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(54) **Liquid detergent composition containing lipase and protease**

Lipase- und proteasehaltige flüssige Waschmittelzusammensetzung

Composition détergente liquide contenant une lipase et une protéase

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(56) References cited:
EP-A- 0 258 068
EP-A- 0 376 705
EP-A- 0 381 262
WO-A-89/04361

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Description

The present invention relates to liquid detergent compositions which contain an enzyme system. The enzyme system is a combination of a modified protease and a lipase.

Background

It is well known in the art that detergent compositions may advantageously comprise enzyme systems. Such enzyme systems include cellulase, protease, lipase and amylases. The present invention is specifically aiming at providing liquid detergent compositions in which the enzyme system comprises a mixture of protease and lipase.

Formulating such a combination in a granular detergent raises no specific issue, since both enzymes can be physically separated. On the contrary, formulating such a combination in a liquid detergent raises a specific technical issue in that the protease is likely to take as a substrate any protein present in the detergent composition.

Specifically, it has been observed that lipases which may also be present in the detergent composition are particularly subject to such proteolytic degradation; as a consequence, the residual activity of the lipase in the detergent composition will rapidly diminish with the storage time of the detergent composition, so that it was up to now impossible to formulate liquid detergent compositions comprising at the same time a lipase and a protease, said detergent compositions being sufficiently stable for a commercial exploitation.

It is thus an object of the present invention to provide a liquid detergent composition comprising an enzyme system comprising a lipase and a protease, wherein said enzyme system is stable; by stable, it is meant that the proteolytic degradation of the lipase is substantially reduced.

It has now been found that this object can be met by using any lipase, or mixtures thereof, together with a bacterial serine protease wherein the methionine adjacent to the serine of the active site has been replaced by another amino acid, or mixtures of such proteases. Indeed, it has been discovered that this specific combination would provide an enzyme system comprising a protease and a lipase, which would be stable in a liquid detergent composition.

This solution has the advantage of being simple because it only requires ingredients which are commercially available; indeed, several modified bacterial serine proteases suitable for the purpose of this invention are commercially available, as well as several lipases suitable for use in a detergent composition. Furthermore, the detergent compositions according to the invention require no addition of specific lipase stabilizers, and are therefore particularly attractive in terms of product cost and environmental compatibility.

Modified bacterial serine proteases including proteases suitable for use in the compositions according to the invention are disclosed for instance in EP-A-0 328 229 as well as their use in detergent compositions. This patent application describes among others a modified bacterial serine protease which is commercially available from GIST-BROCADES under the name MAXAPEM 15^{R}

Biotechnology Newswatch, published March 1988, page 6, and EP-A-O 258 068 describe a lipase enzyme which is commercially available from NOVO NORDISK A/S under the trade name LIPOLASE^{R}. This European Patent application mentions that LIPOLASE^{R} can be combined with proteases to form a granular enzymatic detergent additive.

EP-A-0 381 262 describes detergent compositions comprising a protease and a lipase, preferably LIPOLASE^{R}, together with a stabilizing system. The proteases disclosed in this reference include bacterial proteases.

WO-A-8904361 discloses enzymatic detergent compositions comprising lipases from Pseudomonas and a certain group of proteases showing lipase stability in said composition.

EP 376,705 discloses Humicola-derived lipase and protease of the Subtilisin-type in detergents showing an enhanced storage stability of the lipase by inclusion of lower aliphatic alcohol and lower carboxylic acid.

Summary of the invention

Accordingly, the present invention is a liquid detergent composition comprising an enzyme system, characterized in that the enzyme system comprises a modified bacterial serine protease or mixtures thereof, and a lipase or mixtures thereof. The bacterial serine protease is modified in that the methionine adjacent to the serine of the active site is substituted by another amino acid.

Detailed description of the invention

The enzyme system according to the present invention comprises a lipase and a protease. The lipase to be used in the compositions according to the present invention is a lipase derived from Humicola lanuginosa, as described in EP-A-0 258 068 to NOVO INDUSTRI A/S. This patent application describes how to obtain said specific lipase, but said specific lipase is also commercially available from NOVO NORDISK A/S under the trade name LIPOLASE^{R}.

The compositions according to the present invention typically comprise from 0.1 to 10000 Lipolytic Units per gram

of finished product, preferably from 10 to 2500 Lipolytic Units per gram of finished product. Lipolytic units are defined for instance in EP 0 258 068, page 5 lines 38-40.1 LU is the amount of enzyme which liberates 1 μmol titratable butyric acid per minute at 30°C, pH 7 with gum arabic as an emulsifier. Further details are given in Novo analytical Method AF95/5.

