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(54) Process for preparing liquid enzymatic detergent compositions.

(57) An aqueous liquid enzymatic detergent composition having improved enzyme stability and comprising a detergent active material, a non-phosphate builder and an enzyme may be prepared by adding the enzyme in the form of a slurry of the enzyme in liquid nonionic surfactant.

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TECHNICAL FIELD

This invention relates to a process for preparing liquid enzymatic detergent compositions and to their use, especially for example as laundry detergents.

BACKGROUND AND PRIOR ART

It is well known to prepare detergent compositions in the form of a liquid concentrate to be diluted to give an aqueous wash liquor. Such liquid concentrates can themselves be prepared in the form either of an aqueous or a non-aqueous liquid, and both forms are known.

It is also known to add enzymes to a variety of detergent compositions, especially laundry detergents. The most common enzyme for this purpose is protease, e.g. subtilisin, and others, e.g. amylase, cellulase, lipase, have also been used.

Such enzymes are presented in a variety of forms: as solid compositions, such as marumes or granulates, e.g. multilayer composite granulates, or as powder concentrates; or as liquid compositions such as slurries or stabilized aqueous preparations. The manufacture of stabilized aqueous and some non-aqueous enzyme concentrates is described for example in US-A-4 497 897 (Novo) and DE-A-29 37 012 (Henkel). Enzyme slurries are mentioned for example, along with preparations made up as aqueous (propanediol-water) concentrates, in a brochure 'Novo Enzymes for Household Non-Built Liquid Detergents', which gives some formulations of aqueous enzyme concentrates incorporated into a non-built aqueous detergent composition.

Existing aqueous enzymatic liquid laundry detergents are commonly formulated using as additive a stabilized aqueous liquid enzyme concentrate. 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.

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 nonaqueous slurries) are loosing 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.

US-A-4 090 973 (Procter & Gamble) describes aqueous liquid detergents containing normally-unstable components encapsulated in water-soluble normally-solid alkoxylated nonionic surfactants and/or polyethylene glycol.

EP-A-238 216 and GB-A-2 186 884 (Albright & Wilson and Novo Industri) describe protected enzyme systems for use (inter alia) in liquid detergent compositions, based on dispersing the enzymes in hydrophobic substances (e.g. petroleum jelly or organosiloxane polymer) which do not dissolve on storage and which are liquid under the conditions of use, thus providing a discontinuous phase in the final liquid detergent.

EP-A-351 162 (Albright & Wilson and Novo-Nordisk) describes stabilized aqueous enzyme dispersions obtained by (co)precipitating water-soluble polymer and enzyme from water.

JP-A-47-35192 describes the use of glycerol or sorbitol with borax under certain conditions and proportions, to stabilize enzyme preparations including liquid washing materials.

DE-A-2 728 211 (Unilever) describes the use of polyols containing 2 to 6 hydroxy groups together with boric acid or borate in ratios less than 1, particularly in unbuilt detergents.

GB-A-2 079 305 (Unilever) describes the use of polyols together with boric acid and/or borate and polyacrylate polymers as stabilizing agents, while EP-A-080 223 (Unilever) describes the combined use of boric acid or borate and polyol or polyamino compounds with reducing salts, and EP-A-126 505 (Unilever) describes the use of boric acid or borate and reducing salts, together with succinic or other dicarboxylic acids.

Other prior art, e.g EP-A-028 865 and EP-A-028 866 (Procter & Gamble), and US-A-4 111 855 (Procter & Gamble), discloses use of further stabilizers, such as calcium with short-chain aliphatic acids such as formate or acetate, and ethanol.

