

[0011] The present inventors have found that when a first wash lipase is used in a detergent composition in conjunction with high reserve alkalinity and with a molar ratio of available oxygen (from the peroxide source): peracid of from 1:1 to 35:1, diacyl peroxide formation is controlled such that the disadvantages of this type of hydrophobic peracid or peracid precursor are alleviated.

[0012] In a preferred aspect of the invention, the detergent compositions of the invention comprise less than 15 wt% builders selected from aluminosilicate (zeolite) builder and/or phosphate builder. In a further preferred aspect of the invention, the compositions comprise less than 10 wt% zeolite and/or phosphate builder, or even less than 5 wt% or 4 wt % zeolite and/or phosphate builder.

Detailed Description of the Invention

Peroxide Source

[0013] Inorganic perhydrate salts are a preferred source of peroxide. Preferably these salts are present at a level from 0.05 to 40 wt%, more preferably from 1 to 30 wt% based on the detergent composition, or from 2 to 20 wt%. Examples of inorganic perhydrate salts include perborate, percarbonate, persulphate, perphosphate and persilicate salts. Perborate, usually monohydrate or tetrahydrate, or more especially percarbonate salts are most preferred. These are usually alkali metal salts, preferably sodium salts. The inorganic perhydrate salts are typically incorporated into the detergent compositions of the invention as a crystalline solid, which may be optionally coated for example to achieve improved storage stability. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixture thereof, or organic materials such as waxes, oils or fatty soaps.

Hydrophobic Peracid or Peracid Precursor

[0014] Suitable compounds include compounds of the formula R-(C=O)O-O-M or R-(C=O)-L wherein R is an alkyl group, optionally branched, having from 6 to 14 carbon atoms, more preferably from 8 to 12 carbon atoms; M is a counterion, preferably being sodium, potassium or hydrogen; and L is a leaving group. Preferred leaving groups are benzoic acid and derivatives thereof and especially benzene sulphonate.

[0015] Suitable examples include decanoyl oxybenzoic acid or salt thereof, sodium or potassium salts of dodecanonyl oxybenzene sulphonate, decanoyl oxybenzenesulponate, 3,5,5-trimethyl hexanoyloxybenzene sulphonate, or even more preferred nonanoyloxybenzene sulphonate (NOBS).

[0016] The peracid or peracid precursor is generally present in the composition in an amount of from 0.5 to 10 wt%, preferably from 0.5 to 5 wt%, preferably 0.5 to 4 wt% based on the detergent composition.

[0017] Optionally, in addition to the hydrophobic peracid or peracid precursor, a hydrophilic peracid or peracid precursor may also be incorporated into the detergent compositions of the invention. These include materials of the formulae given above for the hydrophobic peracids/precursors, but with the R group comprising less than 6 carbon atoms, preferably less than 4. A preferred example is TAED. If present it will generally be present in amounts no greater than 7 wt%, generally in amounts from 0.1 to 5 wt%.

[0018] The amounts of hydrogen peroxide source and peracid or peracid precursor are selected such that the molar ratio of Available oxygen (from the peroxide source) to peracid is from 1:1 to 35:1. Preferred molar ratios are from 2:1 to 10:1, or even 3:1 or even 5:1 to 8:1.

Lipase Enzyme

[0019] The reference lipase used in this invention is the wild type lipase derived from Humicola lanuginosa strain DSM 4109. It is described in EP258068 and EP305216 and has the amino acid sequence shown in positions 1-269 of SEQ ID NO: 2 of US5869438 (attached hereto). In this specification, the reference lipase is also referred to as Lipolase.

Substitution with Positive Amino Acid

[0020] The lipase of the invention comprises one or more (e.g. 2-4, particularly two) substitutions of an electrically neutral or negatively charged amino acid near E1 or Q249 with a positively charged amino acid, preferably R.

[0021] The substitution is at the surface of the three-dimensional structure within 15 Å of E1 or Q249, e.g. at any of positions 1-11, 90, 95, 169, 171-175, 192-211, 213-226, 228-258, 260-262.

[0022] The substitution may be within 10 Å of E1 or Q249, e.g. at any of positions 1-7, 10, 175, 195, 197-202, 204-206, 209, 215, 219-224, 230-239, 242-254.

[0023] The substitution may be within 15 Å of E1, e.g. at any of positions 1-11, 169, 171, 192-199, 217-225, 228-240, 243-247, 249, 261-262.

[0024] The substitution is most preferably within 10 Å of E1, e.g. at any of positions 1-7, 10, 219-224 and 230-239.

[0025] Thus, some preferred substitutions are S3R, S224R, P229R, T231R, N23 3R, D234R and T244R.

Peptide Addition at C-Terminal

[0026] The lipase may comprise a peptide addition attached to C-terminal L269. The peptide addition improves the first-wash performance in a variety of detergents.

[0027] The peptide addition preferably consists of 1-5 amino acids, e.g. 2, 3 or 4 amino acids. The amino acids of the peptide addition will be numbered 270, 271, etc.

[0028] The peptide addition may consist of electrically neutral (e.g. hydrophobic) amino acids, e.g. PGL or PG. In an alternative embodiment, the lipase peptide addition consists of neutral (e.g. hydrophobic) amino acids and the amino acid C, and the lipase comprises substitution of an amino acid with C at a suitable location so as to form a disulfide bridge with the C of the peptide addition. Examples are:

270C linked to G23C or T37C
271C linked to K24C, T37C, N26C or R81C
272C linked to D27C, T35C, E56C, T64C or R81C.

Amino Acids at Positions 90-101 and 210

[0029] The lipase used in the invention preferably meets certain limitations on electrically charged amino acids at positions 90-101 and 210. Thus, amino acid 210 may be negative. E210 may be unchanged or it may have the substitution E210D/C/Y, particularly E210D.

[0030] The lipase may comprise a negatively charged amino acid at any of positions 90-101 (particularly 94-101), e.g. at position D96 and/or E99.

[0031] Further, the lipase may comprise a neutral or negative amino acid at position N94, i.e. N94 (neutral or negative), e.g. N94N/D/E.

[0032] Also, the lipase may have a negative or neutral net electric charge in the region 90-101 (particularly 94-101), i.e. the number of negative amino acids is equal to or greater than the number of positive amino acids. Thus, the region may be unchanged from Lipolase, having two negative amino acids (D96 and E99) and one positive (K98), and having a neutral amino acid at position 94 (N94), or the region may be modified by one or more substitutions.

[0033] Alternatively, two of the three amino acids N94, N96 and E99 may have a negative or unchanged electric charge. Thus, all three amino acids may be unchanged or may be changed by a conservative or negative substitution, i.e. N94 (neutral or negative), D(negative) and E99(negative). Examples are N94D/E and D96E. Also, one of the three may be substituted so as to increase the electric charge, i.e. N94 (positive), D96 (neutral or positive) or E99 (neutral or positive). Examples are N94K/R, D96I/L/N/S/W or E99N/Q/K/R/H.

[0034] As discussed in WO00/60063, the substitution of a neutral with a negative amino acid (N94D/E), may improve the performance in an anionic detergent. The substitution of a neutral amino acid with a positive amino acid (N94K/R) may provide a variant lipase with good performance both in an anionic detergent and in an anionic/non-ionic detergent (a detergent with e.g. 40-70 % anionic out of total surfactant). A substitution Q249R/K/H and/or a substitution of R209 with a neutral or negative amino acid (e.g. R209P/S) may be useful. The lipase may optionally comprise the substitution G91A.