The proteases to be used according to the present invention are modified bacterial serine proteases. All native bacterial serine proteases are characterized in that the active site invariably comprises a triade of amino acids which are serine, histidine and aspartic acid. These amino acids are positioned in the native form of the enzyme in such a way that they catalyse the cleavage of internal peptide bonds of proteins. Another common point between these bacterial serine proteases is that there always is a methionine adjacent to the serine of the active site, in the native sequence. The bacterial serine proteases suitable for use according to the present invention are those wherein the methionine adjacent to the serine of the active site has been substituted by another amino acid. The serine of the active site can also be defined as the serine which is homologuous to the serine in position 221 in the amino acid sequence of the bacterial subtilisin protease produced by Bacillus Subtilis; said sequence is listed herein after in figure 1.

In the sequence of this bacterial subtilisin protease produced by Bacillus Subtilis, the methionine is immediately after the serine in position 221 and therefore it is the methionine in position 222 which needs to be substituted by another amino acid. It is possible that, in the sequence of other bacterial serine proteases, this methionine would not be immediately following the serine of the active site; in such a case, it is the methionine homologuous to the methionine in position 222 in the sequence of this bacterial subtilisin protease produced by Bacillus Subtilis which needs to be substituted by another amino acid.

It is to be understood that the present invention does not reside in these modified proteases per se, rather in the particular application of these modified proteases to liquid detergent compositions also comprising a lipase; it is therefore not the aim of the present description to specify how these modified proteases can be obtained; This modification can be done by site-directed mutagenesis or any other genetic engeneering technique well known in the art for this purpose; for instance, EP-A-0 328 229, to GIST-BROCADES N.V. describes how to obtain such proteases. Another suitable method is described in EP 130 756, which also describes a modified bacterial serine protease suitable for use in the compositions according to the invention.

Furthermore, some modified bacterial serine proteases suitable for use in the compositions according to the invention are commercially available, such as DURAZYM ^{R} from NOVO, which is the methionine modified version of SAVINASE ^{R}; another example of available modified protease is MAXAPEM 15 from GIST-BROCADES, which is the modified version of MAXACAL^{R} wherein the methionine in position 216 has been substituted. Also available are experimental samples of modified OPTICLEAN ^{R} and OPTIMASE^{R}, from SOLVAY enzymes; both are modified in that the methionine in position 222 is substituted by a cysteine. Preferred modified bacterial serine protease according to the present invention are MAXAPEM 15^{R} from GIST BROCADES and DURAZYM ^{R} from NOVO.

The compositions according to the present invention typically will contain from 0.005 to 10 mg of active protease per gram of finished product, preferably from 0.01 to 5.0 mg of active protease per gram of finished product. Mixtures of the modified bacterial serine protease described herein above are also suitable for use in the compositions according to the invention.

The rest of the liquid detergent composition according to the present invention is made of conventional detergency ingredients, i.e. water, surfactants, builders and others. The following description of these ingredients is for the sake of completeness of the description and is not to be construed as limiting the compositions of the present invention to those conventional ingredients described.

The liquid detergent compositions herein comprises from 5% to 60% by weight of the total liquid detergent composition, preferably from 10% by weight to 40% by weight of an organic surface-active agent selected from nonionic, anionic, cationic and zwitterionic surface-active agents and mixtures thereof.

Suitable anionic surface-active salts are selected from the group of sulfonates and sulfates. The like anionic surfactants are well-known in the detergent arts and have found wide application in commercial detergents. Preferred anionic water-soluble sulfonate or sulfate salts have in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms.

Examples of such preferred anionic surfactant salts are the reaction products obtained by sulfating C_8-C_{18} fatty alcohols derived from e.g. tallow oil, palm oil, palm kernel oil and coconut oil; alkylbenzene sulfonates wherein the alkyl group contains from about 9 to about 15 carbon atoms; sodium alkylglyceryl ether sulfonates; ether sulfates of fatty alcohols derived from tallow and coconut oils; coconut fatty acid monoglyceride sulfates and sulfonates; and water-soluble salts of paraffin sulfonates having from about 8 to about 22 carbon atoms in the alkyl chain. Sulfonated olefin surfactants as more fully described in e.g. U.S. Patent Specification 3,332,880 can also be used. The neutralizing cation for the anionic synthetic sulfonates and/or sulfates is represented by conventional cations which are widely used in detergent technology such as sodium, potassium or alkanolammonium.

A suitable anionic synthetic surfactant component herein is represented by the water-soluble salts of an alkylbenzene sulfonic acid, preferably sodium alkylbenzene sulfonates, preferably sodium alkylbenzene sulfonates having from

about 10 to 13 carbon atoms in the alkyl group.Another preferred anionic surfactant component herein is sodium alkyl sulfates having from about 10 to 15 carbon atoms in the alkyl group.