Nevertheless, problems remain. Several of the published techniques give a quantitative improvement of enzyme stability in aqueous liquid detergents. Some of them call for stabilizing ingredients and additives which are expensive, or which represent possibly undesirable additions from the point of view of their effects on other components of the compositions, or which are less desirable from an environmental point of view. Therefore it remains desirable to find further techniques for stabilizing enzymes in liquid detergent compositions, which might for example be usefully combinable with existing techniques so as to give increased effect, as well as able to be used alone without also using previously-known technique. It is also desirable to find such techniques which present the advantage of not requiring such costly additives as the existing techniques. The present invention seeks to provide such advantages.

It has now 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.

DEFINITION OF THE INVENTION

According to a first aspect, the invention provides a process for preparing an aqueous liquid enzymatic detergent composition comprising a detergent active compound, a non-phosphate builder and an enzyme, wherein the enzyme is added in the form of a slurry of the enzyme in liquid nonionic surfactant.

The invention also provides an aqueous liquid enzymatic detergent composition prepared by the process of the invention.

DESCRIPTION OF THE INVENTION

'Detergent concentrate' and 'surfactant concentrate' as used herein, do not refer to normally-encountered aqueous wash liquors themselves, but rather refer to surfactant preparations sufficiently concentrated that they can be diluted in a large ratio (water to detergent concentrate), e.g. 15:1 or more, preferably 100:1 or more, to provide a useful aqueous wash liquor.

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 enzymes to be incorporated into a slurry for use in making the compositions of the present invention may be either crude preparations, or partly purified, decolourised, or extensively purified preparations. They may be (and preferably are) dried in any of the usual manners known per se, before slurrying the enzyme in the liquid nonionic surfactant. Examples of suitable purification methods for this purpose include: micro-filtration, high-salt precipitation of the enzyme, e.g. from sodium or ammonium sulphate solutions, or solvent precipitation by adding water-miscible organic solvents (e.g. acetone or ethanol) to aqueous enzyme preparations at any of various stages of their isolation or purification. The compositions may contain either crude or purified enzyme, e.g. enzyme free of cell wall material as described in for example EP-A-322 082 (Gist-Brocades).

Before slurrying, the enzyme preparation can be decolourised, e.g. by the methods described in JP-A-63 119674 (Lion Corp). The enzyme may be crystallized before slurrying by adding halide salts to a concentrated enzyme solution, thus resulting in the formation of microcrystalline enzyme particles, e.g. as described in WO 89/08703 (Genencor). The enzyme composition may be dried by lyophilization or spray-drying, or by using a fluidised bed as detailed in DE-A-2 134 555 (Novo). (The above-mentioned specifications are incorporated herein by reference).

In practice it can happen that certain preparations of enzyme have relatively high concentrations of salt, especially calcium salt, e.g. calcium sulphate or chloride, associated with them. It is preferred for certain purposes to avoid high salt concentrations, especially of calcium. If calcium is present, it is preferably at levels less than 4% w/w of the slurry, more preferably less than 1% or 0.5%, most preferably at trace levels.

In certain embodiments, negatively-charged polymers, such as hetero-polysaccharides including glucuronide and/or galacturonide residues, can help storage stability of the enzymes slurried in the manner described herein. Such polysaccharides may for example include material produced by the organisms from which the enzymes themselves have been produced, and may remain as contaminants in the partially purified enzyme preparations, or they may be added separately, before spray-drying, e.g. in amounts up to about 1 to 5% by weight of the slurry, e.g. in amounts comparable with those of the enzymes themselves.

It is not known why the results of adding enzyme in the form of a slurry should contrast with the results obtainable when the enzyme is added either as a powder concentrate or granule or as a stabilized aqueous liquid. The technique surprisingly leads to improved stability in the final aqueous composition. Thus, the invention opens the way to stabilization without such expensive additives as normally used, and to improving the stability obtainable by the use of other additives.

A suitable example of an enzymatic slurry preparation for use in the present invention is a preparation of Savinase (Trade Mark - subtilisin protease, ex Novo-Nordisk) suspended in liquid Tergitol 15-S-9 (Trade Mark, ex Union Carbide) nonionic detergent consisting substantially of C_{11}-C_{15} secondary alcohol condensed with 9 moles of ethylene oxide.

