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(54) **ENZYMATIC LIQUID DETERGENT COMPOSITIONS AND THEIR USE.**

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Description

Field of the Invention:

5 The present invention relates to enzymatic liquid detergent compositions, e.g. laundry detergents intended for fabric washing, and their manufacture and use. More particularly, it relates to enzymatic liquid detergent compositions which incorporate enzyme(s), for example proteolytic enzymes.

Disclosure of Prior Art:

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It is becoming increasingly common in the detergent industry to present detergent compositions, especially compositions for fabric washing, in liquid form.

Among known presentations and formulations of liquid detergents are compositions which have a structure of dispersed lamellar droplets. Structured liquid detergents showing interesting flow behaviour, turbid appearance and/or ability to suspend particulate solid ingredients of detergent compositions are disclosed, for example, in USP 4 244 840, EP 0 160 342, EP 0 038 101, EP 0 104 452, and EP 0 151 884.

The use of proteolytic enzymes in liquid detergent compositions is well known; although these proteolytic enzymes can be of various types and sources, the proteolytic enzymes commonly used are those produced by *Bacillus* strains, especially *B. subtilis*, i.e. in the form of one or more of the serine proteases often referred to as subtilisin. Although with such proteolytic enzymes satisfactory results as regards wash performance can be achieved, it is frequently necessary to include enzyme-stabilizing systems in the liquid detergent compositions to provide a satisfactory enzyme stability during storage of the enzymatic liquid detergent composition.

We believe that representative examples of relevant prior art concerning proteases and stabilisation of proteases in liquid detergents are as follows.

25 The prior art includes WO 88/03946 (Novo), which discloses, as detergent additives, combinations of *Bacillus* proteases with alkaline fungal or actinomycete proteases, e.g. those proteases obtainable from the genera *Paecilomyces*, *Fusarium*, and *Nocardioopsis*. The disclosure extends to the use of the detergent additive among other things as a liquid, with a known enzyme stabiliser such as propylene glycol, for addition to a liquid detergent.

30 EP 0 238 216 (Albright & Wilson and Novo) discloses further methods for stabilising enzymes in liquid detergents, based on insoluble hydrophobic materials such as silicone oils.

Proteinase K has also been proposed as a protease showing good stability for use in detergents, e.g. in EP 0 317 307 and documents cited therein.

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

DE 27 28 211 (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.

40 GB 2 079 305 (Unilever) describes the use of polyols together with boric acid and/or borate and polyacrylate polymers as stabilising agents, while EP 0 080 223 (Unilever) describes the combined use of boric acid or borate and polyol or polyamino compounds with reducing salts, and EP 0 126 505 (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 0 28 865 and 0 28 866 (Procter & Gamble), and USP 4 111 855 (Procter & Gamble), discloses use of further stabilisers, such as calcium with short-chain aliphatic acids such as formate or acetate, and ethanol.

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Background, Aims and Summary of the Present Invention:

In spite of these proposals it remains a practical problem to stabilise enzymes in liquid detergents.

50 An aim of the present invention is to provide further means for stabilising enzymes in liquid detergent compositions. Another aim is to provide liquid detergents in which such means are used, either alone or together with known stabilisers as disclosed in the prior documents cited above, to provide liquid detergents including enzymes, in which an acceptable degree of enzyme stabilisation can be achieved along with other desirable qualities of the detergent compositions.

55 According to the present invention, in one aspect, there is provided a liquid detergent composition comprising surfactant, electrolyte and water in the form of a dispersion of lamellar droplets in an aqueous continuous phase, and further comprising an enzyme and a deflocculating polymer selected from polymers constituted of nonionic monomers and ionic monomers, wherein the ionic monomer is from 0.1 to 50% by weight of the polymer and polymers comprising a hydrophilic backbone and at least one hydrophobic side chain in the

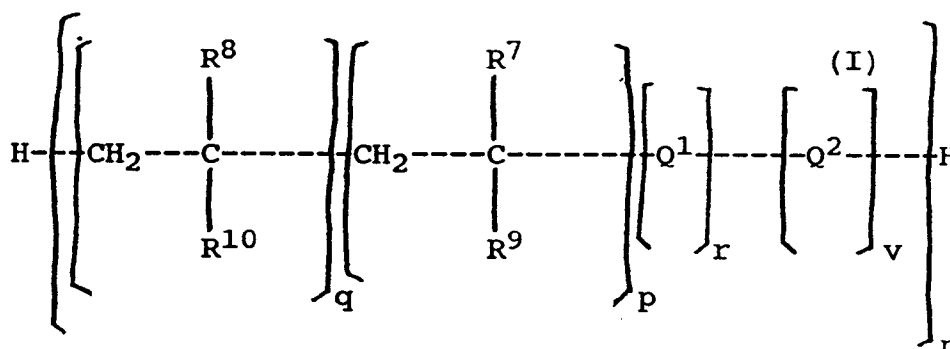
latter case with the provisos that if the enzymes consist of a mixture of Savinase and Amylase, then the relevant composition contains less than 5 wt% glycerol and/or less than 3.5 wt% borax, and if the enzymes consist of Alcalase, then the relevant composition contains less than 3 wt% glycerol and less than 2 wt% borax.