The nonionic surfactants suitable for use herein include those produced by condensing ethylene oxide with a hydrocarbon having a reactive hydrogen atom, e.g., a hydroxyl, carboxyl, or amido group, in the presence of an acidic or basic catalyst, and include compounds having the general formula $RA(CH_2CH_2O)_nH$ wherein R represents the hydrophobic moiety, A represents the group carrying the reactive hydrogen atom and n represents the average number of ethylene oxide moieties. R typically contains from about 8 to 22 carbon atoms They can also be formed by the condensation of propylene oxide with a lower molecular weight compound. n usually varies from about 2 to about 24.

A preferred class of nonionic ethoxylates is represented by the condensation product of a fatty alcohol having from 12 to 15 carbon atoms and from about 4 to 10 moles of ethylene oxide per mole or fatty - alcohol. Suitable species of this class of ethoxylates include : the condensation product of C_{12}-C_{15} oxo-alcohols and 3 to 9 moles of ethylene oxide per mole of alcohol; the condensation product or narrow cut C_{14}-C_{15} oxo-alcohols and 3 to 9 moles of ethylene oxide per mole of fatty(oxo)alcohol; the condensation product of a narrow cut C_{12}-C_{13} fatty(oxo)alcohol and 6,5 moles of ethylene oxide per mole of fatty alcohol; and the condensation products of a C_{10}-C_{14} coconut fatty alcohol with a degree of ethoxylation (moles EO/mole fatty alcohol) in the range from 4 to 8. The fatty oxo alcohols while mainly linear can have, depending upon the processing conditions and raw material olefins, a certain degree of branching, particularly short chain such as methyl branching. A degree of branching in the range from 15% to 50% (weight%) is frequently found in commercial oxo alcohols.

Suitable cationic surfactants include quaternary ammonium compounds of the formula $R_1R_2R_3R_4N^+$ where R_1,R_2 and R_3 are methyl groups, and R_4 is a $C_{12\text{-}15}$ alkyl group, or where R_1 is an ethyl or hydroxy ethyl group, R_2 and R_3 are methyl groups and R_4 is a $C_{12\text{-}15}$ alkyl group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds in which the aliphatic moiety can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 24 carbon atoms and another substituent contains, at least, an anionic water-solubilizing group. Particularly preferred zwitterionic materials are the ethoxylated ammonium sulfonates and sulfates disclosed in U.S. Patents 3,925,262, Laughlin et al., issued December 9, 1975 and 3,929,678, Laughlin et al., issued December 30, 1975.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl or hydroxy alkyl moiety of from about 8 to about 28 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxy alkyl groups, containing from 1 to about 3 carbon atoms which can optionally be joined into ring structures.

Also suitable are Poly hydroxy fatty acid amide surfactants of the formula

$$R^2\text{-}C(=O)\text{-}N(R^1)\text{-}Z,$$

wherein R^1 is H,
$C_{1\text{-}4}$hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R_2 is $C_{5\text{-}31}$ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R_1 is methyl, R_2 is a straight $C_{11\text{-}15}$ alkyl or alkenyl chain or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable, but preferred is a mixture of citric acid and a substituted succinic acid.

The citric acid builder employed in the practice of this invention will be present in the finished product in the form of any water-soluble salt of citric acid. Such salts include, for example, sodium, potassium, ammonium or alkanolammonium salts. In practice it is convenient to use a citric acid monohydrate slurry as a starting material, which will be neutralized in situ, so as to form the above mentioned salts.

The substituted succinic acid builders herein are of the general formula R-CH(COOH)CH_2(COOH), i.e., derivatives of succinic acid, wherein R is C_{10}-C_{16} alkyl or alkenyl, preferably C_{12}-C_{14} alkenyl.

These substituted succinic acid builders are preferably in the finished product in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts (e.g., mono-, di-, or tri-ethanolammonium).

As raw materials, it is preferred to use these succinic acid derivatives in their diacid or anhydride form. The diacid will be neutralized in situ, while the anhydride will undergo a hydrolysis/neutralization process.

Specific examples of substituted succinic acid builders include : lauryl succinic acid, myristyl succinic acid, palmityl succinic acid, 2-dodecenyl succinic acid (preferred), 2-tetradecenyl succinic acid, and the like.

A preferred builder system comprises from 4% to 12% by weight of the total composition of the above substituted succinic acid builders, and from 4% to 12% by weight of the total composition of citric acid. As an alternative builder, the compositions according to the invention may also contain a fatty acid. Preferred are oleic and palmitoleic acid.

It is well known from the man skilled in the art that the pH of the composition may significantly affect the enzyme system's performance. Accordingly, the compositions according to the invention preferably have a pH adjusted in the range of from 6 to 10, preferably from 7.5 to 8.0.