The liquid nonionic detergent of the slurry can otherwise be for example a liquid secondary or primary linear alcohol having 9 to 20 carbon atoms and condensed with about 3 to 20 moles/mole ethylene oxide, or may be a mixture of nonionic surfactants. Alternatively the liquid nonionic surfactant can be chosen from among the liquid surfactants described in "Surface Active Agents" Vol. 1, by Schwartz & Perry, (Interscience 1949), Vol. 2 by Schwartz, Perry & Berch, (Interscience 1958), or in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn. (Carl Hanser Verlag, 1981) (incorporated herein by reference), and can comprise nonionic surfactant chosen from among the groups and examples of nonionic surfactants mentioned in EP-A-346 995 (Unilever) (incorporated herein by reference).

The aqueous liquid enzymatic detergent compositions prepared according to the present invention can for example include protease, lipase, amylase, and/or cellulase enzyme(s). Protease is still the most common enzyme specificity present in laundry detergents. Most often, protease and/or a lipase are used optionally with a further enzyme, e.g. an enzyme selected from lipase, amylase, cellulase and oxidase. It has been found (surprisingly in view of the known adverse effect of proteases on other enzymes in aqueous conditions) that both the protease and optional other enzymes present can be stabilized together in these compositions.

Where at least one enzyme is added in accordance with the present invention as a slurry in liquid nonionic detergent, it is within the scope of the invention to add at least one further enzyme in either a similar or a different form, e.g. as a liquid or a granular composition of enzyme with carrier material (e.g. as described for the case of lipase in EP-A-258 068, but applicable to other enzymes also, and as such compositions are concretely represented e.g. by the Savinase and Lipolase products of Novo).

Protease can for example be used in an amount ranging from about the order of 0.0002 to about the order of 0.05 Anson units per gram of the detergent composition. Expressed in other units, the protease can also be included in the compositions in amounts of the order of from about 1 to 100 GU/mg detergent formulation. Preferably, the amount ranges from 2 to 50 and particularly preferably from 5 to 20 GU/mg.

A GU is a Glycine Unit, defined as the proteolytic enzyme activity which, under standard conditions, during a 15-minute-incubation at 40°C, with N-acetyl casein as substrate, produces an amount of NH_2-group equivalent to 1 micromole of glycine.

Preferred examples of protease enzyme to be used in the present compositions are the subtilisin varieties sold as Savinase (TM of Novo-Nordisk A/S) or Maxacal (TM of Gist-Brocades/IBIS) or as Opticlean (ex Solvay Enzymes) or Biosam (ex Showa Denko), which have an isoelectric point (pl) of approximately 10. Other useful examples of protease include Maxatase, Esperase, Alcalase (Trade Marks), proteinase K and subtilisin BPN'.

Where the compositions comprise lipase enzyme, there can be used for example an amount in the range 50 to 30,000 (LU) lipase units per gram of the surfactant system or of the detergent composition. In this specification lipase units are defined as they are in EP-A-258 068 (Novo).

There is, as is known, a tendency for lipase to be less stable in the presence of protease than in the absence of protease, however, in the presence of protease that is incorporated into the aqueous liquid detergent as a slurry in liquid nonionic surfactant we observe that there is a relative stabilization effect on the lipase also present (e.g. when such lipase is incorporated as a stabilized aqueous liquid preparation). Alternatively, improvement in stability of lipase in the presence of protease is achievable by adding the lipase as a slurry in liquid nonionic detergent, and the protease here may be added e.g. as another slurry in liquid nonionic detergent or even in this case as an aqueous liquid composition. Good results as to enzyme stability during storage are also obtainable where both enzymes (if more than one) are added as slurries in liquid nonionic detergent, either as separate slurries or as an enzyme mixture dispersed in one type of nonionic surfactant.