[0035] The lipase may optionally comprise substitutions of one or more additional amino acids. Such substitutions may, e.g. be made according to principles known in the art, e.g. substitutions described in WO92/05249, WO94/25577, WO95/22615, WO97/04079 and WO97/07202. Specific examples of suitable combinations of substitutions are given in the table bridging pages 4 and 5 of WO00/60063. Nomenclature for amino acid modifications is as described in WO00/60063.

[0036] The preferred lipase enzymes are described in WO00/60063, the most preferred being Lipex (registered tradename of Novozymes), a variant of the *Humicola lanuginosa (Thermomyces lanuginosus)* lipase (Lipolase registered tradename of Novozymes) with the mutations T231R and N23 3R.

[0037] The lipase enzyme incorporated into the detergent compositions of the present invention is generally present in an amount of 10 to 20000 LU/g of the detergent composition, or even 100 to 10000 LU/g. The LU unit for lipase activity is defined in WO99/42566. The lipase dosage in the wash solution is typically from 0.01 to 5 mg/l active lipase protein, more typically from 0.1 to 2mg/l as enzyme protein.

[0038] The lipase enzyme may be incorporated into the detergent composition in any convenient form, generally in the form of a non-dusting granulate, a stabilised liquid or a protected, for example, coated enzyme particle.

Lard First Wash Test

[0039] Whether any specific lipase enzyme gives better First Wash lard removal performance than WT Lipolase (from Novozymes, described in US 5869438, seq#2), can be determined by comparing the performance results of WT Lipolase with the performance results of the specific lipase enzyme according to the following test:

The wash performance of lipolytic enzymes is tested in a one cycle wash trial carried out in a thermostated Terg-O-Tometer (TOM) followed by line-drying. The experimental conditions are as follows:

Wash liquor: 1000ml per beaker
Swatches: 7 flat cotton swatches (9X9cm) (supplied by Warwick-Equest) per beaker Stain: Lard coloured red with sudan red dye (Sigma) (0.75mg sudan red/g lard). 50 µl of lard/sudan red heated to 70°C are applied to the centre of each swatch. After application of the stain the swatches are heated in an oven for 25 minutes at 75°C and then stored overnight at room temperature.
Water for preparing wash liquor: 3.2mM Ca^{2+}/Mg^{2+} (in a ratio of 5:1)
Detergent: 5g/l of detergent composition A.

Detergent Composition A:

[0040]

0.300g/l alkyl sulphate (AS; C_{14-16})
0.650g/l of alcohol ethoxylate (AEO; C_{12-14}, 6EO)
1.750g/l zeolite P
0.145g/l Na_2CO_3
0.020g/l Sokalan CP5 (BASF)
0.050g/l CMC(carboxy methyl cellulose)
5g/l of detergent composition A are mixed into deionised water with added hardness (3.2 mM Ca^{2+}/Mg^{2+} (5:1)) and the pH artificially adjusted to pH 10.2 by adding NaOH. Lipase enzyme is added.
Concentration of lipolytic enzyme: 0 and 12500 LU/1
Wash time: 20 minutes
Wash temperature: 30°C
Rinse: 15 minutes in running tap water
Drying: overnight at room conditions (approx. 20°C, 30 -40 % RH).
Evaluation: the reflectance was measured at 460nm.
The percentage of lard removed is determined as:
Delta reflectance (dR) defined as:

(R(Swatches washed in detergent with lipase)-R(Swatches washed in detergent without lipase)

The reflectance (which may also be termed remission) is measured on an Elrepho 2000 apparatus from Datacolor which illuminates the sample with 2 xenon blitz lamps and measures the amount of reflected light so that entirely white corresponds to a 100% reflectance and entirely black a 0% reflectance. Comparing the results for lard removal due to the presence of enzyme, lipase enzymes giving better performance than WT Lipolase™ are suitable for use in the compositions of the present invention.

Reserve Alkalinity

[0041] As used herein, the term "reserve alkalinity" is a measure of the buffering capacity of the detergent composition (g/NaOH/100g detergent composition) determined by titrating a 1% (w/v) solution of detergent composition with hydrochloric acid to pH 7.5 i.e in order to calculate Reserve Alkalinity as defined herein:

$$\textbf{Reserve Alkalinity} \text{ (to pH 7.5) as \% alkali in g NaOH/100 g product} = \frac{T \times M \times 40 \times Vol}{10 \times Wt \times Aliquot}$$

T = titre (ml) to pH 7.5
M = Molarity of HCl = 0.2
40 = Molecular weight of NaOH
Vol = Total volume (ie. 1000 ml)
W = Weight of product (10 g)
Aliquot = (100 ml)

Obtain a 10g sample accurately weighed to two decimal places, of fully formulated detergent composition. The sample should be obtained using a Pascall sampler in a dust cabinet. Add the 10g sample to a plastic beaker and add 200 ml of carbon dioxide-free deionised water. Agitate using a magnetic stirrer on a stirring plate at 150 rpm until fully dissolved and for at least 15 minutes. Transfer the contents of the beaker to a 1 litre volumetric flask and make up to 1 litre with deionised water. Mix well and take a 100 mls ± 1 ml aliquot using a 100 mls pipette immediately. Measure and record the pH and temperature of the sample using a pH meter capable of reading to +0.01pH units, with stirring, ensuring temperature is 21 °C +/- 2°C. Titrate whilst stirring with 0.2M hydrochloric acid until pH measures exactly 7.5. Note the millilitres of hydrochloric acid used. Take the average titre of three identical repeats. Carry out the calculation described above to calculate RA to pH 7.5.

The RA of the detergent compositions of the invention will be greater than 6.5 and preferably greater than 7.5. The RA may be greater than 8 or even greater than 9 or 9.5 or higher. The RA may be up to 20 or higher.

[0042] Adequate reserve alkalinity may be provided, for example, by one or more of alkali metal silicates (excluding crystalline layered silicate), typically amorphous silicate salts, generally 1.2 to 2.2 ratio sodium salts, alkali metal typically sodium carbonate, bicarbonate and/or sesquicarbonates. STPP and persalts such as perborates and percarbonates also contribute to alkalinity. Buffering is necessary to maintain an alkaline pH during the wash process counteracting the acidity of soils, especially fatty acids liberated by the lipase enzyme.

[0043] The detergent composition preferably comprises from 0 wt% to 50 wt% silicate salt, more usually 5 to 30 wt% silicate salt, or 7 to 20 wt% silicate salt, usually sodium silicate.

[0044] In order to provide the desired reserve alkalinity the detergent compositions of the invention may comprise a carbonate salt, typically from 1 wt% to 70 wt%, or from 5 wt% to 50 wt% or from 10 wt% to 30 wt% carbonate salt. Preferred carbonate salts are sodium carbonate and/or sodium bicarbonate and/or sodium sesquicarbonate. The carbonate salt may be incorporated into the detergent composition wholly or partially via a mixed salt such as Burkeite. A highly preferred carbonate salt is sodium carbonate. Preferably, the composition may comprise from 5 wt% to 50 wt% sodium carbonate, or from 10 to 40 wt% or even 15 to 35 wt% sodium carbonate. It may also be desired for the composition to comprise from 1wt% to 20 wt% sodium bicarbonate, or even 2 to 10 or 8 wt%.

[0045] If zeolite is present, it may be desired for the weight ratio of sodium carbonate and/or sodium silicate to zeolite builder to be at least 5:1, preferably at least 10:1, or at least 15:1, or at least 20:1 or even at least 25:1

[0046] The carbonate salt, or at least part thereof, is typically in particulate form, typically having a weight average particle size in the range of from 200 to 500 micrometers. However, it may be preferred for the carbonate salt, or at least part thereof, to be in micronised particulate form, typically having a weight average particle size in the range of from 4 to 40 micrometers; this is especially preferred when the carbonate salt, or at least part thereof, is in the form of a co-particulate admixture with a detersive surfactant, such as an alkoxylated anionic detersive surfactant.