The compositions according to the invention may also comprise an enzyme stabilizing system. Indeed, the present invention provides a system wherein the protease does not significantly attack the native lipase, but the enzyme system or components thereof may still be subject to unstability problem due to the other detergency ingredients. Therefore, stabilizing agents may be needed, which are conventional and well known in the art. A preferred enzyme stabilizing system is selected from boric acid, 1,2-propanediol, carboxylic acids, and mixtures thereof. These enzyme stabilizing systems are typically present in amounts of from 0.01% to 5% by weight of the total composition.

The compositions of the invention may also comprise other enzymes. such as cellulases or amylases. Amylases, particularly, seem to be stable in the presence of protease, and the compositions of the invention therefore preferably comprise an amylase.

The compositions herein can contain a series of further optional ingredients. Examples of the like additives include : suds regulants, opacifiers, agents to improve the machine compatibility in relation to enamel-coated surfaces, bactericides, dyes, perfumes, bleaches including perborate and percarbonate, brighteners, soil release agents, softening agents and the like.

The liquid compositions herein can contain further additives, typically at levels of from 0.05 to 5%. These additives include polyaminocarboxylates such as ethylenediaminotetracetic acid, diethylenetriaminopentacetic acid, ethylenediamino disuccinic acid or water-soluble alkali metals thereof. Other additives include organo-phosphonic acids; particularly preferred are ethylenediamino tetramethylenephosphonic acid, hexamethylenediamino tetramethylenephosphonic acid, diethylenetriamino pentamethylenephosphonic acid and aminotrimethylenephosphonic acid.

EXAMPLES

The following compositions according to the invention are made by mixing the listed ingredients in the listed proportions.

	1	2	3	4	5
- Linear alkyl benzene sulfonate	12	7	6	7	8
- Sodium C_{12-15} alkyl sulfate	2	2	3	3	2
- C_{14-15} alkyl 2.5 times ethoxylated sulfate	0	0	2	2	0
- C_{12} glucose amide	0	0	6	6	0
- C_{12-15}alcohol 7 times ethoxylated	8	0	0	0	0
- C_{12-15}alcohol 5 times ethoxylated	0	8	0	0	8
- Oleic Acid	2	0	0	0	0
- Citric Acid	3	9	9	13	15
- C_{12-14} alkenyl substituted succinic acid	10	5	5	7	6
- Ethanol	4	4	3	4	5
- 1,2-propanediol	2	3	3	1	2
- NaOH	6	8	8	11	11
- diethylene triamine penta(methylene phosphonic acid)	0.5	0.7	0.7	1	1
- Amylase(143KNU/g)	0.1	0.1	0.05	0.2	0.1
- LipolaseR(100KLU/g commercial solution)	0.4	0.2	0.3	0.3	0.3
- PEM15R(50mg/g Commercial solution)	0.3	0	0	0	0.4
- Durazym^{R} (39 mg/g Commercial solution)	0	0.2	0	0	0
- Opticlean M222C^{R} (experimental sample)	0	0.1	0	0.4	0
- Optimase M222C^{R} (experimental sample)	0	0	0.3	0	0
- CaCl2	0.01	0	0.01	0.01	0.02
- Na metaborate	2.2	2	2	4	3
- TEA	0	0	0	0	0
- Sodium formate	0	0	0	0	0
- Fatty Acids	0	0	0	0	0
- Water and Minors	Balance to 100%				

EXAMPLES

The following compositions according to the invention are made by mixing the listed ingredients in the listed proportions

	6	7	8	9	10
- Linear alkyl benzene sulfonate	5	7	9	8	10
- Sodium C_{12-15} alkyl sulfate	5	2	1.75	0	3
- C_{14-15} alkyl 2.5 times ethoxylated sulfate	2	0	2	0	0
- C_{12} glucose amide	6	0	7	0	0
- C_{12-15}alcohol 7 times ethoxylated	0	0	0.5	0	11.6
- C_{12-15}alcohol 5 times ethoxylated	0	8	0	8	
- Oleic Acid	0	0	0	3.5	2.5
- Citric Acid	10	9	9.5	4	1
- C_{12-14} alkenyl substituted succinic acid	11	0	11.5	0	0
- STPP	0	20	0	0	0
- Zeolite	0	0	0	26	0
- Ethanol	6	4	4	3	6
- 1,2-propanediol	3	2	2	2	1.5
- NaOH	9	9	9.8	9	3.5
- diethylene triamine penta(methylene phosphonic acid)	1.0	1.0	1.0	0.5	0.8
- Amylase(143KNU/g)	0.2	0.1	0.2	0.05	1
- Lipolase^R(100KLU/g commercial solution)	0.5	0.5	0.3	0.2	0.3
- PEM15R(50mg/g Commercial solution)	0.4	0	0	0	0.2
- Durazym^R (39 mg/g Commercial solution)	0	0	0.5	0	0.2
- Opticlean M222C^R (experimental sample)	0	0	0	0.3	0
- Optimase M222C^R (experimental sample)	0	0.5	0	0	0
- CaCl2	0.01	0.01	0.02	0.02	0.01
- Na metaborate	4	2	4	3	0
- TEA	0	0	0	0	6
- Sodium formate	0	0	0	0	1
- Fatty Acids	0	0	0	0	12
- Water and Minors	Balance to 100%				