The added amount of lipolytic enzyme can be chosen within wide limits, for example 50 to 30,000 LU/g of detergent composition, e.g. often at least 100 LU/g, very usefully at least 500 LU/g, sometimes preferably above 1000, above 2000 LU/g or above 4000 LU/g or more, thus very often within the range 50-4000 LU/g and possibly within the range 200-1000 LU/g.

The lipolytic enzyme can be chosen from among a wide range of lipases: in particular the lipases described in for example the following patent specifications, EP-A-214 761 (Novo), EP-A-258 068 (Novo), and EP-A-305 216 (Novo), and especially lipases showing immunological cross-reactivity with antisera raised against lipase from Thermomyces lanuginosus ATCC 22070, EP-A-205 208 (Unilever) and EP-A-206 390 (Unilever), and especially lipases showing immunological cross-reactivity with antisera raised against lipase from Chromobacter viscosum var lipolyticum NRRL B-3673, or against lipase from Alcaligenes PL-679, ATCC 31371 and FERM-P 3783, also the lipases described in specifications WO 87/00859 (Gist-Brocades), WO 89/09263 (Gist-Brocades), EP-A-331 376 (Amano), DE-A-3 908 131 (Toyo Jozo) and EP-A-204 284 (Sapporo Breweries). Suitable in particular are for example the following commercially available lipase preparations: Novo Lipolase, Amano lipases CE, P, B, AP, M-AP, AML, and CES, and Meito lipases MY-30, OF, and PL, also esterase MM, Lipozym, SP225, SP285, Saiken lipase, Enzeco lipase, Toyo Jozo lipase and Diosynth lipase (Trade Marks).

Similar considerations apply mutatis mutandis in the case of the other enzymes. Without limitation: Amylase can for example be used when present in an amount in the range about 1 to about 100 MU (maltose units) per gram of detergent composition, (or 0.014-1.4, e.g. 0.07-0.7, KNU/G (Novo units)). A preferred form of amylase is that sold as Termamyl (TM of Novo), or as Maxamyl (TM of Gist-Brocades).

Cellulase can for example be used when present in an amount in the range about 0.3 to about 35 CEVU units per gram of the detergent composition. Preferred forms of cellulase are Celluzyme (TM of Novo) or KAC500 (TM of Kao).

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. Useful modified lipase enzymes are also described in for example WO 89-09263 (Gist-Brocades), EP-A-218 272 (Gist-Brocades), EP-A-258 068 (Novo), EP-A-407 225 (Unilever) and EP-A-305 216 (Novo).

Typically, the present aqueous liquid detergent compositions comprise from 1-70%, e.g. up to 60%, often in the range of 5% up to 50%, commonly at least 10% and up to 45%, by weight of one or more detergent-active compounds, from 5-60% by weight of one or more organic and/or inorganic non-phosphate builders, and optionally other conventional ingredients such as enzyme stabilizers, soil-suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, silicates, optical brighteners, suds depressants, germicides, anti-tarnishing agents, opacifiers, fabric softening agents, oxygen-liberating bleaches such as hydrogen peroxide or sodium perborate, diperisophthalic anhydride, with or without bleach precursors, oxygen-activating bleaches, buffers and the like.

The detergent-active compounds in the compositions can for example be anionic and/or nonionic surfactants, and the pH of the liquid detergent compositions 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 9 to about pH 11 or more.

In general, the surfactant(s) of the present compositions may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hanser Verlag, 1981. In this respect anionic and nonionic surfactants are especially suitable, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever) (incorporated herein by reference).

Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkylpolyglycoside surfactants described in EP-A-070 074, and the alkyl monoglucosides described in WO88/10147 (Novo).

Preferred anionic surfactants include for example linear and branched-chain alkylbenzene sulphonates and primary alcohol sulphates, e.g. those based on fatty radicals derived from tallow or coconut oil or mixtures thereof, or those defined by carbon ranges as e.g. C_6-C_{16} sodium alkyl sulphates and C_{11}-C_{15} sodium alkylbenzene sulphonates.

