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(54) Liquid detergent composition

(57) The present invention provides an aqueous liquid detergent composition, comprising:

(a) a cleaning effective amount of an enzyme; and
(b) from 0.001 to 0.1% by weight of an anti-oxidant;
said composition being substantially free of boron.

This liquid detergent composition was found to show enhanced stability of the enzyme material contained therein

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Description

Field of the invention

[0001] The present invention relates to detergent compositions containing enzymes, wherein the activity of the enzyme is stabilised against deterioration (e.g. by degradation of the enzyme molecule) during storage. The stabilised liquid enzyme-containing detergent compositions of the invention are particularly useful in methods for removing proteinaceous soils from fabric substrates, so as to clean those substrates.

Background of the invention

[0002] In liquid detergent compositions, especially those for the washing of textile fabrics, it is common to include one or more enzymes for assisting removal of various kinds of soil. Amongst these are proteolytic enzymes, often referred to as "proteases". Proteases are used to assist in the removal of protein-based soil.

[0003] However, the very nature and activity of these enzymes means that they attack any other component in the liquid composition which has a protein-like structure. As a result, they can degrade other enzymes in the liquid, as well as undergo self-degradation. To counteract this, it is usual also to incorporate an enzyme stabilising system. Such stabilising systems commonly consist of a boron compound, e.g. borax, together with a polyol, e.g. glycerol or sorbitol. These components are believed to form an enzyme-inhibiting complex which dissociates by dilution of the composition into the wash liquor, disabling the inhibiting effect so that the protease can act upon the proteinaceous soil.

[0004] Other protease stabilisers such as calcium chloride/calcium format are also known but are not as effective as those systems based on boron. On the other hand, it may be desirable for environmental reasons to reduce the amount of boron in the detergent composition.

[0005] Another type of enzyme stabilising system for use in enzyme-containing liquid detergent compositions is disclosed by US-A-4,238,345. This document discloses that the combination of an antioxidant having a standardised redox potential at least equal to that of ascorbic acid but less than that of sodium hydrosulphite, with hydrophylic polyol is an effective stabilising system for proteolytic enzymes.

[0006] We have now found that it is possible to enhance the stability of enzymes in aqueous liquid detergent compositions by formulating them in a certain way, without the need to employ a boron enzyme stabiliser and preferably also, without the need to employ a non-boron enzyme stabiliser.

Definition of the invention

[0007] Accordingly, in one aspect the present invention provides an aqueous liquid detergent composition, comprising:

a cleaning effective amount of an enzyme; and
from 0 .001 to 0.1% by weight of an anti-oxidant;
said composition being substantially free of boron.

[0008] Furthermore, in a second aspect the invention provides a method of cleaning a fabric substrate, comprising the steps of treating the substrate with a liquid composition of the present invention in an aqueous environment, rinsing the substrate and drying it.

Detailed description of the invention

The liquid detergent composition

[0009] The liquid detergent composition of the invention has been found to show enhanced stability of the enzyme material contained therein. In addition, said liquid detergent composition is environmentally friendly because it is substantially free of any boron-containing compounds. In this connection, "substantially free" is intended to mean that at most 0.05% by weight of boron is present in said liquid detergent composition.

[0010] Preferably, the aqueous liquid detergent composition of the invention has a water content of from 30 to 80% by weight, more preferably from 45 to 80% by weight.

[0011] The liquid detergent composition may generally be either isotropic or structured. Preferably, said liquid composition is isotropic.

Said liquid detergent composition may be formulated as a concentrated liquid for direct application to a substrate, or for application to a substrate following dilution, such as dilution before or during use of the liquid composition by the consumer or in the washing apparatus.

[0012] Preferably, the liquid detergent composition of the invention is used for cleaning a laundry fabric.

Product form

[0013] It should be understood that the liquid compositions according to any aspect of the present invention have a physical form which preferably ranges from a pourable liquid, a pourable gel to a non-pourable gel. These forms are conveniently characterised by the product viscosity. In these definitions, and unless indicated explicitly to the contrary, throughout this specification, all stated viscosity's are those measured at a shear rate of 21 S^{-1} and at a temperature of 25°C.

[0014] Pourable liquid compositions according to any aspect of the present invention preferably have a viscosity of no more than 1,500 mPa.s, more preferably no more than 1,000 mPa.s, still more preferably, no more than 500 mPa.s. Compositions according to any aspect of the present invention which are pourable gels, preferably have a viscosity of at least 1,500 mPa.s but no more than 6,000 mPa.s, more preferably no more than 4,000 mPa.s, still more preferably no more than 3,000 mPa.s and especially no more than 2,000 mPa.s.

[0015] Compositions according to any aspect of the present invention which are non-pourable gels, preferably have a viscosity of at least 6,000 mPa.s but no more than 12,000 mPa.s, more preferably no more than 10,000 mPa.s, still more preferably no more than 8,000 mPa.s and especially no more than 7,000 mPa.s.

[0016] Liquid detergent compositions according to the invention may be suitably contained in water-soluble packages which are preferably made from polyvinyl alcohol (PVOH) film. If so, then the perfume components which are not included in the liquid detergent composition of the invention may be effectively segregated from said composition by including them in the film material of the water soluble package. Alternatively, a water soluble package may be applied wherein the film encloses at least two containers of which the contents are segregated from each other during storage and wherein the perfume components not contained in the liquid detergent composition of the invention are present in a container which is different and segregated from the container holding the composition of the invention.

Physically stable

[0017] For the purpose of this invention a composition is physically stable when less than 2% phase separation occurs after 2 week storage at 37°C. With isotropic liquids this phase separation generally starts with the liquid becoming hazy.