The composition can, for example, include a protease and/or a lipase and optionally a further enzyme, e.g. an enzyme selected from lipase, amylase, and cellulase. It has surprisingly been found that both the protease and optional other enzymes present can be stabilised together in these compositions.

Suitable deflocculating polymers for use in compositions of the present invention are for instance described in our copending European patent application 89201530.6 (EP 346 995), polymers as described in this patent have a hydrophilic backbone and at least one hydrophobic side chain. Generally the hydrophilic backbone of the polymer is predominantly linear (the main chain of the backbone constitutes at least 50 %, preferably more than 75 %, most preferred more than 90% by weight of the backbone), suitable monomer constituents of the hydrophilic backbone are for example unsaturates C_{1-6} acids, ethers, alcohols, aldehydes, ketones or esters, sugar units, alkoxy units, maleic anhydride and saturated polyalcohols such as glycerol. Examples of suitable monomer units are acrylic acid, methacrylic acid, maleic acid, vinyl acetic acid, glucosides, ethylene oxide and glycerol. The hydrophilic backbone made from the backbone constituents in the absence of hydrophilic side-groups is relatively water-soluble at ambient temperature and a pH of between 6.0 and 13.0. Preferably the solubility is more than 1 g/l, more preferred more than 5 g/l most preferred more than 10 g/l.

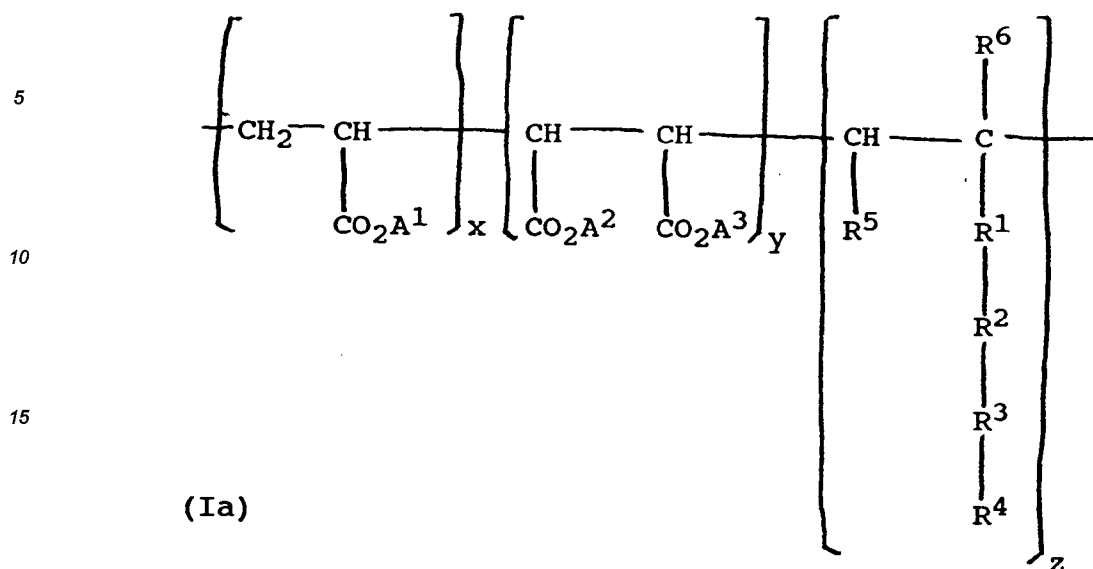
Preferably the hydrophobic sidegroups are composed of relatively hydrophobic alkoxy groups for example butylene oxide and/or propylene oxide and/or alkyl or alkenyl chains having from 5 to 24 carbon atoms. The hydrophobic groups may be connected to the hydrophilic backbone via relatively hydrophilic bonds for example a poly ethoxy linkage.

Preferred polymers are of the formula:



Wherein:

Q^2 is a molecular entity of formula (Ia):



wherein:

R¹ represents -CO-O-, -O-, -O-CO-, -CH₂-, -CO-NH- or is absent;

25 R² represents from 1 to 50 independently selected alkyleneoxy groups preferably ethylene oxide or propylene oxide groups, or is absent, provided that when R³ is absent and R⁴ represents hydrogen or contains no more than 4 carbon atoms, then R² must contain an alkyleneoxy group preferably more than 5 alkyleneoxy groups with at least 3 carbon atoms;

R³ represents a phenylene linkage, or is absent;

R⁴ represents hydrogen or a C₁₋₂₄ alkyl or C₂₋₂₄ alkenyl group, with the provisos that

30 a) when R¹ represents -O-CO-, R² and R³ must be absent and R⁴ must contain at least 5 carbon atoms;-
b) when R² is absent, R⁴ is not hydrogen and when also R³ is absent, then R⁴ must contain at least 5 carbon atoms;

R⁵ represents hydrogen or a group of formula -COOA⁴;

R⁶ represents hydrogen or C₁₋₄ alkyl; and

35 A¹, A², A³ and A⁴ are independently selected from hydrogen, alkali metals, alkaline earth metals, ammonium and amine bases and C₁₋₄, or (C₂H₄O)_t wherein t is from 1-50, and wherein the monomer units may be in random order.

