

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 476 726 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **91201816.5**

(51) Int. Cl.⁵: **C11D 3/386**

(22) Date of filing: **11.07.91**

(30) Priority: **27.07.90 US 559222**

(43) Date of publication of application:
25.03.92 Bulletin 92/13

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

(71) Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)
(84) **CH DE ES FR IT LI NL SE**

(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BO(GB)
(84) **GB**

(72) Inventor: **Kaiserman, Howard Bruce**
Unilever Research US Inc., 45 River Road
Edgewater, NJ 07020(US)
Inventor: **Siuta-Mangano, Patricia**
Unilever Research US Inc., 45 River Road
Edgewater, NJ 07020(US)
Inventor: **van den Bergh, Carlo Johannes**
Unilever Research US Inc., 45 River Road
Edgewater, NJ 07020(US)

(74) Representative: **Kan, Jacob Hendrik, Dr. et al**
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

(54) **Protease-containing liquid detergent compositions.**

(57) The present invention is concerned with the stabilization of proteases in built, aqueous detergent compositions. More particularly, applicants have discovered that propionic acid or a propionic salt capable of forming propionic acid unexpectedly increases stability relative to other stabilizers, e.g., formic acid or acetic acid (or salts thereof), used in these compositions. When the proteolytic enzyme is added in the form of a slurry of the enzyme in liquid nonionic surfactant, a surprising further improvement in stability is obtained.

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TECHNICAL FIELD

This invention relates to the stabilization of proteases in liquid detergent compositions, more in particular built, anionic-rich aqueous detergent compositions.

BACKGROUND AND PRIOR ART

The use of proteases in heavy duty liquid detergent formulations (HDLS) is complicated by their limited stability in solution. Two processes which limit the shelf-life of a protease in an aqueous liquid detergent are denaturation and autolysis (self-digestion). Considerable efforts have been devoted to the stabilization of enzymes in aqueous liquid detergent compositions, which represent a medium that is problematical for the preservation of enzyme activity during storage and distribution.

Denaturation of proteases may be minimized by selection of formulation components (i.e. actives, builders, pH etc.) so that acceptable enzyme stability can be achieved. Self-digestion of proteases may be minimized by inclusion of a protease inhibitor. The inhibitor is released from the enzyme upon dilution in the wash.

Various protease inhibitors are known in the art. For example, US-A-4 261 868 (Unilever) teaches the use of borax as a protease inhibitor and both US-A-4 243 546 (Drackett) and GB-A-1 354 761 (Henkel) teach the use of carboxylic acids as protease inhibitors. Various combinations of these protease inhibitors are also known in the art. US-A-4 305 837 (Procter & Gamble), for example, teaches the combination of carboxylic acids and simple alcohols and US-A-4 404 115 (Unilever) teaches the combination of borax and polyols as protease inhibitors. US-A-4 537 707 (Procter & Gamble) teaches the combination of borax and carboxylates as protease inhibitors.

As mentioned above, the use of carboxylates in detergent compositions as protease inhibitors is known. US-A-4 318 818, for example, teaches stabilized, liquid enzyme compositions in which the inhibitor is a short chain length carboxylic acid salt selected from the group consisting of formates, acetates, propionates and mixtures thereof. This patent teaches that formates are surprisingly much more effective than other short chain salts such as acetates and propionates. The reference also teaches that at a pH range above 8.5, only formates can be used. The detergent compositions used in this patent are unbuilt, i.e., contain no builders.

US-A-4 243 546 (Drackett) teaches aqueous enzyme compositions wherein the enzyme stabilizer is selected from the group consisting of mono and diacids having from 1 to 18 carbon atoms. Acetic acid is said to be preferred. Compositions of the invention are also unbuilt. The patent seems to be primarily directed to compositions having a pH below 8 (most of the examples have a pH of 7.5) and the one example which has a pH of 9.5 appears to require the presence of alcohol (ethanol). In addition, the composition not only are not anionic rich, but appear to comprise no anionics at all.

GB-A-1 354 761 (Henkel) teaches compositions which may contain 2 to 8 carbon carboxylic acids. All the examples show use of acetic acid and the detergent compositions of the invention are also unbuilt.

Thus, where carboxylic acid stabilizers are used in the prior art, there is a preference for 1 or 2 carbon carboxylic acids (acetate and formate). When compositions of high pH (i.e. greater than 8.5) are used in the prior art, either the use of formate is dictated (as in US-A-4 318 818) or the carboxylic acid is used in combination with an alcohol or in an environment which is not anionic rich. The compositions of the prior art are also unbuilt and there appears to be no recognition of the importance of using anionic rich compositions with specific stabilizers.