Anionic surfactants can be present for example in amounts in the range from about 5% to about 50% by weight of the liquid detergent concentrate. Preferably nonionic detergent is present in amounts greater than 1%, e.g. 2-20% by weight of the composition.

Among the compositions of the present invention are aqueous liquid detergents having incorporated therein nonionic-based enzyme slurries, and 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.

The compositions prepared according to the invention further comprise a builder of the zero-P type. For example they can be built with zeolite particles. Typical examples of non-phosphorus-containing builders include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous alumino-silicates. More specific examples are sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonate, silicates, and zeolites, e.g. zeolite A.

The compositions may contain in aggregate form for example from 1-50%, e.g. at least about 5% and often up to about 35-40% by weight, of one or more organic and/or inorganic builders, especially 5-40%, e.g. 5-25% of non-soap builders.

In the context of several such builders, e.g. inorganic builders and/or zeolites, we prefer to include electrolytes which promote the solubility of other electrolytes, for example the use of potassium salts to promote the solubility of sodium salts. Thereby the amount of dissolved electrolyte can be increased, as described in GB-A-1 302 543.

Organic detergency builders include for example alkali metal and ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetal carboxylates, and polyhydroxy sulphonates. Specific examples include sodium, potassium and lithium ammonium and substituted ammonium salts of EDTA, NTA, oxydisuccinic acid, mellitic acid, benzenepolycarboxylic acids, CMOS, tartrate monosuccinate, tartrate disuccinate, and citrate.

When organic builders are used, it is often desirable to incorporate polymers which are only partly dissolved in the aqueous continuous phase, as described in EP-A-301 882. This allows viscosity reduction (due to dissolved polymer) while incorporating high enough amounts to achieve secondary benefits such as building, because the undissolved part does not bring about instability that might occur if all were dissolved. Typical amounts are from 0.5-4.5% w/w.

Further polymers may be incorporated as well as or instead of these partly-dissolved polymers, i.e. substantially totally-soluble polymers having an average molecular weight of at least 1000, having an electrolyte resistance of more than 5 grams Na-NTA in 100ml of a 5% aqueous solution of the polymer, and also having vapour pressure in 20% aqueous solution equal to or less than the vapor pressure of a 2% aqueous solution of polyethylene glycol of average molecular weight 6000. These are as described in EP-A-301 882 (Unilever).

We have also found that the storage stability of the enzyme incorporated into an aqueous detergent in the form of a slurry may be significantly improved by inclusion of electrolytes that cause salting-out of proteins into the final product. Typical examples of suitable salting-out electrolytes are alkali metal or ammonium salts of -borate, -sulphate, -citrate, -carbonate and -nitrilotriacetate. When sodium salts are used, the lyotropic number must be less than 9.5 (see also US-A-4 530 780).

The total level of salting-out electrolytes may vary from about 2 to about 45% by weight of the final product, preferably from 5 to 30% by weight.

According to convenience, e.g. to ensure desired pH in the wash liquor during use, it can be convenient to include a pH buffer such as triethanolamine (/HCl), optionally with monoethanolamine.

Silicates and carbonates included for other reasons e.g. as builders may provide some (possibly adequate) buffering capacity. Tris buffer can also have an auxiliary stabilizing effect on the enzymes of the composition.

The detergent compositions may also include usual further detergent ingredients in usual amounts. Further optional ingredients of the liquid detergent compositions include e.g. lather boosters such as alkanolamides, especially monoethanolamides from palm kernel and/or coconut fatty acids, lather/foam depressants, anti-corrosion agents, soil-suspending agents, sequestering agents, anti-soil redeposition agents, perfumes, dyes, colourants and so on.