Perfume composition

[0018] The liquid composition of the present invention is either substantially free from perfume or comprises between 0.001 to 3 % by weight, preferably between 0.1 to 2 % by weight, of a perfume composition which does not contain a perfume component selected from the group consisting of saturated and unsaturated linear aldehydes, lilial, cyclal c, vanillin, citral, cinnamic aldehyde, pulegone, terpinolene, gamma terpinene, alpha methylionone.

[0019] It has been found in this connection that the indicated perfume components have a clearly negative effect on the storage stability of any protease, amylase and lipase enzyme present in the liquid detergent composition of the invention.

[0020] Particular examples of (un)saturated linear aldehydes are octanal and tridecylenic aldehyde. These types of linear aldehydes should clearly be excluded from the liquid detergent composition of the invention.

[0021] On the other hand, it has been found that the following perfume components do not -or to a much lesser extent- negatively interact with the indicated types of enzyme:

citronellal, trifernal, precyclemone, hexylcinnamic aldehyde, benzaldehyde, anis aldehyde, vertofix coeur, alpha damascone, iso e super, tetra hydrolinalool,
methyl anthranilate, benzyl acetate, rose oxide, peonile, and
limonene. It is therefore preferred to apply these perfume components in the perfume composition of the present invention.

Enzymes

[0022] "Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry application. Enzymes are included in the liquid detergent composition of the present ivention for a variety of purposes, including removal of protein-based, saccharide-based, or triglyceride-based stains, for the prevention of refugee dye transfer, and for fabric restoration.

[0023] The composition of the invention preferably contains an enzyme selected from the group consisting of a protease, an amylase, a lipase, a cellulase and mixtures thereof. Preferably, said composition contains a protease enzyme and/or

an amylase. Other enzymes which are usually present in liquid detergent compositions, include peroxidases of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermo-stability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

[0024] Enzymes are normally incorporated into detergent compositions at levels sufficient to provide a "cleaning-effective amount".

[0025] The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.001 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.0001% to 10%, preferably from 0.001% to 5%, more preferably 0.005%-1% by weight of a commercial enzyme preparation.

The Proteolytic Enzyme

[0026] Endopeptidases (proteolytic enzymes or proteases) of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins, which can be obtained from particular strains of B. subtilis, B. lentus, B. amyloliquefaciens and B. licheniformis, such as the commercially available subtilisins Savinase™, Alcalase™, Relase™, Kannase™ and Everlase™ as supplied by Novo Industri A/S, Copenhagen, Denmark or Purafect™, PurafectOxP™ and Properase™ as supplied by Genencor International. Chemically or genetically modified variants of these enzymes are included such as described in WO-A-99/02632 pages 12 to 16 and in WO-A-99/20727 and also variants with reduced allergenicity as described in WO-A-99/00489 and WO-A-99/49056.

[0027] It should be understood that the protease is present in the liquid detergent composition of the invention in a dissolved or dispersed form, i.e., the protease is not encapsulated to prevent the protease from the liquid composition. Instead the protease in more or less in direct contact with the liquid composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis. One suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE™ by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE™ and SAVINASE™ from Novo and MAXATASE™ from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, and Protease B as disclosed in EP 303,761 A and EP 130,756 A. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A. Other preferred proteases include those of WO 9510591 A. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583.

[0028] Useful proteases are also described in PCT publications: WO 95/30010, WO 95/30011, WO 95/29979.

[0029] Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those described in EP-A-251446 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in EP-A- 199404, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein, Protease A as disclosed in EP-A-130756.

[0030] The preferred liquid laundry detergent compositions according to the present invention comprise at least 0.001% by weight, of a protease enzyme. However, an effective amount of protease enzyme is sufficient for use in the liquid laundry detergent compositions described herein. The term "an effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.001 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Typically, the proteolytic enzyme content is up to 0.2%, preferably from 4 x 10^{-5}% to 0.06% by weight of the composition of pure enzyme.

Lipolytic enzyme

[0031] As outlined above, the present invention may also provide the use of a lipase enzyme a combination with a liquid detergent composition of the present invention, as specified in claim 1. Said lipase enzyme may be present in the liquid detergent composition of the invention at a level of 10 - 20,000 LU per gram. The lipase enzyme is preferably

selected from the group consisting of Lipolase, Lipolase ultra, LipoPrime, Lipomax, Liposam, and lipase from *Rhizomucor miehei* (e.g. as described in EP-A-238 023 (Novo Nordisk).

[0032] A characteristic feature of lipases is that they exhibit interfacial activation. This means that the enzyme activity is much higher on a substrate which has formed interfaces or micelles, than on fully dissolved substrate. Interface activation is reflected in a sudden increase in lipolytic activity when the substrate concentration is raised above the critical micel concentration (CMC) of the substrate, and interfaces are formed. Experimentally this phenomenon can be observed as a discontinuity in the graph of enzyme activity versus substrate concentration. Contrary to lipases, however, cutinases do not exhibit any substantial interfacial activation.

[0033] Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. LIPOLASE™ enzyme derived from Humicola lanyginosa and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249. Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

[0034] The lipolytic enzyme suitable for use in the present invention can usefully be added to the detergent composition in any suitable form, i.e. the form of a granular composition, a slurry of the enzyme, or with carrier material (e.g. as in EP-A-258 068 and the Savinase (TM) and Lipolase (TM) products of Novozymes). A good way of adding the enzyme to a liquid detergent product is in the form of a slurry containing 0.5 to 50 % by weight of the enzyme in a ethoxylated alcohol nonionic surfactant, such as described in EP-A-450 702 (Unilever).

