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(54) Benævnelse: **VASKE- OG RENGØRINGSMIDLER MED EN KOMBINATION AF AMYLASE OG PROTEASE**

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WASHING AND CLEANING AGENTS COMPRISING A COMBINATION OF AMYLASE AND PROTEASE

[0002] The invention relates to a washing and cleaning agent, comprising an enzyme combination of an amylase and a protease, the amino acid sequences of which were modified in particular with respect to the use in washing and cleaning agents, and all sufficiently similar amylases and proteases having a corresponding modification. The invention also relates to methods and uses of these washing and cleaning agents.

[0003] Proteases are some of the technically most important enzymes. They are the enzymes that have been established the longest for washing and cleaning agents, and can be found in practically all modern, powerful washing and cleaning agents. They bring about the decomposition of protein-containing stains on the item to be cleaned. Of these, in turn, proteases of the subtilisin type (subtilases, subtilopeptidases, EC 3.4.21.62) are particularly important, and are serine proteases due to the catalytically active amino acids. They act as non-specific endopeptidases and hydrolyze any acid amide bonds inside peptides or proteins. Their optimum pH is usually in the distinctly alkaline range. An overview of this family can be found, for example, in the article "Subtilases: Subtilisin-like Proteases" by R. Siezen, and pages 75-95 in "Subtilisin enzymes," published by R. Bott and C. Betzel, New York, 1996. Subtilases are formed naturally from microorganisms. Among these, the subtilisins formed and secreted by the Bacillus species in particular are the most significant group of subtilases.

[0004] Examples of subtilisin-type proteases preferably used in washing and cleaning agents are the subtilisins BPN' and Carlsberg, the protease PB92, the subtilisins 147 and 309, the protease from Bacillus lentus and in particular from Bacillus lentus DSM 5483, subtilisin DY and the thermitase enzymes, proteinase K, and the proteases TW3 and TW7, which can be classified as subtilases but not as subtilisins in the narrower sense, and variants of the aforementioned proteases which have a modified amino acid sequence compared to the starting protease. Proteases are modified deliberately or randomly using methods known from the prior art and thus optimized for use in washing and cleaning agents, for example. These methods include point mutagenesis, deletion or insertion mutagenesis, or fusion with other proteins or protein fragments. Appropriately optimized variants are therefore known for the majority of proteases known from the prior art.

[0005] Other enzymes that can be used in washing and cleaning agents are amylases. Synonymous terms can be used for amylases, such as 1,4-alpha-D-glucan-glucanohydrolase or glycogenase. The α-amylases are preferred amylases according to the invention.

[0006] The decisive factor as to whether an enzyme is an α-amylase within the meaning of the invention is its ability to hydrolyze α-(1-4)-glycosidic linkages in the amylose of starch. Amylases known in the prior art and, in particular, their improved further developments for use in washing or cleaning agents are described below. The α-amylase from Bacillus licheniformis (available as Termamyl® from Novozymes or as Purastar®ST from Danisco/Genencor) and the further development products thereof Duramyl® and Termamyl®ultra (Novozymes), Purastar®OxAm (Danisco/Genencor) and Keistase® (Daiwa Seiko Inc.), and the α-amylases from Bacillus amyloliquefaciens or from Bacillus stearothermophilus are suitable amylases. The α-amylase from Bacillus amyloliquefaciens is sold by Novozymes under the name BAN®, and derived variants from the α-amylase from Bacillus stearothermophilus are available under the names BSG® and Novamyl®, also from Novozymes. Further known amylases are the α-amylase from Bacillus sp. A 7-7 (DSM 12368) and the cyclodextrin glucanotransferase (CGTase) from Bacillus agaradherens (DSM 9948) as well as the further developments of the α-amylase from Aspergillus niger and A. oryzae available from Novozymes under the trade name Fungamyl®. Other commercial products that can advantageously be used in washing and cleaning agents are, for example, Amylase-LT® and Stainzyme® or Stainzyme ultra® or Stainzyme plus®, the latter also being from Novozymes. It is also possible to use variants of these enzymes obtained by way of point mutations in washing and cleaning agents. Particularly preferred amylases are disclosed in international applications WO 00/60060, WO 03/002711, WO 03/054177 and WO07/079938.

[0007] Amylases and proteases suitable for washing and cleaning agents are also known from WO 2011/100410, EP 2679679, WO 2015/044448, EP 2100948, and WO 99/63040.

[0008] Surprisingly, it has now been found that an α-amylase according to the invention improves the stability and the performance of a protease in a washing and cleaning agent.

[0009] The present invention therefore relates to a washing and cleaning agent containing a combination of an α-amylase and a protease, wherein the α-amylase is characterized by being at least 89%, and increasingly preferably at least 90%, 90.5%, 91%, 91.5%, 92%, 92.5%, 93%, 93.5%, 94%, 94.5%, 95%, 95.5%, 96%, 96.5%, 97%, 97.5%, 98%, 98.5%, 99%, 99.5%, and up to 100% identical to the sequence given in SEQ ID N0.1 over the entire length thereof and, in the numbering according to SEQ ID NO. 1, has a deletion at one or more of positions 180, 181, 182, 183, and 184, and wherein the protease is characterized by having an amino acid sequence which is at least 80%, and increasingly preferably at least 81%, 82%, 83%, 84%, 85%, 86%, 87%, 88%, 89%, 90%, 90.5%, 91%, 91.5%, 92%, 92.5%, 93%, 93.5%, 94%, 94.5%, 95%, 95.5%, 96%, 96.5%, 97%, 97.5%, 98%, 98.5%, and 99% identical to the amino acid sequence given in SEQ ID NO. 2 over the entire length thereof, wherein the α-amylase improves the stability and performance of the protease in the washing and cleaning agents.

[0010] Particularly preferred is a deletion of two positions selected from 180+181, 181+182, 182+183, and 183+184, and especially particularly preferred are deletions at positions 183+184 in the numbering according to SEQ ID NO. 1, and the deletions H183*+G184* are particularly preferred.

[0011] Preferably, in the numbering according to SEQ ID NO. 1, the α-amylase according to the invention furthermore has an amino acid substitution at one or more of positions 405, 421, 422, and 428. The substitutions I405L, A421H, A422P, and A428T are particularly preferred.

[0012] In a particularly preferred embodiment, the α-amylase according to the invention has the deletions H183*+G184*, and additionally the substitutions I405L, A421H, A422P, and A428T, in the numbering according to SEQ ID NO. 1.

[0013] The protease according to the invention comprises an amino acid sequence which is at least 80%, and increasingly preferably 81%, 82%, 83%, 84%, 85%, 86%, 87%, 88%, 89%, 90%, 90.5%, 91%, 91.5%, 92%, 92.5%, 93%, 93.5%, 94%, 94.5%, 95%, 95.5%, 96%, 96.5%, 97%, 97.5%, 98%, 98.5%, 99%, or 100% identical to the amino acid sequence given in SEQ ID NO. 2 over the entire length thereof.

[0014] A preferred protease is one that includes an amino acid sequence that is at least 80%, and increasingly preferably at least 81%, 82%, 83%, 84%, 85%, 86%, 87%, 88%, 89%, 90%, 90.5%, 91%, 91.5%, 92%, 92.5%, 93%, 93.5%, 94%, 94.5%, 95%, 95.5%, 96%, 96.5%, 97%, 97.5%, 98%, 98.5%, 99% identical to the amino acid sequence indicated in SEQ ID NO. 2 over the total length thereof and comprises the amino acid glutamic acid (E) at position 99.

[0015] A protease according to SEQ ID NO.4 is particularly preferred.

[0016] Amino acid positions that, within the scope of the present invention, are indicated by the expression “numbering according to SEQ ID NO. 1” shall be understood to mean the following: the further amino acid positions are defined by an alignment of the amino acid sequence of an amylase or a protease according to the invention with the amino acid sequence as indicated in SEQ ID NO. 1. The assignment of the positions is furthermore dependent on the mature protein. This assignment should, in particular, also be used when the amino acid sequence of a protein according to the invention comprises a higher number of amino acid residues than the amylase or protease in SEQ ID NO. 1. Proceeding from the aforementioned positions in the amino acid sequence, the modification positions in an amylase or protease according to the invention are those which are assigned to precisely these positions in an alignment.

[0017] The combination according to the invention of an α-amylase according to the invention with a protease in washing and cleaning agents brings about improved cleaning performance of the washing and cleaning agent on at least one protease-sensitive stain. The α-amylases according to the invention have a performance-enhancing effect on the protease likewise present in the washing and cleaning agent and consequently, due inter alia to the protease-stabilizing action thereof, enable improved removal of at least one, and preferably of multiple, protease-sensitive stains on textiles and/or hard surfaces, such as dishes. Particularly advantageous cleaning performance is exhibited by preferred embodiments of washing and cleaning agents according to the invention on stains containing blood, such as the blood/milk/ink stain: product no. CFT C-05, available from CFT (Center For Testmaterials) B.V. Vlaardingen, Netherlands.

[0018] As a result of preferred embodiments of the present invention, washing and cleaning agents having improved cleaning performance are produced deliberately with respect to protease-sensitive soiling.

[0019] Preferred embodiments of amylase and protease combinations according to the invention also already achieve this advantageous cleaning performance at low temperatures, and in particular in the temperature ranges between 10 °C and 60 °C, preferably between 15 °C and 50 °C, and particularly preferably between 20 °C and 40 °C. Further preferred embodiments of amylase and protease combinations according to the invention achieve this advantageous cleaning performance in a wide temperature range, for example between 15 °C and 90 °C, and preferably between 20 °C and 60 °C.

[0020] Cleaning performance within the scope of the invention shall be understood to mean the lightening performance on one or multiple stains, in particular on laundry or dishes. Within the scope of the invention, both the washing or cleaning agent that comprises the combination of amylase and protease, or the washing or cleaning liquor formed by this agent, and the protease and amylase themselves exhibit a particular cleaning performance. The cleaning performance of the enzymes thus contributes to the cleaning performance of the agent, or of the washing or cleaning liquor formed by the agent. The cleaning performance is preferably ascertained as described hereafter.

[0021] For the present invention, primarily the cleaning performance of the protease will be highlighted, wherein the synergistic effect of the α-amylase according to the invention is shown indirectly by the improved cleaning performance of the protease on protease-containing stains.