[0047] In order to provide the required reserve alkalinity, preferably the levels of carbonate and/or silicate salts, typically sodium carbonate and sodium silicate will be from 10 to 70 wt%, or from 10 or even 15 to 50 wt% based on the total weight of the composition.

Builders

[0048] In accordance with the present invention, preferably, the amount of strong builder selected from phosphate and/or zeolite builder is less than 15 wt% based on the total weight of the detergent composition, preferably below 10 wt%, or even below 8 or 5 or 4 or 3 or 2 wt%.

[0049] In a further preferred aspect of the invention, the total level of weak builders selected from layered silicate (SKS-6), citric acid, citrate salts and nitrilo triacetic acid or salt thereof is below 15 wt%, more preferably below 8 wt%, more preferably below 4 wt% or even below 3 or 2 wt% based on the total weight of the detergent composition. Typically the level of each of layered silicate, citric acid, citrate salts and nitrilo triacetic acid or salt thereof will be below 10 wt% or even below 5 wt% or wt% based on the total weight of the composition.

Surfactant

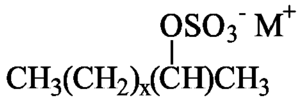
[0050] A highly preferred adjunct component of the compositions of the invention is a surfactant. Preferably, the detergent composition comprises one or more surfactants. Typically, the detergent composition comprises (by weight of the composition) from 0% to 50%, preferably from 5% and more preferably from 10 or even 15 wt% to 40%, or to 30%, or to 20% one or more surfactants. Preferred surfactants are anionic surfactants, non-ionic surfactants, cationic surfactants, zwitterionic surfactants, amphoteric surfactants, cationic surfactants and mixtures thereof.

Anionic surfactants

[0051] Suitable anionic surfactants typically comprise one or more moieties selected from the group consisting of carbonate, phosphate, phosphonate, sulphate, sulphonate, carboxylate and mixtures thereof. The anionic surfactant may be one or mixtures of more than one of C_{8-18} alkyl sulphates and C_{8-18} alkyl sulphonates. Suitable anionic surfactants incorporated alone or in mixtures in the compositions of the invention are also the C_{8-18} alkyl sulphates and/or C_{8-18} alkyl sulphonates optionally condensed with from 1 to 9 moles of C_{1-4} alkylene oxide per mole of C_{8-18} alkyl sulphate and/or C_{8-18} alkyl sulphonate. The alkyl chain of the C_{8-18} alkyl sulphates and/or C_{8-18} alkyl sulphonates may be linear or branched, preferred branched alkyl chains comprise one or more branched moieties that are C_{1-6} alkyl groups. More particularly, suitable anionic surfactants include the C_{10}-C_{20} primary, branched-chain, linear-chain and random-chain alkyl sulphates (AS), typically having the following formula:

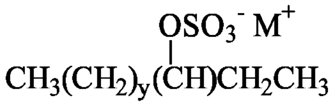
$$CH_3(CH_2)_xCH_2\text{-}OSO_3^- M^+$$

wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations are sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9; C_{10}-C_{18} secondary (2,3) alkyl sulphates, typically having the following formulae:



$$CH_3(CH_2)_x\underset{}{\overset{\overset{OSO_3^- M^+}{|}}{(CH)}}CH_3$$

or



$$CH_3(CH_2)_y\overset{\overset{OSO_3^- M^+}{|}}{(CH)}CH_2CH_3$$

wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations include sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9, y is an integer of at least 8, preferably at least 9; C_{10}-C_{18} alkyl alkoxy carboxylates; mid-chain branched alkyl sulphates as described in more detail in US 6,020,303 and US 6,060,443; modified alkylbenzene sulphonate (MLAS) as described in more detail in WO 99/05243, WO 99/05242, WO 99/05244, WO 99/05082, WO 99/05084, WO 99/05241, WO 99/07656, WO 00/23549, and WO 00/23548 and mixtures thereof.

[0052] Preferred anionic surfactants are C_{8-18} alkyl benzene sulphates and/or C_{8-18} alkyl benzene sulphonates. The alkyl chain of the C_{8-18} alkyl benzene sulphates and/or C_{8-18} alkyl benzene sulphonates may be linear or branched, preferred branched alkyl chains comprise one or more branched moieties that are C_{1-6} alkyl groups.

[0053] Other preferred anionic surfactants are selected from the group consisting of: C_{8-18} alkenyl sulphates, C_{8-18} alkenyl sulphonates, C_{8-18} alkenyl benzene sulphates, C_{8-18} alkenyl benzene sulphonates, C_{8-18} alkyl di-methyl benzene sulphate, C_{8-18} alkyl di-methyl benzene sulphonate, fatty acid ester sulphonates, di-alkyl sulphosuccinates, and combinations thereof. Other useful anionic surfactants herein include the esters of alpha-sulfonated fatty acids, typically containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; 2-acyloxy-alkane-1-sulfonic acid and salts thereof, typically containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to 23 carbon atoms in the alkane moiety; alpha-olefin sulfonates (AOS), typically containing from about 12 to 24 carbon atoms; and beta-alkoxy alkane sulfonates, typically containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety. Also useful are the sulphonation products of fatty acid esters containing an alkyl group typically with from 10 to 20 carbon atoms. Preferred are C_{1-4}, most preferably methyl ester sulphonates. Preferred are C_{16-18} methyl ester sulphonates (MES).

[0054] The anionic surfactants may be present in the salt form. For example, the anionic surfactant(s) may be an alkali metal salt of any of the above. Preferred alkali metals are sodium, potassium and mixtures thereof.

[0055] Preferred anionic detersive surfactants are selected from the group consisting of: linear or branched, substituted or unsubstituted, C_{12-18} alkyl sulphates; linear or branched, substituted or unsubstituted, C_{10-13} alkylbenzene sulphonates, preferably linear C_{10-13} alkylbenzene sulphonates; and mixtures thereof. Highly preferred are linear C_{10-13} alkylbenzene sulphonates. Highly preferred are linear C_{10-13} alkylbenzene sulphonates that are obtainable, preferably obtained, by sulphonating commercially available linear alkyl benzenes (LAB); suitable LAB include low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®.

[0056] It may be preferred for the anionic detersive surfactant to be structurally modified in such a manner as to cause the anionic detersive surfactant to be more calcium tolerant and less likely to precipitate out of the wash liquor in the presence of free calcium ions. This structural modification could be the introduction of a methyl or ethyl moiety in the vicinity of the head group of the anionic detersive surfactant, as this can lead to a more calcium tolerant anionic detersive surfactant due to steric hindrance of the head group, which may reduce the affinity of the anionic detersive surfactant for complexing with free calcium cations in such a manner as to cause precipitation out of solution. Other structural modifications include the introduction of functional moieties, such as an amine moiety, in the alkyl chain of the anionic detersive surfactant; this can lead to a more calcium tolerant anionic detersive surfactant because the presence of a functional group in the alkyl chain of an anionic detersive surfactant may minimise the undesirable physicochemical property of the anionic detersive surfactant to form a smooth crystal structure in the presence of free calcium ions in the wash liquor. This may reduce the tendency of the anionic detersive surfactant to precipitate out of solution.

Alkoxylated anionic surfactants

[0057] The composition may comprise an alkoxylated anionic surfactant. Where present such a surfactant will generally be present in amounts from 0.1 wt% to 40 wt%, generally 0.1 to 10 wt%based on the detergent composition as a whole. It may be preferred for the composition to comprise from 3wt% to 5wt% alkoxylated anionic detersive surfactant, or it may be preferred for the composition to comprise from 1wt% to 3wt% alkoxylated anionic detersive surfactant.