Amylolytic enzymes

[0035] The present invention may also provide the use of an amylase enzyme in a liquid detergent formulation of the invention. Suitable amylases include those of bacterial or fungal origin. Chemically or genetically modified variants of these enzymes are included as described in WO-A-99/02632 pages 18,19. Commercial cellulase are sold under the tradename Purastar™, Purastar OxAm™ (formerly Purafact Ox Am™) by Genencor; Termamyl™, Fungamyl™, Duramyl™, Natalase™, all available from Novozymes.

[0036] Amylases suitable herein include, for example, alfa-amylases described in GB 1,296,839 to Novo; RAPIDASE™, International Bio-Synthetics, Inc. and TERMAMYL™, Novo. FUNGAMYL™ from Novo is especially useful. See, for example, references disclosed in WO 9402597.

Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the Baccillus amylases, especially the Bacillus cc- amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors.

[0037] Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to WO 9402597, known as TERMAMYL™,

Particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee,

Novo, as DURAMYL™. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo Or WO 9509909 A to Novo.

Other enzymes

[0038] Other optional suitable enzymes that may be included alone or in combination with any other enzyme may, for example, be oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases. 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.

[0039] Examples of the oxidoreductases are oxidases such as glucose oxidase, methanol oxidase, bilirubin oxidase, catechol oxidase, laccase, peroxidases such as ligninase and those described in WO-A-97/31090, monooxygenase, dioxygenase such as lipoxygenase and other oxygenases as described in WO-A-99/02632, WO-A-99/02638, WO-A-99/02639 and the cytochrome based enzymatic bleaching systems described in WO-A-99/02641.

[0040] Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen

peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo- peroxidase.

[0041] A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al.

[0042] A process for enhancing the efficacy of the bleaching action of oxidoreductases is by targeting them to stains by using antibodies or antibody fragments as described in WO-A-98/56885. Antibodies can also be added to control enzyme activity as described in WO-A-98/06812.

[0043] Suitable cellulases include those of bacterial or fungal origin. Chemically or genetically modified variants of these enzymes are included as described in WO-A-99/02632 page 17. Particularly useful cellulases are the endoglucanases such as the EGIII from *Trichoderma longibrachiatum* as described in WO-A-94/21801 and the E5 from *Thermomonospora fusca* as described in WO-A-97/20025. Endoglucanases may consist of a catalytic domain and a cellulose binding domain or a catalytic domain only. Preferred cellulolytic enzymes are sold under the tradename Carezyme™, Celluzyme™ and Endolase™ by Novo Nordisk A/S; Puradax™ is sold by Genencor and KAC™ is sold by Kao corporation, Japan.

[0044] Detergent enzymes are usually incorporated in an amount of 0.00001% to 2%, and more preferably 0.001% to 0.5%, and even more preferably 0.005% to 0.2% in terms of pure enzyme protein by weight of the composition. Detergent enzymes are commonly employed in the form of granules made of crude enzyme alone or in combination with other components in the detergent composition. Granules of crude enzyme are used in such an amount that the pure enzyme is 0.001 to 50 weight percent in the granules. The granules are used in an amount of 0.002 to 20 and preferably 0.1 to 3 weight percent. Granular forms of detergent enzymes are known as Enzoguard™ granules, prills, marumes or T-granules. Other suitable forms of enzymes are liquid forms such as the "L" type liquids from Novo Nordisk, slurries of enzymes in nonionic surfactants such as the "SL" type sold by Novo Nordisk and microencapsulated enzymes marketed by Novo Nordisk under the tradename "LDP" and "CC".

[0045] The enzymes can be added as separate single ingredients (prills, granulates, stabilised liquids, etc. containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates). Enzymes in liquid detergents can be stabilised by various techniques as for example disclosed in US-A-4 261 868 and US-A-4 318 818.

[0046] The detergent compositions of the present invention may additionally comprise one or more biologically active peptides such as swollenin proteins, expansins, bacteriocins and peptides capable of binding to stains.

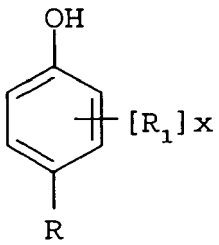
Antioxidant

[0047] The liquid detergent composition of the invention comprises an anti-oxidant in an amount of from 0.001 to 0.1% by weight so as to further increase the storage stability of the liquid composition of the invention. Preferably, the anti-oxidant is present at a concentration in the range of from 0.002 to less than 0.08%, by weight.

[0048] This low concentration range of the antioxidant is most preferred for economical reasons and because the risk of discoloration of the treated fabric is reduced when applying such low antioxidant contents.

Antioxidants are substances as described in Kirk-Othmers (Vol 3, pg 424) and in Uhlmanns Encyclopedia (Vol 3, pg 91).

[0049] One class of antioxidants suitable for use in the present invention is alkylated phenols having the general formula:



wherein R is C1-C22 linear or branched alkyl, preferably methyl or branched C3-C6 alkyl; C3-C6 alkoxy, preferably methoxy; R1 is a C3-C6 branched alkyl, preferably tert-butyl; x is 1 or 2. Hindered phenolic compounds are a preferred type of alkylated phenols having this formula.

A preferred hindered phenolic compound of this type is 2,6-di-tert-butyl-hydroxy-toluene (BHT). Another preferred type of antioxidant is 1,2-benzisothiazoline-3-one (Proxel GXL).

[0050] Other suitable antioxidants are derivatives of α-tocopherol, beta-tocopherol, gamma-tocopherol, delta-tocopherol, 6-hydroxy-2,5,7,8-tetra-methylchroman-2-carboxylic acid (Trolox™).

