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Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)
Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)

72

Inventor: **Hora, Jiri**
De Nolle 3
NL-3237 KA Vierpolders(NL)

74

Representative: **Van Gent, Jan Paulus et al**
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

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Enzymatic detergent composition.

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The invention pertains to detergent compositions which comprise a peroxy-type bleaching agent, other than an alkali metal percarbonate, and enzymes. By inclusion of an alkali metal metaborate in such compositions, preferably affixed to the surface of the particulate peroxy-type bleaching agent, the storage stability of the enzymes in the compositions is significantly improved.

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ENZYMATIC DETERGENT COMPOSITION

The present invention relates to enzymatic detergent compositions with improved enzyme-storage stability. More particularly, the invention relates to a detergent composition which contains a bleaching agent, in addition to the enzymes, with improved enzyme-storage stability.

It is well-known in the detergent art that the inclusion of enzymes and bleaching agents in a detergent composition may give rise to enzyme-stability problems. Without precautionary measures, the enzymes may be negatively affected by the bleaching agent, resulting in a decrease of the enzymatic activity. Numerous proposals have already been made in the prior art to stabilize the enzymes in such bleach-containing detergent compositions, such as coating the enzymes and/or the bleaching agent with a protective coating or adding specific stabilizing agents to the composition.

Recently it has been proposed in German Patent Application 3321082, laid open to public inspection on 15 December 1983, to improve the storage stability of sodium percarbonate in a detergent composition by coating the sodium percarbonate with a coating which contains a borate, such as sodium tetraborate (either the anhydrous salt or the different hydrates thereof), sodium octaborate, sodium pentaborate and sodium metaborate. The sodium metaborate-dihydrate and -tetrahydrate are preferred.

These compositions may also contain enzymes and it is stated that such enzyme-containing detergent compositions have an improved enzyme-storage stability.

We have now surprisingly found that the storage stability of enzymes in detergent compositions which contain other peroxy-type bleaching agents can be improved by inclusion in such compositions of sodium metaborate. Whereas in the above discussed reference sodium perborate is stated and shown to be much more stable than uncoated sodium percarbonate and as stable as coated sodium percarbonate, it is unexpected that the addition of sodium metaborate according to our invention to other peroxy-type bleaching agents increases the enzyme stability even more.

In addition, whereas the above reference advocates the use of various borates, we have found that in our compositions only alkali metal metaborates are effective as enzyme storage stability improving agents.

The present invention therefore relates to an enzymatic detergent composition which comprises a peroxy-type bleaching agent other than an alkali metal percarbonate, and enzymes, the storage stability of which is improved by the inclusion in the composition of an alkali metal metaborate.

The invention will hereafter be discussed in further detail.

The first essential ingredient is a bleaching agent of the peroxy-type other than alkali metal percarbonate. Typical examples of such peroxy-type bleaching agents are alkali metal persulphates, -perphosphates, -perborates, alkali metal and alkaline earth metal salts of organic peracids, such as perphthalic acid, mono- and diperoxy azelaic acid, peroxy acetic acid, diperdodecane dioic acid and so on.

The preferred peroxy-type bleaching agents are those which have, under the same storage conditions, a better storage stability in terms of available oxygen than percarbonate. A particularly preferred bleaching agent is sodium perborate, both in its tetrahydrate as well as in its monohydrate form. In general the amount of peroxy-type bleaching agent in the compositions of the invention ranges from

1-40%, preferably 3-35%, and particularly preferably from 5-30% by weight. The compositions of the invention may in this respect also contain bleach precursors, such as tetraacetyl ethylene diamine, tetraacetyl glycoluril, glucose pentaacetate and so on, to provide with the peroxy-type bleaching agent for a low temperature bleaching detergent composition. Usually the amount of such a bleach precursor ranges from 0.5-20% by weight.

The second essential ingredient is the alkali metal metaborate. Typical suitable examples thereof are sodium and potassium metaborate, either anhydrous or in its various hydrate forms, e.g. K-metaborate. 1.5 aq, Na-metaborate. 2 aq. and .4 aq.

The alkali metal metaborate can be added in powdered form to the compositions of the invention or can be affixed to the surface of the peroxy-type bleaching agent when the latter is used in a particulate form. In this respect it has been found that even better enzyme storage stability results are obtained if the particulate peroxy-type bleaching agent is first treated with a potassium salt having a lower equilibrium humidity than the particulate peroxy-type bleaching agent, followed by a treatment with sodium metaborate. Typical examples of a suitable potassium salt is potassium metaborate. Both the potassium salts and the sodium metaborate are affixed to the particulate peroxy-type bleaching agent in the dry, powdered form. It is also possible to cause formation of the metaborate on the surface of the peroxy-type bleaching agent in situ, e.g. by addition of metaborate-forming substances which react with the peroxy-type bleaching agent, e.g. dimethyl sulfoxide.