[0022] A protease exhibits proteolytic activity, which is to say it is capable of hydrolyzing peptide bonds of a polypeptide or protein, in particular in a washing or cleaning agent. A protease is thus an enzyme that catalyzes the hydrolysis of peptide bonds, and thus is able to cleave peptides or proteins. The amylases and proteases according to the invention are preferably the mature amylase/protease, which is to say the catalytically active molecule having no signal peptide(s) and/or propetide(s). Unless stated otherwise, the sequences given each also refer to mature enzymes.

[0023] The identity of nucleic acid or amino acid sequences is determined by a sequence comparison. This sequence comparison is based on the commonly used BLAST algorithm established in the prior art (see, for example, Altschul, S.F., Gish, W., Miller, W., Myers, E.W. & Lipman, D.J. (1990) “Basic local alignment search tool.” J. Mol. Biol. 215:403–410, and Altschul, Stephan F., Thomas L. Madden, Alejandro A. Schaffer, Jinghui Zhang, Hheng Zhang, Webb Miller, and David J. Lipman (1997): “Gapped BLAST and PSI-BLAST: a new generation of protein database search programs” Nucleic Acids Res., 25, pp. 3389–3402) and is in principle carried out by assigning similar successions of nucleotides or amino acids in the nucleic acid sequences or amino acid sequences to each other. A tabular assignment of the particular positions is referred to as an alignment. Another algorithm available in the prior art is the FASTA algorithm. Sequence comparisons (alignments), in particular multiple sequence comparisons, are created using computer programs. The Clustal series (cf. for example Chenna et al. (2003): Multiple sequence alignment with the Clustal series of programs. Nucleic Acid Research 31, 3497-3500), T-Coffee (see, for example, Notredame et al. (2000): T-Coffee: A novel method for multiple sequence alignments. J. Mol. Biol. 302, 205-217) or programs based on these programs or algorithms are frequently used. In the present patent application, all sequence comparisons (alignments) were created using the computer program Vector NTI® Suite 10.3 (Invitrogen Corporation, 1600 Faraday Avenue, Carlsbad, California, USA) with the specified standard parameters, the AlignX module of which program for the sequence comparisons is based on ClustalW.

[0024] A comparison of this kind makes it possible to specify the similarity between the compared sequences. It is usually given in percent identity, i.e. the proportion of identical nucleotides or amino acid residues in said sequences or in an alignment of corresponding positions. The broader concept of homology takes conserved amino acid exchanges into account in the case of amino acid sequences, i.e. amino acids having similar chemical activity, since they usually perform similar chemical activities within the protein. Therefore, the similarity between the compared sequences can also be expressed in percent homology or percent similarity. Identity and/or homology information can be provided for whole polypeptides or genes or only for individual regions. Homologous or identical regions of different nucleic acid or amino acid sequences are therefore defined by matches in the sequences. Such regions often have identical functions. They can be small and comprise only a few nucleotides or amino acids. Often, such small regions perform essential functions for the overall activity of the protein. It may therefore be useful to relate sequence matches only to individual, optionally small regions. Unless stated otherwise, however, identity or homology information in the present application relates to the entire length of the particular nucleic acid or amino acid sequence indicated.

[0025] The cleaning performance is determined in a washing system comprising a washing agent in a dose between 3.5 and 6.5 grams per liter of washing liquor and the protease and the amylase. The amylases to be compared are used in the same concentration (based on active protein). The cleaning performance of the protease with respect to a blood stain is determined by measuring the degree of whiteness of the washed textiles. The washing process takes place for 70 minutes at a temperature of 40 °C, wherein the water has a hardness between 13.5 and 16.5 ° (German degree of hardness).

[0026] The concentration of the protease in the washing agent intended for this washing system is 0.001 to 0.1 wt.%, and preferably 0.01 to 0.06 wt.%, based on active protein. The concentration of the amylase in the washing agent intended for this washing system is 0.001 to 0.15 wt.%, and preferably 0.005 to 0.012 wt.%, based on active protein.

[0027] A preferred liquid washing agent for such a washing system has the following composition (all information in percent by weight): 0.3 to 0.5% xanthan gum, 0.2 to 0.4% anti-foaming agent, 6 to 7% glycerol, 0.3 to 0.5% ethanol, 4 to 7% FAEOS (fatty alcohol ether sulfate), 5 to 15% non-ionic surfactants, 5 to 15% anionic surfactants (LAS), 1% boric acid, 1 to 4% sodium citrate (dihydrate), 2 to 4% soda, 2 to 6% coconut fatty acids, 0.5 to 2.5% HEDP (1-hydroxyethane-(1,1-diphosphonate)), 0 to 0.4% PVP (polyvinylpyrrolidone), 0 to 0.15% optical brighteners, 0 to 0.001% dye, the remainder being demineralized water. Preferably, the dosage of the liquid washing agent is between 3.5 and 6.0 grams per liter of washing liquor, for example 4.7, 4.9 or 5.9 grams per liter of washing liquor. The washing process preferably takes place in a pH range between pH 8 and pH 10.5, preferably between pH 8 and pH 9.

[0028] A preferred powdered washing agent for such a washing system has the following composition (all information in percent by weight): 10% linear alkylbenzene sulfonate (sodium salt), 1.5% C12-C18 fatty alcohol sulfate (sodium salt), 2.0% C12-C18 fatty alcohol having 7 EO, 20% sodium carbonate, 6.5% sodium hydrogen carbonate, 4.0% amorphous sodium silicate, 17% sodium carbonate peroxohydrate, 4.0% TAED, 3.0% polyacrylate, 1.0% carboxymethyl cellulose, 1.0% phosphonate, 27% sodium sulfate, the remainder being: suds suppressors, optical brighteners and fragrances. The dose of the powdered washing agent is preferably between 4.5 and 7.0 grams per liter of washing liquor, for example and particularly preferably 4.7 grams per liter of washing liquor, or 5.5, 5.9 or 6.7 grams per liter of washing liquor. The washing process preferably takes place in a pH range between pH 9 and pH 11.

[0029] The degree of whiteness, which is to say the lightening of the stains, as a measure of the cleaning performance, is preferably determined by way of optical measurement methods, and preferably photometrically. A suitable device for this purpose is for example the Minolta CM508d spectrometer. Usually, the devices used for the measurement are calibrated beforehand with a white standard, preferably a supplied white standard.

[0030] The protein concentration can be determined using known methods, such as the BCA method (bicinchoninic acid; 2,2'-biquinoline-4,4'-dicarboxylic acid) or the biuret method (A. G. Gornall, C. S. Bardawill and M.M. David, J. Biol. Chem., 177 (1948), pp. 751-766). The active protein concentration can be determined in this regard by titrating the active centers using a suitable irreversible inhibitor (e.g. phenylmethylsulfonylfluoride (PMSF) for proteases) and determining the residual activity (cf. M. Bender et al., J. Am. Chem. Soc. 88, 24 (1966), pp. 5890-5913).

[0031] In addition to the amino acid alterations discussed above, amylases and proteases according to the invention can have other amino acid alterations, in particular amino acid substitutions, insertions or deletions. Such amylases and proteases are, for example, developed by deliberate genetic modification, i.e. by mutagenesis methods, and optimized for specific applications or with regard to specific properties (for example with regard to their catalytic activity, stability, etc.). Furthermore, nucleic acids according to the invention can be introduced into recombination approaches and can thus be used to generate completely new types of amylases and proteases or other polypeptides.

[0032] The goal is to introduce deliberate mutations such as substitutions, insertions, or deletions into the known molecules in order, for example, to improve the cleaning performance of enzymes according to the invention. For this purpose, in particular the surface charges and/or the isoelectric point of the molecules and thus their interactions with the substrate can be modified. For instance, the net charge of the enzymes can be modified in order to influence the substrate binding, in particular for use in washing and cleaning agents. Alternatively or in addition, the stability of the amylase or protease can be still further increased by one or more corresponding mutations, thereby improving its cleaning performance. Advantageous properties of individual mutations, e.g. individual substitutions, can complement one another. A protease or amylase which has already been optimized with regard to specific properties, for example with respect to the stability thereof to surfactants and/or bleaching agents and/or other components, can thus additionally be further developed within the scope of the invention.

[0033] The following convention applies to the description of substitutions that relate to precisely one amino acid position (amino acid exchanges): initially, the naturally present amino acid is denoted in the form of the internationally customary single letter code, then follows the associated sequence position, and finally the inserted amino acid. Several exchanges within the same polypeptide chain are separated by forward slashes. In the case of insertions, additional amino acids are named following the sequence position. In the case of deletions, the missing amino acid is replaced by a symbol, for example a star or a dash. For example, A95G describes the substitution of alanine at position 95 by glycine, A95AG describes the insertion of glycine after the amino acid alanine at position 95, and A95* describes the deletion of alanine at position 95. This nomenclature is known to a person skilled in the field of enzyme technology.

[0034] The present invention therefore also relates to a washing and cleaning agent comprising a combination of an α-amylase and a protease, wherein the α-amylase is characterized by being obtainable from an amylase according to the invention as the starting molecule by one or more conservative amino acid substitutions. The expression "conservative amino acid substitution" refers to the exchange (substitution) of one amino acid residue for another amino acid residue, wherein this exchange does not result in a change in the polarity or charge at the position of the exchanged amino acid, such as the exchange of a non-polar amino acid residue for another non-polar amino acid residue. Conservative amino acid substitutions within the scope of the invention include, for example: G=A=S, I=V=L=M, D=E, N=Q, K=R, Y=F, S=T, G=A=I=V=L=M=Y=F=W=P=S=T.

[0035] The present invention therefore also relates to a washing and cleaning agent comprising a combination of an α-amylase and a protease, wherein the α-amylase is characterized by being obtainable from an amylase according to the invention as the starting molecule by way of fragmentation, deletion mutagenesis, insertion mutagenesis, or substitution mutagenesis and comprises an amino acid sequence that matches the starting molecule over a length of at least 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 475, 480, 482, 484, or 485 contiguous amino acids.