Compositions of the invention can be prepared by any conventional method for the preparation of liquid detergent compositions. A preferred method comprises dispersing the electrolyte ingredient(s) and minors (except for any temperature-sensitive items such as enzymes and perfumes) in water, followed by builder, and the detergent active ingredient(s), optionally as a premix, with stirring. After cooling, if necessary, the remaining ingredients are added. Deflocculating polymer can be suitably added just after the electrolyte ingredients, or just after the builder ingredients or after adding the detergent-active ingredients. If zeolite is present, it is preferably added as the last ingredient.

The final liquid formulation is adjusted to the desired pH. The preferred stage for adding the enzyme slurry as described above, as well as minor constituents such as perfumes and colourants, etc, is after the stage of pH-adjustment.

The use of the present invention enables easy mixing of the enzyme in the final liquid detergent. The liquidity of the practically anhydrous slurry can give a benefit during handling of the enzyme preparation as compared with the handling of solid preparations.

The compositions can be used for the washing of textile materials, especially but without limitation cotton-, nylon-and polyesterbased textiles and mixtures thereof. Especially suitable are for example washing processes carried out at temperatures of about 60-65 °C or lower, e.g. about 30-35 °C or lower. It can be very suitable to use the compositions in an amount sufficient to provide about 0.4-0.8 g/l surfactant in the wash liquor, although it is of course possible to use greater concentrations if desired. Without limitation it can for example be stated that a range up to about 6% of detergent liquid in the wash liquor, but often below 3% and usually below 1%, can be suitable for use in the case when the liquids are formulated as in the Examples below.

It is within the scope of the present invention to incorporate other 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 short-chain aliphatic acid salt, 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.

The invention is further illustrated, without intent to limit its scope, by the following examples, in which amounts and percentages are by weight unless otherwise indicated.

EXAMPLES 1-5

The following aqueous liquid detergent compositions were prepared by mixing the following ingredients:

Example	1	2	3	4	5
Anionic detergent					
(Dodecyl benzene sulphonic acid)	10.3	6.7	8.4	23.0	10.0
(Linear alkyl ethoxysulphate)	3.4	--	--	--	6.0
Nonionic detergent (C_{13}-C_{15}-primary linear alkyl.7EO)	1.7	2.4	3.0	10.0	8.0
Nonionic detergent (C_{13}-C_{15}-primary linear alkyl.3EO)	--	2.4	3.0	--	--
Zeolite 4A	20	20	--	--	--
Citric Acid	--	3.9	4.9	--	4.5
Sodium citrate. 2aq	7.5	--	--	16.5	--
Polymer Narlex LD31	0.7	--	--	--	--
Polymer Sokalan PA50	--	0.2	0.3	--	--
Deflocculating Polymer	--	--	--	1.0	--
Monoethanolamine	--	--	--	--	2.0
Triethanolamine	--	--	--	--	2.0
Sodium xylenesulphonate	--	--	--	--	3.0
Minors	0.2	1.8	2.3	0.1	0.5
Enzyme preparation	0.5	0.5	0.6	0.5	0.5
Water		- Balance -			
pH adjusted to:	8.5	8.5	8.5	8.5	10.0

The compositions of Examples 1 to 4 were structured liquids, the composition of Example 5 was an isotropic liquid. The composition of Example 4 was prepared according to the technique disclosed in EP-A-346 995 (incorporated herein by reference), and the Deflocculating Polymer corresponded to the polymer A11 of the Examples of that specification. The enzyme was a slurry of Savinase (Trade Mark, Novo-Nordisk) in Tergitol 15-S-9 nonionic detergent (Trade Mark), having a specific activity of 8 KNPU (s) (kilo Novo protease units)/g. Subsequently, the storage stability of the enzyme of the compositions of Examples 1 to 5 was determined at 37°C. The results are shown in Table A.

EXAMPLES 6-10

The Examples 1-5 were repeated, except that the enzyme was a slurry of Savinase (Trade Mark, Novo-Nordisk) in Tergitol 15-S-9 nonionic detergent (Trade Mark), having a higher specific activity of 16 KNPU (s) (kilo Novo protease units)/g. Subsequently, the storage stability of the enzyme was determined at 37°C. The results are shown in Table A.