Existing aqueous enzymatic liquid laundry detergents are commonly formulated using as additive a stabilized aqueous liquid enzyme concentrate. In his article in Tenside 27(1), p.30 (1990), G. Jensen describes the difficulty of formulating built liquid detergent compositions comprising proteolytic enzymes. Such products are said to require a special type of enzyme in order to obtain a satisfactory storage stability. The normal liquid enzymes (i.e. aqueous concentrates and non-aqueous slurries) are losing their activity too fast due to denaturation of enzyme protein structure by the alkaline ingredients and sequestering agent present in the composition. To solve this problem, the author believes it is necessary to use a protected enzyme system comprising a dispersion of the enzyme in a silicone matrix, so-called silicone slurries. An example is given of a liquid detergent product comprising a phosphate-builder and a proteolytic enzyme in the form of a slurry, which indeed shows a poor enzyme stability.

Unexpectedly, applicants have discovered that, when the detergent composition is a built, preferably anionic rich composition having a pH greater than 7.0, preferably greater than 8.5 and more preferably 9.0 and above, enzyme stability is enhanced relative to other carboxylic acid stabilizers (i.e. acetate or formate) by the use of propionate rather than acetate or formate.

Furthermore, it has surprisingly been found that improved stability of enzyme can be achieved in aqueous liquid detergent concentrates when the enzyme is added to the formulation as a slurry of the enzyme in a nonionic detergent which is normally liquid.

5 DEFINITION OF THE INVENTION

Accordingly, the present invention provides a stable, aqueous enzymatic detergent composition comprising:

- (a) from about 5 to about 65% by weight of a surfactant;
 - 10 (b) from about 0.5 to about 50% by weight of a builder;
 - (c) a protease enzyme added in sufficient quantity to have an activity level of 0.01 to 200,000 GU/gm;
 - (d) from about 0.1 to about 15% by weight propionic acid or a propionic acid salt capable of forming propionic acid;
- the remainder being water and minor ingredients;
- 15 wherein the pH of the composition is greater than 7.0. Preferably, the pH of the composition is greater than 8.5, more preferably 9.0 and above.

The invention also provides a process for preparing such aqueous liquid enzymatic detergent compositions, wherein the proteolytic enzyme is preferably added in the form of a slurry of the enzyme in liquid nonionic surfactant.

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DETAILED DESCRIPTION OF THE INVENTION

Detergent Active

- 25 The compositions of the invention comprise from about 5% to about 65% by weight of (a) anionic surfactant or (b) anionic surfactant and one or more detergent actives wherein the ratio of anionic to non-anionic by weight is greater than 1:1.

- The detergent active material other than anionic surfactant may be an alkali metal or alkanolamine soap or a 10 to 24 carbon atom fatty acid, including polymerized fatty acids, or a nonionic, cationic, zwitterionic or amphoteric synthetic detergent material, or mixtures of any of these.
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- Examples of the anionic synthetic detergents are salts (including sodium, potassium, ammonium and substituted ammonium salts such as mono-, di- and triethanolamine salts of 9 to 20 carbon alkylbenzenesulphonates, 8 to 22 carbon primary or secondary alkanesulphonates, 8 to 24 carbon olefinsulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in GB-A-1 082 179, 8 to 22 carbon alkylsulphates, 8 to 24 carbon alkylpolyglycoether-sulphates, -carboxylates and -phosphates (containing up to 10 moles of ethylene oxide); further examples are described in "Surface Active Agents and Detergents" (Vol. I and II) by Schwartz, Perry and Berch. Any suitable anionic may be used and the examples are not intended to be limiting in any way.
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- 40 Examples of nonionic synthetic detergents which may be used with the invention are the condensation products of ethylene oxide, propylene oxide and/or butylene oxide with 8 to 18 carbon alkylphenols, 8 to 18 carbon primary or secondary aliphatic alcohols, 8 to 18 carbon fatty acid amides; further examples of nonionics include tertiary amine oxides with one 8 to 18 carbon alkyl chain and two 1 to 3 carbon alkyl chains. The above reference also describes further examples of nonionics.

- 45 The average number of moles of ethylene oxide and/or propylene oxide present in the above nonionics varies from 1-30; mixtures of various nonionics, including mixtures of nonionics with a lower and a higher degree of alkoxylation, may also be used. Preferred are ethoxylated C12-C15 fatty alcohols having 3-9 EO-groups, 5-7 EO-groups being especially preferred.

