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(71) Applicant: **NOVO-NORDISK A/S**
Novo Allé
DK-2880 Bagsvaerd (DK)

BEROL NOBEL NACKA AB
Box 11536
S-100 61 Stockholm (SE)

(72) Inventor: **Aaslyng, Dorrit**
Fyrren 8
D-4000 Roskilde (DK)

Palicka, Jadwiga
Ekbackevägen 26
S-181 46 Lidingö (SE)

(74) Representative: **Schöld, Zaid et al**
Nobel Industries Sweden AB Patent Department Box 11554
S-100 61 Stockholm (SE)

(54) **Stabilized enzymatic liquid detergent.**

(57) Stabilized enzymatic liquid detergent compositions for cleaning a wide range of items including hard surfaces and soft goods such as textiles both for commercial and home use. The detergent compositions comprise a relatively unstable enzyme and certain amphoteric compounds.

EP 0 352 244 A2

Description

STABILIZED ENZYMATIC LIQUID DETERGENT

TECHNICAL FIELD

This invention concerns stabilized enzymatic liquid detergent compositions for cleaning a wide range of items including hard surfaces and soft goods such as textiles both for commercial and home use. More particularly, the invention relates to a stabilized composition comprising a relatively unstable enzyme.

BACKGROUND ART

Liquid enzymatic detergents are well-known in the prior art. The enzymes incorporated in liquid detergents have mostly been Bacillus proteases, but the prior art also suggests that incorporation of enzymes other than Bacillus proteases may be useful, e.g. other enzyme types (such as amylases, lipases and cellulases) as well as enzymes of non-Bacillus origin (e.g. fungal enzymes). A major problem which is encountered with such compositions is that of ensuring a sufficient stability of the enzymes in the compositions during storage.

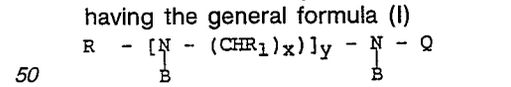
One approach to overcoming this stability problem lies in selecting, from among the available enzymes, one with relatively good stability in conventional liquid detergents. One such enzyme is Esperase(R) (product of Novo-Nordisk A/S), a protease from an alkalophilic Bacillus, prepared according to US 3,723,250. However, other less stable enzymes may be desirable due to economy, washing performance etc. This invention relates to liquid detergents comprising such a relatively unstable enzyme and particularly to improving the stability of the enzyme during storage.

The prior art deals extensively with stabilization of enzymes in liquid detergents. It is known that a number of commonly used detergent ingredients, such as detergent builders, may destabilize enzymes, so enzyme stability can be improved by eliminating these or reducing their amount. The prior art also teaches stabilization of enzymes by incorporation of various compounds that are not detergent active. JP-A 57-158,718 discloses enzyme stabilization in toothpaste by addition of dimethyl alkyl betaine.

It is the object of this invention to provide a liquid detergent composition comprising a relatively unstable enzyme having improved enzyme stability during storage without the need for incorporating detergent-inactive materials. The amphoteric compounds which are used for enzyme stabilization in detergents according to the present invention are advantageous in comparison with alkyl betaines in that they in addition to the enzyme stabilization effect have very good washing performance in combination with nonionic tensides. They also give a fabric softening and bactericidal effect.

STATEMENT OF THE INVENTION

The object of the invention is achieved by providing a stabilized enzymatic liquid detergent composition comprising an effective amount of a microbial enzyme,
said enzyme having less than 30% residual activity when tested by adding the enzyme to a liquid test detergent and storing for 2 weeks at 40° C, said test detergent containing 12% of alcohol ethoxylate (C12/C13 alcohol with an average of 6.5 moles of ethylene oxide), 5% of linear alkylbenzene sulfonate (dodecylbenzene sulfonate), 5% of citric acid and 4% of triethanolamine (% by weight) in water adjusted to a pH of 9.2 with NaOH
said stabilized detergent composition comprising from about 1 to 50% by weight of an amphoteric surfactant having the general formula (I)



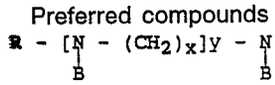
(I)

R is C_7 - C_{22} hydrocarbon group
R_1 is H or C_1 - C_6 alkyl,
X is 2 or 3,
y is 1 to 4
Q is (R_2 COOM) where
R_2 is C_1 - C_6 alkylene and
M is H, an alkali metal, alkaline earth metal, and ammonium or substituted ammonium ion,
and B is hydrogen or has the same meaning as Q.