[0051] Anti-oxidants/radical scavengers such as tocopherol sorbate, other esters of tocopherol, butylated hydroxy benzoic acids and their salts, gallic acid and its alkyl esters, especially propyl gallate, uric acid and its salts and alkyl esters, sorbic acid and its salts, the ascorbyl esters of fatty acids, amines (e.g. N,N-diethylhydroxylamine, amino-guanidine, amine alcohols), sulfhydryl compounds (e.g., glutathione), and dihydroxy fumaric acid and its salts may also be used.

[0052] Non-limiting examples of anti-oxidants suitable for use in the present invention include phenols, inter alia 2,6-di-tertbutylphenol, 2,6-di-tert-butyl-4-methylphenol, mixtures of 2 and 3- tert-butyl-4-methoxyphenol, and other ingredients including include propyl gallate, tert- butylhydroquinone, benzoic acid derivatives such as methoxy benzoic acid, methylbenzoic acid, dichloro benzoic acid, dimethyl benzoic acid, 5-hydroxy-2,2,4,6,7- pentamethyl-2,3-dihydro-1-benzofuran-3-one, 5-hydroxy-3-methylene-2,2,4,6,7-pentamethyl-2,3-dihydro-benzofuran, 5-benzyloxy-3-hydroxymethyl-2,2,4,6,7-pentamethyl-2,3-dihydro-1-benzofuran, 3-hydroxymethyl-5-methoxy-2,2,4,6,7-pentamethyl-2,3-dihydro-1-benzofuran, vitamin C(ascorbic acid), and Ethoxyquine (1,2-dihydro-6-ethoxy-2,2,4-trimethylchinolin)marketed under the name Raluquin™ by the company Raschig™.

[0053] Highly preferred antioxidants for use herein include 2,6-di-tert-butyl hydroxy toluene (BHT), α-tocopherol, ethoxyquine, 2,2,4-trimethyl-1,2-dihydroquinoline, 2,6-di-tert-butyl hydroquinone, tert-butyl-hydroxy anisole, lignosulphonic acid, 6-hydroxy-2,5,7,8-tetra-methylchroman-2-carboxylic acid (Trolox™), 1,2-benzisothiazoline-3-one (Proxel GXL) and salts thereof, and mixtures thereof. The most preferred types of antioxidant for use in the present invention are 2,6-di-tert-butyl hydroxy toluene (BHT, alpha-tocopherol, 1,2-benzisothiazoline-3-one (Proxel GXL) and mixtures thereof.

Fatty acid soap

[0054] In order to further increase the storage stability of the liquid detergent composition of the invention, said composition preferably comprises a fatty acid soap of increased saturation. The extent of saturation of the fatty acid is expressed in terms of iodine value: the lower the iodine value, the higher the degree of saturation. Desirably, the fatty acid soap has a iodine value lower than 1.0, more preferably lower than 0.3.

[0055] In this connection, the iodine value of the fatty acid soap is defined as the weight of halogens expressed as iodine absorbed by 100 parts by weight of fatty acid soap. It follows that a lower iodine value will be measured if the level of saturation of the fatty acid soap will be higher.

The iodine value is determined by the Wijs' method described by IFFO (ISO 3961:1996, May 1998) in which the test sample is dissolved in a solvent and Wijs' reagent added. After about one hour reaction time, potassium iodide and water are added to the mixture. Iodine liberated by the process is titrated with sodium thiosulphate solution.

[0056] Preferably, the fatty acid soap has a degree of saturation of more than 95%, said degree of saturation being most preferably 100%.

Reason is that such saturated fatty acid soaps have been found to perform favourably for improving storage stability of the enzyme present in the liquid detergent composition of the invention.

[0057] Good results with respect to this storage stability were obtained when the fatty acid contained in the soap is a mixture of lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, and behenic acid.

[0058] It will be recognised that the fatty acid soaps optionally used in the composition of the invention, consist of a fatty acid and a cation. Suitable cations include, sodium, potassium, ammonium, monoethanol ammonium diethanol ammonium, triethanol ammonium, tetraalkyl ammonium, e.g., tetra methyl ammonium up to tetradecyl ammonium etc. cations.

Preferably, the level of the fatty acid soap in the liquid composition of the invention is at most 8%, more preferably at most 4% by weight, most preferably at most 2% by weight based on the full liquid composition of the invention.

Surfactant

[0059] The liquid composition of the invention may comprise from 1 to 90%, preferably from 10 to 70% by weight of a surfactant, preferably selected from anionic, nonionic, cationic, zwitterionic active detergent materials or mixtures thereof. Preferably, the compositions herein comprise 12 to 60% by weight of surfactant, more preferably 15 to 40% by weight.

[0060] The compositions of the invention are preferably substantially free of aklylbenzene sulphonate surfactant,but may contain small amounts of eg. C_{11}- C_{18} alkylbenzene sulphonates, eg up to 5% by weight or up to 1% by weight.

[0061] Non-limiting examples of surfactants useful herein typically at levels from about 10 % to about 70%, by weight, include the C_{10}-C_{18} secondary (2,3) alkyl sulphates of the formula $CH_3(CH_2)_x(CHOSO_3\text{-}M+)CH_3$ and $CH_3(CH_2)_y(CHOS0_3\text{-}M+)CH_2CH_3$ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilising cation, especially sodium, unsaturated sulphates such as oleyl sulphate, C_{10}-C_{18} alkyl alkoxy carboxylates (especially the EO 1-7 ethoxycarboxylates), the C_{10}-C_{18} glycerol ethers, the C_{10}-C_{18} alkyl polyglycosides and their corresponding sulphated polyglycosides, and C_{12}-C_{18} alpha-sulphonated fatty acid esters. If desired, the conventional

nonionic and amphoteric surfactants such as the C_{12}-C_{18} alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C_6-C_{12} alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C_{12}-C_{18} betaines and sulphobetaines ("sultaines"), C_{10}-C_{18} amine oxides, and the like, can also be included in the overall compositions. The C_{10}-C_{18} N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C_{12}-C_{18} N-methylglucamides. See WO-92/06,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C_{10}-C_{18} N-(3 - methoxypropyl) glucamide. C_{10}-C_{20} conventional soaps may also be used. If high sudsing is desired, the branched-chain C_{10}-C_{16} soaps may be used.