- Examples of cationic detergents are the quaternary ammonium compounds such as alkyldimethylammonium halogenides.
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- Examples of amphoteric or zwitterionic detergents which may be used with the invention are N-alkylamino acids, sulphobetaines, condensation products of fatty acids with protein hydrolysates; but owing to their relatively high costs they are usually used in combination with an anionic or a nonionic detergent. Mixtures of the various types of active detergents may also be used, and preference is given to mixtures of an anionic and a nonionic detergent active. Soaps (in the form of their sodium, potassium and substituted ammonium salts) of fatty acids may also be used, preferably in conjunction with an anionic and/or nonionic synthetic detergent.
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Among the compositions of the present invention are aqueous liquid detergents having for example a

homogeneous physical character, e.g. they can consist of a micellar solution of surfactants in a continuous aqueous phase, so-called isotropic liquids.

Alternatively, they can have a heterogeneous physical phase and they can be structured, for example they can consist of a dispersion of lamellar droplets in a continuous aqueous phase, for example comprising a deflocculating polymer having a hydrophilic backbone and at least one hydrophobic side chain, as described in EP-A-346 995 (Unilever) (incorporated herein by reference). These latter liquids are heterogeneous and may contain suspended solid particles such as particles of builder materials e.g. of the kinds mentioned below.

Builders

Builders which can be used according to this invention include conventional alkaline detergency builders, inorganic or organic, which can be used at levels from about 0.5% to about 50% by weight of the composition, preferably from 3% to about 35% by weight. More particularly, when non-structured compositions are used, preferred amounts of builder are 3 to 10% and when structured compositions are used, preferred amounts of builder are 5%-35% by weight.

By structured liquid composition is meant a composition in which at least some of the detergent active forms a structured phase. Preferably such structured phase is capable of suspending a solid particulate material.

More particularly, when a structured liquid is contemplated, the composition requires sufficient electrolyte to cause the formation of a lamellar phase by the surfactant to endow solid suspending capability. The selection of the particular type(s) and amount of electrolyte to bring this into being for a given choice of surfactant is effected using methodology very well known to those skilled in the art. It utilizes the particular techniques described in a wide variety of references. One such technique entails conductivity measurements. The detection of the presence of such a lamellar phase is also very well known and may be effected by, for example, optical and electron microscopy or X-ray diffraction, supported by conductivity measurement.

As used herein, the term electrolyte means any water-soluble salt. The amount of electrolyte should be sufficient to cause formation of a lamellar phase by the surfactant to endow solid suspending capability. Preferably, the composition comprises at least 1.0% by weight, more preferably at least 5.0% by weight, most preferably at least 17.0% by weight of electrolyte. The electrolyte may also be a detergency builder, such as the inorganic builder sodium tripolyphosphate, or it may be a non-functional electrolyte such as sodium sulphate or chloride. Preferably, the inorganic builder comprises all or part of the electrolyte.

Such structured compositions are capable of suspending particulate solids, although particularly preferred are those systems where such solids are actually in suspension. The solids may be undissolved electrolyte, the same as or different from the electrolyte in solution, the latter being saturated in electrolyte. Additionally, or alternatively, they may be materials which are substantially insoluble in water alone. Examples of such substantially insoluble materials are aluminosilicate builders and particles of calcite abrasive.

Examples of suitable inorganic alkaline detergency builders which may be used (in structured or unstructured compositions) are water-soluble alkalimetal phosphates, polyphosphates, borates, silicates and also carbonates. Specific examples of such salts are sodium and potassium triphosphates, pyrophosphates, orthophosphates, hexametaphosphates, tetraborates, silicates and carbonates.

Examples of suitable organic alkaline detergency builder salts are: (1) water-soluble amino polycarboxylates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates and N-(2 hydroxyethyl)-nitrilodiacetates; (2) water-soluble salts of phytic acid, e.g., sodium and potassium phytates (see US-A-2 379 942); (3) water-soluble polyphosphonates, including specifically, sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium and lithium salts of methylene diphosphonic acid; sodium, potassium and lithium salts of ethylene diphosphonic acid; and sodium, potassium and lithium salts of ethane-1,1,2-triphosphonic acid. Other examples include the alkali metal salts of ethane-2-carboxy-1,1-diphosphonic acid hydroxymethane diphosphonic acid, carboxyldiphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-2-hydroxy-1,1,2-triphosphonic acid, propane-1,1,3,3-tetrakisphosphonic acid, propane-1,1,2,3-tetrakisphosphonic acid, and propane-1,2,2,3-tetrakisphosphonic acid; (4) water-soluble salts of polycarboxylate polymers and copolymers as described in US-A-3 308 067.