[0058] Preferably, the alkoxylated anionic detersive surfactant is a linear or branched, substituted or unsubstituted C_{12-18} alkyl alkoxylated sulphate having an average degree of alkoxylation of from 1 to 30, preferably from 1 to 10. Preferably, the alkoxylated anionic detersive surfactant is a linear or branched, substituted or unsubstituted C_{12-18} alkyl ethoxylated sulphate having an average degree of ethoxylation of from 1 to 10. Most preferably, the alkoxylated anionic detersive surfactant is a linear unsubstituted C_{12-18} alkyl ethoxylated sulphate having an average degree of ethoxylation of from 3 to 7.

[0059] The alkoxylated anionic detersive surfactant may also increase the non-alkoxylated anionic detersive surfactant activity by making the non-alkoxylated anionic detersive surfactant less likely to precipitate out of solution in the presence of free calcium cations. Preferably, the weight ratio of non-alkoxylated anionic detersive surfactant to alkoxylated anionic detersive surfactant is less than 5:1, or less than 3:1, or less than 1.7:1, or even less than 1.5:1. This ratio gives optimal whiteness maintenance performance combined with a good hardness tolerency profile and a good sudsing profile. However, it may be preferred that the weight ratio of non-alkoxylated anionic detersive surfactant to alkoxylated anionic detersive surfactant is greater than 5:1, or greater than 6:1, or greater than 7:1, or even greater than 10:1. This ratio gives optimal greasy soil cleaning performance combined with a good hardness tolerency profile, and a good sudsing profile.

Suitable alkoxylated anionic detersive surfactants are: Texapan LEST™ by Cognis; Cosmacol AES™ by Sasol; BES151™ by Stephan; Empicol ESC70/U™; and mixtures thereof.

Non-ionic detersive surfactant

[0060] The compositions of the invention may comprise non-ionic surfactant. Where present it is generally present in amounts of from 0.5wt% to 20, more typically 0.5 to 10 wt% based on the total weight of the composition. The composition may comprise from 1wt% to 7wt% or from 2wt% to 4wt% non-ionic detersive surfactant. The inclusion of non-ionic detersive surfactant in the composition helps to provide a good overall cleaning profile, especially when laundering at high temperatures such as 60°C or higher.

[0061] The non-ionic detersive surfactant can be selected from the group consisting of: C_{12}-C_{18} alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C_6-C_{12} alkyl phenol alkoxylates wherein 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; C_{14}-C_{22} mid-chain branched alcohols, BA, as described in more detail in US 6,150,322; C_{14}-C_{22} mid-chain branched alkyl alkoxylates, BAE_x, wherein x = from 1 to 30, as described in more detail in US 6,153,577, US 6,020,303 and US 6,093,856; alkylpolysaccharides as described in more detail in US 4,565,647, specifically alkylpolyglycosides as described in more detail in US 4,483,780 and US 4,483,779; polyhydroxy fatty acid amides as described in more detail in US 5,332,528, WO 92/06162, WO 93/19146, WO 93/19038, and WO 94/09099; ether capped poly(oxyalkylated) alcohol surfactants as described in more detail in US 6,482,994 and WO 01/42408; and mixtures thereof.

[0062] The non-ionic detersive surfactant could be an alkyl polyglucoside and/or an alkyl alkoxylated alcohol. Preferably the non-ionic detersive surfactant is a linear or branched, substituted or unsubstituted C_{8-18} alkyl ethoxylated alcohol having an average degree of ethoxylation of from 1 to 50, more preferably from 3 to 40. Non-ionic surfactants having a degree of ethoxylation from 3 to 9 may be especially useful either. Nonionic surfactants having an HLB value of from 13 to 25, such as C_{8-18} alkyl ethoxylated alcohols having an average degree of ethoxylation from 15 to 50, or even from 20 to 50 may also be preferred non-ionic surfactants in the compositions of the invention. Examples of these latter non-ionic surfactants are Lutensol AO30 and similar materials disclosed in WO04/041982 These may be beneficial as they have good lime soap dispersant properties.

[0063] The non-ionic detersive surfactant not only provides additional soil cleaning performance but may also increase the anionic detersive surfactant activity by making the anionic detersive surfactant less likely to precipitate out of solution in the presence of free calcium cations. Preferably, the weight ratio of non-alkoxylated anionic detersive surfactant to non-ionic detersive surfactant is in the range of less than 8:1, or less than 7:1, or less than 6:1 or less than 5:1, preferably from 1:1 to 5:1, or from 2:1 to 5:1, or even from 3:1 to 4:1.

Cationic detersive surfactant

[0064] In one aspect of the invention, the detergent compositions are free of cationic surfactant. However, the composition optionally may comprise from 0.1wt% to 10 or 5wt% cationic detersive surfactant. When present however, preferably the composition comprises from 0.5wt% to 3wt%, or from 1% to 3wt%, or even from 1wt% to 2wt% cationic detersive surfactant. This is the optimal level of cationic detersive surfactant to provide good cleaning. Suitable cationic detersive surfactants are alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, and alkyl ternary sulphonium compounds. The cationic detersive surfactant can be selected from the group consisting of: alkoxylate quaternary ammonium (AQA) surfactants as described in more detail in US 6,136,769; dimethyl hydroxyethyl quaternary ammonium as described in more detail in US 6,004,922; polyamine cationic surfactants as described in more detail in WO 98/35002, WO 98/35003, WO 98/35004, WO 98/35005, and WO 98/35006; cationic ester surfactants as described in more detail in US 4,228,042, US 4,239,660, US 4,260,529 and US 6,022,844; amino surfactants as described in more detail in US 6,221,825 and WO 00/47708, specifically amido propyldimethyl amine; and mixtures thereof. 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 C_{6-18} alkyl or alkenyl moiety, R^1 and R^2 are independently selected from methyl or ethyl moieties, R^3 is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, preferred anions include halides (such as chloride), sulphate and sulphonate. Preferred cationic detersive surfactants are mono-C_{6-18} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly preferred cationic detersive surfactants are mono-C_{8-10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C_{10-12} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C_{10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride. Cationic surfactants such as Praepagen HY (tradename Clariant) may be useful and may also be useful as a suds booster.

[0065] The cationic detersive surfactant provides additional greasy soil cleaning performance. However, the cationic detersive surfactant may increase the tendency of any non-alkoxylated anionic detersive surfactant to precipitate out of solution. Preferably, the cationic detersive surfactant and any non-alkoxylated anionic detersive surfactant are separated in the detergent composition of the invention, for example if cationic surfactant is present, preferably the cationic a dn any anionic surfactant, particularly non-alkoxylated anionic surfactant will be present in the composition in separate particles. This minimises any effect that any cationic detersive surfactant may have on the undesirable precipitation of the anionic detersive surfactant, and also ensures that upon contact with water, the resultant wash liquor is not cloudy. If cationic surfactant is present, preferably the weight ratio of non-alkoxylated anionic detersive surfactant to cationic detersive surfactant is in the range of from 5:1 to 25:1, more preferably from 5:1 to 20:1 or from 6:1 to 15:1, or from 7:1 to 10:1, or even from 8:1 to 9:1.

[0066] Typically, the detergent composition comprises from 1 to 50 wt% anionic surfactant, more typically from 2 to 40 wt%. Alkyl benzene sulphonates are preferred anionic surfactants.