Q¹ is a multifunctional monomer, allowing the branching of the polymer, wherein the monomers of the polymer may be connected to Q¹ in any direction, in any order, therewith possibly resulting in a branched polymer. Preferably Q¹ is trimethyl propane triacrylate (TMPTA), methylene bisacrylamide or divinyl glycol.

40 n is at least 1; z and v are 1; and (x + y + p + q + r) : z is from 4 : 1 to 1,000 : 1, preferably from 6 : 1 to 250 : 1; in which the monomer units may be in random order; and preferably either p and q are zero, or r is zero;

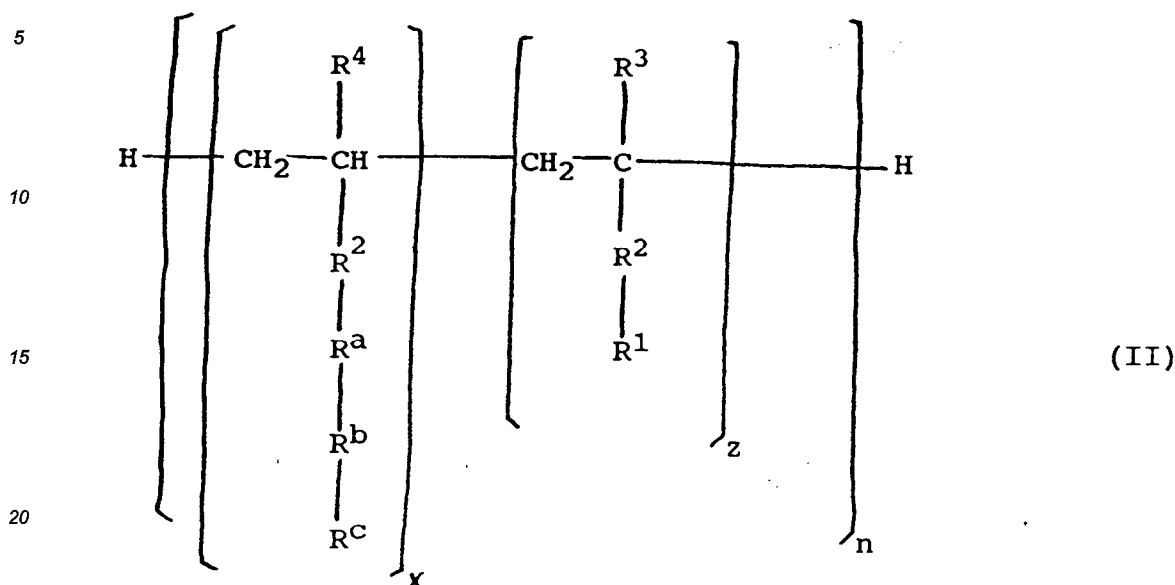
R⁷ and R⁸ represent -CH₃ or -H;

45 R⁹ and R¹⁰ represent substituent groups such as amino, amine, amide, sulphonate, sulphate, phosphonate, phosphate, hydroxy, carboxyl and oxide groups, preferably they are selected from -SO₃Na, -CO-O-C₂H₄-OSO₃Na, -CO-O-NH-C(CH₃)₂-SO₃Na, -CO-NH₂, -O-CO-CH₃, -OH;

50 Preferably polymers for use in compositions of the invention which are of relatively high pH (say 10 or more) are substantially free of hydrolysable groups such as carbonyl groups for increased polymer stability at high pH values. Particularly preferred polymers for use in high pH compositions of the invention comprise hydrophilic backbones constituted by acid groups such as acrylic acid and at least one hydrophobic side chain which is constituted of from 5 to 75 relatively water-insoluble alkoxy groups such as propoxy units optionally linked to the hydrophilic backbone via an -poly-alkoxy linkage constituted of from 1-10 relatively watersoluble alkoxy groups such as ethoxy units.