In addition, polycarboxylate builders can be used satisfactorily, including water-soluble salts of mellitic acid, citric acid, and carboxymethyloxysuccinic acid and salts of polymers of itaconic acid and maleic acid.

Certain zeolites or aluminosilicates can be used. One such aluminosilicate which is useful in the compositions of the invention is an amorphous water-insoluble hydrated compound, said amorphous

material being characterized by a Mg^{++} exchange capacity of from about 50 mg eq. $CaCO_3/g$ and a particle diameter of from about 0.01 micron to about 5 microns. This ion-exchange builder is more fully described in GB-A-1 470 250.

A second water-insoluble synthetic aluminosilicate ion exchange material useful herein is crystalline in nature and has the formula $Na_z[(AlO_2)_y.(SiO_2)].xH_2O$, wherein z and y are integers of at least 6; the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264; said aluminosilicate ion exchange material having a particle size diameter from about 0.1 micron to about 100 microns; a calcium ion exchange capacity on an anhydrous basis of at least about 200 milligrams equivalent of $CaCO_3$ hardness per gram; and a calcium exchange rate on an anhydrous basis of at least about 2 grains/gallon/minute/ gram. These synthetic aluminosilicates are more fully described in GB-A-1 429 143.

The Enzymes

The proteolytic enzyme used in the present invention can be of vegetable, animal or microorganism origin. Preferably, it is of the latter origin, which includes yeasts, fungi, moulds and bacteria. Particularly preferred are bacterial subtilisin type proteases, obtained from e.g. particular strains of **B. subtilis** and **B. licheniformis**. Examples of suitable commercially available proteases are Alcalase, Savinase, Esperase, all of NOVO Industri A/S; Maxatase and Maxacal of Gist-Brocades; Kazusase of Showa Denko; Subtilisin BPN' and Subtilisin BPN'-derived proteases and so on.

Genetic engineering of any of the above-mentioned enzymes can be achieved e.g. by extraction of an appropriate gene, and introduction and expression of the gene or derivative thereof in a suitable producer organism. EP-A-130 756 (Genentech), EP-A-214 435 (Henkel), WO 87/04461 (Amgen), WO 87/05050 (Genex), EP-A-405 901 (Unilever) and EP-A-303 761 (Genentech) describe useful modified subtilisin proteases.

The amount of proteolytic enzyme included in the composition ranges from 0.01 to 200,000 GU/g, preferably from 1 to 100,000 GU/g, most preferably from 1000 to 50,000 GU/g, based on the final composition. Naturally, mixtures of different proteolytic enzymes may be used.

A GU is a glycine unit, which is the amount of proteolytic enzyme which under standard incubation conditions produces an amount of terminal NH_2 -groups equivalent to 1 microgramme/ml of glycine.

The proteolytic enzymes are usually added in the form of concentrated aqueous solutions. However, it has now surprisingly been found that even further improved stability of the proteolytic enzymes can be achieved in aqueous liquid detergent concentrates of the invention, when the enzyme is added to the formulation as a slurry of the enzyme in a nonionic detergent which is normally liquid.

As described in our copending European patent application 91200677.2 (incorporated herein by reference), the enzyme slurry contains the enzyme in the dispersed form of e.g. powder or particles suspended in a non-aqueous (nonionic) liquid surfactant, especially one which is substantially anhydrous. The enzyme particles may for example be spray-dried or lyophilized, and can for example be milled after spray-drying and before dispersion in (e.g. anhydrous) nonionic liquid detergent. Alternatively, they may be milled after dispersing the enzyme in the nonionic detergent.

The enzyme level in the slurry can be from about 0.5 to about 50% by weight, e.g. from about 1 to about 20% by weight. Commonly the enzyme slurry which is used in the manufacture of the compositions of the present invention is substantially anhydrous, with water content less than about 10%, preferably less than about 5% w/w, sometimes less than about 1%. Using this slurry technique it is possible to use a practically anhydrous liquid nonionic surfactant as the continuous phase of the slurry. The liquid state of the slurry enables a thorough mixing of the enzyme in the final liquid detergent, and allows easy liberation of the enzyme after dilution of the liquid detergent in the wash liquor.

The compositions of the invention may also contain other enzymes in addition to the proteases of the invention such as lipases, amylases and cellulases. When present, the enzymes may be used in an amount from 0.001% to 5% of the compositions.

Stabilizer

As mentioned above, the stabilizer used according to the subject invention is a propionic acid added neat or propionic acid added as salt at a level of about 0.1 to about 15% of the composition.

It is within the scope of the present invention to incorporate further stabilizing systems for the enzymes, and for this purpose it is possible to use the measures set out in the specifications acknowledged by number above in connection with enzyme stabilization (which are specifically incorporated herein by reference).

