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(54) **LIQUID DISHWASHING DETERGENT**

(57) The invention concerns liquid, phosphate free dishwashing detergents that are essentially free of bleach and comprise a polymer combination of polyaspartic acid or modified polyaspartic acid and graft polymers based on oligo- and polysaccharides that improves shine on glass.

EP 4 386 071 A1

Description

[0001] The invention concerns liquid, phosphate free dishwashing detergents that are essentially free of bleach and comprise a polymer combination of polyaspartic acid or modified polyaspartic acid and graft polymers based on oligo- and polysaccharides that improves shine on glass.

[0002] WO 2019/211231 A1 describes compositions containing a polymer mix of polyaspartic acid or modified polyaspartic acid and graft polymers based on oligo- and polysaccharides to improve shine on glass ware during automatic dishwashing.

[0003] In WO2015/197379 A1 formulations are disclosed that contain a complexing agent selected from GLDA and MGDA and a graft copolymer based on oligo- and polysaccharides.

[0004] It is an object of the invention to provide a composition that is biodegradable without reduction of cleaning performance and better shine on glass. It reduces or prevents filming and spotting, enhances inhibition of spot formation, leads to an overall better rinse performance and additionally reduces scale built up. Furthermore, it takes care of the interior of the automatic dishwashing machine. Especially, it shows a reduction of limescale built up at the inner parts of the machine.

[0005] In a first aspect the invention relates to a phosphate free dishwashing detergent formulation, liquid at 20 °C, that is essentially free of bleach, comprising

(i) 1 - 5 % by weight of the total composition of

(a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,

(b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

(b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and

(b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 3 to 25% by weight of the total composition of complexing agent selected from the group of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts thereof as complexing agent;

(iii) from 0.2 to 6 % by weight of the total composition of thickener;

(iv) at least 20 % by weight of the total composition of water and

(v) optionally from 4 to 15% by weight of the total composition of builders and/or cobuilders;

(vi) optionally from 1 to 8% by weight of the total composition of nonionic surfactants;

(vii) optionally from 0.001 to 3% by weight of the total composition of enzymes;

(viii) optionally from 2 to 30 wt% of the total composition of organic solvents.

[0006] The compositions according to the invention provide a comparable or even better cleaning performance than other liquid dishwashing compositions with the polymer mixture. The shine of glassware washed in an automatic dishwasher with these compositions is improved and also glass corrosion is reduced. Furthermore, the compositions are beneficial because the biodegradability is enhanced. Preferably the active ingredients of the compositions are biodegradable which leads to a high percentage of biodegradability, preferably above 85 % by weight of the composition. This means that 85 % by weight of the components in the composition are biodegradable. More preferably more than 90 wt% of the composition is biodegradable, most preferred more than 98 % of the composition is biodegradable. Biodegradability of the components is defined according to OECD 301.

[0007] The dishwashing detergent formulations according to the invention are suitable in particular as dishwashing

detergent composition for machine dishwashing. In one embodiment, the dishwashing detergent composition according to the invention is therefore a machine dishwashing detergent composition. The dishwashing detergent formulations according to the invention can be provided in liquid or gel-like form, as one or more phases.

[0008] Preferred embodiments are set out in the dependent claims.

[0009] When wt.-% (% by weight) values are given, they are based on the total weight of the liquid composition, except explicitly stated otherwise. Numerical ranges given in the format "from x to y" include the above values. When multiple preferred numerical ranges are given in this format, it is understood that all ranges resulting from the combination of the various endpoints are also included.

[0010] In the present specification, the terms "a" and "an" and "at least one" are the same as the term "one or more" and can be employed interchangeably.

[0011] "One or more", as used herein, relates to at least one and comprises 1, 2, 3, 4, 5, 6, 7, 8, 9 or more of the referenced species. Similarly, "at least one," as used herein, includes but is not limited to 1, 2, 3, 4, 5, 6, and more. With respect to an ingredient, it refers to the type of ingredient and not to the absolute number of molecules. "At least one surfactant" thus means, for example, at least one type of surfactant, meaning that one type of surfactant or a mixture of several different surfactants may be meant. Together with weight indications, the indication refers to all compounds of the indicated type contained in the composition/mixture, i.e., that the composition does not contain any further compounds of this type beyond the indicated amount of the corresponding compounds.

[0012] Where reference is made herein to molar masses, this information always refers to the number-average molar mass M_n , unless explicitly stated otherwise. The number average molar mass can be determined, for example, by gel permeation chromatography (GPC) according to DIN 55672-1 :2007-08 with THF as eluent. The weight average molecular weight M_w can also be determined by GPC as described for M_n .