The group R is, as said above, a hydrocarbon group with 7 to 22 carbon atoms, suitably 12 to 22 and preferably 12 to 20. The hydrocarbon group can be straight or branched, saturated or unsaturated and optionally contain substituents such as hydroxyl or carboxyl groups. The group R may also contain one or several, up to about 20, ethylene oxide groups. The group R is preferably an alkyl or alkenyl group but may also be a cycloalkyl-alkyl group, an aralkyl or aralkenyl group wherein the alkyl or alkenyl group contains at least 6

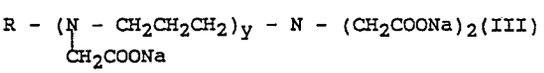
carbon atoms. It is preferred that R is a hydrocarbon group originating from coconut, tallow or oleic fatty acid.

Preferred compounds of formula (I) have the formula (II):



where Q is CH_2-COOM or CH_2CH_2-COOM,
y is 1, 2 or 3, and
where M, R, x and B are as indicated above. Preferably all groups B are groups Q.

Particularly preferred compounds of formula (II) have the formula (III):



where R is defined as above, and y is 1, 2 or 3. Mixtures of compounds having different values for y of above formulae II and III respectively are also preferred. R in these compounds preferably originates from tallow acid.

According to the invention, enzyme stabilization is obtained by incorporation of a certain type of amphoteric surfactant that is itself detergent active. Thus, the incorporation of non-active material solely for the purpose of enzyme stabilization can be avoided or reduced.

Amphoteric compounds of the type disclosed above as well as their use in detergents are previously known and reference is made to European patent applications 160507, 162600 and 214868 and to 2nd Word Surfactants Congress, Paris, 24-27 May 1988, Proceedings pp. 449-475, J. Palicka. These references disclose the amphoteric compounds and their general bactericidal, detergent properties etc and their use together with various additives such as other surfactants, bleaching agents, enzymes, builders, foaming agents etc.

DETAILED DESCRIPTION OF THE INVENTION

Microbial enzyme

The enzyme used in the composition of the invention is relatively unstable in the sense that it retains less than 30% of its activity after two weeks storage at 37° C in a test detergent of specified composition (detergent C-LAS of example I). Microbial enzymes suitable for the present compositions include proteases, lipases, amylases and cellulases. The enzymes are derived from microbial sources, such as Bacillus and fungi. Some specific examples of detergent enzymes follow, each identified by enzyme type, microbial source and reference to a commercial product and/or a patent publication:

- Protease of Bacillus, especially from B. licheniformis (e.g. Alcalase(R) and from alkalophilic Bacillus strains according to US 3,723,250 (e.g. Savinas(R)) (both available from Novo Industri A/S)
- Alpha-amylase of Bacillus, especially B. licheniformis. Termamyl(R) (Novo Industri A/S).
- Protease of Fusarium, especially F. oxysporum, US 3,652,399 (Takeda), PCT/DK 89/00001.
- Cellulase of Humicola, especially H. insolens. Celluzyme(R) (Novo Industri A/S), US 4,435,307 (Novo).
- Lipase of Humicola, especially H. lanuginosa. Lipolase(R) (Novo), EP 305,216 (Novo) and US 4,810,414 (Novo).

The detergent of the invention may contain two or more detergent enzymes. Examples are combinations of any two of the above enzymes, especially combinations of a Bacillus protease and any one of the above enzymes.

Other surfactants

The detergent composition of the invention will usually also contain a nonionic surfactant, e.g. about 3-20% by weight. Further, the composition may optionally contain anionic surfactant and/or a second amphoteric surfactant, e.g. about 3-15% by weight. It may be preferable that the composition is essentially free of anionic surfactant, as this may destabilize some enzymes.

Examples of suitable surfactants are:

- Nonionics: Nonyl phenol ethoxylate, alcohol ethoxylate.
- Anionics: linear alkylbenzene sulfonate, secondary alkane sulfonate, alcohol ethoxylate sulfate, alpha olefin sulfonate.
- 2nd amphoteric: Iminodipropionate (e.g. Ampholak YCE, available from Berol Nobel Nacka AB, Sweden), iminopropionate and ampho carboxyglycinate (e.g. Ampholak XCO-30)

Other ingredients

The liquid detergent of the invention may be aqueous, e.g. containing 20-70% of water and 0-20% of solvent, or containing 1-20% of water and 5-25% of solvent. Satisfactory enzyme stability may be obtained even at water contents above 50%. Alternatively, it may be essentially free of water (e.g. water content below 1%), and will then typically contain 10-30% of solvent.

Typical solvents are mono- and divalent lower alcohols and glycol ethers.

The detergent composition of the invention may be built (i.e. comprising a detergent builder) or unbuilt (i.e. essentially free of a detergent builder). Enzyme stability is generally better in an unbuilt composition, but it may

be desired to include a builder for improved detergency. A built composition typically contains about 1-40%, by weight, of a builder such as zeolite, phosphate, phosphonate, citrate, NTA, EDTA or DTPA.