[0062] Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

[0063] Other anionic surfactants useful for detersive purposes can also be included in the liquid compositions hereof. These can include C_8-C_{22} primary or secondary alkanesulphonates, C_8-C_{24} olefinsulphonates, sulphonated polycarboxylic acids, alkyl glycerol sulphonates, fatty acyl glycerol sulphonates, fatty oleyl glycerol sulphates, alkyl phenol ethylene oxide ether sulphates, paraffin sulphonates, alkyl phosphates, isothionates such as the acyl isothionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinamates and sulphosuccinates, monoesters of sulphosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulphosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates, sulphates of alkylpolysaccharides such as the sulphates of alkylpolyglucoside, branched primary alkyl sulphates, alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO\text{-}M+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt- forming cation, and fatty acids esterified with isethionic acid and neutralised with sodium hydroxide. Further examples are given in Surface Active Agents and Detergents (Vol. I and II by Schwartz, Perry and Berch).

[0064] Alkyl alkoxylated sulphate surfactants are another category of preferred anionic surfactant. These surfactants; are water soluble salts or acids typically of the formula $RO(A)mSO_3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is hydrogen or a water soluble cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulphates as well as alkyl propoxylated sulphates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines, e.g., monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulphate, C_{12}- C_{18} alkyl polyethoxylate (2.25) sulphate, C_{12}-C_{18} alkyl polyethoxylate (3.0) sulphate, and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulphate wherein M is conveniently selected from sodium and potassium.

[0065] The liquid detergent compositions of the present invention preferably comprise at least about 5%, preferably at least 10%, more preferably at least 12% and less than 70%, more preferably less than 60% by weight, of an anionic surfactant.

Preferred nonionic surfactants such as C12-C18 alkyl ethoxylates ("AE") including the so- called narrow peaked alkyl ethoxylates and C_6-C_{12} alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), block alkylene oxide condensate of C_6 to C_{12} alkyl phenols, alkylene oxide condensates ofC_8-C_{22} alkanols and ethylene oxide/propylene oxide block polymers (Pluronic™-BASF Corp.), as well as semi polar nonionics (e.g., amine oxides and phosphine oxides) can be used in the present liquid compositions. An extensive disclosure of these types of surfactants is found in U.S. Patent 3,929,678.

[0066] Alkylpolysaccharides such as disclosed in U.S. Patent 4,565,647 are also preferred nonionic surfactants in the liquid compositions of the invention.

Further preferred nonionic surfactants are the polyhydroxy fatty acid amides.

A particularly desirable surfactant of this type for use in the liquid compositions herein is alkyl-N-methyl glucamide.

[0067] Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C_{10}-C_{18} N-(3-methoxypropyl) glucamide. The N-propyl through N- hexyl C_{12}-C_{18} glucamides can be used for low sudsing. C_{10}-C_{20} conventional soaps may also be used. If high sudsing is desired, the branched-chain C_{10}-C_{16} soaps may be used.

[0068] The liquid detergent compositions of the present invention preferably comprise at least about 5%, preferably at least 10%, more preferably at least 12% and less than 70%, more preferably less than 60% by weight, of a nonionic surfactant.

Carriers

[0069] Liquid detergent compositions of the invention may contain various solvents as carriers.

Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Other suitable carrier materials are glycols, such as mono-, di-, tri-propylene glycol, glycerol and polyethylene glycols (PEG) having a molecular weight of from 200 to 5000.

The compositions may contain from 1% to 50%, typically 5% to 30%, preferably from 2% to 10%, by weight of such carriers.

Detergency builders

[0070] One or more detergency builders may be suitably present in the liquid detergent composition of the invention.

[0071] Examples of suitable organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates, carboxymethyloxysuccinates, carboxymethyloxymalonates, ethylene diamine-N,N-disuccinic acid salts, polyepoxysuccinates, oxydiacetates, triethylene tetramine hexa-acetic acid salts, N-alkyl imino diacetates or dipropionates, alpha sulpho- fatty acid salts, dipicolinic acid salts, oxidised polysaccharides, polyhydroxysulphonates and mixtures thereof.

[0072] Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamino-tetraacetic acid, nitrilo-triacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid, tartrate mono succinate and tartrate di succinate.

Other optional ingredients

[0073] The compositions herein can further comprise a variety of optional ingredients. A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, hydrotropes, processing aids, dyes or pigments, solid fillers for bar compositions, etc.

[0074] If high sudsing is desired, suds boosters such as the C_{10}-C_{16} alkanolamides can be incorporated into the compositions, typically at 1%- 10% levels. The C_{10}-C_{14} monoethanol and diethanol amides illustrate a typical class of such suds boosters. If desired, soluble magnesium salts such as $MgCl_2$, $MgS0_4$, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Chelating Agents

[0075] The liquid detergent compositions herein may also optionally contain one or more iron, copper and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally- substituted aromatic chelating agents and mixtures therein, all as hereinafter defined.

[0076] If utilised, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilised the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

[0077] Suitable types of phosphonates for use as chelating agents in the composition of the invention are ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate.