In general the alkali metal metaborate is present in the composition in an amount ranging from 0.1 % to 50 %, preferably 0.2 to 30%, and particularly preferably 0.5 to 20% by weight.

The third essential ingredient in the compositions of the invention is an enzyme. Typical examples of enzymes which can be used according to the invention are proteases, amylases, lipases and cellulases as they are usually proposed in the detergent art for inclusion in detergent compositions.

Suitable examples of proteolytic enzymes are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*, such as the commercially available Maxatase [®] (ex Gist-Brocades N.V., Delft, Holland) and Alcalase [®] (ex Novo Industri A/S, Copenhagen, Denmark). Particularly suitable are proteases obtained from a strain of *Bacillus* having maximum activity in the pH-range of 8-12, developed and sold by Novo Industri A/S under the registered trade-names Esperase [®] and Savinase [®]. The preparation of such enzymes is described in British Patent Specification 1,243,784.

Suitable examples of amylolytic enzymes are commercially available amylases, such as Maxamyl [®] (ex Gist-Brocades) and Termamyl [®] (ex Novo Industri A/S). Amylases as described in British Patent Specification 1,296,839 are also suitable.

Typical examples of commercial lipolytic enzymes are e.g. Lipase YL, Amano CE, Wallerstein AW, Lipase MY, and typical examples of cellulolytic enzymes are cellulases ex *Humicola insolens* as described in German Patent Application 3,117,250.

The benefits of the present invention are especially pronounced in amylase-containing formulations. The amount of enzymes present in the compositions of the invention is dictated by the activity of the enzyme preparation used. The

higher this activity, the lower the level of enzymes required. In general the amount will vary between 0.001 and 10% by weight, and for most practical purposes between 0.1 and 5% by weight of the composition.

The compositions of the present invention can furthermore contain other ingredients commonly encountered in bleaching and detergent compositions. Thus they may comprise one or more surfactants in an amount of up to 60%, such as soaps, anionic, nonionic, cationic and/or amphoteric synthetic detergents. In addition they may comprise one or more inorganic and/or organic builder salts, such as the condensed phosphates, silicates, carbonates, nitrilotriacetates and so on, in amounts up to 60% by weight. In this respect it has been found that the benefits of the present invention are particularly pronounced in formulations which contain a phosphate builder salt.

Furthermore, other optional ingredients include soil-suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, optical brighteners, suds-depressants, germicides, anti-tarnishing agents, other enzyme stabilizers, softening agents, sequestering agents, such as the amino polyphosphonic acids, clays and so on.

Thus, a typical formulation for use in machine dishwashing may contain from 20-50% of sodium tripolyphosphate, 2-20% sodium silicate, 0-50% sodium carbonate, 5-25% sodium perborate, amylase plus protease up to 4%, TAED up to 10%, and amino polyphosphonic acid up to 1%.

The compositions of the present invention can be prepared in any suitable particulate form, such as powders, granules, tablets, flakes, ribbons, noodles and the like, and they can be used for fabric washing, hard surface cleaning, dishwashing and general purpose cleaning.

The invention will be further illustrated by way of Example.

EXAMPLE 1

The following dry-mixed formulations were prepared :

	Particulate sodium tri- polyphosphate % by weight	Granular sodium perborate tetrahydrate % by weight	Particulate sodium meta- borate % by weight	Termamyl % by weight
A	86.4	9.6	0	4
B	81.6	9.6	4.8	4
C	76.8	9.6	9.6	4

Termamyl is an amylase according to British Patent 1,296,839, sold by Novo Industri AS.

These products were stored under the conditions as given in the Table below and the residual enzymatic activity (REA) was determined at the end of the storage period. The results were as follows : REA (expressed as % of initial activity) after

	22 days at 30°C in closed con- tainer	2.7 days at 37°C/ 70% RH in open container	5.7 days at 37°C/ 70% RH in open container
A	54.0	19.8	7.7
B	85.9	56.2	32.9
C	89.5		

EXAMPLE 2

% by weight

	Sodium tri- polyphosphate	Sodium per- borate tetrahydrate	Sodium metaborate tetrahydrate	Enzyme
A	88.4	9.6	0	2 SP 227
B	83.6	9.6	4.8	2 SP 227
C	90	9.6	0	0.4 Savinase
D	85.2	9.6	4.8	0.4 Savinase

SP 227 is a cellulase as described in German Patent Application 3,117,250, manufactured by NOVO Industri AS, and Savinase is a protease as described in British Patent 1,243,784, manufactured by NOVO Industri AS.