[0067] Preferred compositions of the present invention comprise at least two different surfactants in combination comprising at least one selected from a first group, the first group comprising alkyl benzene sulphonate and MES surfactant; and at least one selected from a second group, the second group comprising alkoxylated anionic surfactant, MES and alkoxylated non-ionic surfactant and alpha olefin sulfonates (AOS). A particularly preferred combination comprises alkyl benzene sulphonate, preferably LAS in combination with MES. A further particularly preferred combination comprises alkyl benzene sulphonate, preferably LAS with an alkoxylated anionic surfactant, preferably C_{8-18} alkyl alkoxylated sulphate having an average degree of alkoxylation of from 1 to 10. A third particularly preferred combination comprises alkyl benzene sulphonate, preferably LAS in combination with an alkoxylated non-ionic surfactant, preferably C_{8-18} alkyl ethoxylated alcohol having a degree of alkoxylation of from 15 to 50, preferably from 20 to 40.

[0068] The weight ratio of the surfactant from the first group to the weight ratio of the surfactant from the second group is typically 1:5 to 100:1, preferably 1:2 to 100:1 or 1:1 to 50:1 or even to 20:1 or 10:1. The levels of the surfactants are as described above under the specific classes of surfactants. Presence of AE3S and/or MES in the system is preferred on account of their exceptional hardness-tolerance and ability to disperse lime soaps which are formed during the wash by lipase.

[0069] In a further embodiment, the surfactant in the detergent compositions of the invention comprises at least three surfactants, at least one from each of the first and second groups defined above and in addition a third surfactant, preferably also from the first or second groups defined above.

[0070] The detergent compositions of the invention may surprisingly contain relatively low levels of surfactant and yet still perform good cleaning, on account of the soil removal functionality delivered by the lipase, so that the overall level of surfactant may be below 12 wt%, or 10 wt% or 8 wt% based on total weight of the composition

[0071] In a preferred embodiment of the invention, the detergent composition also comprises a suds booster, typically in amounts from 0.01 to 10 wt%, preferably in amounts from 0.02 to 5 wt% based on the total weight of the composition. Suitable suds boosters include fatty acid amides, fatty acid alkalonamides, betaines, sulfobetaines and amine oxides. Particularly preferred materials are cocamidopropyl betaine, cocomonoethanolamide and amine oxide. A suitable amine oxide is Admox 12, supplied by Albemarle.

Lime Soap Dispersants

[0072] Since these lipase enzymes release soil into the wash water, it may be particularly preferred for the detergent compositions of the invention to additionally comprise anti-redeposition polymers such as the polymeric polycarboxylates described below. In addition, or alternatively, cellulose ethers such as carboxymethyl cellulose (CMC) will be useful. A suitable CMC is Tylose CR1500 G2, sold by Clariant. Suitable polymers are also sold by Andercol, Colombia under the Textilan brand name.

[0073] It is especially preferred to include additives with lime soap dispersancy functionality such as the aforementioned MES, AES, highly ethoxylated nonionic surfactant or polymers showing excellent lime soap dispersancy such as Acusol 460N (Rohm & Haas). Lists of suitable lime soap dispersants are given in the following references and documents cited therein.

[0074] WO9407974 (P&G), WO9407984 (P&G), WO9407985 (P&G), WO9504806 (P&G), WO9703379 (P&G), US6770610 (Clariant), EP0324568 (Rohm & Haas), EP0768370 (Rohm & Haas), M.K. Nagarajan and W.F. Masler, Cosmetics and Toiletries, 1989, 104, pp71-73, W. M. Linfield, Tenside Surf. Det, 1990, 27, pp159-161, R.G. Bistline et al, J. Am. Oil Chem. Soc, 1972, 49, pp63-69

[0075] Presence of a soil release polymer has been found to be especially beneficial in further strengthening the stain removal and cleaning benefits of the development, especially on synthetic fibres. Modified cellulose ethers such as methyl hydroxyethyl cellulose (MHEC), for example as sold by Clariant as Tylose MH50 G4 and Tylose MH300 G4, are preferred. Polyester-based Soil Release Polymers are especially preferred as they can also be effective as lime soap dispersants. Examples of suitable materials are Repel-o-Tex PF (supplied by Rhodia), Texcare SRA100 (supplied by Clariant) and Sokalan SR100 (BASF)

[0076] The formulations may contain one or more other enzymes in addition to the first wash lipase, for example protease, amylase, cellulase (especially endoglucanase), pectate lyase and/or mannanase.

[0077] The detergent compositions of the invention may be in any convenient form such as solids such as powdered or granular or tablet solids, bars, or liquids which may be aqueous or on-aqueous, gels or liquigels. Any of these forms may be partially or completely encapsulated. However, the present invention particularly relates to solid detergent compositions, especially granular compositions. Where the detergent compositions of the invention are solid, conventionally, surfactants are incorporated into agglomerates, extrudates or spray dried particles along with solid materials, usually builders, and these may be admixed to produce a fully formulated detergent composition according to the invention. When present in the granular form the detergent compositions of the present invention are preferably those having an overall bulk density of from 350 to 1200 g/l, more preferably 450 to 1000g/l or even 500 to 900g/l. Preferably, the detergent particles of the detergent composition in a granular form have a size average particle size of from 200μm to 2000μm, preferably from 350μm to 600μm.

[0078] Generally the detergent compositions of the invention will comprise a mixture of detergent particles including combinations of agglomerates, spray-dried powders and/or dry added materials such as bleaching agents, enzymes etc.

[0079] In one aspect of the invention the detergent compositions of the invention comprise an anionic surfactant from the list above which is a non-alkoxylated anionic detersive surfactant and this is preferably incorporated into the detergent composition in particulate form, such as via an agglomerate, a spray-dried powder, an extrudate, a bead, a noodle, a needle or a flake. Spray-dried particles are preferred. If via an agglomerate, the agglomerate preferably comprises at least 20%, by weight of the agglomerate, of a non-alkoxylated anionic detersive surfactant, more preferably from 25wt% to 65wt%, by weight of the agglomerate, of a non-alkoxylated anionic detersive surfactant. It may be preferred for part of the non-alkoxylated anionic detersive surfactant to be in the form of a spray-dried powder (e.g. a blown powder), and for part of the non-alkoxylated anionic detersive surfactant to be in the form of a non-spray-dried powder (e.g. an agglomerate, or an extrudate, or a flake such as a linear alkyl benzene sulphonate flake; suitable linear alkyl benzene sulphonate flakes are supplied by Pilot Chemical under the tradename F90®, or by Stepan under the tradename Nacconol 90G®). This is especially preferred when it is desirable to incorporate high levels of non-alkoxylated anionic detersive surfactant in the composition.

[0080] Any alkoxylated anionic detersive surfactant may be incorporated into the detergent compositons of the invention via a spray-dried particle of a non-spray-dried powder such as an extrudate, agglomerate, preferably an agglomerate. Non- spray dried particles are preferred when it is desirable to incorporate high levels of alkoxylated anionic detersive surfactant in the composition

[0081] Any non-ionic detersive surfactant, or at least part thereof, can be incorporated into the composition in the form of a liquid spray-on, wherein the non-ionic detersive surfactant, or at least part thereof, in liquid form (e.g. in the form of a hot-melt) is sprayed onto the remainder of the composition. The non-ionic detersive surfactant, or at least part thereof, may be in included into a particulate for incorporation into the detergent composition of the invention and the non-ionic detersive surfactant, or at least part thereof, may be dry-added to the remainder of the composition. The non-ionic surfactant, or at least part thereof, may be in the form of a co-particulate admixture with a solid carrier material such as carbonate salt, sulphate salt, burkeite, silica or any mixture thereof.