Suitable examples of carboxylates for use as chelating agents are ethylene diamine disuccinate (EDDS), ethylene diamine tetraacetate (EDTA), diethylene triamine pentaacetic acid (DTPA), and imino disuccinic acid (IDS).

Clay Soil Removal/Anti-redeposition Agents

[0078] The compositions of the present invention can also optionally contain water- soluble ethoxylated amines having clay soil removal and antiredeposition properties.

Liquid detergent compositions typically contain 0.0 1% to 5% of these agents.

[0079] One preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, Other types of preferred antiredeposition agent include the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Brightener

[0080] Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the liquid detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, cournarin, carboxylic acid, methinecyanines, dibenzothiphene-5,5-dioxide, azoles, 5-and 6-membered- ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Suds Suppressors

[0081] Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

[0082] A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430- 447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

[0083] The detergent compositions herein may also contain non-surfactant suds suppressors. These include; for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C 1 8-C40 ketones (e.g., stearone), etc.

Fabric Softeners

[0084] Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647 as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416 and U.S. Patent 4,291,071.

Dye Transfer Inhibiting Agents

[0085] The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N- vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

Bleaches

[0086] The liquid detergent composition of the present invention may also comprise bleaching material.

[0087] Particularly preferred bleaching ingredients are those capable of yielding hydrogen peroxide in aqueous solution, the so-called peroxyl species. Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide and PAP (N,N-phthaloylaminoperoxy caproic acid), and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Mixtures of two or more such compounds may also be suitable.

[0088] Particularly preferred types of H_2O_2-sources are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons. The amount thereof in the composition of the invention usually will be within the range of about 1-35% by weight, preferably from 5-25% by weight. One skilled in the art will appreciate that these amounts may be reduced in the presence of a bleach precursor e.g., N,N,N'N'-tetraacetyl ethylene diamine (TAED), SNOBS (sodium nonanoyloxybenzene sulfonate) and NACOBS ((6-nonamidocaproyl) oxybenzene sulfonate). When used, the bleach precursors generate peroxyacids after reaction with hydrogen peroxide. Alternatively, peracids, as such, for instance PAP (N,N-phthaloylaminoperoxy caproic acid), may be employed. Cationic nitriles may also be used to activate peroxyl species.

[0089] Alternatively or in addition to, a transition metal catalyst may be used with the peroxyl species, see, for example WO-02/48301. A transition metal catalyst may also be used in the absence of peroxyl species where the bleaching is termed to be via atmospheric oxygen, see, for example WO-00/52124 and WO-02/48301. The transition metal catalysts disclosed in WO-00/52124 and WO-02/48301 are generally both applicable to what is known in the art as "air mode" and "peroxyl mode" bleaching. Another example of a suitable class of transition metal catalysts is found in WO-02/48301 and references found therein. The transition metal catalysts have also been found to enhance enzyme stability.

[0090] If a peroxygen bleach is present in the composition the presence of a transition metal chelating agent is preferred to stabilise the peroxygen bleach.

Photobleaches, including singlet oxygen photobleaches, may also be used in the liquid detergent composition of the invention.

[0091] When the composition is in the form of a liquid, segregation of various components may be necessary and these will be evident to one skilled in the art. One form of segregation that is preferred is that of coacevation. The use of pH-Jump compositions and antioxidants are also applicable to preserving the integrity of certain components within the composition.

[0092] Since many bleaches and bleach systems are unstable in aqueous liquid detergents and/or interact unfavourably with other components in the composition, e.g. enzymes, they may for example be protected, e.g. by encapsulation or by formulating a structured liquid composition, whereby they are suspended in solid form.

Another suitable form of segregation is that of coacervation. The use of a pH-jump system may also be desirable for preserving the integrity of certain components within the liquid composition of the invention.

[0093] The invention will now be illustrated by way of the following non-limiting examples, in which all parts and percentages are by weight unless otherwise indicated.

Example 1

[0094] The following liquid detergent formulations were prepared:

Example no.	1A	1B
Ingredient	(%wt)	(%wt)
sLES (3EO)	9	9
NI 9EO	9	9
Perfume A	0.4	0.4
Tinopal BMX	0.02	0.02
Stainzyme 12L	0.1	0.1
Relase 16.0 L EXI	0.4	0.4
Proxel GXL	0.016	0.016
Prifac 7908	1.75	-
Prifac 5908	-	1.75
Water	balance to 100%	

wherein:

sLES (3EO)= sodium lauryl ether sulphate (with on average 3 ethylene oxide groups).

NI 9 EO = C_{12}-C_{13} fatty alcohol ethoxylated with an average of 9 ethylene oxide groups.

Perfume A= 'Nicola' (ex Firminich): a perfume composition of which roughly 20% consists of components selected from saturated and unsaturated linear aldehydes, lilial, cyclal c, vanillin, citral, cinnamic aldehyde, pulegone, terpinolene, gamma terpinene, and alpha methylionone.

Tinopal CB5 = biphenyl disteryl derivate ex Ciba

Stainzyme 12L= amylase enzyme (ex Novozymes)

Relase 16.0 L EXI = protease enzyme (ex Novozymes)

Proxel GXL = anti-oxidant (20% 1,2-benzisothiazoline-3-one) Prifac 5908 and Prifac 7908 = saturated and unsaturated types of palm kernel fatty acid, having a iodine value of < 1 respectively 16-21

The above liquid detergent formulations had a pH-value of 8.5. In addition, a similar liquid detergent formulation was prepared the only difference with the above formulations being that the pal kernel fatty acid (I.e. Prifac 7908 respectively Prifac 5908) was replaced by water.

[0095] In this example, the residual activity of the protease enzyme in all above-mentioned liquid detergent formulations after 4 weeks of storage at 37°C was determined.