[0036] It is thus possible, for example, to delete individual amino acids at the termini or in the loops of the enzyme without the proteolytic activity thereby being lost or decreased. Furthermore, such fragmentation, deletion mutagenesis, insertion mutagenesis, or substitution mutagenesis can also be used to lower the allergenicity of the enzymes in question, and thus the overall usability can be improved. Advantageously, the enzymes preserve the proteolytic activity thereof even after the mutagenesis, which is to say the proteolytic activity thereof corresponds at least to that of the starting enzyme. Substitutions can also exhibit advantageous effects. Both single and multiple contiguous amino acids can be exchanged for other amino acids.

[0037] An amylase according to the invention can additionally be stabilized, in particular by one or more mutations, such as substitutions, or by coupling to a polymer. An increase in stability during storage and/or during use, for example during the washing process, causes the enzymatic activity to last longer, whereby the cleaning performance is improved. In principle, all stabilization options which are described in the prior art and/or are appropriate are considered. Those stabilizations are preferred which are achieved by mutations of the enzyme itself, since such stabilizations do not require any further work steps following the recovery of the enzyme. Suitable sequence changes for this purpose are known from the prior art.

[0038] Further possibilities for stabilization are, for example:

- changing the binding of metal ions, in particular the calcium binding sites, for example by exchanging one or more of the amino acid(s) that are involved in the calcium binding with one or more negatively charged amino acids and/or by introducing sequence alterations in at least one of the sequences of the two amino acids arginine and glycine;
- protecting against the influence of denaturing agents such as surfactants by mutations that cause an alteration of the amino acid sequence on or at the surface of the protein;
- exchanging amino acids near the N-terminus with those likely to contact the rest of the molecule via non-covalent interactions, thus contributing to the maintenance of the globular structure.

[0039] Preferred embodiments are those in which the enzyme is stabilized in several ways, as several stabilizing mutations act additively or synergistically.

[0040] The invention also relates to an amylase as described above, which is characterized in that it has at least one chemical modification. An amylase with such a modification is referred to as a derivative, which is to say that the amylase is derivatized.

[0041] Derivatives, within the meaning of the present application, shall thus be understood to mean those proteins in which the pure amino acid chain has been chemically modified. Such derivatizations can be achieved, for example, in vivo by the host cell that expresses the protein. In this regard, couplings of low-molecular-weight compounds such as lipids or oligosaccharides are particularly noteworthy. However, the derivatizations may also be carried out in vitro, for example by the chemical conversion of a side chain of an amino acid or by covalent bonding of another compound to the protein. For example, it is possible to couple amines to carboxyl groups of an enzyme in order to alter the isoelectric point. Another such compound may also be another protein that is bound to a protein according to the invention via bifunctional chemical compounds, for example. Derivatization is also understood to mean the covalent bonding to a macromolecular carrier or a non-covalent inclusion in suitable macromolecular cage structures. Derivatizations may, for example, affect the substrate specificity or bonding strength to the substrate or cause a temporary blockage of the enzymatic activity when the coupled substance is an inhibitor. This can be expedient, for example, for the period of storage. Such modifications may further affect the stability or enzymatic activity. They can also be used to reduce the allergenicity and/or immunogenicity of the protein and thus, for example, increase its skin compatibility. For example, couplings with macromolecular compounds, for example polyethylene glycol, can improve the protein in terms of stability and/or skin tolerability.

[0042] In the broadest sense, derivatives of a protein according to the invention can also be understood to mean preparations of these proteins. Depending on the recovery, processing or preparation, a protein can be combined with various other substances, for example from the culture of the producing microorganisms. A protein may also have been deliberately added to other substances, for example to increase its storage stability. All preparations of a protein according to the invention are thus also covered by the invention. This holds true regardless of whether or not the protein indeed develops this enzymatic activity in a certain preparation. This is because it may be desirable for the protein to have no, or only low, activity during storage and to develop the enzymatic function thereof only at the time of use. This can be controlled via appropriate accompanying substances, for example.

[0043] This subject matter of the invention includes all conceivable types of washing or cleaning agents, both concentrates and undiluted agents, for use on a commercial scale, in washing machines or for hand washing or cleaning. These include, for example, washing agents for textiles, carpets, or natural fibers, for which the term washing agent is used. These also include, for example, dishwasher detergents for dishwashers or manual dishwashing detergents or cleaners for hard surfaces such as metal, glass, porcelain, ceramics, tiles, stone, painted surfaces, plastics, wood, or leather, for which the term cleaning agent is used, i.e. in addition to manual and mechanical dishwashing detergents, for example, also scouring agents, glass cleaners, scented automatic toilet bowl cleaners and the like. Within the scope of the invention, the washing and cleaning agents furthermore include washing auxiliaries, which are dosed to the washing agent proper when washing textiles manually or automatically so as to achieve further action. Washing and cleaning agents within the scope of the invention furthermore also include textile pre- and after-treatment agents, which is to say agents with which the piece of laundry is brought in contact prior to the actual washing process, for example to partially loosen stubborn stains, and also agents that impart further desirable properties, such as a pleasant feel, crease resistance, or low static electricity, to the item to be washed in a step downstream from the actual textile washing process. The agents mentioned last include fabric softeners, for example.

[0044] The washing or cleaning agents according to the invention can comprise further enzymes. Further enzymes that can be used are, for example, lipases or cutinases, in particular for the triglyceride-liberating activities thereof, but also so as to create peroxy acids in situ from suitable precursors. These include, for example, the lipases that can originally be obtained from Humicola lanuginosa (Thermomyces lanuginosus) or those that have been developed therefrom, in particular those having the amino acid exchange D96L. These include, for example, the lipases that can originally be obtained from Humicola lanuginosa (Thermomyces lanuginosus) or have been developed therefrom, in particular those having one or more of the following amino acid exchanges in positions D96L, T213R and/or N233R, particularly preferably T213R and N233R, proceeding from the mentioned lipase. Moreover, the cutinases which have been originally isolated from Fusarium solani pisi and Humicola insolens can also be used, for example. Lipases and/or cutinases of which the starting enzymes have been isolated originally from Pseudomonas mendocina and Fusarium solanii can also be used.

[0045] The agents according to the invention can also contain cellulases or hemicellulases, such as mannanases, xanthan lyases, pectin lyases (= pectinases), pectinesterases, pectate lyases, xyloglucanases (= xylanases), pullulanases or β-glucanases.

[0046] In order to increase the bleaching effect, oxidoreductases such as oxidases, oxygenases, catalases, peroxidases such as halo-, chloro-, bromo-, lignin, glucose, or manganese peroxidases, dioxygenases, or laccases (phenoloxidases, polyphenoloxidases) can be used according to the invention. Advantageously, organic, particularly preferably aromatic compounds that interact with the enzymes are additionally added in order to enhance the activity of the relevant oxidoreductases (enhancers) or, in the event of greatly differing redox potentials, to ensure the flow of electrons between the oxidizing enzymes and the stains (mediators).

[0047] Amylases can also be used as further enzymes, all of the amylases already described above being suitable.

[0048] In addition to the ingredients described above, the washing or cleaning agents can contain substances having a cleaning action, substances from the group of surfactants, builders, polymers, glass corrosion inhibitors, corrosion inhibitors, fragrances and perfume carriers being preferred. These preferred ingredients are described in more detail below.

[0049] Preferred components of the washing or cleaning agents according to the invention are non-ionic surfactants, non-ionic surfactants of the general formula R^1-$CH(OH)CH_20$-$(AO)_w$-$(A'O)_x$-$(A''O)_y$-$(A'''O)_z$-R^2, in which

- R^1 represents a straight-chain or branched, saturated or mono- or polyunsaturated C_{6-24}-alkyl or alkenyl functional group;
- R^2 represents a linear or branched hydrocarbon functional group having 2 to 26 carbon atoms;
- A, A', A'', and A''' represent, independently of one another, a functional group from the group consisting of
  $-CH_2CH_2$, $-CH_2CH_2$-CH_2, $-CH_2$-$CH(CH_3)$, $-CH_2$-CH_2-CH_2-CH_2,
  $-CH_2$-$CH(CH_3)$-CH_2-, $-CH_2$-$CH(CH_2$-$CH_3)$, and
- w, x, y, and z represent values of between 0.5 and 120, where x, y, and/or z can also be 0,

being preferred.

[0050] By adding the above-mentioned non-ionic surfactants of the general formula R^1-$CH(OH)CH_2O$-$(AO)_w$-$(A'O)_x$-$(A''O)_y$-$(A'''O)_z$-R^2, subsequently also referred to as "hydroxy mixed ethers," the cleaning performance of enzyme-containing preparations according to the invention can be significantly improved, both in comparison with surfactant-free systems and in comparison with systems containing alternative non-ionic surfactants, for example from the group of polyalkoxylated fatty alcohols.

[0051] By using these non-ionic surfactants having one or more free hydroxyl groups on one or both terminal alkyl functional groups, the stability of the enzymes contained in the washing or cleaning agent preparations according to the invention can be improved substantially.

[0052] Particularly preferred are end-capped, poly(oxyalkylated) non-ionic surfactants which, according to the formula $R^1O[CH_2CH_2O]_xCH_2CH(OH)R^2$, also comprise, in addition to a functional group R^1, which represents linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon functional groups having 2 to 30 carbon atoms, preferably having 4 to 22 carbon atoms, a linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon functional group R^2 having 1 to 30 carbon atoms, wherein x represents values between 1 and 90, preferably values between 30 and 80, and in particular values between 30 and 60.

[0053] Surfactants of the formula $R^1O[CH_2CH(CH_3)O]_x[CH_2CH_2O]_yCH_2CH(OH)R^2$ are particularly preferred, in which R^1 represents a linear or branched aliphatic hydrocarbon functional group having 4 to 18 carbon atoms or mixtures thereof, R^2 represents a linear or branched hydrocarbon functional group having 2 to 26 carbon atoms or mixtures thereof, and x represents values between 0.5 and 1.5, and y represents a value of at least 15.

[0054] The group of these non-ionic surfactants includes, for example C_{2-26} fatty alcohol-$(PO)_1$-$(EO)_{15-40}$-2-hydroxyalkyl ethers, in particular the C_{8-10} fatty alcohol-$(PO)_1$-$(EO)_{22}$-2-hydroxydecylether.