COMPARATIVE EXAMPLES 1A-5A

The Examples 1-5 were repeated, except that the Savinase enzyme was applied as a stabilized aqueous enzyme solutions: Savinase 16.0LDX ex Novo-Nordisk.. Subsequently, the storage stability of the Savinase enzyme was determined at 37°C. The results are shown in Table A.

COMPARATIVE EXAMPLE P

The following (phosphate-built) aqueous liquid detergent composition was prepared by mixing the following ingredients:

Anionic detergent (Dodecyl benzene sulphonic acid)	9.0
Nonionic detergent (C12-C15 primary linear alcohol condensed with 7 moles of ethylene oxide)	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). Savinase enzyme was added in the form of a slurry in nonionic detergent (as described in Example 6). Subsequently, the storage stability of the enzyme of the composition was determined at 37°C. The results are shown in Table A.

COMPARATIVE EXAMPLE Q

Comparative Example P was repeated, except that the Savinase enzyme was applied as a stabilized aqueous enzyme solution:
Savinase 16.0LDX ex Novo-Nordisk. Subsequently, the storage stability of the Savinase enzyme was determined at 37°C. The results are shown in Table A.

EXAMPLES 11-12

The following aqueous liquid detergent compositions were prepared by mixing the following ingredients:

Example	11	12
Anionic detergent (Dodecyl benzene sulphonic acid)	12.0	25.6
Nonionic detergent (C12-C15 primary linear alcohol condensed with 7 moles of ethyleneoxide)	12.0	12.0
Fatty acid	6.0	--
Sodium citrate .2aq	10.0	9.9
Glycerol	2.0	4.9
Borax.10aq	1.5	3.5
Potassium hydroxide	3.2	--
Sodium hydroxide	--	2.8
Zeolite 4A	15.0	--
Deflocculating Polymer	1.0	1.0
Triethanolamine	--	2.0
Monoethanolamine	--	2.0
Enzyme preparation	1.0	1.0
Water and minors	- Balance -	
pH adjusted to	8.7	9.2

The above liquid compositions were prepared according to the technique disclosed in EP-A-346 995 (incorporated herein by reference), and the polymer corresponded to the polymer A11 of the examples of that specification. The enzyme preparation was a mixture of Savinase and Lipolase (Trade Marks, Novo-Nordisk). Both enzymes were obtained from Novo-Nordisk. Savinase was applied as a slurry in Tergitol 15-S-9 nonionic detergent (TM), having a specific activity of 16 KNPU (s) (kilo Novo protease units)/g, and Lipolase as a stabilized aqueous liquid preparation: Lipolase 100L ex Novo-Nordisk. Subsequently, the storage stability of the Lipolase enzyme was determined at 37°C. The results are shown in Table B.

EXAMPLES 13-14

The Examples 11-12 were repeated, except that the Lipolase enzyme was a slurry in Tergitol 15-S-9 nonionic detergent (Trade Mark) obtained from Novo-Nordisk as Lipolase 100SL. Subsequently, the storage stability of the Lipolase enzyme of the compositions was determined at 37°C. The results are shown in Table B.

EXAMPLES 15-16

The Examples 13-14 were repeated, except that the Savinase enzyme was applied as a stabilized aqueous enzyme solution: Savinase 16.0LDX ex Novo-Nordisk. Subsequently, the storage stability of the Lipolase enzyme of the compositions was determined at 37°C. The results are shown in Table B.

COMPARATIVE EXAMPLES 11A-12A

The Examples 11-12 were repeated, except that the Savinase enzyme was applied as a stabilized aqueous enzyme solution: Savinase 16.0LDX ex Novo-Nordisk. Subsequently, the storage stability of the Lipolase enzyme of the compositions was determined at 37°C. The results are shown in Table B.