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These formulations were stored in closed cups at 37°C and the residual enzymatic activity (in %) was measured after the storage period as indicated below. The following results were obtained.

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REA after x days

	x = 12	x = 19	x = 33
A	65	58	49
B	77	73	59
C	77	75	70
D	94	85	76

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EXAMPLE 3

The following formulations were prepared by dry mixing:

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	Sodium tri- polyphosphate	Magnesium mono- peroxy phthalate	Metaborate dihydrate	Termamyl
G	88.4	9.6	0	2
H	81.73	9.6	6.67	2

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After storage for 2.7 days in open containers at 37°C/70% RH, the following residual enzymatic activities were measured :

G 16.9%

H 41.9%

EXAMPLE 4

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The following compositions were prepared by dry mixing:

% by weight

	J	K	L	M	N
Sodium tripolyphosphate	88.4	86.4	83.6	83.6	83.6
Sodium perborate tetrahydrate	9.6	9.6	9.6	9.6	9.6
Termamyl	2	2	2	2	2
Boric acid	-	2	-	-	-
Sodium pentaborate decahydrate	-	-	4.8	-	-
Borax (decahydrate)	-	-	-	4.8	-
Sodium metaborate tetrahydrate	-	-	-	-	4.8

These products were stored for x days in open containers at 37°C/70% RH and in closed containers at 37°C. The residual enzymatic activities were as follows :

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37°C/70% RH	x =	2	5	8	37°C	13	28	35
J		14	4	1		57	47	45
K		4	1	0		29	22	17
L		4	0	0		54	43	39
M		6	3	1		20	17	14
N		65	18	6		69	46	36

EXAMPLE 5

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Compositions were prepared consisting of 2.1% Termamyl, 10% sodium perborate tetrahydrate, alkali metal metaborate as specified in the Table below, and sodium tripolyphosphate up to 100%. The residual enzymatic activity after x days' storage in open containers at 37°C/70% RH was as follows :

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		REA	
Metaborate		x = 3	x = 6
O	-	16	6
P	1.2% K-metaborate. 1.5 H ₂ O	39	23
Q	0.76% Na-metaborate dry	39	19
R	1.11% Na-metaborate. 2 H ₂ O	42	20
S	1.5% Na-metaborate. 4 H ₂ O	36	20

EXAMPLE 6

Granulated sodium perborate (73.92 kg) was mixed in a Lödige mixer at 20°C for one hour with powdered potassium metaborate.1.5 H₂O (2.94 kg). The metaborate melted within the surface of the perborate granules, causing a fluidized surface thereon. Subsequently, powdered dry sodium metaborate (7.14 kg) was added to the mixer, which

15 adhered to the fluidized surface and restored the free-flowing character of the granulate. After sieving and collecting the particles with a diameter of more than 230 micrometer, 79.5 kg of a granulate containing up to 87.3% sodium perborate were obtained.

20 Formulations were made with this granulate, with or without separately added dry sodium disilicate, and these formulations were compared with the same formulations but without the metaborate. The formulations had the following compositions :

	%			
	A	B	C	D
Termamyl	2	2	2	2
Sodium perborate.4H ₂ O	9.2	-	9.6	-
Sodium perborate)	-	9.6	-	9.6
(co-granulate))				
Alkali metal metaborate)	-	1.3	-	1.3
Sodium disilicate	-	-	9.6	9.6
Sodium tripolyphosphate	88.4	87.1	78.8	77.5

The residual enzymatic activity after x days' storage at 30°C/60-65% RH in open containers was as follows :

	x = 0	8	14
A	96	54	34
B	98	74	65
C	98	61	48
D	99	81	69

Claims

1. An enzymatic detergent and bleaching composition comprising enzymes and a peroxy-type bleaching agent, other than an alkali metal percarbonate, and an enzyme-storage stability improving agent, characterised in that the enzyme-storage stability improving agent comprises an alkali metal metaborate. 5

2. A composition according to claim 1, characterised in that the alkali metal metaborate is affixed to the surface of a particulate form of the peroxy-type bleaching agent. 10

3. A composition according to claim 2, characterized in that sodium metaborate is affixed to the surface of a particulate form of the peroxy-type bleaching agent which has first been treated with potassium metaborate. 15

4. A composition according to any one of claims 1 to 3, characterised in that the enzyme is an amylase and the peroxy-type bleaching agent is sodium perborate. 20

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