55 Other preferred polymers for use in compositions of the invention are described in our copending British patent applications 8924479.2, 8924478.4 and 8924477.6. Of the polymers described in those patent applications, especially the use of polymers in accordance with british patent application 8924478.4 is preferred. These polymers are constituted of nonionic monomers and ionic monomers, wherein the ionic monomer is from

0.1 to 50 % by weight of the polymer. Especially preferred polymers of this type are of the formula:

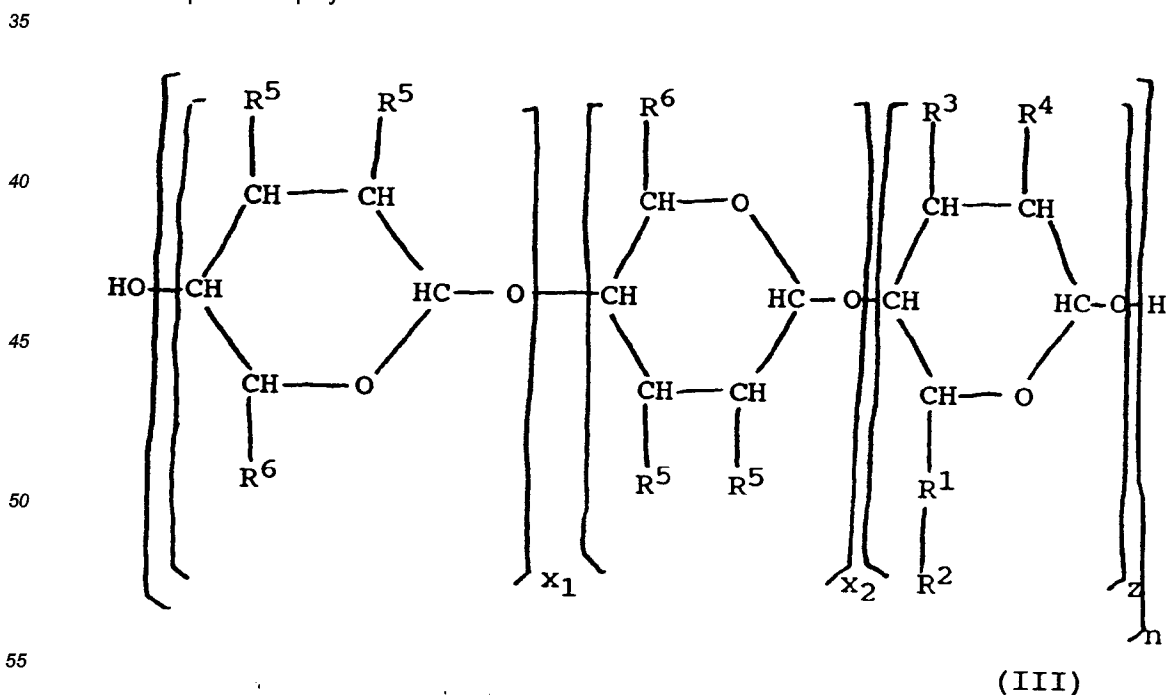


wherein: x, z and n are as above;

- 25
- R³ and R⁴ represent hydrogen or C₁₋₄ alkyl;
 - R² represents -CO-O-, -O-, -O-CO-, -CH₂-, -CO-NH-, or is absent;
 - R¹ represents -C₃H₆-N⁺-(CH₃)₃(Cl⁻), -C₂H₄-OSO₃⁻(Na⁺), -SO₃⁻(Na⁺), -C₂H₄ N⁺(CH₃)₃ Cl⁻, -C₂H₄ N⁺(C₂H₅)₃ Cl⁻, -CH₂ N⁺(CH₃)₃ Cl⁻, -CH₂ N⁺(C₂H₅)₃ Cl⁻ or benzyl-SO₃⁻(Na⁺);
 - R^a is CH₂, C₂H₄, C₃H₆ or is absent;
 - R^b represents from 1 to 50 independently selected alkylene oxide groups, preferably ethylene oxide groups or is absent;
 - R^c represents -OH or -H;
- 30

and wherein if R², R^a and R^b are absent, then R^c is not -H.

Other preferred polymers have the formula:



Wherein:

- $x = x_1 + x_2$

- x, z and n are as defined above
- R¹ represents -CH₂O- or -O-;
- R² represents -CH₂COO⁻Na⁺, -C₃H₆ON⁺(CH₃)₃Cl⁻ or -C₃H₃N⁺(CH₃)₃Cl⁻
- R³ and R⁴ represents -OH, CH₂OH, -O(C₃H₆O)_p-H, -CH₂-O(C₃H₆O)_p-H or -OCH₂COO⁻Na⁺ or -O-C₃H₆ON⁺(CH₃)₃Cl⁻ or -O-C₃H₆N⁺(CH₃)₃Cl⁻
- R⁵ represents -OH, -NH-CO-CH₃ or -O(C₃H₆O)_p-H
- R⁶ represents -OH, -CH₂OH, -CH₂-OCH₃, -O(C₃H₆O)_p-H or -CH₂-O-(C₃H₆O)_p-H
- p is from 1 - 10.

Preferably polymers for use in compositions have a molecular weight (as determined as in our co-pending european patent application 89201530.6) of between 500 and 100,000, more preferred from 1,000 to 20,000, especially preferred from 1,500 to 10,000 most preferred from 2,800 to 6,000. Polymers for use in compositions of the invention may for example be prepared by using conventional aqueous polymerisation procedures, suitable methods are for example described in the above mentioned co-pending European patent application.