[0055] Particularly preferred are also end-capped poly(oxyalkylated) non-ionic surfactants of the formula $R^1O[CH_2CH_2O]_x[CH_2CH(R^3)O]_yCH_2CH(OH)R^2$, in which R^1 and R^2 represent, independently of one another, a linear or branched, saturated or mono- or polyunsaturated hydrocarbon functional group having 2 to 26 carbon atoms, R^3 is selected, independently of one another, from $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2-CH_3$, $-CH(CH_3)_2$, but preferably represents $-CH_3$, and x and y represent, independently of one another, values between 1 and 32, non-ionic surfactants having $R^3 = -CH_3$ and values for x of from 15 to 32 and for y of 0.5 and 1.5 being very particularly preferred.

[0056] Further non-ionic surfactants that can preferably be used are the end-capped poly(oxyalkylated) non-ionic surfactants of the formula $R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$, in which R^1 and R^2 represent linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon functional groups having 1 to 30 carbon atoms, R^3 represents H or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl or 2-methyl-2-butyl functional group, x represents values between 1 and 30, and k and j represent values between 1 and 12, preferably between 1 and 5. If the value x is ≥ 2, every R^3 in the above formula $R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$ can be different. R^1

and R^2 are preferably linear or branched, saturated or unsaturated, aliphatic, or aromatic hydrocarbon functional groups having 6 to 22 carbon atoms, with functional groups having 8 to 18 C atoms being particularly preferred. For the functional group R^3, H, $-CH_3$, or $-CH_2CH_3$ are particularly preferred. Particularly preferred values for x are in the range from 1 to 20, in particular from 6 to 15.

[0057] As described above, every R^3 in the above formula can be different if $x \geq 2$. In this way, the alkylene oxide unit in square brackets can be varied. For example, if x represents 3, the functional group R^3 can be selected in order to form ethylene oxide (R^3 = H) or propylene oxide ($R^3 = CH_3$) units, which can be joined together in any sequence, for example (EO)(PO)(EO), (EO)(EO)(PO), (EO)(EO)(EO), (PO)(EO)(PO), (PO)(PO)(EO), and (PO)(PO)(PO). The value 3 for x has been selected here by way of example and can by all means be greater, in which case the range of variation increases as the values for x increase and includes a large number of (EO) groups combined with a small number of (PO) groups, for example, or vice versa.

[0058] Particularly preferred end-capped poly(oxyalkylated) alcohols of the above formula have values of k = 1 and j = 1, and therefore the previous formula is simplified to $R^1O[CH_2CH(R^3)O]_xCH_2CH(OH)CH_2OR^2$. In the aforementioned formula, R^1, R^2 and R^3 are as defined above and x represents numbers from 1 to 30, preferably 1 to 20, and in particular 6 to 18. Surfactants in which the functional groups R^1 and R^2 comprise 9 to 14 C atoms, R^3 represents H, and x assumes values from 6 to 15 are particularly preferred.

[0059] Finally, the non-ionic surfactants of general formula $R^1\text{-}CH(OH)CH_2O\text{-}(AO)_w\text{-}R^2$ have proven to be particularly effective, in which

- R^1 represents a straight-chain or branched, saturated or mono- or polyunsaturated $C_{6\text{-}24}$-alkyl or alkenyl functional group;
- R^2 represents a linear or branched hydrocarbon functional group having 2 to 26 carbon atoms;
- A represents a functional group from the group consisting of CH_2CH_2, $-CH_2CH_2CH2$, $-CH_2CH(CH_3)$, and
- w represents values between 1 and 120, preferably 10 to 80, and in particular 20 to 40.

The group of these non-ionic surfactants includes, for example, the $C_{4\text{-}22}$ fatty alcohol-$(EO)_{10\text{-}80}$-2-hydroxyalkyl ethers, and in particular also the $C_{8\text{-}12}$ fatty alcohol-$(EO)_{22}$-2-hydroxydecyl ethers and the $C_{4\text{-}22}$ fatty alcohol-$(EO)_{40\text{-}80}$-2-hydroxyalkyl ethers.

[0060] Preferred washing or cleaning agents are characterized in that the washing or cleaning agent contains at least one non-ionic surfactant, preferably a non-ionic surfactant from the group of hydroxy mixed ethers, the percentage by weight of the non-ionic surfactant with respect to the total weight of the washing or cleaning agent preferably being from 0.2 to 10 wt.%, more preferably from 0.4 to 7.0 wt.% and in particular from 0.6 to 6.0 wt.%.

[0061] Preferred washing or cleaning agents according to the invention for use in automatic dishwashing methods comprise further surfactants, and in particular amphoteric surfactants, in addition to the above-described non-ionic surfactants. However, the proportion of anionic surfactants with respect to the total weight of these washing or cleaning agents is preferably limited. Preferred automatic dishwasher detergents are therefore characterized in that they contain less than 5.0 wt.%, preferably less than 3.0 wt.%, particularly preferably less than 2.0 wt.%, of anionic surfactant, based on the total weight thereof. Larger quantities of anionic surfactants are not used, in particular so as to avoid excessive foaming.

[0062] Another preferred component of washing or cleaning agents according to the invention are complexing agents. Phosphonates are particularly preferred complexing agents. In addition to 1-hydroxyethane-1,1-diphosphonic acid, the complexing phosphonates comprise a number of different compounds, such as diethylenetriamine penta(methylene phosphonic acid) (DTPMP). Hydroxy alkane or aminoalkane phosphonates are particularly preferred in this application. Among the hydroxy alkane phosphonates, 1-hydroxyethane-1,1-diphosphonate (HEDP) is of particular importance as a cobuilder. It is preferably used as a sodium salt, wherein the disodium salt reacts in a neutral manner and the tetrasodium salt reacts in an alkaline manner (pH 9). Possible preferred aminoalkane phosphonates include ethylenediamine tetramethylene phosphonate (EDTMP), diethylentriamine pentamethylene phosphonate (DTPMP) and the higher homologs thereof. They are preferably used in the form of the neutrally reacting sodium salts, for example as the hexasodium salt of EDTMP or as the hepta- and octasodium salt of DTPMP. Of the class of phosphonates, HEDP is preferably used as a builder. The aminoalkane phosphonates additionally have a pronounced ability to bind heavy metals. Accordingly, it may be preferred, in particular if the agents also contain bleach, to use aminoalkane phosphonates, in particular DTPMP, or to use mixtures of the aforementioned phosphonates.

[0063] A preferred washing or cleaning agent within the scope of this application comprises one or more phosphonate(s) from the group consisting of

a) aminotrimethylene phosphonic acid (ATMP) and/or the salts thereof;
b) ethylenediamine tetra(methylene phosphonic acid) (EDTMP) and/or the salts thereof;
c) diethylenetriamine penta(methylene phosphonic acid) (DTPMP) and/or the salts thereof;
d) 1-hydroxyethane-1,1-diphosphonic acid (HEDP) and/or the salts thereof;
e) 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) and/or the salts thereof;
f) hexamethylenediamine tetra(methylene phosphonic acid) (HDTMP) and/or the salts thereof;
g) nitrilotri(methylene phosphonic acid) (NTMP) and/or the salts thereof.

[0064] Particularly preferred are washing or cleaning agents that comprise 1-hydroxyethane-1,1-diphosphonic acid (HEDP) or diethylenetriamine penta(methylene phosphonic acid) (DTPMP) as phosphonates. The washing or cleaning agents according to the invention can, of course, comprise two or more different phosphonates. Preferred washing or cleaning agents according to the invention are characterized in that the washing or cleaning agent comprises at least one complexing agent from the group of phosphonates, preferably 1-hydroxyethane-1,1-diphosphonate, wherein the percentage by weight of the phosphonate, based on the total weight of the washing or cleaning agent, is preferably 0.1 to 8.0 wt.%, preferably 0.2 to 5.0 wt.%, and in particular 0.5 to 3.0 wt.%.

[0065] The washing or cleaning agents according to the invention furthermore preferably comprise builders. The builders include in particular the silicates, carbonates, organic cobuilders, and—where there is no ecological bias against their use—phosphates.

[0066] Organic cobuilder substances can be present in amounts of up to 40 wt.%, in particular up to 25 wt.%, and preferably from 1 wt.% to 8 wt.%, if desired.

[0067] Among the large number of commercially available phosphates, alkali metal phosphates have the greatest significance for the agents according to the invention, pentasodium triphosphate, $Na_5P_3O_{10}$ (sodium tripolyphosphate) or pentapotassium triphosphate, $K_5P_3O_{10}$ (potassium tripolyphosphate) being particularly preferred. If phosphates are used as substances providing cleaning action in the washing or cleaning agent within the scope of the present application, preferred agents comprise said phosphate or phosphates, preferably pentapotassium triphosphate, wherein the percentage by weight of the phosphate based on the total weight of the washing or cleaning agent is in particular 5.0 to 40 wt.%, preferably 10 to 30 wt.%, and in particular 12 to 25 wt.%.

[0068] Polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, aspartic acid, polyacetals, dextrins, other organic cobuilders, and phosphonates are particularly noteworthy as organic cobuilders. These substance classes are described below.

[0069] Usable organic builder substances are, for example, the polycarboxylic acids that can be used in the form of the free acids and/or the sodium salts thereof, wherein polycarboxylic acids shall be understood to mean those carboxylic acids that carry more than one acid function. These include, for example, citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, saccharic acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), provided that such use is not objectionable for ecological reasons, and mixtures thereof. In addition to their builder effect, the free acids typically also have the property of being an acidifying component and are thus also used to set a lower and milder pH of washing or cleaning agents. Particularly noteworthy here are citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid, and any mixtures thereof. Citric acid or salts of citric acid are particularly preferably used as builder substances. Further particularly preferred builder substances are selected from methylglycine diacetic acid (MGDA), glutamine diacetic acid (GLDA), aspartic acid diacetate (ASDA), hydroxyethyl-iminodiacetate (HEIDA), iminodisuccinate (IDS), ethylenediamine disuccinate (EDDS), carboxymethyl inulin and polyaspartate.

[0070] Builders moreover include polymeric polycarboxylates. These are, for example, the alkali metal salts of polyacrylic acid or of polymethacrylic acid, e.g. those having a relative molar mass from 500 to 70,000 g/mol.