EXAMPLES

The following compositions according to the invention are made by mixing the listed ingredients in the listed proportions

	11	12	13	14	15
- Linear alkyl benzene sulfonate	5	7	9	8	10
- Sodium C_{12-15} alkyl sulfate	5	2	1.75	0	3
- C_{14-15} alkyl 2.5 times ethoxylated sulfate	2	0	2	0	0
- C_{12} glucose amide	6	0	7	0	0
- C_{12-15}alcohol 7 times ethoxylated	0	0	0.5	0	11.6
- C_{12-15}alcohol 5 times ethoxylated	0	8	0	8	
- Oleic Acid	0	0	0	3.5	2.5
- Citric Acid	10	9	9.5	4	1
- C_{12-14} alkenyl substituted succinic acid	11	0	11.5	0	0
- Tartrate monosuccinate	0	15	0	17	20
- Diethoxylated poly (1,2 propylene terephtalate)	1.0	0.5	0.7	0	0.5

(continued)

	11	12	13	14	15
- Ethanol	6	4	4	3	6
- 1,2-propanediol	3	2	2	2	1.5
- NaOH	9	9	9.8	9	3.5
- diethylene triamine penta(methylene phosphonic acid)	1.0	1.0	1.0	0.5	0.8
- Amylase(143KNU/g)	0.2	0.1	0.2	0.05	1
- LipolaseR(100KLU/g commercial solution)	0.5	0.5	0.3	0.2	0.3
- PEM15^{R}(50mg/g Commercial solution)	0.4	0	0	0	0.2
- Durazym^{R} (39 mg/g Commercial solution)	0	0	0.5	0	0.2
- Opticlean M222C^{R} (experimental sample)	0	0	0	0.3	0
- Optimase M222C^{R} (experimental sample)	0	0.5	0	0	0
- CaCl2	0.01	0.01	0.02	0.02	0.01
- Na metaborate	4	2	4	3	0
- TEA	0	0	0	0	6
- Sodium formate	0	0	0	0	1
- Fatty Acids	0	0	0	0	12
- Water and Minors	Balance to 100%				

Claims

1. A liquid detergent composition comprising conventional detergent ingredients and an enzyme system comprising a lipase derived from Humicola lanuginosa and a bacterial serine protease modified such that the methionine adjacent to the serine of the active site in the amino acid sequence has been replaced by another amino acid.

2. A liquid detergent composition according to claim 1 wherein the bacterial serine protease is derived from Bacillus subtilis and has the methionine at position 222 of the amino acid sequence replaced by another amino acid.

3. A detergent composition according to claim 1 which comprises a lipase in amounts so as to obtain from 0.1 to 10 000 Lipolytic Units per gram of finished product.

4. A detergent composition according to claim 1 which comprises a protease, in amounts such as to obtain from 0.005 to 10 mg of active protease per gram of finished product.

5. A detergent composition according to claim 1 wherein the modified bacterial serine protease is modified by substituting cysteine for said methionine.

6. A detergent composition according to any of the preceding claims which additionally comprises an amylase.

7. A detergent composition according to any of the preceding claims which additionally comprises an enzyme stabilization system.

8. A detergent composition according to claim 7 wherein the enzyme stabilization system comprises from 0.01% to 5% by weight of the total composition of boric acic.

9. A detergent composition according to claim 7 wherein the enzyme stabilization system comprises at least one of 1,2-propane diol and carboxylic acids.

10. A detergent composition according to any of the preceding claims which has a pH in the range of from 6 to 10.

Patentansprüche

1. Flüssige Waschmittelzusammensetzung, umfassend herkömmliche Waschmittelbestandteile und ein Enzymsystem, das eine von Humicola lanuginosa abgeleitete Lipase und eine bakterielle Serin-Protease umfaßt, welche in der Weise modifiziert ist, daß das zu dem Serin benachbarte Methionin der aktiven Stelle in der Aminosäuresequenz durch eine andere Aminosäure ersetzt ist.

2. Flüssige Waschmittelzusammensetzung nach Anspruch 1, wobei die bakterielle Serin-Protease von Bacillus subtilis abgeleitet ist und das Methionin an Position 222 der Aminosäuresequenz durch eine andere Aminosäure ersetzt hat.