[0082] Any non-ionic detersive surfactant, or at least part thereof, may be in a co-particulate admixture with either an alkoxylated anionic detersive surfactant, a non-alkoxylated anionic detersive surfactant or a cationic detersive surfactant. The non-ionic detersive surfactant, or at least part thereof, may be agglomerated or extruded with either an alkoxylated anionic detersive surfactant, a non-alkoxylated anionic detersive surfactant or a cationic detersive surfactant.

[0083] The cationic detersive surfactant if present may be incorporated into the composition by incorporation in a particulate, such as a spray-dried powder, an agglomerate, an extrudate, a flake, a noodle, a needle, or any combination thereof. Preferably, the cationic detersive surfactant, or at least part thereof, is in the form of a spray-dried powder or an agglomerate.

Optional Detersive Adjuncts

[0084] Optionally, the detergent ingredients can include one or more other detersive adjuncts or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition. Usual detersive adjuncts of detergent compositions include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al. and in Great Britain Patent Application No. 9705617.0, Trinh et al., published September 24, 1997. Such adjuncts are included in detergent compositions at their conventional art-established levels of use, generally from 0 wt% to about 80 wt% of the detergent ingredients, preferably from about 0.5 wt% to about 20wt % and can include color speckles, suds boosters, suds suppressors, anti-tarnish and/or anticorrosion agents, soil-suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, enzymes, enzyme stabilizing agents, solvents, solubilizing agents, chelating agents, clay soil removal/anti-redeposition agents, polymeric dispersing agents, processing aids, fabric softening components, static control agents, bleaching agents, bleaching activators, bleach stabilizers, dye-transfer inhibitors, flocculants, fabric softeners, suds supressors, fabric integrity agents, perfumes, whitening agents, photobleach, alkali metal sulphate salts, sulphamic acid, sodium sulphate and sulphamic acid complexes, etc and combinations thereof. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition or component, and the precise nature of the washing operation for which it is to be used.

[0085] Preferred zwitterionic surfactants comprise one or more quaternized nitrogen atoms and one or more moieties selected from the group consisting of: carbonate, phosphate, sulphate, sulphonate, and combinations thereof. Preferred zwitterionic surfactants are alkyl betaines. Other preferred zwitterionic surfactants are alkyl amine oxides. Catanionic surfactants which are complexes comprising a cationic surfactant and an anionic surfactant may also be included. Typically, the molar ratio of the cationic surfactant to anionic surfactant in the complex is greater than 1:1, so that the complex has a net positive charge.

[0086] The compositions of the invention may comprise bleach boosters. Preferred bleach boosters are selected from the group consisting of: zwitterionic imines, anionic imine polyions, quaternary oxaziridinium salts, and combinations thereof. Highly preferred bleach boosters are selected from the group consisting of aryliminium zwitterions, aryliminium polyions, and combinations thereof. Suitable bleach boosters are described in US360568, US5360569 and US5370826.

[0087] A preferred adjunct component is an anti-redeposition agent. Preferably, the detergent composition comprises one or more anti-redeposition agents. Preferred anti-redeposition agents are cellulosic polymeric components, most preferably carboxymethyl celluloses.

[0088] A preferred adjunct component is a chelant. Preferably, the detergent composition comprises one or more chelants. Preferably, the detergent composition comprises (by weight of the composition) from 0.01 % to 10% chelant, or 0.01 to 5 wt% or 4 wt% or 2 wt%. Preferred chelants are selected from the group consisting of: hydroxyethane-dimethylene-phosphonic acid, ethylene diamine tetra(methylene phosphonic) acid, diethylene triamine pentacetate, ethylene diamine tetraacetate, diethylene triamine penta(methyl phosphonic) acid, ethylene diamine disuccinic acid, and combinations thereof.

[0089] A preferred adjunct component is a dye transfer inhibitor. Preferably, the detergent composition comprises one or more dye transfer inhibitors. Typically, dye transfer inhibitors are polymeric components that trap dye molecules and retain the dye molecules by suspending them in the wash liquor. Preferred dye transfer inhibitors are selected from the group consisting of: polyvinylpyrrolidones, polyvinylpyridine N-oxides, polyvinylpyrrolidone-polyvinylimidazole copolymers, and combinations thereof.

[0090] Preferred adjunct components include other enzymes. Preferably, the detergent composition comprises one or more additional enzymes. Preferred enzymes are selected from then group consisting of: amylases, arabinosidases, carbohydrases, cellulases, chondroitinases, cutinases, dextranases, esterases, β-glucanases, gluco-amylases, hyaluronidases, keratanases, laccases, ligninases, lipoxygenases, malanases, mannanases, oxidases, pectinases, pentosanases, peroxidases, phenoloxidases, phospholipases, proteases, pullulanases, reductases, tannases, transferases, xylanases, xyloglucanases, and combinations thereof. Preferred additional enzymes are selected from the group consisting of: amylases, carbohydrases, cellulases, proteases, and combinations thereof.

[0091] A preferred adjunct component is a fabric integrity agent. Preferably, the detergent composition comprises one or more fabric integrity agents. Typically, fabric integrity agents are polymeric components that deposit on the fabric surface and prevent fabric damage during the laundering process. Preferred fabric integrity agents are hydrophobically modified celluloses. These hydrophobically modified celluloses reduce fabric abrasion, enhance fibre-fibre interactions and reduce dye loss from the fabric. A preferred hydrophobically modified cellulose is described in WO99/14245. Other preferred fabric integrity agents are polymeric components and/or oligomeric components that are obtainable, preferably obtained, by a process comprising the step of condensing imidazole and epichlorhydrin.

[0092] A preferred adjunct component is a salt. Preferably, the detergent composition comprises one or more salts. The salts can act as alkalinity agents, buffers, builders, co-builders, encrustation inhibitors, fillers, pH regulators, stability agents, and combinations thereof. Typically, the detergent composition comprises (by weight of the composition) from 5% to 60% salt. Preferred salts are alkali metal salts of aluminate, carbonate, chloride, bicarbonate, nitrate, phosphate, silicate, sulphate, and combinations thereof. Other preferred salts are alkaline earth metal salts of aluminate, carbonate, chloride, bicarbonate, nitrate, phosphate, silicate, sulphate, and combinations thereof. Especially preferred salts are sodium sulphate, sodium carbonate, sodium bicarbonate, sodium silicate, sodium sulphate, and combinations thereof. Optionally, the alkali metal salts and/or alkaline earth metal salts may be anhydrous.

[0093] A preferred adjunct component is a soil release agent. Preferably, the detergent composition comprises one or more soil release agents. Typically, soil release agents are polymeric compounds that modify the fabric surface and prevent the redeposition of soil on the fabric. Preferred soil release agents are copolymers, preferably block copolymers, comprising one or more terephthalate unit. Preferred soil release agents are copolymers that are synthesised from dimethylterephthalate, 1,2-propyl glycol and methyl capped polyethyleneglycol. Other preferred soil release agents are anionically end capped polyesters.

[0094] It may be desired for the compositions of the invention to comprise at least 0.1wt%, or at least 0.5 wt%, or at least 2 or 3 wt%, or even at least 5 wt% polymeric polycarboxylates up to levels of 30 wt% or 20 wt% or 10 wt%. Preferred polymeric polycarboxylates include polyacrylates and co-polymers of maleic acid and acrylic acid. Suitable polycarboxylates are the Sokalan CP, PA and HP ranges (BASF) such as Sokalan CP5, PA40 and HP22, and the Alcosperse range of polymers (Alco) such as Alcosperse 725, 747, 408, 412 and 420.