We believe that in these compositions the combination of the lamellar dispersion structure and the deflocculating polymer is instrumental in providing good enzyme stabilisation.

The composition can, for example, have a pH of less than 12.5, for example from 6-12, more preferred 7-11, most preferred 8-10. The protease can have an isoelectric point higher than the pH of the liquid detergent composition. The protease can, for example, have pI of about 10 and the composition a pH of about 9.

There can, for example, be further included a quantity of an enzyme-stabilising system selected from (a) an enzyme-stabilising system comprising calcium and short-chain aliphatic acid salt, and (b) a borate-containing enzyme-stabilising system.

The invention also includes, for example, a liquid detergent composition comprising surfactant, electrolyte and water and forming a dispersion of lamellar droplets in an aqueous continuous phase, the composition yielding no more than 2% by volume phase separation when stored at 25°C for 21 days from the time of preparation, and further comprising a deflocculating polymer having a hydrophilic backbone and at least one hydrophobic side-chain, the composition usually having a pH less than e.g. 12.5, and comprising protease enzyme, e.g. a subtilisin-type protease, e.g. with pI greater than about 9, and optionally another enzyme, e.g. lipase. It is important for the stabilising effect described herein that the physical form of the liquid detergent composition be a lamellar dispersion. Homogenising agents (hydrotropes) that remove the lamellar structure leaving an isotropic liquid have been found to worsen the stability of the enzyme.

Our earlier patent application (non-prepublished) EP 0 346 995 (incorporated herein by references describes the use of deflocculating polymers in the preparation of liquid detergent compositions and includes certain examples which include protease enzyme together with substantial quantity of conventional enzyme-stabiliser. Even if the description of our patent application thus incorporated were to be taken into account, it would still be surprising that enzyme-stabilisation can be achieved in systems incorporating the deflocculating polymers as described herein, without requiring such quantities, or any quantities, of stabiliser. In general, the use of conventional stabiliser is not excluded from the present invention because one skilled in the art will recognise that the novel means of enzyme stabilisation disclosed herein may, on occasion, be employed either instead of, or together with, prior known stabilising systems. Compositions as exemplified in EP 346 995 are disclaimed from the scope of the present invention

Often the deflocculating polymer may be used in the range 0.1-5%, e.g. 0.5-4%, e.g. about 1%-3%, of the detergent compositions. The stability of enzyme under conditions described herein has in several cases been found to be better as the quantity of polymer is higher, at least in the range up to about 3% polymer concentration.

Although it is not excluded that previously-known enzyme-stabilising ingredients are also present in the compositions, e.g. glycerol-borate stabiliser, one advantage of the compositions defined herein is that good enzyme stability can be achieved also in the absence of such conventional stabilising materials, or in the presence of amounts of such materials which in themselves confer an insubstantial degree of stabilisation.

In certain embodiments of the compositions of the present invention, glycerol-borax/boric acid stabiliser may be present in small amounts such as, for example, glycerol < 3%, e.g. < 1% with borax < 2% and/or boric acid < 1.7%, e.g. < 0.5%.

Higher amounts or glycerol-borax/boric acid-stabiliser may be present, if desired, to provide enhanced stabilisation.

Correspondingly, embodiments of the present invention may include either small and insubstantial amounts, or higher amounts, of stabilising systems as mentioned in EP 0 028 865-6, e.g. calcium formate/acetate-stabiliser.

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 NH₂-group equivalent to 1 micromole of glycine.

A preferred example of a protease enzyme to be used in the present compositions is the subtilisin variety sold as Savinase (TM of Novo-Nordisk A/S) or Maxacal (TM of Gist-Brocades/IBIS) or as Opticlean (ex MKC) or API22 (ex Showa Denko), which has pI approximately 10. Other useful examples of protease include Maxatase, Esperase, Alcalase (Trade Marks), proteinase K and subtilisin BPN'.

Proteases with high isoelectric point (e.g. preferred Savinase or Maxacal) have been found more stable under the conditions encountered in the compositions of this invention than proteases of lower isoelectric point. So far, particularly good results as to stability have been achieved with the combination of a high-pI protease (e.g. Savinase, pI about 10) and a lower pH of the liquid detergent (e.g. about 9).

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 0 258 068 (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, the presence of polymer ingredients mentioned herein have been found to have a relative stabilising effect on the lipase. This stabilising effect is initially proportional to the quantity used of the polymer, at least in the range up to about 3% polymer.

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 0 214 761 (Novo), EP 0 258 068 (Novo), and EP 0 305 216 (Novo), and especially lipases showing immunological cross-reactivity with antisera raised against lipase from *Thermomyces lanuginosus* ATCC 22070, EP 0 205 208 (Unilever) and EP 0 206 390 (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 0 331 376 (Amano), DE 39 08 131 (Toyo Jozo) and EP 0 204 284 (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).

Cellulose can, for example, be used when present in an amount in the range of about 0.3 to about 35 CEVU units per gram of the detergent composition. A preferred form of cellulase is Celluzyme (TM of Novo).