[0071] Within the meaning of this application, the molar masses indicated for the polymeric polycarboxylates are weight average molar masses M_w of the respective acid form, which were generally determined by way of gel permeation chromatography (GPC) in which a UV detector was used. The measurement was carried out against an external polyacrylic acid standard which, due to the structural relationship to the tested polymers, yields realistic molecular weight values. These specifications differ significantly from the molecular weight specifications for which polystyrene sulfonic acids are used as the standard. The molar masses measured against polystyrene sulfonic acids are generally considerably higher than the molar masses indicated in the present application.

[0072] Suitable polymers are in particular polyacrylates which preferably have a molecular mass of from 2000 to 20,000 g/mol. Due to their superior solubility, short-chain polyacrylates having molar masses from 2000 to 10,000 g/mol, and particularly preferably from 3000 to 5000 g/mol, may in turn be preferred from this group.

[0073] Also suitable are copolymeric polycarboxylates, in particular those of acrylic acid with methacrylic acid, and of acrylic acid or methacrylic acid with maleic acid. Copolymers of acrylic acid with maleic acid, comprising 50 to 90 wt.% acrylic acid and 50 to 10 wt.% maleic acid, have proven to be particularly suitable. The relative molecular mass thereof, based on free acids, is generally 2000 to 70,000 g/mol, preferably 20,000 to 50,000 g/mol, and in particular 30,000 to 40,000 g/mol.

[0074] Oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate, are also suitable cobuilders. In this case, ethylenediamine-N,N'-disuccinate (EDDS) is preferably used in the form of the sodium or magnesium salts thereof. Glycerol disuccinates and glycerol trisuccinates are also preferred in this context.

[0075] In order to improve the cleaning performance and/or set the viscosity, preferred washing or cleaning agents comprise at least one hydrophobically modified polymer, and preferably a hydrophobically modified carboxylic acid group-containing polymer, wherein the percentage by weight of the hydrophobically modified polymer, based on the total weight of the washing or cleaning agent, is in particular 0.1 to 10 wt.%, preferably between 0.2 and 8.0 wt.%, and in particular 0.4 to 6.0 wt.%.

[0076] In addition to the above-described builders, polymers providing cleaning action can also be present in the washing or cleaning agent. The percentage by weight of the polymers providing cleaning action, based on the total weight of automatic washing or cleaning agents according to the invention, is in particular 0.1 to 20 wt.%, preferably 1.0 to 15 wt.%, and in particular 2.0 to 12 wt.%.

[0077] Polymers containing sulfonic acid groups, in particular from the group of copolymeric polysulfonates, are preferably used as polymers providing cleaning action. In addition to sulfonic acid group-containing monomer(s), these copolymeric polysulfonates comprise at least one monomer from the group of the unsaturated carboxylic acids.

[0078] Unsaturated carboxylic acids of formula $R^1(R^2)C=C(R^3)COOH$ are particularly preferably used as unsaturated carboxylic acid(s), in which R^1 to R^3, independently of one another, denote -H, $-CH_3$, a straight-chain or branched saturated alkyl functional group having 2 to 12 carbon atoms, a straight-chain or branched, monounsaturated or polyunsaturated alkenyl functional group having 2 to 12 carbon atoms, alkyl functional groups or alkenyl functional groups substituted with $-NH_2$, -OH or -COOH as defined above, or -COOH or $-COOR^4$, wherein R^4 is a saturated or unsaturated, straight-chain or branched hydrocarbon functional group having 1 to 12 carbon atoms.

[0079] Particularly preferred unsaturated carboxylic acids are acrylic acid, methacrylic acid, ethacrylic acid, α-chloroacrylic acid, α-cyanoacrylic acid, crotonic acid, α-phenylacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, citraconic acid, methylene malonic acid, sorbic acid, cinnamic acid, or mixtures thereof. It is also possible, of course, to use the unsaturated dicarboxylic acids.

[0080] Among the sulfonic acid group-containing monomers, those of the formula $R^5(R^6)C=C(R^7)-X-SO_3H$ are preferred, in which R^5 to R^7 denote, independently of one another, -H, $-CH_3$, a straight-chain or branched saturated alkyl functional group having 2 to 12 carbon atoms, a straight-chain or branched, mono- or polyunsaturated alkenyl functional group having 2 to 12 carbon atoms, $-NH_2$, -OH, or -COOH-substituted alkyl or alkenyl functional groups, or represent -COOH or $-COOR^4$, where R^4 is a saturated or unsaturated, straight-chain or branched hydrocarbon functional group having 1 to 12 carbon atoms, and X represents an optionally present spacer group that is selected from $-(CH_2)_n-$, where n = 0 to 4, $-COO-(CH_2)_k-$, where k = 1 to 6, $-C(O)-NH-C(CH_3)_2-$, $-C(O)-NH-C(CH_3)_2-CH_2-$ and $-C(O)-NH-CH(CH_2CH_3)-$.

[0081] Among these monomers, those of formulas $H_2C=CH-X-SO_3H$, $H_2C=C(CH_3)-X-SO_3H$, and

$HO_3S\text{-}X\text{-}(R^6)C{=}C(R^7)\text{-}X\text{-}SO_3H$ are preferred, in which R^6 and R^7, independently of one another, are selected from -H, $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$ and $-CH(CH_3)_2$, and X denotes an optionally present spacer group that is selected from $-(CH_2)_n-$, where n = 0 to 4, $-COO-(CH_2)_k-$, where k = 1 to 6, -C(O)-NH-$C(CH_3)_2$-, -C(O)-NH-$C(CH_3)_2$-CH_2- and -C(O)-NH-$CH(CH_2CH_3)$-.

[0082] Particularly preferred sulfonic acid group-containing monomers are 1-acrylamido-1-propanesulfonic acid, 2-acrylamido-2-propanesulfonic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid, 2-methacrylamido-2-methyl-1-propanesulfonic acid, 3-methacrylamido-2-hydroxy-propanesulfonic acid, allyl sulfonic acid, methallyl sulfonic acid, allyloxybenzene sulfonic acid, methallyloxybenzene sulfonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulfonic acid, 2-methyl-2-propene-1-sulfonic acid, styrene sulfonic acid, vinylsulfonic acid, 3-sulfopropylacrylate, 3-sulfopropylmethacrylate, sulfomethacrylamide, sulfomethylmethacrylamide, as well as mixtures of the above acids or water-soluble salts thereof.

[0083] The sulfonic acid groups can be present entirely or partially in neutralized form in the polymers. The use of partially or fully neutralized sulfonic acid group-containing copolymers is preferred according to the invention.

[0084] The molar mass of the sulfo-copolymers that are preferably used according to the invention can be varied in order to adapt the properties of the polymers to the desired intended purpose. Preferred automatic dishwasher detergents are characterized in that the copolymers have molar masses of from 2000 to 200,000 $gmol^{-1}$, preferably from 4000 to 25,000 $gmol^{-1}$, and in particular from 5000 to 15,000 $gmol^{-1}$.

[0085] In a further preferred embodiment, the copolymers also comprise at least one non-ionic, preferably hydrophobic, monomer, in addition to the carboxyl group-containing monomer and the sulfonic acid group-containing monomer. Through the use of these hydrophobically modified polymers, it was possible to improve, in particular, the rinsing performance of automatic dishwasher detergents according to the invention.

[0086] Washing or cleaning agents containing a copolymer comprising

i) carboxylic acid group-containing monomer(s)
ii) sulfonic acid group-containing monomer(s)
iii) non-ionic monomer(s)

are therefore preferred according to the invention. Through the use of these terpolymers, it was possible to improve the rinsing performance of automatic dishwasher detergents according to the invention over comparable dishwasher detergents comprising sulfo-polymers without the addition of non-ionic monomers.

[0087] The non-ionic monomers used are preferably monomers of the general formula $R^1(R^2)C=C(R^3)-X-R^4$, in which R^1 to R^3 denote, independently of one another, -H, $-CH_3$ or $-C_2H_5$, X denotes an optionally present spacer group selected from $-CH_2-$, -C(O)O- and -C(O)-NH-, and R^4 denotes a straight-chain or branched saturated alkyl functional group having 2 to 22 carbon atoms or an unsaturated, preferably aromatic functional group having 6 to 22 carbon atoms.

[0088] Particularly preferred non-ionic monomers are butene, isobutene, pentene, 3-methylbutene, 2-methylbutene, cyclopentene, hexene, hexene-1, 2-methlypentene-1, 3-methlypentene-1, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, 2,4,4-trimethylpentene-1, 2,4,4-trimethylpentene-2, 2,3-dimethylhexene-1, 2,4-dimethylhexene-1, 2,5-dimethylhexene-1, 3,5-dimethylhexene-1, 4,4-dimethylhexane-1, ethylcyclohexene, 1-octene, α-olefins having 10 or more carbon atoms such as 1-decene, 1-dodecene, 1-hexadecene, 1-octadecene and C22-α-olefin, 2-styrene, α-methylstyrene, 3-methylstyrene, 4-propylstyrene, 4-cyclohexylstyrene, 4-dodecylstyrene, 2-ethyl-4-benzylstyrene, 1-vinyl naphthalene, 2-vinyl naphthalene, acrylic acid methyl ester, acrylic acid ethyl ester, acrylic acid propyl ester, acrylic acid butyl ester, acrylic acid pentyl ester, acrylic acid hexyl ester, methacrylic acid methyl ester, N-(methyl)acrylamide, acrylic acid-2-ethylhexyl ester, methacrylic acid-2-ethylhexyl ester, N-(2-ethylhexyl)acrylamide, acrylic acid octyl ester, methacrylic acid octyl ester, N-(octyl)acrylamide, acrylic acid lauryl ester, methacrylic acid lauryl ester, N-(lauryl)acrylamide, acrylic acid stearyl ester, methacrylic acid stearyl ester, N-(stearyl)acrylamide, acrylic acid behenyl ester, methacrylic acid behenyl ester and N-(behenyl)acrylamide, or mixtures thereof.

[0089] The percentage by weight of the sulfonic acid group-containing copolymers based on the total weight of washing or cleaning agents according to the invention is preferably from 0.1 to 15 wt.%, more preferably from 1.0 to 12 wt.% and in particular from 2.0 to 10 wt.%.

[0090] The washing or cleaning agents according to the invention can be present in production forms known to a person skilled in the art, i.e. for example in solid or liquid form or as a combination of solid and liquid product formats. Powder, granules, extrudates or compacted products, in particular tablets, are particularly suitable as solid product formats.