There can for example be further included a quantity of an enzyme-stabilizing system e.g. selected from (a) an enzyme-stabilizing system comprising calcium and formate or acetate, and (b) a polyol-and-borate-containing enzyme-stabilizing system.

Polyol at 2-25% w/w, e.g. glycerol or propylene glycol or other polyol, with sodium borate or borax at 2-15% w/w, may be used e.g. in compositions formulated according to EP-A-080 223 (Unilever) (incorporated herein by reference).

In addition or alternatively, low-molecular weight mono carboxylates (in salt or acid form) such as formate or acetate (0.1-10%), enzyme accessible calcium ions (0.1-1 mmole/kg) and lower alcohols e.g. ethanol or propylene glycol (up to 20%), may be used e.g. in compositions formulated according to EP-A-028 865 (Procter & Gamble) (incorporated herein by reference).

It can be quite acceptable to use lesser quantities of these stabilizers than those pointed out by the above-cited specifications.

Calcium Salt

The compositions of the invention may also comprise a calcium salt which is used to provide free calcium ions to the solution. The calcium ions impart stabilization to the enzyme either alone or in combination with the propionate. Examples of calcium salts which may provide free calcium ions to the system include calcium chloride dihydrate and calcium sulphate. The calcium salt may comprise from 0.01 to 1% of the composition, preferably 0.01 to 0.2%, most preferably 0.03 to 0.1%.

Optional Components

In addition to the essential ingredients described hereinbefore, the preferred compositions herein frequently contain a series of optional ingredients which are used for the known functionality in conventional levels. While the inventive compositions are premised on aqueous enzyme-containing detergent compositions, it is frequently desirable to use a phase regulant. This component together with water constitutes then the solvent matrix for the claimed liquid compositions. Suitable phase regulants are well-known in liquid detergent technology and, for example, can be represented by hydrotropes such as salts of alkyl arylsulphonates having up to 3 carbon atoms in the alkylgroup, e.g., sodium, potassium, ammonium and ethanolamine salts of xylene-, toluene-, ethylbenzene-, cumene-, and isopropylbenzene sulphonic acids. Alcohols may also be used as phase regulants. This phase regulant is frequently used in an amount from about 0.5% to about 20%, the sum of phase regulant and water is normally in the range from 35% to 65%.

The preferred compositions herein can contain a series of further optional ingredients which are mostly used in additive levels, usually below about 5%. Examples of the like additives include: polyacids, suds regulants, opacifiers, antioxidants, bactericides, dyes, perfumes, brighteners and the like.

The beneficial utilization of the claimed compositions under various usage conditions can require the utilization of a suds regulant. While generally all detergent suds regulants can be utilized, preferred for use herein are alkylated polysiloxanes such as dimethylpolysiloxane also frequently termed silicones. The silicones are frequently used in a level not exceeding 0.5%, most preferably between 0.01% and 0.2%.

It can also be desirable to utilize opacifiers inasmuch as they contribute to create a uniform appearance of the concentrated liquid detergent compositions. Examples of suitable opacifiers include: polystyrene commercially known as LYTRON 621 manufactured by MONSANTO CHEMICAL CORPORATION. The opacifiers are frequently used in an amount from 0.3% to 1.5%.

The compositions herein can also contain known antioxidants for their known utility, frequently radical scavengers in the art established levels, i.e. 0.001% to 0.25% (by reference to total composition). These antioxidants are frequently introduced in conjunction with fatty acids.

Another optional ingredient which may be used particularly in structured liquids, is a deflocculating polymer. In general, a deflocculating polymer comprises a hydrophobic backbone and one or more hydrophobic side chains, as described in EP-A-346 995 (Unilever) (incorporated herein by reference). They allow, if desired, the incorporation of greater amounts of surfactants and/or electrolytes than would otherwise be compatible with the need for a stable, low-viscosity product as well as the incorporation, if desired, of greater amounts of other ingredients to which lamellar dispersions are highly stability-sensitive.

The deflocculating polymer generally will comprise, when used, from about 0.1 to about 5% of the composition, preferably 0.1 to about 2% and most preferably, about 0.5 to about 1.5%.

Product pH

The pH of the liquid detergent compositions of the invention can be chosen at will from a wide range, e.g. from about pH 7 to about pH 12, e.g. a milder alkaline range from about pH 7.5 to about pH 9.5 or a stronger alkaline range from about pH 8.5 to about pH 11.5, preferably from above 8.5 to 11, and most preferably from 9 to 10.5.

5 The following examples are intended to illustrate the invention and facilitate its understanding and are not meant to limit the invention in any way.