3. Waschmittelzusammensetzung nach Anspruch 1, welche eine Lipase in solchen Mengen umfaßt, um 0,1 bis 10.000 Lipolyseeinheiten pro Gramm fertiges Produkt zu erzielen.

4. Waschmittelzusammensetzung nach Anspruch 1, welches eine Protease in solchen Mengen umfaßt, um 0,005 bis 10 mg aktive Protease pro Gramm fertiges Produkt zu erzielen.

5. Waschmittelzusammensetzung nach Anspruch 1, wobei die modifizierte bakterielle Serin-Protease mittels Substitution von Methionin durch Cystein modifiziert ist.

6. Waschmittelzusammensetzung nach mindestens einem der vorangehenden Ansprüche, welche weiterhin eine Amylase umfaßt.

7. Waschmittelzusammensetzung nach mindestens einem der vorangehenden Ansprüche. welche weiterhin ein Enzymstabilisierungssytem umfaßt.

8. Waschmittelzusammensetzung nach Anspruch 7, wobei das Enzymstabilisierungssystem 0,01 bis 5 Gew.-% der gesamten Zusammensetzung an Borsäure umfaßt.

9. Waschmlttelzusammensetzung nach Anspruch 7, wobei das Enzymstabilisierungssystem mindestens eines von 1,2-Propandiol und Carbonsäuren umfaßt.

10. Waschmittelzusammensetzung nach mindestens einem der vorangehenden Ansprüche, welche einen pH im Bereich von 6 bis 10 aufweist.

Revendications

1. Composition détergente liquide comprenant des ingrédients détergents classiques et un système d'enzymes comprenant une lipase dérivée de "Humicola lanuginosa" et une protéase sérine bactérienne modifiée de telle sorte que la méthionine contiguë à la sérine du site actif dans la séquence d'amino-acide a été remplacée par un autre amino-acide.

2. Composition détergente liquide selon la revendication 1, dans laquelle la protéase sérine bactérienne est dérivée du Bacillus subtilis, et a la méthionine en position 222 de la séquence d'amino-acide remplacée par un autre amino-acide.

3. Composition détergente selon la revendication 1, qui comprend une lipase en quantité telle que l'on obtient de 0,1 à 10 000 unités lipolytiques par gramme de produit fini.

4. Composition détergente selon la revendication 1, qui comprend une protéase, en quantité telle que l'on obtient de 0,005 à 10 mg de protéase active par gramme de produit fini.

5. Composition détergente selon la revendication 1, dans laquelle la protéase sérine bactérienne modifiée est modifiée en substituant la cystéine à ladite méthionine.