Genetic engineering of any of the 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. The techniques described in WO 88/02775 (Novo), EP 0 243 338 (Labofina), EP 0 268 452 (Genencor) and EP 0 305 216 (Novo) may be applied and adapted.

EP 0 130 756 (Genentech) (corresponding to USP 4,760,025 (Genencor), EP 0 214 435 (Henkel), WO 87/04461 (Amgen), WO 87/05050 (Genex) and EP 0 303 761 (Genentech) describe useful modified subtilisin proteases.

Further useful modified (lipase) enzymes are also described in, for example, WO 89-09263 (Gist-Brocades) and EP 0 218 272 (Gist-Brocades) as well as EP 0 258 068 (Novo) and EP 0 305 216 (Novo).

The enzyme(s) can usefully be added in the form of a liquid or a slurry or a powder concentrate or a granular composition of enzyme with carrier material (e.g. as described for the case of lipase in EP 0 258 068, but applicable to other enzymes also, and as such compositions are concretely represented, e.g. by the Savinase and Lipolase products of Novo). The compositions may contain either crude or purified enzyme, e.g. enzyme free of cell wall material as described in, for example, EP 0 322 082 (Gist-Brocades).

In certain embodiments, the detergent compositions of the invention may include citrate, e.g. as alkali metal citrate, and be free or substantially free of solid (e.g. builder) particles.

The amount of salt present in the formulations may be up to saturation (for example). Salt levels may also

exceed solubility, since in many cases the liquids can carry suspended solids.

The compositions can contain electrolyte in any amount sufficient to bring about lamellar structuring of the detergent-active material. A salting-out electrolyte (that is an electrolyte having a lyotropic number of less than 9.5, see, for explanation, EP-A-0 079 646 (Unilever)) can be present in, for example, amounts in the range of 1-60% w/w, e.g. 10-45. Optionally some salting-in electrolyte, see for explanation EP 79 646 may also be present.

The detergent compositions may also include usual further detergent ingredients in usual amounts.

Compositions of the invention also comprise detergent active materials, preferably at a level of from 0.1 to 60 % by weight of the composition, more preferred at a level of 20 to 50 % by weight, most preferred from 30 to 45 % by weight.

In the case of blends of surfactants, the precise proportions of each component which will result in lamellar structures will depend on the type(s) and amount(s) of the surfactants and the electrolytes (if present), as is the case with conventional structured systems such as liquids.

In the widest definition the detergent-active material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol.I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol.II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H.Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C₆-C₁₈) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulfoxides.

Preferably the level of nonionic surfactants is more than 0.2 % by weight of the composition, preferably from 5 to 40 % by weight of the composition, more preferred from 7 to 30 %.

Compositions of the present invention may contain synthetic anionic surfactant ingredients, which are preferably present in combination with the above mentioned nonionic materials. Suitable anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C₈-C₁₈) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl (C₉-C₂₀) benzene sulphonates, particularly sodium linear secondary alkyl (C₁₀-C₁₅) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C₈-C₁₈) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C₈₋₂₀) with sodium bisulphite and those derived from reacting paraffins with SO₂ and Cl₂ and then hydrolyzing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C₁₀-C₂₀ alpha-olefins, with SO₃ and then neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C₁₁-C₁₅) alkyl benzene sulphonates and sodium (C₁₆-C₁₈) alkyl sulphates.

Generally the level of the above mentioned anionic surfactant materials is from 0.5-60 % by weight of the composition, preferably from 20-45 %, more preferred from 20 to 40 %, most preferred from 25-35 %.

It is also possible, and sometimes preferred, to include an alkali metal soap of a mono- or di-carboxylic acid, especially a soap of an acid having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. For example the sodium, potassium, ammonium and alkanol amine soaps of these acids can be used. Preferably the level of soap in compositions of the invention is from 0.1 to 30 % by weight of the composition, more preferred from 3 to 20 %, especially preferred from 5 to 15%.

Also possible is the use of salting out resistant active materials such as for example described in EP 328 177, especially the use of alkyl poly glycoside surfactants such as for example disclosed in EP 70 074. Also alkyl mono glucosides may be used.

They may be built or unbuilt. Detergent builder is preferably present in the compositions, some or all of which may be electrolyte. Some surfactants, e.g. soaps, also have builder properties.

Typical examples of phosphorus-containing builders include alkali metal ortho, pyro, hexa-, meta- and tri-
 5 polyphosphates, alkali metal carbonates, either alone or in admixture with calcite, alkali metal citrates, alkali metal nitrilotriacetates, carboxymethyloxysuccinates, zeolites, polyacetalcarboxylates and so on. Phosphonate sequestrant builders may be used.

They may alternatively be of the zero-P type (i.e. not containing any phosphorus-containing builders). For example, they can be built with zeolite particles. Typical examples of non-phosphorus-containing builders include
 10 water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. More specific examples are sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonate, silicates, and zeolites, e.g. zeolite A. Mixed phosphorus- and non-phosphorus-containing builders can be used.