In the Examples the following abbreviations will be used:

LAS	Sodium linear C12-alkyl benzene sulphonate
LES	Lauryl ether sulphate
10 Nonionic	Ethoxylated C12-C15 fatty alcohol

Compositions of the Invention

The compositions of the invention are as follows:

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Composition A (Isotropic Non-Structured Composition)

<u>Ingredients</u>	<u>Weight</u>
LAS	10.0
Nonionic.9EO (Neodol 25-9)	8.0
LES (Neodol 25-3S)	6.0
Sodium xylene sulphonate	3.0
Builder	7.0
Triethanolamine	2.0
Monoethanolamine	2.0
Fatty acid	0.8
Protease (Savinase)	0.38
NaOH	to pH 10
Carboxylic acid stabilizer (Na-salt)	.31 molar*
Calcium chloride dihydrate	.035
Water	to 100%

* .31 molar corresponds to 2.1% by weight for formate, 2.6% by weight for acetate and 3.0% by weight for propionate.

Composition B (Structured, Built Composition)

<u>Ingredients</u>	<u>Weight</u>
LAS	6.72
Nonionic, average 5EO	4.8
Sodium xylene sulphonate	0.8
Builder	23.85
Alkali metal salts	2.44
Protease	0.38

Minors plus water	to 100%
Carboxylic acid stabilizer	.31 Molar
5 Calcium chloride dihydrate	0.1
pH	8.4

10 * Corresponding to 2.1% by weight formate, 2.5% by weight acetate, or 3.0% by weight propionate

Composition C (Structured, Built Composition)

15 <u>Ingredients</u>	<u>Weight</u>
LAS	16.5
Nonionic, average 5EO	9.0
20 Builder	23.23
Fatty Acid	4.5
Alkali Metal Salts	10.5
25 Deflocculating polymer	1.0
Protease	0.38
Minors plus water	to 100%
Carboxylic acid stabilizer	.31 Molar *
30 Calcium chloride dihydrate	0.1
pH	9.1

35 * Corresponding to 2.1% by weight formate, 2.6% by weight acetate, or 3.0% by weight propionate.

40 The liquid preparations were prepared according to the technique disclosed in EP-A-346 995 and the deflocculating polymer corresponds to polymer A11 of that specification.

Compositions D and E (structured liquids, containing a deflocculating polymer)

	<u>D</u>	<u>E</u>
LAS	23	23
Nonionic.7EO	10	10
50 Sodium citrate	16.5	11.5
Triethanolamine	-	-
Na-carbonate	-	-

Na-propionate	-	5
Protease	0.38	0.38
Deflocculating polymer	1	1
Water & minors	... to 100% ...	
pH	8.5	8.5

The liquid preparations were prepared according to the technique disclosed in EP-A-346 995 and the deflocculating polymer corresponds to polymer A11 of that specification.

Compositions F, G and H (structured liquids, containing a deflocculating polymer)

	<u>F</u>	<u>G</u>	<u>H</u>
LAS	28	28	28
Nonionic.7EO	12	12	12
Na-citrate	10	10	10
Triethanolamine	4	4	4
Na-propionate	-	5	-
Na-acetate	-	-	7.7
Protease	0.38	0.38	0.38
Deflocculating polymer	1	1	1
Water & minors	... to 100% ...		
pH	9.3	9.3	9.3

The liquid preparations were prepared according to the technique disclosed in EP-A-346 995 and the deflocculating polymer corresponds to polymer A11 of that specification.

Compositions K and L (structured liquids, containing a deflocculating polymer)

	<u>K</u>	<u>L</u>
LAS	28	28
Nonionic.7EO	12	12
Na-citrate	8	8
Na-carbonate	4	4
Na-propionate	-	5
Protease	0.38	0.38

Deflocculating polymer	1	1
Water & minors	...	to 100% ...
pH	9.2	9.2

The liquid preparations were prepared according to the technique disclosed in EP-A-346 995 and the deflocculating polymer corresponds to polymer A11 of that specification.

Composition M (structured, built liquid)

<u>Ingredients</u>	<u>Weight</u>
LAS	6.7
Nonionic, average 5EO	4.8
Sodium xylene sulphonate	0.2
Builder	20.0
Alkali metal salts	6.5
Protease	0.3
Minors plus water	to 100%
Carboxylic acid stabilizer	0.52 Molar*)
Calcium chloride dihydrate	0.15
pH	8.5

*)corresponding to 5% by weight of propionate

COMPOSITION N (structured, phosphate-built liquid)

LAS	9.0
Nonionic.7EO	2.25
Pentasodium triphosphate	27.0
Sodium hydroxide	1.1
Enzyme preparation	0.5
Water	Balance

The pH of the composition was adjusted to 9.0. The composition was prepared in accordance with EP-A-266 199 (Unilever).