6. Composition détergente selon l'une quelconque des revendications précédentes qui comprend de plus une amylase.

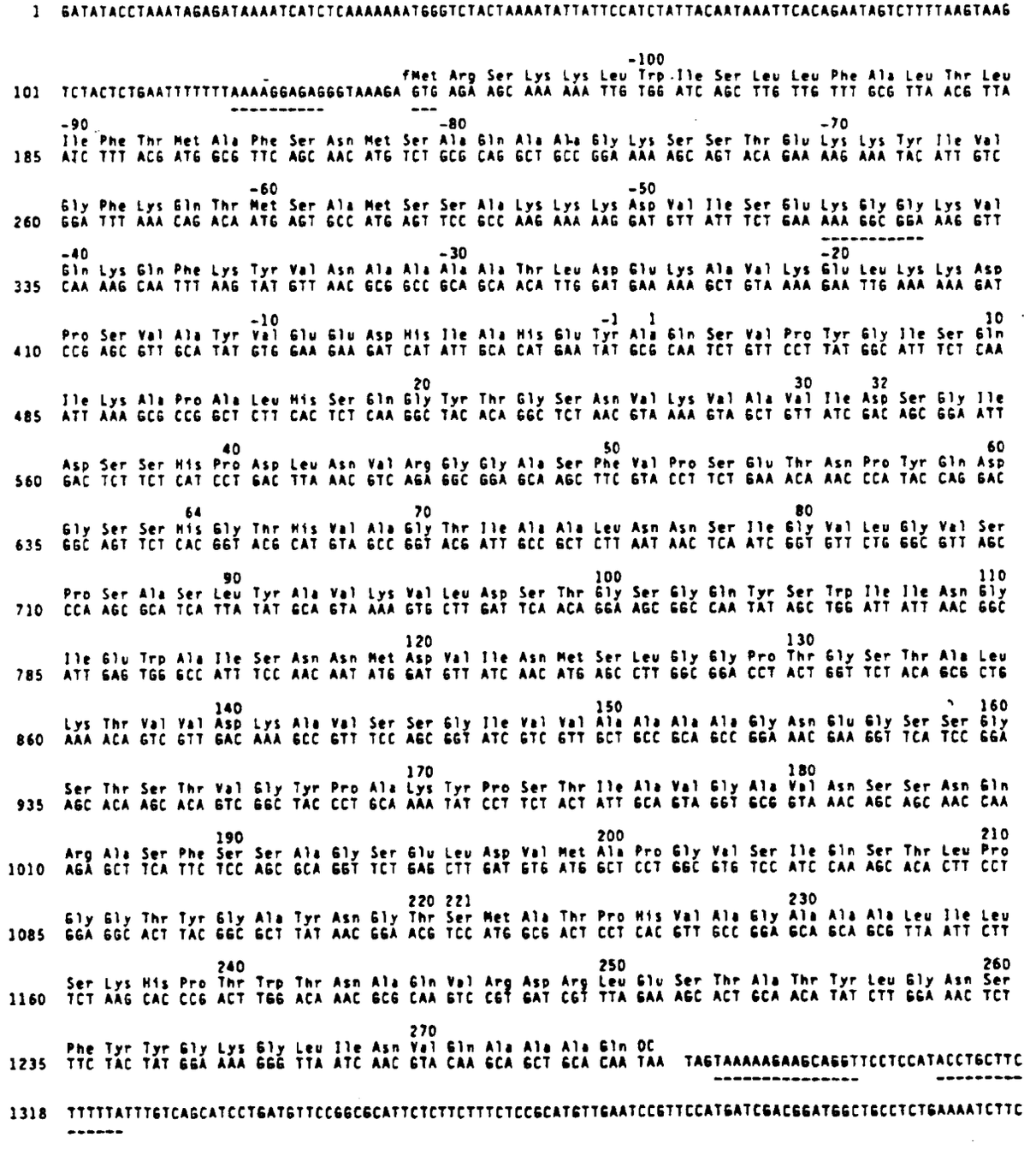
7. Composition détergente selon l'une quelconque des revendications précédentes qui comprend, de plus, un système de stabilisation d'enzymes.

8. Composition détergente selon la revendication 7, dans laquelle le système de stabilisation d'enzymes comprend de 0,01% à 5% en poids de la composition totale d'acide borique.

9. Composition détergente selon la revendication 7, dans laquelle le système de stabilisation d'enzymes comprend au moins un des composés du groupe formé par le 1,2-propane diol et les acides carboxyliques.