For this determination, the protease enzyme activity was measured at 40°C in a TRIS pH 9 buffer and using tetrapeptide as substrate.

More particularly, the following protocol was used:

Samples of 70 mg of the tested liquid formulation were diluted in 10 ml MilliQ water. 10 μl of this solution was added to an assay of 205 μl containing 74.4 mMol TRIS pH 9 and 0.494 mMol tetrapeptide (succinyl-Ala-Ala-Pro-Phe-p-Nitroanilide).

The absorbance of the tested samples at a wavelength of 450 nm was measured for 15 minutes at 40°C using a spectrometer.

The absolute changes in absorbance as compared to the absorbance measured on the freshly prepared calibration

sample were correlated to the measured activity of such freshly prepared sample. The measured protease enzyme activity is expressed as GU/ml.
The residual enzyme activity (expressed as %) is the enzyme activity after 4 weeks of storage (at 37°C) of the liquid detergent formulation concerned divided by the enzyme activity of that formulation at t=0.
Table 1 shows the residual enzyme activities in the various liquid compositions as described above.

Table 1

soap type	
no soap	34
Prifac 7908	24
Prifac 5908	30

When considering these results, it can be clearly noticed that the residual enzyme activity in the formulations containing the saturated fatty acid Prifac 5908 is significantly higher than in the formulations containing the unsaturated fatty acid Prifac 7908.

Example 2

[0096] The following liquid detergent formulations were prepared:

Example no.	2A	2B
Ingredient	(%wt)	(%wt)
LAS acid	6	6
sLES (3EO)	6	6
NI 9EO	6	6
Bleach catalyst	0.03	0.03
Relase 16.0 L EXI	0.4	0.4
$CaCl_2.2H_2O$	-	0.4
Water	balance to 100%	

Wherein
LAS acid = C10-C14 alkyl benzene sulphonic acid.
Bleach catalyst = 3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate) iron (II)-chloride hydrate.
[0097] More information about the bleach catalyst in these formulations can be found in WO-02/48301. It is also noted that these composition have a pH-value of 7 and that the calcium chloride present therein acts as an enzyme stabilizer.
[0098] Furthermore, three liquid detergent formulations similar to the above formulation of example 2A and three liquid detergent formulation similar to the above formulation of example 2B were also prepared, the only difference with the above formulations being that 0.016% Proxel GXL, respectively 0.008% 2,6-di-tert-butyl hydroxy toluene (BHT), respectively both Proxel GXL and BHT were added,
[0099] The residual activity of the protease enzyme in all above-mentioned liquid detergent formulations after 4 weeks of storage at 37°C was determined using the protocol described in example 1.
Table 2 shows the residual enzyme activities in these various liquid compositions.

Table 2

Added material	liquid 2A	liquid 2B
0% BHT and 0% Proxel GXL	1	5
0% BHT and 0.016% Proxel GXL	1	20
0.008% BHT and 0% Proxel GXL	1	4
0.008% BHT and 0.016% Proxel GXL	9	46

[0100] It can be derived from these results that the calcium chloride present in the liquid 2B has a considerable effect on the residual enzyme activity: when this type of enzyme stabilizer is present, the residual activity is much higher than when it I not contained in the liquid.

Smaller improvements in residual enzyme activity are obtained after adding the anti-oxidants Proxel GXL and BHT.

Example 3

[0101] The following liquid detergent formulations were prepared:

Example no.	3A	3B	3C
Ingredient	%wt	%wt	%wt
LAS acid	6	6	6
sLES (3EO)	6	6	6
NI 9EO	6	6	6
Relase 16.0 L EXI	0.4	0.4	0.4
Proxel GXL	0.016	0.016	0.016
Perfume A	-	0.4	-
Perfume B	-	-	0.4
Water	balance to 100%		

wherein perfume B = a perfume composition which does not contain perfume components selected from the group consisting of saturated and unsaturated linear aldehydes, lilial, cyclal c, vanillin, citral, cinnamic aldehyde, pulegone, terpinolene, gamma terpinene, alpha methylionone.

[0102] The above liquid detergent formulations had a pH-value of 7. Furthermore, three liquid detergent formulations similar to the above three formulations were also prepared, the only difference with the above formulations being that 1% Prifac 7908 was added.

[0103] The residual activity of the protease enzyme in all these liquid detergent formulations after 4 weeks of storage at 37°C was determined using the protocol described in example 1.

Table 3 shows the residual enzyme activities in these various liquid compositions.

Table 3

Soap	Liquid 3A	Liquid 3B	Liquid 3C
No soap	92	76	94
1% Prifac 7908	84	11	86

When comparing the results for liquid 3A and 3B, it can be derived that the residual enzyme activity is reduced by adding a 'full' perfume composition (perfume A).

When comparing the results for liquids 3B and 3C, it can be noticed that the residual activiity can be restored by applying a perfume which does not contain various perfume components (perfume B).

Example 4

[0104] The following liquid detergent compositions were prepared:

Example no.	4A	4B
Ingredient	%wt	%wt
LAS acid	6	6
sLES (3EO)	6	6
NI (9EO)	6	6
Relase 16.0 L EXI	0.4	0.4
Stainzyme	0.1	0.1
Proxel GXL	0.016	0.016
BHT	-	0.008
Bleach catalyst	0.03	0.03
Perfume A	0.4	0.4
Water	balance to 100%	

[0105] The above liquid detergent formulations had a pH-value of 7 Furthermore, two liquid detergent formulations similar to the above formulation of example 4A and two liquid detergent formulations similar to the above formulation of example 4B were prepared, the only difference with the above formulation being 0% respectively 0.2% of perfume A were used.