EXAMPLE 1

When equal mole percentages of the formate salt, acetate salt and propionate salt (i.e. 0.31 molar) were added and compared in Composition A above, stability results were as follows:

Carboxylate Salt Added	Stability $t_{1/2}$ (days)
none	5
formate	20
acetate	23
propionate	31

The stability of the protease was determined by measuring protease activity (spectrophotometric techniques using tetrapeptide substrate) as a function of storage time at 37 ° C. Half-lives were determined by plotting Ao/At versus time and performing non-linear regression analysis.

These results establish that the half-life stability for Savinase in built anionic-rich detergent compositions having a pH higher than 8.5, preferably higher than 9.0, was superior when propionate was used compared to where either formate or acetate were used. The result was unexpected in view of the superior stability data for formate and acetate stabilizers relative to propionate in the art. It is clear that in the specifically defined compositions of the invention (anionic-rich, built compositions having defined pH ranges), different results are found.

EXAMPLE 2

Equal mole percentages of formate salt, acetate salt and propionate salt (i.e. 0.31 molar) were added and tested in structured composition B and C above and the following results were observed:

Composition B

		<u>% Protease</u>	
<u>Carboxylate</u>		<u>Activity Left</u>	<u>%</u>
<u>Salt Added</u>	<u>Protease</u>	<u>After 215 hrs.</u>	<u>Improvement</u>
none	Savinase	44	-
formate	Savinase	66	52
acetate	Savinase	69	58
propionate	Savinase	81	85

		<u>% Protease</u>	
<u>Carboxylate</u>		<u>Activity Left</u>	<u>%</u>
<u>Salt Added</u>	<u>Protease</u>	<u>After 215 hrs.</u>	<u>Improvement</u>
none	BPN'	17	-
formate	BPN'	27	58
acetate	BPN'	28	63
propionate	BPN'	44	155

Composition C

		<u>% Protease</u>	
<u>Carboxylate</u>		<u>Activity Left</u>	<u>%</u>
<u>Salt Added</u>	<u>Protease</u>	<u>After 215 hrs.</u>	<u>Improvement</u>
none	BPN'	38	-
formate	BPN'	49	27
acetate	BPN'	48	24
propionate	BPN'	59	55

These results show that propionate provides significant improvement in protease stability over time in structured, anionic rich compositions of defined pH. These results are unexpected in view of the teachings

of the prior art.

EXAMPLE 3

5 Equal mole percentages of formate salt, acetate salt and propionate salt were tested in a composition essentially the same as structured Composition B except that the pH range was varied. The following results were observed:

10 Composition B at PH 8.0

		<u>% Protease</u>	
<u>Carboxylate</u>		<u>Activity Left After</u>	<u>%</u>
<u>Salt Added</u>	<u>Protease</u>	<u>About 195 hrs.</u>	<u>Improvement</u>
15 none	BPN'	23	-
formate	BPN'	36	55
acetate	BPN'	36	55
20 propionate	BPN'	51	118

25 Composition B at pH 8.6

		<u>% Protease</u>	
<u>Carboxylate</u>		<u>Activity Left After</u>	<u>%</u>
<u>Salt Added</u>	<u>Protease</u>	<u>About 195 hrs.</u>	<u>Improvement</u>
30 none	BPN'	21	-
formate	BPN'	30	41
acetate	BPN'	31	47
35 propionate	BPN'	41	94

40 Composition B at pH 9.0

		<u>% Protease</u>	
<u>Carboxylate</u>		<u>Activity Left After</u>	<u>%</u>
<u>Salt Added</u>	<u>Protease</u>	<u>About 195 hrs.</u>	<u>Improvement</u>
45 none	BPN'	17	-
formate	BPN'	27	61
acetate	BPN'	28	64
50 propionate	BPN'	38	125

As can be clearly seen from the above results, an unexpected increase in stability, using propionate stabilizer relative to formate or acetate stabilizer, was observed across various pH ranges.

55 EXAMPLE 4

Stability of Savinase is determined in compositions D and E. Savinase (ex NOVO-Nordisk) is added

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either as liquid concentrate or as a liquid nonionic-slurry; both preparations have 16 KNPU/g (KNPU = kilo NOVO Protease Units) proteolytic activity. The stability is expressed as half-life of deactivation (in days) at 37° C.