Organic detergency builders include, for example, alkali metal and ammonium and substituted ammonium
 15 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.

Citrate-containing builders are often preferred for use in this invention.

In the context of organic builders, it is often desirable to incorporate polymers which are only partly dissolved in the aqueous continuous phase, as described in EP 0 301 882. This allows viscosity reduction (due
 20 to dissolved polymer) while incorporating amounts that are high enough 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 of average molecular weight at least 1000, having an electrolyte resistance
 25 of more than 5 grams Na-NTA in 100 ml of a 5% aqueous solution of the polymer, and also having vapour pressure in 20% aqueous solution equal to, or less than, the vapour pressure of a 2% aqueous solution of polyethyleneglycol of average molecular weight 6000.

These are as described in EP 0 301 882 (Unilever).

The composition may contain in aggregate 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
 30 non-soap builders.

According to convenience, e.g. to ensure desired pH in the wash liquor during use, it can be convenient
 35 to include a pH buffer such as triethanolamine (HCl), optionally with monoethanolamine. Silicates and carbonates as well as phosphates included for other reasons, e.g. as builders, may provide some (possibly adequate) buffering capacity. Tris buffer can also have an auxiliary stabilising effect on the enzymes of the composition.

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
 40 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
 45 for any temperature-sensitive items such as enzymes and perfumes) in water, followed by builder, if any, and the detergent-active ingredient(s) (optionally as a premix), with stirring. After cooling where necessary, the remaining ingredients are added.

The deflocculating polymer can usefully be added for example just after the electrolyte ingredients, or just after the builder ingredients or after adding the detergent-active ingredients. If zeolites are present, they are
 50 preferably added as the final ingredient.

The compositions can be used for the washing of textile materials, especially but without limitation cotton-, nylon- and polyester-based 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
 55 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%, can be suitable for use in the case when the liquids are formulated as in the Examples below.

The invention is further illustrated by the following non-limitative Examples, in which the example of deflocculating polymer is as described above:

Example 1

A structured liquid detergent composition comprising a deflocculating polymer is prepared to the following formulation:

	Anionic surfactant	
	(linear alkylbenzenesulphonate)	16% (w/w)
10	Nonionic surfactant (Synperonic A7)	7%
	Sodium citrate	20%
	Deflocculating polymer (A11 of EP 346 995)	2%
15	Protease (Savinase)	0.25%

Minors (e.g. fluorescer such as Tinopal (TM) anti-foam such as silicone oil, chelating agent such as Dequest (TM), soluble silicate such as Gasil (TM) or other anti-redeposition agent, perfume, buffer) and water to 100%.

The composition is preferably prepared by adding the ingredients to water at room temperature, with stirring, in the following order: citrate, sodium hydroxide (for neutralising the anionic surfactant to be added in its acid form), a premix of the nonionic surfactant and the acid form of the anionic surfactant. Remaining ingredients including the deflocculating polymer but excluding enzyme are then added; the pH is adjusted to 9.0 using triethanolamine at 2%, followed by HC1, and the protease is added last at room temperature.

In alternative preparative techniques, the deflocculating polymer may be added just before the surfactant premix.

The Savinase enzyme is found to have a good storage stability in this composition.

Examples 2 - 4

Further structured liquid detergent compositions incorporating deflocculating polymer are prepared to formulations similar to that of Example 1. except that the quantity of deflocculating polymer is varied: in Ex. 2 -- 1%; in Ex. 3 -- 3%; and in Ex. 4 -- 4%.

The half-life of deactivation at 37°C (in days) for example 1-4 was as follows:

35	<u>% polymer</u>	<u>half-life (days)</u>
	1	6.6
40	2	9.2
	3	12.4
	4	10.5

The longest storage life of the enzyme was observed in Example 3, with 3% of the polymer.

When 6% of a hydrotrope material such as SXS was added and 10% instead of 20% citrate was used to the composition, the resulting product was no longer structured. The half-life deactivation time at 37°C (in days) for such a system was only 0.6.

Example 5

A structured liquid detergent composition incorporating deflocculating polymer has the following formulation:

55

5	Anionic surfactant (linear alkylbenzenesulphonate)	16%
	Nonionic surfactant (Synperonic A7)	7%
	Sodium citrate	20%
	Deflocculating polymer(A11 of EP 346 995)	0.2%
10	Protease (Savinase)	0.25%
	Lipase (Lipolase)	0.2%

15 Minors and method of preparation are as Examples 1-4. Both the Savinase and the Lipolase enzymes are found to be stabilised in this composition. Higher concentrations of polymer are usable, and about 2-3% polymer concentration has been found to give particularly good enzyme-stabilising effect. At a polymer concentration of 2% the half-life deactivation time at 37°C is 16 days for Savinase and 2 days for the lipase.