[0095] It may also be preferred for the composition to comprise a soil dispersant, for example having the formula:

$$\mathrm{bis}((C_2H_5O)(C_2H_4O)n)(CH_3)\text{-}N^+\text{-}C_xH_{2x}\text{-}N^+\text{-}(CH_3)\text{-}\mathrm{bis}((C_2H_5O)(C_2H_4O)n)$$

wherein, n = from 20 to 30, and x = from 3 to 8. Other suitable soil dispersants are sulphonated or sulphated soil dispersants having the formula:

$$\text{sulphonated or sulphated } \mathrm{bis}((C_2H_5O)(C_2H_4O)n)(CH_3)\text{-}N^+\text{-}C_xH_{2x}\text{-}N^+\text{-}(CH_3)\text{- }\mathrm{bis}((C_2H_5O)(C_2H_4O)n)$$

wherein, n = from 20 to 30, and x = from 3 to 8. Preferably, the composition comprises at least 1wt%, or at least 2wt%, or at least 3wt% soil dispersants.

Softening system

[0096] The detergent compositions of the invention may comprise softening agents for softening through the wash such as clay optionally also with flocculant and enzymes.

[0097] Further more specific description of suitable detergent components can be found in WO97/11151.

Washing Method

[0098] The invention also includes methods of washing textiles comprising contacting textiles with an aqueous solution comprising the detergent composition of the invention. The invention may be particularly beneficial at low water temperatures such as below 30°C or below 25 or 20°C. Typically the aqueous wash liquor will comprise at least 100 ppm, or at least 500ppm of the detergent composition

Examples

[0099] The following are examples of the invention.

Ingredient	A	B	C	D
Sodium linear C_{11-13} alkylbenzene sulfonate	19	14.5	5	6
$R_2N^+(CH_3)_2(C_2H_4OH)$, with $R_2 = C_{12-14}$ alkyl gp	Nil	0.5	Nil	Nil
$R_2N^+(CH_3)_2(C_2H_4OH)$, with $R_2 = C_{8-10}$ alkyl group	0.55	Nil	0.6	0.9
Sodium C_{12}-C_{15} alcohol ether sulfate with average 3 moles of ethylene oxide	1.0	1.0	3.6	Nil
Sodium C_{16-18} methyl ester sulphonate (MES)	Nil	3.0	Nil	3.0
C_{12-18} linear alcohol ethoxylate condensed with an av. of 3-9 moles of EO/ mole of alkyl alcohol	Nil	Nil	Nil	9.2
C_{13-15} alcohol ethoxylate condensed with av. of 30 moles of EO/mole of alkyl alcohol (Lutensol AO30 from BASF)	Nil	Nil	Nil	Nil
Citric acid	Nil	Nil	3.2	2.6
STPP(anhydrous)	9.0	3.0	Nil	Nil
Zeolite A	Nil	3.4	0.5	Nil
Sodium carboxymethyl cellulose	0.6	0.5	0.2	0.7
Sodium polyacrylate polymer with wt av. M. wt. 3000 to 5000	1.0	1.0	Nil	Nil
Copol.of maleic/acrylic	Nil	Nil	10.9	12.0

(continued)

Ingredient	A	B	C	D
acid, with wt av.molecular wt.50,000-90,000, ratio of maleic:acrylic acid from 1:3 to 1:4 (Sokalan CP5 from BASF)				
Lime soap dispersant (Acusol 460N from Rohm & Haas)	Nil	Nil	Nil	Nil
DTPA	0.3	0.3	Nil	Nil
EDDS	Nil	Nil	0.3	0.2
Protease enzyme -enzyme activity of from 15 -70mg/g	0.2	0.2	0.3	0.3
Amylase enzyme -enzyme activity 25 - 50mg/g	0.1	0.1	0.2	0.4
Lipex® from Novozymes-enzyme activity 5-25 mg/g	0.15	0.10	0.2	0.12
Anhydrous sodium perborate monohydrate	4.4	Nil	Nil	Nil
Sodium percarbonate	Nil	4.4	15	15
Magnesium sulfate	0.5	0.5	0.3	0.4
Nonanoyl oxybenzene sulfonate	1.0	1.9	4	3
Tetraacetylethylenediamine	0.28	0.6	1.2	1.0
Brightener	0.16	0.30	0.3	0.5
Sodium carbonate	20.0	17.0	17.0	20.0
Sodium silicate (2.0 R)	12.0	12.0	15.0	12.0
Photobleach	0.0035	0.0035	0.0014	0.0012
Perfume spray-on	0.2	0.2	0.34	0.37
Starch encapsulated perfume	0.2	0.2	0.1	0.2
Suds suppressor granule	0.3	0.2	0.3	0.4
Soap	Nil	Nil	Nil	1.0
Na_2SO_4, misc & moisture	to 100	to 100	to 100	to 100

(i) SEQUENCE CHARACTERISTICS:
(A) LENGTH: 291 amino acids
(B) TYPE: amino acid
(D) TOPOLOGY: linear

(ii) MOLECULE TYPE: protein
(xi) SEQUENCE DESCRIPTION: SEQ ID No: 2:

Met	Arg	Ser	Ser	Leu	Val	Leu	Phe	Phe	Val	Ser	Ala	Trp	Thr	Ala	Leu
-22		-20					-15					-10			
Ala	Ser	Pro	Ile	Arg	Arg	Glu	Val	Ser	Gln	Asp	Leu	Phe	Asn	Gln	Phe
	-5					1				5					10
Asn	Leu	Phe	Ala	Gln	Tyr	Ser	Ala	Ala	Ala	Tyr	Cys	Gly	Lys	Asn	Asn
				15					20					25	
Asp	Ala	Pro	Ala	Gly	Thr	Asn	Ile	Thr	Cys	Thr	Gly	Asn	Ala	Cys	Pro
			30					35					40		
Glu	Val	Glu	Lys	Ala	Asp	Ala	Thr	Phe	Leu	Tyr	Ser	Phe	Glu	Asp	Ser
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Gly	Val	Gly	Asp	Val	Thr	Gly	Phe	Leu	Ala	Leu	Asp	Asn	Thr	Asn	Lys
	60					65					70				
Leu	Ile	Val	Leu	Ser	Phe	Arg	Gly	Ser	Arg	Ser	Ile	Glu	Asn	Trp	Ile
75					80					85					90
Gly	Asn	Leu	Asn	Phe	Asp	Leu	Lys	Glu	Ile	Asn	Asp	Ile	Cys	Ser	Gly
				95					100					105	
Cys	Arg	Gly	His	Asp	Gly	Phe	Thr	Ser	Ser	Trp	Arg	Ser	Val	Ala	Asp
			110					115					120		
Thr	Leu	Arg	Gln	Lys	Val	Glu	Asp	Ala	Val	Arg	Glu	His	Pro	Asp	Tyr
		125					130					135			
Arg	Val	Val	Phe	Thr	Gly	His	Ser	Leu	Gly	Gly	Ala	Leu	Ala	Thr	Val
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Ala	Gly	Ala	Asp	Leu	Arg	Gly	Asn	Gly	Tyr	Asp	Ile	Asp	Val	Phe	Ser
155					160					165					170
Tyr	Gly	Ala	Pro	Arg	Val	Gly	Asn	Arg	Ala	Phe	Ala	Glu	Phe	Leu	Thr
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Val Gln Thr Gly Gly Thr Leu Tyr Arg Ile Thr His Thr Asn Asp Ile
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Val Pro Arg Leu Pro Pro Arg Glu Phe Gly Tyr Ser His Ser Ser Pro
        205                 210                 215

Glu Tyr Trp Ile Lys Ser Gly Thr Leu Val Pro Val Thr Arg Asn Asp
    220                 225                 230