Composition	Stabiliser	Savinase liquid	Savinase slurry
D	none	2.1	25
E	propionate	4.5	>>30

EXAMPLE 5

Stability of Savinase is determined in composition F, G and H. Savinase (ex NOVO-Nordisk) is added either as liquid concentrate or as a liquid nonionic-slurry; both preparations have 16 KNPU/g (KNPU = kilo NOVO Protease Units) proteolytic activity. The stability is expressed as half-life of deactivation (in weeks) at 37° C.

<u>Composition</u>	<u>Stabiliser</u>	<u>Savinase liquid</u>	<u>Savinase slurry</u>
F	none	0.3	1
G	acetate	0.6	nd
H	propionate	1.6	4
(nd = not determined)			

Example 6

Stability of Savinase is determined in composition K and M. Savinase (ex NOVO-Nordisk) is added either as liquid concentrate or as a liquid nonionic-slurry; both preparations have 16 KNPU/g (KNPU = kilo NOVO Protease Units) proteolytic activity. The stability is expressed as half-life of deactivation (in weeks) at 37° C.

Composition	Stabiliser	Savinase liquid	Savinase slurry
K	none	0.5	3
L	propionate	0.8	7

Example 7

Stability of Savinase is determined in compositions F, G and H. Savinase (ex NOVO-Nordisk) is added either as liquid concentrate or as a liquid nonionic-slurry; both preparations have 16 KNPU/g (KNPU = kilo NOVO Protease Units) proteolytic activity. The stability is expressed as half-life of deactivation (in weeks) at 37° C.

Composition	Stabiliser	Savinase liquid	Savinase slurry
M	none	0.5	1.5
M	propionate	15	20

Example 8

Stability of Savinase is determined in composition N. Savinase (ex NOVO-Nordisk) is added either as liquid concentrate or as a liquid nonionic-slurry; both preparations have 16 KNPU/g proteolytic activity. The stability is expressed as half-life of deactivation (in days) at 37 °C.

Composition	Stabiliser	Savinase liquid	Savinase slurry
N	none	<<1	<1
N	propionate	3.4	4.5

Claims

1. A stable aqueous enzymatic detergent composition comprising:
 - (a) from about 5 to about 65% by weight of a surfactant;
 - (b) from about 0.5 to about 50% by weight of a builder;
 - (c) a protease enzyme added in sufficient quantity to have an activity level of 0.01 to 200,000 GU/gm;
 - (d) from about 0.1 to about 15% by weight propionic acid or a propionic acid salt capable of forming propionic acid;
 the remainder being water and minor ingredients;
 wherein the pH of the composition is greater than 7.0.
2. A composition according to claim 1, wherein the surfactant is an anionic surfactant.
3. A composition according to claim 1, wherein the surfactant is a mixture of an anionic surfactant and one or more detergent actives, the ratio of anionic to non-anionic by weight being greater than 1:1.
4. A composition according to claims 1-3, wherein if the composition is structured, 5 to 35% by weight builder is used.
5. A composition according to claims 1-3, wherein if the composition is not structured, 3 to 10% by weight builder is used.
6. A stable aqueous enzymatic detergent composition according to claims 1-4, further comprising from about 0.1 to about 5% of a deflocculating polymer.
7. A stable aqueous enzymatic detergent composition according to claims 1-6, further comprising from about 0.01 to about 1% of a calcium salt.
8. Process for preparing an aqueous liquid enzymatic detergent composition according to claims 1-7, wherein the proteolytic enzyme is added in the form of a slurry of the enzyme in liquid nonionic surfactant.



European
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EUROPEAN SEARCH REPORT

Application Number

EP 91 20 1816

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A-2 178 054 (COLGATE-PALMOLIVE) * claims 1-7,14 * -- --	1,2	C 11 D 3/386
A	EP-A-0 378 261 (THE PROTECTOR & GAMBLE COMPANY) * claims; page 3, lines 27-52; page 5, lines 33-35, lines 41-43 * -- --	1	
A	EP-A-0 324 568 (ROHM & HAAS CO.) * abstract; claims 13-15; page 12, lines 23-43; page 36, lines 1-37 * -- --	1,4,6	
A	US-A-4 497 897 (J.H. EILERTSEN) * claims; column 3, lines 26-45 * -- --	1,7	
A,D	EP-A-0 028 865 (THE PROTECTOR & GAMBLE COMPANY) * claims * -- --	1,2,7	
A,P	WO-A-9 109 102 (UNILEVER PLC) * whole document * -- -- -- --	1-4,6	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 11 D
Place of search		Date of completion of search	Examiner
Berlin		29 October 91	PELLI-WABLAT B
CATEGORY OF CITED DOCUMENTS			
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