10. Composition détergente selon l'une quelconque des revendications précédentes, qui a un pH dans la gamme de 6 à 10.

FIGURE 1


1 GATATACCTAAATAGAGATAAAATCATCTCAAAAAAATGGGTCTACTAAAATATTATTCCATCTATTACAATAAATTCACAGAATAGTCTTTTAAGTAAG
-100
fMet Arg Ser Lys Lys Leu Trp Ile Ser Leu Leu Phe Ala Leu Thr Leu
101 TCTACTCTGAATTTTTTTAAAAGGAGAGGGTAAAGA GTG AGA AGC AAA AAA TTG TGG ATC AGC TTG TTG TTT GCG TTA ACG TTA
-90 -80 -70
Ile Phe Thr Met Ala Phe Ser Asn Met Ser Ala Gln Ala Ala Gly Lys Ser Ser Thr Glu Lys Lys Tyr Ile Val
185 ATC TTT ACG ATG GCG TTC AGC AAC ATG TCT GCG CAG GCT GCC GGA AAA AGC AGT ACA GAA AAG AAA TAC ATT GTC
-60 -50
Gly Phe Lys Gln Thr Met Ser Ala Met Ser Ser Ala Lys Lys Lys Asp Val Ile Ser Glu Lys Gly Gly Lys Val
260 GGA TTT AAA CAG ACA ATG AGT GCC ATG AGT TCC GCC AAG AAA AAG GAT GTT ATT TCT GAA AAA GGC GGA AAG GTT
-40 -30 -20
Gln Lys Gln Phe Lys Tyr Val Asn Ala Ala Ala Ala Thr Leu Asp Glu Lys Ala Val Lys Glu Leu Lys Lys Asp
335 CAA AAG CAA TTT AAG TAT GTT AAC GCG GCC GCA GCA ACA TTG GAT GAA AAA GCT GTA AAA GAA TTG AAA AAA GAT
-10 -1 1 10
Pro Ser Val Ala Tyr Val Glu Glu Asp His Ile Ala His Glu Tyr Ala Gln Ser Val Pro Tyr Gly Ile Ser Gln
410 CCG AGC GTT GCA TAT GTG GAA GAA GAT CAT ATT GCA CAT GAA TAT GCG CAA TCT GTT CCT TAT GGC ATT TCT CAA
20 30 32
Ile Lys Ala Pro Ala Leu His Ser Gln Gly Tyr Thr Gly Ser Asn Val Lys Val Ala Val Ile Asp Ser Gly Ile
485 ATT AAA GCG CCG GCT CTT CAC TCT CAA GGC TAC ACA GGC TCT AAC GTA AAA GTA GCT GTT ATC GAC AGC GGA ATT
40 50 60
Asp Ser Ser His Pro Asp Leu Asn Val Arg Gly Gly Ala Ser Phe Val Pro Ser Glu Thr Asn Pro Tyr Gln Asp
560 GAC TCT TCT CAT CCT GAC TTA AAC GTC AGA GGC GGA GCA AGC TTC GTA CCT TCT GAA ACA AAC CCA TAC CAG GAC
64 70 80
Gly Ser Ser His Gly Thr His Val Ala Gly Thr Ile Ala Ala Leu Asn Asn Ser Ile Gly Val Leu Gly Val Ser
635 GGC AGT TCT CAC GGT ACG CAT GTA GCC GGT ACG ATT GCC GCT CTT AAT AAC TCA ATC GGT GTT CTG GGC GTT AGC
90 100 110
Pro Ser Ala Ser Leu Tyr Ala Val Lys Val Leu Asp Ser Thr Gly Ser Gly Gln Tyr Ser Trp Ile Ile Asn Gly
710 CCA AGC GCA TCA TTA TAT GCA GTA AAA GTG CTT GAT TCA ACA GGA AGC GGC CAA TAT AGC TGG ATT ATT AAC GGC
120 130
Ile Glu Trp Ala Ile Ser Asn Asn Met Asp Val Ile Asn Met Ser Leu Gly Gly Pro Thr Gly Ser Thr Ala Leu
785 ATT GAG TGG GCC ATT TCC AAC AAT ATG GAT GTT ATC AAC ATG AGC CTT GGC GGA CCT ACT GGT TCT ACA GCG CTG
140 150 160
Lys Thr Val Val Asp Lys Ala Val Ser Ser Gly Ile Val Val Ala Ala Ala Ala Gly Asn Glu Gly Ser Ser Gly
860 AAA ACA GTC GTT GAC AAA GCC GTT TCC AGC GGT ATC GTC GTT GCT GCC GCA GCC GGA AAC GAA GGT TCA TCC GGA
170 180
Ser Thr Ser Thr Val Gly Tyr Pro Ala Lys Tyr Pro Ser Thr Ile Ala Val Gly Ala Val Asn Ser Ser Asn Gln
935 AGC ACA AGC ACA GTC GGC TAC CCT GCA AAA TAT CCT TCT ACT ATT GCA GTA GGT GCG GTA AAC AGC AGC AAC CAA
190 200 210
Arg Ala Ser Phe Ser Ser Ala Gly Ser Glu Leu Asp Val Met Ala Pro Gly Val Ser Ile Gln Ser Thr Leu Pro
1010 AGA GCT TCA TTC TCC AGC GCA GGT TCT GAG CTT GAT GTG ATG GCT CCT GGC GTG TCC ATC CAA AGC ACA CTT CCT
220 221 230
Gly Gly Thr Tyr Gly Ala Tyr Asn Gly Thr Ser Met Ala Thr Pro His Val Ala Gly Ala Ala Ala Leu Ile Leu
1085 GGA GGC ACT TAC GGC GCT TAT AAC GGA ACG TCC ATG GCG ACT CCT CAC GTT GCC GGA GCA GCA GCG TTA ATT CTT
240 250 260
Ser Lys His Pro Thr Trp Thr Asn Ala Gln Val Arg Asp Arg Leu Glu Ser Thr Ala Thr Tyr Leu Gly Asn Ser
1160 TCT AAG CAC CCG ACT TGG ACA AAC GCG CAA GTC CGT GAT CGT TTA GAA AGC ACT GCA ACA TAT CTT GGA AAC TCT
270
Phe Tyr Tyr Gly Lys Gly Leu Ile Asn Val Gln Ala Ala Ala Gln OC
1235 TTC TAC TAT GGA AAA GGG TTA ATC AAC GTA CAA GCA GCT GCA CAA TAA TAGTAAAAAGAAGCAGGTTCCTCCATACCTGCTTC
1318 TTTTTATTTGTCAGCATCCTGATGTTCCGGCGCATTCTCTTCTTTCTCCGCATGTTGAATCCGTTCCATGATCGACGGATGGCTGCCTCTGAAAATCTTC
1418 ACAAGCACCGGAGGATCAACCTGCTCAGCCCCGTCACGGCCAAATCCTGAAACGTTTTAACACTGGCTTCTCTGTTCTCTGTC