20 Example 6

A structured liquid detergent composition incorporating deflocculating polymer has the following formulation:

25	Anionic surfactant (linear alkylbenzenesulphonate)	23%
	Nonionic surfactant (Synperonic A7)	10%
30	Sodium citrate	17%
	Deflocculating polymer(A11 of EP 346 995)	1%
	Protease (Savinase or Alcalase)	0.25%

35 Minors and method of preparation are as Examples 1-4. In an alternative composition, the pH can usefully be made less alkaline, e.g pH 8.5. At a pH of 8.5 the half-life deactivation time at 37°C (in days) for Savinase was 13.1 day and for Alcalase 4.6.

40 The Savinase enzyme is found to have a good storage stability in this composition, the Alcalase enzyme stability is somewhat less good, though still usefully stabilised compared with the situation in the absence of the polymer.

Example 7

45 The following formulation was made as in example I

	Anionic (LAS)	35%
	Nonionic (Synperonic A7)	10%
50	Sodium citrate	13.5%
	Deflocculating polymer (A11)	1%
	Protease (Savinase or Alcalase)	0.25%

55 If Savinase was used as the protease, the half-life deactivation time at 37°C was 4 weeks, if Alcalase was used the half-life time was about 1 week. This result confirms a particularly good enzyme stability for systems of high active level say from 20-60%.

Claims

1. A liquid detergent composition comprising surfactant, electrolyte and water in the form of a dispersion of lamellar droplets in an aqueous continuous phase, and further comprising an enzyme and a deflocculating polymer selected from polymers constituted of nonionic monomers and ionic monomers, wherein the ionic monomer is from 0.1 to 50% by weight of the polymer and polymers comprising a hydrophilic backbone and at least one hydrophobic side chain in the latter case with the provisos that if the enzymes consist of a mixture of Savinase and Amylase, then the relevant composition contains less than 5 wt% glycerol and/or less than 3.5 wt% borax, and if the enzymes consist of Alcalase, then the relevant composition contains less than 3 wt% glycerol and less than 2 wt% borax.
2. A liquid detergent composition according to claim 1 comprising from 10-45% of electrolytes.
3. A liquid detergent composition according to claim 1 or 2 comprising from 20-60% by weight of surfactants.
4. A liquid detergent composition according to claim 1, 2 or 3 comprising 0.1 to 5% by weight of deflocculating polymers.

Patentansprüche

1. Flüssige Waschmittelzusammensetzung, umfassend Tensid, Elektrolyt und Wasser in Form einer Dispersion lamellarer Tröpfchen in einer wässrigen kontinuierlichen Phase, und zusätzlich umfassend ein Enzym und ein entfloccendes Polymer, ausgewählt aus Polymeren, bestehend aus nichtionischen Monomeren und ionischen Monomeren, wobei das ionische Monomer 0,1 bis 50 Gew.-% des Polymers ausmacht, und Polymeren, umfassend ein hydrophiles Gerüst mit mindestens einer hydrophoben Seitenkette; im letzteren Fall mit den Maßgaben, daß wenn die Enzyme aus einem Gemisch von Savinase und Amylase bestehen, die betreffende Zusammensetzung dann weniger als 5 Gew.-% Glycerin und/oder weniger als 3,5 Gew.-% Borax enthält, und wenn die Enzyme aus Alcalase bestehen, die betreffende Zusammensetzung dann weniger als 3 Gew.-% Glycerin und weniger als 2 Gew.-% Borax enthält.
2. Flüssige Waschmittelzusammensetzung nach Anspruch 1, umfassend 10 bis 45 % Elektrolyte.
3. Flüssige Waschmittelzusammensetzung nach Anspruch 1 oder 2, umfassend 20 bis 60 Gew.-% Tenside.
4. Flüssige Waschmittelzusammensetzung nach Anspruch 1, 2 oder 3, umfassend 0,1 bis 5 Gew.-% entfloccende Polymere.

Revendications

1. Composition détergente liquide comprenant un tensioactif, un électrolyte et de l'eau sous forme d'une dispersion de gouttelettes lamellaires dans une phase aqueuse continue, et qui comprend en outre une enzyme et un polymère défloculant choisi parmi les polymères constitués de monomères non ioniques et de monomères ioniques, les monomères ioniques représentant de 0,1 à 50% en poids du polymère et les polymères comprenant un édifice de base hydrophile et au moins une chaîne latérale hydrophobe, dans ce dernier cas à la condition que si les enzymes consistent en un mélange de Savinase et Amylase, alors la composition considérée renferme moins de 5% en poids de glycérol et/ou moins de 3,5% en poids de borax, et si les enzymes consistent en Alcalase, alors la composition considérée renferme moins de 3% en poids de glycérol et moins de 2% en poids de borax.
2. Composition détergente liquide selon la revendication 1, qui comprend de 10 à 45% d'électrolytes.
3. Composition détergente liquide selon la revendication 1 ou 2, qui comprend de 20 à 60% en poids de tensioactifs.
4. Composition détergente liquide selon la revendication 1, 2 ou 3, qui comprend de 0,1 à 5% en poids de polymères défloculants.