[0091] A substance (e.g. a composition or an agent) is solid according to the definition of the invention if it is in the solid state of aggregation at 25 °C and 1013 mbar.

[0092] A substance (e.g. a composition) is liquid according to the definition of the invention if it is in the liquid state of aggregation at 25 °C and 1013 mbar. Liquid also includes gel form.

[0093] In addition to the enzymes according to the invention, solid, and in particular powdered, washing or cleaning agents according to the invention can, in principle, comprise all known ingredients customary in such agents, wherein at least one further ingredient is present in the agent. The agents according to the invention can, in particular, comprise builder substances, surface-active surfactants, bleaching agents based on organic and/or inorganic peroxygen compounds, bleach activators, water-miscible organic solvents, enzymes, sequestering agents, electrolytes, pH regulators, and further auxiliary agents, such as optical brighteners, graying inhibitors, foam regulators, dyes and fragrances, and combinations thereof.

[0094] In one embodiment, a washing or cleaning agent further comprises

- 5 wt.% to 70 wt.%, and in particular 5 wt.% to 30 wt.% surfactants and/or
- 10 wt.% to 65 wt.%, and in particular 12 wt.% to 60 wt.% water-soluble or water-dispersible inorganic builder material and/or
- 0.5 wt.% to 10 wt.%, and in particular 1 wt.% to 8 wt.% water-soluble organic builder substances and/or
- 0.01 to 15 wt.% solid inorganic and/or organic acids or acid salts and/or
- 0.01 to 5 wt.% complexing agents for heavy metals and/or
- 0.01 to 5 wt.% graying inhibitor and/or
- 0.01 to 5 wt.% dye transfer inhibitor and/or
- 0.01 to 5 wt.% suds suppressor.

[0095] Optionally, the agent can furthermore comprise optical brighteners, preferably from 0.01 to 5 wt.%.

[0096] The preparation of solid agents according to the invention presents no difficulties and can be carried out in a known manner, for example by spray-drying or granulation, wherein enzymes and possibly other thermally sensitive ingredients, such as bleaching agents, are optionally added separately later. For the preparation of agents according to the invention having an increased bulk density, in particular in the range of from 650 g/l to 950 g/l, a method having an extrusion step is preferred.

[0097] To produce solid agents according to the invention in tablet form, which can be single-phase or multiphase, single-color or multi-color, and in particular can be composed of one layer or of multiple, in particular of two, layers, the procedure is preferably such that all components—optionally one layer each—are mixed with one another in a mixer, and the mixture is compressed using conventional tablet presses, such as eccentric presses or rotary presses, using pressures in the range of approximately 50 to 100 kN, preferably 60 to 70 kN. In the case of multilayer tablets in particular, it can be advantageous if at least one layer is pre-pressed. This is preferably carried out at pressures of between 5 and 20 kN, in particular at 10 to 15 kN. This readily yields break-resistant tablets that nonetheless dissolve sufficiently quickly under usage conditions, normally with breaking and flexural strengths of 100 to 200 N, but preferably above 150 N. A tablet thus produced preferably has a weight of 10 g to 50 g, and in particular of 15 g to 40 g. The tablets can have any physical shape. They can be round, oval, or angular, and intermediate shapes are also possible. Corners and edges are advantageously rounded. Round tablets preferably have a diameter of 30 mm to 40 mm. In particular, the size of angular or cuboid tablets, which are predominantly introduced via the dosing device, for example of the dishwasher, is dependent on the geometry and the volume of this dosing device. By way of example, preferred embodiments have a base area of (20 to 30 mm) x (34 to 40 mm), and in particular of 26x36 mm or of 24x38 mm.

[0098] A solid agent according to the invention preferably contains at least one water-soluble and/or water-insoluble, organic and/or inorganic builder. The water-soluble organic builder substances include the above-described organic builders.

[0099] In particular, alkali silicates, alkali carbonates and alkali phosphates, which can be present in the form of the alkaline, neutral, or acidic sodium or potassium salts, can be used as water-soluble inorganic builder materials. Examples in this regard are described above in the present application.

[0100] Water-dispersible inorganic builder materials for solid agents are, in particular, crystalline or amorphous alkali aluminosilicates, used in amounts of up to 50 wt.%, preferably no more than 40 wt.% and, in liquid agents, in particular in amounts from 1 wt.% to 5 wt.%. Among these, the crystalline sodium aluminosilicates in washing agent quality, in particular zeolite A, P, and optionally X, either alone or in mixtures, for example in the form of a co-crystallizate of the zeolites A and X (Vegobond® AX, a commercial product of Condea Augusta S.p.A.), are preferred. Amounts close to the stated upper limit are preferably used in solid, particulate agents. Suitable aluminosilicates have in particular no particles having a particle size greater than 30 μm and preferably comprise at least 80 wt.% of particles having a size smaller than 10 μm. Their calcium binding capacity, which can be determined according to the specifications in German patent DE 24 12 837, is generally in the range of from 100 to 200 mg CaO per gram.

[0101] Suitable substitutes or partial substitutes for the stated aluminosilicate are crystalline alkali silicates, which may be present alone or in a mixture with amorphous silicates. The alkali silicates that can be used as builders in the agents according to the invention preferably have a molar ratio of alkali oxide to SiO_2 of less than 0.95, in particular 1:1.1 to 1:12, and may be present in amorphous or crystalline form. Preferred alkali silicates are sodium silicates, in particular amorphous sodium silicates, having a $Na_2O:SiO_2$ molar ratio of 1:2 to 1:2.8. Crystalline phyllosilicates of the general formula $Na_2Si_xO_{2x+1} \cdot y\, H_2O$, where x, referred to as the module, is a number from 1.9 to 22, in particular 1.9 to 4, and y is a number from 0 to 33, and preferred values for x are 2, 3, or 4, are preferably used as crystalline silicates, which may be present alone or in a mixture with amorphous silicates. Preferred crystalline phyllosilicates are those in which x in the stated general formula assumes the values 2 or 3. In particular, both ß- and δ-sodium disilicates ($Na_2Si_2O_5 \cdot y\ H_2O$) are preferred. Practically anhydrous crystalline alkali silicates of the above general formula, in which x is a number from 1.9 to 2.1 and which are produced from amorphous alkali silicates, may also be used in agents according to the invention. In a further preferred embodiment of agents according to the invention, a crystalline sodium phyllosilicate having a module of from 2 to 3, as can be produced from sand and soda, is used. Crystalline sodium silicates having a module in the range of from 1.9 to 3.5 are used in a further preferred embodiment of agents according to the invention. Crystalline phyllosilicates of the above formula (I) are sold by Clariant GmbH under the trade name Na-SKS, for example Na-SKS-1 ($Na_2Si_{22}O_{45} \cdot xH_2O$, kenyaite), Na-SKS-2 ($Na_2Si_{14}O_{29} \cdot xH_2O$, magadiite), Na-SKS-3 ($Na_2Si_8O_{17} \cdot xH_2O$) or Na-SKS-4 ($Na_2Si_4O_9 \cdot xH_2O$, macatite). Of these, Na-SKS-5 (α-$Na_2Si_2O_5$), Na-SKS-7 (β-$Na_2Si_2O_5$, natrosilite), Na-SKS-9 ($NaHSi_2O_5 \cdot 3H_2O$), Na-SKS-10 ($NaHSi_2O_5 \cdot 3H_2O$, kanemite), Na-SKS-11 (t-$Na_2Si_2O_5$), and Na-SKS-13 ($NaHSi_2O_5$), and in particular Na-SKS-6 (δ-$Na_2Si_2O_5$), are particularly suitable. In a preferred embodiment of agents according to the invention, a granular compound made of crystalline phyllosilicate and citrate, crystalline phyllosilicate and the above-described (co)polymeric polycarboxylic acid, or alkali silicate and alkali carbonate is used, as it is commercially available under the name Nabion® 15, for example.

[0102] Builder substances are preferably present in the solid agents according to the invention in amounts of up to 75 wt.%, and in particular of 5 wt.% to 50 wt.%.

[0103] Possible peroxygen compounds suitable for use in the solid agents according to the invention include, in particular, organic peroxy acids or peracid salts of organic acids, such as phthalimidopercaproic acid, perbenzoic acid, or salts of diperdodecanoic diacid, hydrogen peroxide and inorganic salts giving off hydrogen peroxide under the washing conditions, which include perborate, percarbonate, persilicate, and/or persulfates such as caroate. If solid peroxygen compounds are intended to be used, these may be used in the form of powders or granules, which may also be coated in a manner known in principle. If an agent according to the invention contains peroxygen compounds, these are present in amounts of preferably up to 50 wt.%, in particular from 5 wt.% to 30 wt.%. The addition of small amounts of known bleaching agent stabilizers such as phosphonates, borates or metaborates, metasilicates, and magnesium salts such as magnesium sulfate may be expedient.

[0104] Compounds which, under perhydrolysis conditions, result in aliphatic peroxocarboxylic acids having preferably 1 to 10 C atoms, in particular 2 to 4 C atoms, and/or optionally substituted perbenzoic acid, may be used as bleach activators in the solid agents. Suitable substances are those that carry O- and/or N-acyl groups having the described carbon atomic number and/or optionally substituted benzoyl groups. Preferred are polyacylated alkylene diamines, in particular tetraacetylethylenediamine (TAED), acylated triazine derivatives, in particular 1,5-diacetyl-2,4-

dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, in particular tetraacetylglycoluril (TAGU), N-acylimides, in particular N-nonanoyl succinimide (NOSI), acylated phenolsulfonates, in particular n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), carboxylic acid anhydrides, in particular phthalic acid anhydride, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate, 2,5-diacetoxy-2,5-dihydrofuran and enol ester, and acetylated sorbitol and mannitol or the described mixtures thereof (SORMAN), acylated sugar derivatives, in particular pentaacetyl glucose (PAG), pentaacetyl fructose, tetraacetyl xylose and octaacetyl lactose, and acetylated, optionally N-alkylated glucamine and gluconolactone, and/or N-acylated lactams, for example N-benzoylcaprolactam. The hydrophilically substituted acyl acetals and the acyl lactams are likewise preferably used. Combinations of conventional bleach activators can also be used. Such bleach activators can, in particular in the presence of the above-mentioned hydrogen peroxide-yielding bleaching agents, be present in the customary quantity range, preferably in amounts of 0.5 wt.% to 10 wt.%, and in particular 1 wt.% to 8 wt.%, based on the total agent, but are preferably entirely absent when percarboxylic acid is used as the sole bleaching agent.