[0106] The residual activity of the stainzyme (amylase) enzyme in all these liquid detergent formulations after 4 weeks of storage at 37°C was determined using a method based on the amylolytic action of α-amylases on 4,6-ethylidene-p-nitrophenyl-a,D-maltoheptaoside (ethylidene-G7PNP). The ethylidene-G7PNP reacts with the α-amylase to G2PNP+G3PNP+G4PNP. Subsequently, the G2PNP+G3PNP+G4PNP react with α-glucosidase to glucose and the yellow p-nitrophenol (PNP). This reaction is followed in situ and the change in absorbance at 405 nm per time unit is measured. The amylolytic activity is automatically calculated by referring to a calibration curve of the corresponding reference standard.
The residual stainzyme enzyme activity (expressed as %) is the stainzyme activity after 4 weeks of storage (at 37°C) of the liquid detergent formulation concerned divided by the stainzyme activity of that formulation at t=0.
Table 4 shows the residual stainzyme activities in these various liquid compositions.

Table 4

Perfume A (in %)	Liquid 4A	Liquid 4B
0	71	91
0.2	40	90
0.4	30	85

[0107] When considering these results, it can be derived that the residual stainzyme activity is significantly increased by the presence of BHT. Furthermore, it can be noticed that this residual activity is reduced when the level of perfume A is increased. However, the extent of said reduction is much smaller when BHT is present.

Claims

1. An aqueous liquid detergent composition, comprising:

   (a) a cleaning effective amount of an enzyme; and
   (b) from 0.001 to 0.1% by weight of an anti-oxidant; said composition being substantially free of boron.

2. A composition according to claim 1, comprising from 0.002 to less then 0.08% by weight of the anti-oxidant.

3. A liquid composition according to any preceding claim, wherein the composition further comprises a fatty acid soap having an iodine value lower than 1.0, preferably lower than 0.3.

4. A composition according to any preceding claim, being substantially free of alkyl benzene sulphonate surfactant.

5. A composition according to any preceding claim, being substantially free of perfume or else containing from 0.001 to 3% by weight of a perfume composition, the perfume composition not containing a perfume component selected from the group consisting of saturated and unsaturated linear aldehydes, lilial, cyclal c, vanillin, citral, cinnamic aldehyde, pulegone, terpinolene, gamma terpinene, alpha methylionone.

6. A composition according to any preceding claim, further comprising a bleach catalyst.

7. A liquid detergent composition according to any preceding claim, wherein the enzyme is selected from the group consisting of a proteolytic enzyme, an amylolytic enzyme, a lipolytic enzyme, a cellulolytic enzyme and mixtures thereof.

8. A liquid composition according to any preceding claim, wherein the antioxidant is selected from the group consisting of 2,6-di-tert-butyl-hydroxy-toluene (BHT), alpha-tocopherol, ethoxyquine, 2,2,4-trimethyl-1,2-dihydroquinoline, 2,6-di-tert-butyl-hydroquinone, 2-tert-butyl-hydroquinone, tert-butyl-hydroxy anisole, lignosulphonic acid, 6-hydroxy-2,5,7,8-tetra-methylchroman-2-carboxylic acid (Trolox™), 1,2-benzisothiazoline-3-one and salts thereof, and mixtures thereof.

9. A liquid composition according to claim 8, wherein the antioxidant is selected from 2,6-di-tert-butyl-hydroxy-toluene (BHT), alpha-tocopherol, 1,2-benzisothiazoline-3-one (Proxel GXL) and mixtures thereof.

10. A liquid composition according to any preceding claim, wherein the composition comprises water in an amount of from 30 to 80% by weight.

11. A method of cleaning a fabric substrate, comprising the steps of treating the substrate with a liquid composition as defined in any preceding claim in an aqueous environment, rinsing the substrate and drying it.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 07 5593

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 95/29980 A (THE PROCTER & GAMBLE COMPANY) 9 November 1995 (1995-11-09) * page 1, line 25 - page 2, line 13; claims; examples 3-6 * * page 18, line 12 - page 19, line 12 *	1-11	C11D3/386 C11D10/04 C11D3/50
X	WO 00/36062 A (UNILEVER N.V; UNILEVER PLC; HINDUSTAN LEVER LTD) 22 June 2000 (2000-06-22) * page 2, line 20 - page 4, line 12; claims *	1-11	
X	GB 2 021 142 A (ECONOMICS LABORATORY INC) 28 November 1979 (1979-11-28) * page 6, line 44 - line 53; claims; examples *	1-11	
X	WO 98/16607 A (UNILEVER N.V; UNILEVER PLC) 23 April 1998 (1998-04-23) * examples 5,6 *	1,2,5, 7-11	
X	US 2002/082181 A1 (HUMPHREY VICKIE L ET AL) 27 June 2002 (2002-06-27) * claims 1,5; examples *	1,2,4,5, 7-9,11	TECHNICAL FIELDS SEARCHED (IPC) C11D
E	WO 2005/059077 A (UNILEVER N.V; UNILEVER PLC; HINDUSTAN LEVER LIMITED; OUWENDIJK-VRIJENH) 30 June 2005 (2005-06-30) * page 6, line 1 - page 8, line 2; claims *	1,2,4, 7-9,11	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	16 December 2005	Hillebrecht, D

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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EUROPEAN SEARCH REPORT

Application Number
EP 05 07 5593

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
E	WO 2005/080540 A (NOVOZYMES A/S) 1 September 2005 (2005-09-01) * page 6, line 13 - page 7, line 12; claims; examples * -----	1,7,11	

TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	16 December 2005	Hillebrecht, D

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