TABLE A

Example	Enzyme type	Half-life of protease-activity at 37°C (days)
1	Savinase Slurry[1])	3.5
2	,, ,,	5
3	,, ,,	8
4	,, ,,	10
6	Savinase Slurry[2])	7.8
7	,, ,,	10
8	,, ,,	20
9	,, ,,	25
10	,, ,,	6.5
P	,, ,,	0.8
1A	Savinase Liquid[3])	1.9
2A	,, ,,	3
3A	,, ,,	6.5
4A	,, ,,	2
5A	,, ,,	2.8
Q	,, ,,	0.2

[1]) Savinase-slurry containing 8KNPU/g; 8.0SL ex Novo

[2]) Savinase-slurry containing 16KNPU/g; ex Novo

[3]) Stabilized liquid concentrate containing 16KNPU/g; 16.0LDX ex Novo

Substantial improvements in stabilization are evident from the oomparison, in favor of the compositions prepared according to the invention, by incorporating the proteolytic enzyme in the form of the slurry.

TABLE B

Example	Enzyme types	Half-life of lipase-activity at 37°C (days)
11	Savinase Slurry1)/Lipolase Liquid2)	16
12	,, ,, / ,, ,,	3
13	,, ,, /Lipolase Slurry3)	12
15	Savinase Liquid4)/ ,, ,,	8
11A	,, ,, /Lipolase Liquid2)	4
12A	,, ,, / ,, ,,	0.6

1)Savinase-slurry containing 16KNPU/g; ex Novo

2)Lipolase-liquid containing 100LU/g; 100L ex Novo

3)Lipolase-slurry containing 100LU/g; 100SL ex Novo

4)Stabilized liquid concentrate containing 16KNPU/g; 16.0LDX ex Novo

Substantial improvements in stabilization are evident from the comparison, in favor of the compositions prepared according to the invention, by incorporating the lipolytic enzyme in the form of the slurry. When the lipolytic enzyme is present in the form of a liquid concentrate, its stability is surprisingly improved when any additional proteolytic enzyme is present in the form of a slurry.

Claims

1. Process for preparing an aqueous liquid enzymatic detergent composition comprising a detergent active compound, a non-phosphate builder and an enzyme, wherein the enzyme is added in the form of a slurry of the enzyme in liquid nonionic surfactant.

2. Process according to Claim 1, wherein the enzyme is selected from the group consisting of proteases, lipases and mixtures thereof.

3. Process according to any one of the preceding Claims, wherein the enzyme slurry has a water content of less than 10% by weight.

4. Process according to any one of the preceding Claims, wherein the liquid nonionic surfactant is an ethoxylated fatty alcohol having 9 to 20 carbon atoms and ethoxylated with 3 to 20 ethylene oxide moieties.

5. Process according to any one of the preceding Claims, wherein the non-phosphate builder is selected from the group consisting of zeolites, citrates and mixtures thereof.

6. Process according to any one of the preceding Claims, wherein the aqueous liquid enzymatic detergent composition comprises 5 to 50% by weight of one or more detergent-active compounds.

7. Process according to any one of the preceding Claims, wherein the aqueous liquid enzymatic detergent composition further comprises one or more enzymes in the form of a stabilized aqueous liquid composition.

8. Process according to any one of the preceding Claims, wherein the aqueous liquid enzymatic detergent composition comprises surfactant in the form of a dispersion of lamellar droplets in an aqueous continuous phase.

9. Process according to Claim 8, wherein the aqueous liquid enzymatic detergent composition comprises surfactant in the form of a dispersion of lamellar droplets in an aqueous continuous phase, and a deflocculating polymer.

10. Process according to Claim 8, wherein the aqueous liquid enzymatic detergent composition comprises from 2 to 45% by weight salting-out electrolytes.

11. Aqueous liquid enzymatic detergent composition prepared by the process of any one of the preceding Claims.