[0105] In addition to or instead of the conventional bleach activators, sulfonimines and/or bleach-boosting transition metal salts or transition metal complexes may also be contained as what are referred to as bleach catalysts.

[0106] The solid application forms according to the invention include extrudates, granules, tablets, or pouches comprising solid agents, which can be present in large packages or packaged into portions. The agent may alternatively be present as a pourable powder, in particular having a bulk density of 300 g/l to 1200 g/l, in particular 500 g/l to 900 g/l or 600 g/l to 850 g/l.

[0107] Embodiments of the present invention include all solid, powdered, liquid, gel, or pasty application forms of agents, which may optionally also consist of a plurality of phases and can be present in compressed or uncompressed form. Thus, agents that are characterized by being present in the form of a monocomponent system represent another embodiment of the invention. Such agents preferably consist of one phase. Agents according to the invention, however, can of course also be composed of multiple phases, for example two liquid phases, two solid phases, or one liquid and one solid phase. In a further embodiment of the invention, the washing or cleaning agent is therefore characterized by being divided into several components.

[0108] The liquid presentation forms based on water and/or organic solvents can be present in thickened form, in the form of gels.

[0109] The washing or cleaning agents according to the invention are preferably present in liquid form. Preferred washing or cleaning agents contain more than 40 wt.%, preferably between 50 and 90 wt.% and in particular between 60 and 80 wt.%, water, based on the total weight thereof.

[0110] The washing or cleaning agents according to the invention can contain an organic solvent as a further component. Adding organic solvents has an advantageous effect on the enzyme stability and cleaning performance of these agents. Preferred organic solvents are derived from the group of monohydric or polyhydric alcohols, alkanolamines or glycol ethers. The solvents are preferably selected from ethanol, n- or i-propanol, butanol, glycol, propanediol or butanediol, glycerol, diglycol, propyl diglycol or butyl diglycol, hexylene glycol, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, propylene glycol methyl ether, propylene glycol ethyl ether or propylene glycol propyl ether, dipropylene glycol methyl ether or dipropylene glycol ethyl ether, methoxytriglycol, ethoxytriglycol, butoxytriglycol, 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol, propylene-glycol-t-butylether, and mixtures of these solvents. The percentage by weight of these organic solvents with respect to the total weight of the washing or cleaning agents according to the invention is preferably from 0.1 to 10 wt.%, more preferably from 0.2 to 8.0 wt.% and in particular from 0.5 to 5.0 wt.%. A particularly preferred organic solvent which is particularly effective in stabilizing the washing or cleaning agents is glycerol, as well as 1,2-propylene glycol. Liquid washing or cleaning agents which contain at least one polyol, preferably from the group of glycerol and 1,2-propylene glycol, are preferred according to the invention, the percentage by weight of the polyol with respect to the total weight of the washing or cleaning agent preferably being from 0.1 to 10 wt.%, more preferably from 0.2 to 8.0 wt.%, and in particular from 0.5 to 5.0 wt.%.

[0111] Other preferred organic solvents are the organic amines and alkanolamines. The washing or cleaning agents according to the invention preferably contain these amines in amounts of from 0.1 to 10 wt.%, more preferably from 0.2 to 8.0 wt.% and in particular from 0.5 to 5.0 wt.%, in each case based on the total weight thereof. Ethanolamine is a particularly preferred alkanolamine.

[0112] A further preferred component of the washing or cleaning agents according to the invention is a sugar alcohol (alditol). The group of alditols includes non-cyclic polyols of the formula $HOCH_2[CH(OH)]_nCH_2OH$. The alditols include, for example, mannitol, isomalt, lactitol, sorbitol and xylitol, threitol, erythritol and arabitol. Sorbitol has been found to be particularly advantageous with regard to enzyme stability. The percentage by weight of the sugar alcohol with respect to the total weight of the washing or cleaning agent is preferably from 1.0 to 10 wt.%, more preferably from 2.0 to 8.0 wt.% and in particular from 3.0 to 6.0 wt.%.

[0113] Liquid washing or cleaning agents according to the invention are preferably formulated in multiphase form, i.e. by combining two or more different liquid washing or cleaning agents which are separate from one another. This type of formulation increases the stability of the washing or cleaning agent and improves the cleaning performance thereof. A preferred washing or cleaning agent according to the invention is characterized by comprising a packaging means and two liquid washing or cleaning agents A and B which are separate from one another in said packaging means, wherein composition A comprises

a) at least one modified protease according to the invention;
b) at least one further enzyme different from the protease according to the invention,
c) 10 to 84.9 wt.% builder(s),
d) 15 to 89.9 wt.% water, and composition B comprises
e) 10 to 75 wt.% builder(s);
f) 25 to 90 wt.% water.

[0114] The invention also relates to a method for cleaning textiles or hard surfaces, which is characterized in that an agent according to the invention is used in at least one method step.

[0115] This covers both manual and automatic methods, with automatic methods being preferred. Methods for cleaning textiles are generally characterized in that, in a plurality of method steps, various substances providing cleaning action are applied to the material to be cleaned and washed off after the exposure time, or in that the material to be cleaned is otherwise treated with a washing agent or a solution or dilution of this agent. The same applies to methods for cleaning all materials other than textiles, in particular hard surfaces. All conceivable washing or cleaning methods can be enhanced in at least one of the method steps by the use of a washing or cleaning agent according to the invention or a combination of amylase and protease according to the invention, and therefore represent embodiments of the present invention. All aspects, subject matter, and embodiments described for the combination of amylase and protease according to the invention and agents comprising same can also be applied to this subject matter of the invention. Express reference is therefore made here to the disclosure at the appropriate point, with the note that this disclosure also applies to the above-described methods according to the invention.

[0116] Alternative embodiments of the present subject matter of the invention also include methods for treating textile raw materials or for textile care in which a protease according to the invention becomes active in at least one method step. Among these, methods for textile raw materials, fibers, or textiles with natural constituents are preferred, very particularly methods for textile raw materials, fibers, or textiles with wool or silk.

[0117] The invention also relates to the use of an agent according to the invention for cleaning textiles or hard surfaces, in particular in such a way that the combination of amylase and protease is used in an amount of 40 µg to 4 g, preferably from 50 µg to 3 g, particularly preferably from 100 µg to 2 g, and most particularly preferably from 200 µg to 1 g.

[0118] All aspects, subject matter, and embodiments described for the proteases according to the invention and agents comprising same can also be applied to this subject matter of the invention.

Express reference is therefore made here to the disclosure at the appropriate point, with the note that this disclosure also applies to the above-described use according to the invention.

Example

[0120] The following example describes the invention, without limiting it to this example:

[0121] Examination of the combinations according to the invention of amylase and protease in the washing machine.

[0122] Textiles soiled with standardized stains were used for this example. The following stain was used:

- blood/milk/ink on cotton: product No. C-05, available from CFT (Center For Testmaterials) BV Vlaardingen, Netherlands

[0123] The combination according to the invention of the protease according to SEQ ID NO. 4 and an amylase according to the invention (batch 1), and a comparative batch containing the protease according to SEQ ID NO. 4 and Stainzyme® (batch 2) were washed for comparison in the washing machine, wherein the washing experiments were carried out once directly after the washing agent was formulated (0 weeks) and once after the washing agent had been stored for 16 weeks (16 weeks).

[0124] The same amount of active enzyme was used in each case. The proteases and amylases were dosed on top to an aqueous liquid washing agent (containing, in addition to water, 5.5 wt.% 7-fold ethoxylated C12/14 fatty alcohol, 5.3 wt.% sodium-C9-13 alkylbenzene sulfonate, 4.9 wt.% sodium-C12/14 fatty alcohol ether sulfate comprising 2 EO, 1.8 wt.% citric acid, 3 wt.% C12-18 fatty acid, 0.1 wt.% diethylenetriamine penta(methylene phosphonic acid)-hepta sodium salt, 1.3 wt.% NaOH, 3.6 wt.% ethanol/glycerol) having a pH of 8.5 and washed at 30 °C, water hardness 16 °dH, in a Miele W 1935, total washing time 70 minutes.

[0125] A 6-fold determination was carried out, and various stain monitors were washed and measured with a colorimeter after washing.

[0126] The following delta Y values were obtained for batch 1 compared to batch 2:

Storage time (weeks)	delta Y values (batch 1 - batch 2)
0	2.1
16	3.2

[0127] It is clearly apparent that the washing performance of the washing agent comprising the protease according to SEQ ID NO. 4 and the amylase according to the invention is significantly higher both after 0 weeks and after 16 weeks. In particular, a greater effect is apparent after a storage period of 16 weeks, which additionally allows the conclusion that the protease is stabilized by the amylase according to the invention.