Ile Val Lys Ile Glu Gly Ile Asp Ala Thr Gly Gly Asn Asn Gln Pro
235                 240                 245                 250

Asn Ile Pro Asp Ile Pro Ala His Leu Trp Tyr Phe Gly Leu Ile Gly
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Thr Cys Leu
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SEQUENCE LISTING

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<110>  The Procter & Gamble Company

<120>  Detergent Compositions

<130>  CM2956M

<140>  06110531.8
<141>  2006-02-28

<150>  05251269.6
<151>  2005-03-03

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<170>  PatentIn 3.3

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<212>  PRT
<213>  Humicola lanuginosa

<400>  1

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Ala Ser Pro Ile Arg Arg Glu Val Ser Gln Asp Leu Phe Asn Gln Phe
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Asn Leu Phe Ala Gln Tyr Ser Ala Ala Ala Tyr Cys Gly Lys Asn Asn
        35                  40                  45

Asp Ala Pro Ala Gly Thr Asn Ile Thr Cys Thr Gly Asn Ala Cys Pro
    50                  55                  60

Glu Val Glu Lys Ala Asp Ala Thr Phe Leu Tyr Ser Phc Glu Asp Scr
65                  70                  75                  80

Gly Val Gly Asp Val Thr Gly Phc Leu Ala Leu Asp Asn Thr Asn Lys
                85                  90                  95

Leu Ile Val Leu Ser Phe Arg Gly Ser Arg Ser Ile Glu Asn Trp Ile
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```

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Gly  Asn  Leu  Asn  Phe  Asp  Leu   Lys  Glu  Ile  Asn  Asp  Ile  Cys  Ser  Gly
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Cys  Arg  Gly  His  Asp  Gly  Phe   Thr  Ser  Ser  Trp  Arg  Ser  Val  Ala  Asp
     130                      135                       140

Thr  Leu  Arg  Gln  Lys  Val  Glu   Asp  Ala  Val  Arg  Glu  His  Pro  Asp  Tyr
145                      150                       155                      160

Arg  Val  Val  Phe  Thr  Gly  His   Ser  Leu  Gly  Gly  Ala  Leu  Ala  Thr  Val
                    165                       170                      175

Ala  Gly  Ala  Asp  Leu  Arg  Gly   Asn  Gly  Tyr  Asp  Ile  Asp  Val  Phe  Ser
               180                       185                      190

Tyr  Gly  Ala  Pro  Arg  Val  Gly   Asn  Arg  Ala  Phe  Ala  Glu  Phe  Leu  Thr
          195                       200                      205

Val  Gln  Thr  Gly  Gly  Thr  Leu   Tyr  Arg  Ile  Thr  His  Thr  Asn  Asp  Ile
     210                      215                       220

Val  Pro  Arg  Leu  Pro  Pro  Arg   Glu  Phe  Gly  Tyr  Ser  His  Ser  Ser  Pro
225                      230                       235                      240

Glu  Tyr  Trp  Ile  Lys  Ser  Gly   Thr  Leu  Val  Pro  Val  Thr  Arg  Asn  Asp
                    245                       250                      255

Ile  Val  Lys  Ile  Glu  Gly  Ile   Asp  Ala  Thr  Gly  Gly  Asn  Asn  Gln  Pro
               260                       265                      270

Asn  Ile  Pro  Asp  Ile  Pro  Ala   His  Leu  Trp  Tyr  Phe  Gly  Leu  Ile  Gly
          275                       280                      285

Thr  Cys  Leu
     290
```

Claims

1. A detergent composition comprising a hydrogen peroxide source, a hydrophobic peracid and/or precursor thereof having the formula R-(C=O)-L where R is an alkyl group having from 6 to 14, preferably from 8 to 12 carbon atoms, and L is a leaving group, and a lipase enzyme which is a polypeptide having an amino acid sequence which: (a) has at least 90% identity with the wild-type lipase derived from *Humicola lanuginosa* strain DSM 4109; (b) compared to said wild-type lipase, comprises a substitution of an electrically neutral or negatively charged amino acid at the surface of the three-dimensional structure within 15Å of E1 or Q249 with a positively charged amino acid; and (c) comprises a peptide addition at the C-terminal; and/or (d) comprises a peptide addition at the N-terminal and/or (e) meets the following limitations: i) comprises a negative amino acid in position E210 of said wild-type lipase; ii) comprises a negatively charged amino acid in the region corresponding to positions 90-101 of said wild-type lipase; and iii) comprises a neutral or negative amino acid at a position corresponding to N94 of said wild-type lipase and/or has a negative or neutral net electric charge in the region corresponding to positions 90-101 of said wild-type lipase; the detergent composition having a reserve alkalinity of greater than 6.5, the quantity of available oxygen (from the peroxide source) and peracid and/or precursor thereof being such as to provide the detergent composition with a molar ratio of Available oxygen (from the peroxide source): peracid of from 1:1 to 35:1.

2. A detergent composition according to claim 1 having a reserve alkalinity greater than 8, or greater than 9.

3. A detergent composition according to claim 1 or claim 2 having an available oxygen:peracid ratio of 2:1 to 8:1.

4. A detergent composition according to any preceding claim in which the hydrophobic bleach activator comprises nonanoyloxybenzene sulphonate.

5. A detergent composition according to any preceding claim comprising from 0.1 to 40 wt% alkoxylated alkyl sulphate surfactant and/or from 0.1 to 40 wt% C_{1-4} alkyl ester sulphonate, preferably methyl ester sulphonate (MES), preferably in combination with alkyl benzene sulphonate surfactant in an amount from 5 to 40 wt%.

6. A detergent composition according to any preceding claim comprising a suds booster in an amount from 0.05 to 2

wt%, preferably selected from fatty acid amides, fatty acid alkanolamides, betaines, sulfobetaines and amine oxides or mixtures thereof.

7. A detergent composition according to any preceding claim comprising from 0.05 to 5, preferably from 0.1 to 1 wt% tetra acetyl ethylene diamine (TAED).

8. A detergent composition according to any preceding claim which is a solid detergent composition, preferably granular.

9. A washing process comprising laundering textile articles in an aqueous solution comprising the detergent composition according to any preceding claim.

10. A washing process according to claim 9 in which the aqueous solution is at a temperature below 30°C.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 11 0531

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,Y	US 5 869 438 A (SVENDSEN ET AL) 9 February 1999 (1999-02-09) * column 17, line 57 - column 21, line 55 *	1-10	INV. C11D3/386 C11D3/395 C11D3/39
D,Y	WO 00/60063 A (NOVO NORDISK A/S; VIND, JESPER; SVENDSEN, ALLAN; PATKAR, SHAMKANT, ANA) 12 October 2000 (2000-10-12) * page 2, line 17 - line 21 * * page 9, line 30 - page 10, line 16; claims 1-21 *	1-10	
D,A	WO 99/42566 A (NOVO NORDISK A/S; BORCH, KIM; VIND, JESPER; SVENDSEN, ALLAN; PETERSEN,) 26 August 1999 (1999-08-26) * page 10, line 12 - page 13, line 32 *	1-10	
A	EP 0 258 068 A (NOVO INDUSTRI A/S; NOVO NORDISK A/S) 2 March 1988 (1988-03-02) * claims 1-22 *	1-10	TECHNICAL FIELDS SEARCHED (IPC)
A	EP 0 305 216 A (NOVO INDUSTRI A/S; NOVO NORDISK A/S) 1 March 1989 (1989-03-01) * claims 1-43 *	1-10	C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	22 June 2006	Richards, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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& : member of the same patent family, corresponding document

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The members are as contained in the European Patent Office EDP file on
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22-06-2006

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82