A soluble calcium salt is preferably included in an amount giving about 1-20 μ-mol/l as Ca, as calcium stabilizes many detergent enzymes. pH will typically be neutral or alkaline, particularly preferred between 8-10.

The compositions may also contain, depending on the intended use, additives such as fabric conditioner (e.g. quaternary ammonium salts, typically 1-5%), foam boosters (e.g. 1-5%), bactericides (e.g. 1-5%), optical brighteners (eg 0.1-1%), dyes e.g. 0.1-1%) and perfumes (eg 0.1-1%).

EXAMPLE I

Samples of essentially unbuilt and zeolite-built liquid detergents with various water content were prepared with the following general composition (% by weight, as active material):

Detergent	B	BI	ZI	C
Water	54.9%	64.9%	65.6%	65.1%
Triethanolamine	10	8	2.8	3.7
Fatty acid (C12-C14)	7	5.6	-	-
Ethanol	5	4	-	3.0
Polyacrylate	-	-	0.7	-
Propylene glycol	5	3	0.7	-
Zeolite S	-	-	18.9	-
Phosphonate (60%)	2	1.6	-	1.6
$CaCl_2 \cdot 2H_2O$	0.1	0.1	0.1	-
Citric acid	-	-	-	5.0
NaOH	-	-	-	2.4
Diethyleneglycol monoethylether	-	-	-	3.0
Nonionic surfactant	10	8	7	12.0
Anionic/amphoteric surfactant	6	4.8	4.2	4.8
	100%	100%	100%	100%
pH, adjusted to	9.0	9.0	9.0	9.2

The polyacrylate was Alcosperse 409, and the phosponate was Dequest 2006. The non-ionic surfactant was alcohol ethoxylate; for detergents B, BI and Z it consisted of the following Dobanol types (Shell): 25-9, 23-6.5 and 23-3 in the ratio 3:1:1, and for detergent C it consisted of Dobanol 23-6.5 only.

The anionic/amphoteric surfactant in each formulation was one of the following:

Reference:
- LAS (anionic), linear dodecylbenzene sulfonate, Sulfosoft (Berol)
- SAS (anionic), secondary alkane (C12) sulfonate, Hostapur SAS 60 (Hoechst)
- AES (anionic), alcohol ethoxylate sulfate (C12/C15 alcohol with 3 ethoxysulfate groups), Dobanol 25-3S (Shell)
- AOS (anionic), alpha olefin sulfonate (Ethyl corp.)

Invention:
- Ampholak 7TX (amphoteric of invention mixture of compounds of formula III with different values for y)
- 7TX + LAS, ratio 2:1
- 7TX + Ampholak YCE (2nd amphoteric), in the ratio 3:1

One of the following enzymes was added to each detergent sample:
- 1% of Savinase 8.0L (alkalophilic Bacillus protease)
- 1.5% of Celluzyme (Humicola cellulase)
- 0.5% of Lipolase(R) 100L (fungal lipase).

The samples were stored at 37°C for two weeks, the enzyme activity was measured before and after storage, and the results were expressed as residual activity in % of initial activity:

	Reference				Invention		
% residual activity	LAS	SAS	AES	AOS	7TX	LAS+7TX	7TX+YCE
Det.B:							
Savinase	60	67	71	70	91	61	
Alcalase	5		15		21	22	
Celluzyme	45	47	55	56	80	67	
Lipolase	53				79		
Det. BI:							
Alcalase	6				31		
Savinase	36	40	45	45	83	81	51
Celluzyme	52	59	51	63	73	66	74
Det.ZI:							
Savinase	9	20	5	6	26	21	29
Det.C:							
Alcalase	7				22		
Savinase	10				63		
Celluzyme	24				57		

For all formulations tried, it is seen that complete substitution of anionic with amphoteric surfactant according to the invention improves the storage stability of the enzyme.

EXAMPLE II

Washing tests were made with three different detergents of formulation BI of Example I, containing 0.5% (by weight) of Savinase 8.0L (alkalophilic Bacillus protease). The tests were made with freshly prepared detergent, and with detergent after two weeks storage at 37° C. The anionic/surfactant in each of the three detergents was as follows:

Reference: LAS (anionic).

Invention: Ampholak 7TX (amphoteric), 7TX+LAS (2:1).

The following standard soiled fabrics (available from Eidgenössische Material-Prüfungs-Anstalt, St. Gallen, Switzerland) were used:

EMPA 116, cotton soiled with blood, milk and ink.

EMPA 112, cotton soiled with cocoa, milk and sugar.

EMPA 117, polyester/cotton soiled with milk and ink.