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Thr Gly Lys Asn Met Phe Ala Val Ala Glu Phe Trp Lys Asn Asp Leu
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Gly Ala Ile Glu Asn Tyr Leu Gln Lys Thr Asn Trp Asn His Ser Val
        275                 280                 285

Phe Asp Val Pro Leu His Tyr Asn Leu Tyr Asn Ala Ser Lys Ser Gly
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Gly Asn Tyr Asp Met Arg Asn Ile Phe Asn Gly Thr Val Val Gln Arg
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His Pro Ser His Ala Val Thr Phe Val Asp Asn His Asp Ser Gln Pro
                325                 330                 335

Glu Glu Ala Leu Glu Ser Phe Val Glu Glu Trp Phe Lys Pro Leu Ala
            340                 345                 350

Tyr Ala Leu Thr Leu Thr Arg Glu Gln Gly Tyr Pro Ser Val Phe Tyr
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Gly Asp Tyr Tyr Gly Ile Pro Thr His Gly Val Pro Ala Met Arg Ser
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Lys Ile Asp Pro Ile Leu Glu Ala Arg Gln Lys Tyr Ala Tyr Gly Pro
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Glu Thr Trp Tyr Asp Ile Thr Gly Asn Arg Ser Asp Thr Val Lys Ile
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Thr Gly Ile Ser Thr His Pro Asp Leu Asn Ile Arg Gly Gly Ala Ser
        35                  40                  45


Phe Val Pro Gly Glu Pro Ser Thr Gln Asp Gly Asn Gly His Gly Thr
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His Val Ala Gly Thr Ile Ala Ala Leu Asn Asn Ser Ile Gly Val Leu
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Gly Val Ala Pro Ser Ala Glu Leu Tyr Ala Val Lys Val Leu Gly Ala
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Asn Asn Asn Arg Ala Ser Phe Ser Gln Tyr Gly Ala Gly Leu Asp Ile
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Val Ala Pro Gly Val Asn Val Gln Ser Thr Tyr Pro Gly Ser Thr Tyr
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Ala Ser Leu Asn Gly Thr Ser Met Ala Thr Pro His Val Ala Gly Ala
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Ala Ala Leu Val Lys Gln Lys Asn Pro Ser Trp Ser Asn Val Gln Ile
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Ser Gly Ile Asp Ser Ser His Pro Asp Leu Lys Val Ala Gly Gly Ala
        35                  40                  45


Ser Met Val Pro Ser Glu Thr Asn Pro Phe Gln Asp Asn Asn Ser His
    50                  55                  60


Gly Thr His Val Ala Gly Thr Val Ala Ala Leu Asn Asn Ser Ile Gly
65                  70                  75                  80
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            100                 105                 110

Trp Ala Ile Ala Asn Asn Met Asp Val Ile Asn Met Ser Leu Gly Gly
        115                 120                 125

Pro Ser Gly Ser Ala Ala Leu Lys Ala Ala Val Asp Lys Ala Val Ala
    130                 135                 140

Ser Gly Val Val Val Val Ala Ala Ala Gly Asn Glu Gly Thr Ser Gly
145                 150                 155                 160

Ser Ser Ser Thr Val Gly Tyr Pro Gly Lys Tyr Pro Ser Val Ile Ala
                165                 170                 175

Val Gly Ala Val Asp Ser Ser Asn Gln Arg Ala Ser Phe Ser Ser Val
            180                 185                 190

Gly Pro Glu Leu Asp Val Met Ala Pro Gly Val Ser Ile Gln Ser Thr
        195                 200                 205

Leu Pro Gly Asn Lys Tyr Gly Ala Tyr Asn Gly Thr Ser Met Ala Ser
    210                 215                 220

Pro His Val Ala Gly Ala Ala Ala Leu Ile Leu Ser Lys His Pro Asn
225                 230                 235                 240

Trp Thr Asn Thr Gln Val Arg Ser Ser Leu Glu Asn Thr Thr Thr Lys
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Thr Gly Ile Ser Thr His Pro Asp Leu Asn Ile Arg Gly Gly Ala Ser
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Phe Val Pro Gly Glu Pro Ser Thr Gln Asp Gly Asn Gly His Gly Thr
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His Val Ala Gly Thr Ile Ala Ala Leu Asn Asn Ser Ile Gly Val Leu
65                  70                  75                  80

Gly Val Ala Pro Ser Ala Glu Leu Tyr Ala Val Lys Val Leu Gly Ala
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Asp Gly Glu Gly Ala Ile Ser Ser Ile Ala Gln Gly Leu Glu Trp Ala
            100                 105                 110

Gly Asn Asn Gly Met His Val Ala Asn Leu Ser Leu Gly Ser Pro Ser
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Pro Ser Ala Thr Leu Glu Gln Ala Val Asn Ser Ala Thr Ser Arg Gly
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Val Leu Val Val Ala Ala Ser Gly Asn Ser Gly Ala Ser Ser Ile Ser
145                 150                 155                 160

Tyr Pro Ala Arg Tyr Ala Asn Ala Met Ala Val Gly Ala Thr Asp Gln
                165                 170                 175

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

Val Ala Pro Gly Val Asn Val Gln Ser Thr Tyr Pro Gly Ser Thr Tyr
        195                 200                 205

Ala Ser Leu Asn Gly Thr Ser Met Ala Thr Pro His Val Ala Gly Ala
    210                 215                 220

Ala Ala Leu Val Lys Gln Lys Asn Pro Ser Trp Ser Asn Val Gln Ile
225                 230                 235                 240

Arg Asn His Leu Lys Asn Thr Ala Thr Ser Leu Gly Ser Thr Asn Leu
                245                 250                 255
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Tyr Gly Ser Gly Leu Val Asn Ala Glu Ala Ala Thr Arg
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Patentkrav

1. Vaske- eller rengøringsmiddel der indeholder en kombination af en α-amylase og en protease, hvilken α-amylase er **kendetegnet ved, at** den over hele dens længde er mindst 89 % og i stigende grad fortrinsvis mindst 90 %, 90,5% , 91 %, 91,5 %, 92 %, 92,5 %, 93 %, 93,5 %, 94 %, 94,5 %, 95 %, 95,5 %, 96 %, 96,5 %, 97 %, 97,5 %, 98 %, 98,5 %, 99 %, 99,5 % og op til 100 % identisk med sekvensen, der er angivet i SEQ ID NO.1, og omfatter deletioner ved en eller flere af positionerne: 180, 181, 182, 183 og 184 i nummereringen ifølge SEQ ID NO.1, og proteasen er **kendetegnet ved, at** den omfatter en aminosyresekvens, der over hele dens længde er mindst 80 % og i stigende grad fortrinsvis mindst 81 %, 82 %, 83 %, 84 %, 85 %, 86 %, 87 %, 88 %, 89 %, 90 %, 90,5 %, 91 %, 91,5 %, 92 %, 92,5 %, 93 %, 93,5 %, 94 %, 94,5 %, 95 %, 95,5 %, 96 %, 96,5 %, 97 %, 97,5 %, 98 %, 98,5 % og 99 % identisk med aminosyresekvensen, der er specificeret i SEQ ID NO. 2, hvilken α-amylase forbedrer stabiliteten og ydeevnen af proteasen i vaske- og rengøringsmidlet.

2. Vaske- eller rengøringsmidlet ifølge krav 1, hvor amylasen omfatter deletioner i mindst to positioner, som er valgt blandt positionerne: 180 + 181, 181 + 182, 182 + 183 og 183 + 184 i nummereringen ifølge SEQ ID NO.1, og særligt foretrukket i positionerne 183 + 184 i nummereringen ifølge SEQ ID NO. 1.

3. Vaske- eller rengøringsmiddel ifølge krav 1 og 2, hvor amylasen omfatter deletionerne H183* + G184* i nummereringen ifølge SEQ ID NO. 1.

4. Vaske- eller rengøringsmiddel ifølge krav 1 til 3, hvor amylasen også omfatter aminosyresubstitutioner i en eller flere af positionerne: 405, 421, 422 og 428 i nummereringen ifølge SEQ ID NO. 1.

5. Vaske- eller rengøringsmiddel ifølge krav 1 til 4, hvor amylasen omfatter substitutionerne: I405L; A421H, A422P og A428T i nummereringen ifølge til SEQ ID NO. 1.

6. Vaske- eller rengøringsmidlet ifølge krav 1, hvor proteasen omfatter en aminosyresekvens, der over hele dens længde er mindst 80 % og i stigende grad fortrinsvis mindst 81 %, 82 %, 83 %, 84 %, 85 %, 86 %, 87 %, 88 %, 89 %, 90 %, 90,5 %, 91 %, 91,5 %, 92 %, 92,5 %, 93 %, 93,5 %, 94 %, 94,5 %, 95 %, 95,5 %, 96 %, 96,5 %, 97 % , 97,5 %, 98 %, 98,5 % og 99 % identisk med aminosyresekvensen, der er specificeret i SEQ ID NO. 2, og omfatter aminosyren glutaminsyre (E) i position 99 i nummereringen ifølge SEQ ID NO. 2.

7. Vaske- eller rengøringsmiddel ifølge krav 1 til 6, hvor proteasen er en protease ifølge SEQ ID NO.4.

8. Vaske- eller rengøringsmiddel ifølge krav 1 til 7, **kendetegnet ved, at** proteasen er indeholdt i midlet i en mængde på 0,001 til 0,1 vægt-%, fortrinsvis 0,01 til 0,06 vægt-%, og amylasen er indeholdt i midlet i en mængde på 0,001 til 0,15 vægt-%, fortrinsvis på 0,005 til 0,012 vægt-%, baseret på den samlede vægt af vaske- eller rengøringsmidlet.

9. Anvendelse af et vaske- eller rengøringsmiddel ifølge et af kravene 1 til 8 til vask af tekstiler eller rengøring af hårde overflader.

10. Fremgangsmåde til rengøring af tekstiler eller hårde overflader, **kendetegnet ved, at** et vaske- eller rengøringsmiddel ifølge et af kravene 1 til 8 anvendes i mindst et fremgangsmådetrin.

11. Anvendelse af en α-amylase til forbedring af stabiliteten og ydeevnen af en protease i et vaske- og rengøringsmiddel, hvilken α-amylase er **kendetegnet ved, at** den over hele dens længde er mindst 89 % og i stigende grad fortrinsvis mindst 90 %, 90,5 %, 91 %, 91,5 %, 92 %, 92,5 %, 93 %, 93,5 %, 94 %, 94,5 %, 95 %, 95,5 %, 96 %, 96,5 %, 97 %, 97,5 %, 98 %, 98,5 %, 99 %, 99,5 % og op til 100 % identisk med sekvensen, der er angivet i SEQ ID NO. 1, og omfatter deletioner på en eller flere af positionerne: 180, 181, 182, 183 og 184 i nummereringen ifølge SEQ ID NO.1, og proteasen er **kendetegnet ved, at** den omfatter en aminosyresekvens, der over hele dens længde er mindst 80 % og i stigende grad fortrinsvis mindst 81 %, 82 %, 83 %, 84 %, 85 %, 86 %, 87 %, 88 %, 89 %, 90 %, 90,5 %, 91 %, 91,5 %, 92 %, 92,5 %, 93 %, 93,5 %, 94 %, 94,5 %, 95 %, 95,5 %, 96 %, 96,5 %, 97 %, 97,5 %, 98 %, 98,5 % og 99 % identisk med aminosyresekvensen, der er specificeret i SEQ ID NO. 2.