The washing conditions were as follows:

Machine: Cylinda 9500 (frontloaded)

Program: Main wash 60° C

Number of washing cycles: 3

Water: 5 l

Detergent dosage: 5 ml/l

Water hardness: 5 °dH (degrees German hardness)

Wash load: 1 kg clean fabrics + 40x40 cm test fabric

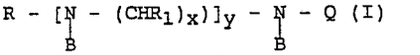
Light reflectance was measured on washed fabric (W), soiled fabric (S) and clean fabric (C), and % detergency was calculated as (W-S)/(C-S). Finally, the % retention of detergency was calculated from detergency before and after storage. Results:

	LAS	7TX	7TX+LAS
EMPA 116			
Detergency before storage	36.6	43.4	38.6
Detergency after storage	7.6	37.3	24.7
% retention	20.8	85.9	64.1
EMPA 112			
Detergency before storage	46.9	38.8	44.7
Detergency after storage	28.6	34.4	36.3
% retention	60.9	88.4	81.2
EMPA 117			
Detergency before storage	64.0	66.0	69.3
Detergency after storage	16.3	57.0	22.7
% retention	25.5	86.3	32.7

It is seen that on each of the three test fabrics, detergents according to the invention (columns 2 and 3) show clearly improved detergency after storage and retention of detergency. Particularly, the detergent with complete substitution of anionic surfactant with amphoteric according to the invention (column 2) shows a remarkable retention of detergency: better than 85% on each test fabric.

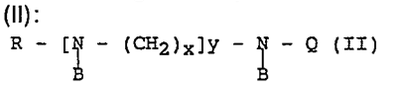
Claims

1. A stabilized enzymatic liquid detergent composition, characterized in that it comprises an effective amount of a microbial enzyme, said enzyme having less than 30% residual activity when tested by adding the enzyme to a liquid test detergent and storing for 2 weeks at 40° C, said test detergent containing 12% of alcohol ethoxylate, 5% of linear alkylbenzene sulfonate, 5% of citric acid and 4% of triethanolamine (% by weight) in water at a pH of 9.2, said stabilized detergent composition being characterized by comprising from about 1 to 50% by weight of an amphoteric surfactant having the general formula (I)



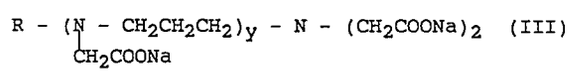
wherein R is a C_7 - C_{22} hydrocarbon group, R_1 is H or C_1-C_6 alkyl, X is 2 or 3, y is 1 to 4, and Q is (R_2 COOM) where R_2 is C_1 - C_6 alkylene, M is H, an alkali metal, alkaline earth metal, ammonium or substituted ammonium ion and B is hydrogen or has the same meaning as Q.

2. A detergent composition according to Claim 1, wherein said amphoteric surfactant has the formula (II):



where Q is CH_2-COOM or CH_2CH_2-COOM, y is 1, 2 or 3, and where M, R, x and B are as indicated in claim 1.

3. A detergent composition according to Claim 1, wherein said amphoteric surfactant has the formula (III):



where R is defined as above, and y is 1, 2 or 3.

4. A detergent composition according to any of claims 1-3 wherein the enzyme is a Bacillus enzyme, preferably a protease, an amylase or a cellulase.

5. A detergent composition according to any of Claims 1-3 wherein the enzyme is a fungal detergent

enzyme, preferably a protease, a lipase or a cellulase.

6. A detergent composition according to Claim 5, wherein the enzyme is a Fusarium protease, a Humicola lipase or a Humicola cellulase.

7. A detergent composition according to any of Claims 1-6 further containing an effective amount of a second microbial enzyme.

8. A detergent composition according to any of Claims 1-7 containing from about 3 to 40% by weight of said amphoteric surfactant.

9. A detergent composition according to any of Claims 1 - 8, further containing from about 1 to 20% by weight of a nonionic surfactant.

10. A detergent composition according to Claims 1 - 9 further containing from about 1 to 20% by weight of an anionic and/or a second amphoteric surfactant.

11. A detergent composition according to Claims 1-10, which is substantially free of a anionic surfactant.

12. A detergent composition according to Claims 1-11 further containing from about 20 to 70% by weight of water and from 0 to about 20% by weight of a solvent.

13. A detergent composition according to Claims 1-11 which contains from about 10 to 30% of a solvent, and is essentially free of water.

14. A detergent composition according to Claims 1-13 which is substantially free of a detergent builder.

15. A detergent composition according to Claims 1 -13 containing from about 1 to 40% by weight of a detergent builder.

16. A detergent composition according to Claims 1-15, containing a soluble calcium salt in an amount giving from about 1 to 20 millimoles of calcium per liter.