[0013] Whenever alkaline earth metals are mentioned in the following as counterions for monovalent anions, this means that the alkaline earth metal is naturally present only in half the amount of substance - sufficient for charge balance - as the anion.

[0014] In the context of the present invention, fatty acids or fatty alcohols or derivatives thereof - unless otherwise indicated - are representative of branched or unbranched carboxylic acids or alcohols or derivatives thereof preferably having 6 to 22 carbon atoms. The former are preferred for ecological reasons, in particular because of their vegetable basis as being based on renewable raw materials, without, however, limiting the teaching according to the invention to them. In particular, the oxo-alcohols obtainable, for example, according to the ROELEN oxo-synthesis or their derivatives can also be used accordingly.

[0015] The cleaning composition according to the invention is provided in form of a liquid. The term "liquid" as used herein includes liquids and gels. The term "liquid", as used herein, refers to compounds or mixtures of compounds that are flowable and pourable at 20° C, 1 bar.

[0016] The cleaning composition according to the invention is phosphate-free. "Phosphate-free" as used herein is to be understood as the cleaning composition being substantially free of phosphate (including orthophosphate, polyphosphate and/or pyrophosphate), in particular as comprising phosphates in an amount of less than 0.1 wt.%, preferably less than 0.01 wt.%, based on the total weight of the composition.

[0017] The expression "essentially free of" means that the respective compound may in principle be contained, but is then present in an amount that does not impair a function of the other components. In the context of the present invention, therefore, the property "essentially free of" a particular compound is preferably taken to mean a total weight of less than 0.1 % by weight, more preferably less than 0.001 % by weight, in particular free of it, based on the total weight of the composition.

[0018] The cleaning composition according to the invention is essentially free of bleach. This means in the context of the invention that the compositions comprise less than 0.1 % by weight of percarbonate salts, alkali metal hypochlorite, H_2O_2 and its precursors, based on the total weight of the composition. Preferably the compositions comprise less than 0.01 wt% by weight, more preferred less than 0.001 % by weight of these components based on the total weight of the composition.

[0019] "Bleach-free" as used herein is to be understood as the cleaning composition being substantially free of active ingredients, that are capable to release bleach, especially peroxy-containing compounds, hypohalogenic compounds or H_2O_2 to the wash liquor in an automatic dishwashing. In a preferred embodiment "bleach-free" means that the composition comprises bleach compounds (compounds that release bleach) in an amount of less than 0.1 wt.%, preferably less than 0.01 wt.%, based on the total weight of the composition.

[0020] It was surprisingly found that liquid compositions that contain a polymer mix according to i) containing biodegradable polyaspartic acid or modified polyaspartic acid or salts thereof (a) and biodegradable graft polymer (b) prepared by grafting of at least one ethylenic unsaturated mono- or dicarboxylic acid and at least one N-containing cationic monomer onto oligo- and polysaccharides leads to dramatically improved cleaning re-suit. The combination is especially effective in preventing film formation (scaling) on glass.

[0021] The weight ratio of aspartic or modified aspartic acid (a) to graft polymer (b) is preferably from 18:1 to 5:1, more

preferably from 11 : 1 to 8 : 1 particularly preferably from 11 : 1 to 9 : 1.

[0022] The sum of components (a) and (b) accounts for 1 to 4% by weight of the total composition. When the dishwashing detergent formulation of the invention is being formulated, components (a) and (b) can be added separately, or can be added as a pre-compounded film inhibiting composition.

[0023] In a preferred embodiment in the dishwashing detergent formulation the amount of the component according to (i) is from 1.2 % to 4.5%, preferably from 1.5 % to 4.0 % by weight of the total composition.

[0024] Polyaspartic acid is well known as biodegradable dispersing and scale inhibiting polymer. Modified polyaspartic acid which can be used according to the present invention is preparable by polycondensation of (a1) 50 to 99 mol%, preferably 60 to 95 mol%, particularly preferably 80 to 95 mol%, of aspartic acid; and (a2) 1 to 50 mol%, preferably 5 to 40 mol%, particularly preferably 5 to 20 mol%, of at least one carboxyl-containing compound, and subsequent hydrolysis of the cocondensates with the addition of a base, for example sodium hydroxide solution, wherein (a2) is not an aspartic acid.

[0025] The carboxyl-containing compound (a2) used in connection with the preparation of the polyaspartic acid to be used according to the invention can be, inter alia, a carboxylic acid (monocarboxylic acid or polycarboxylic acid), a hydroxycarboxylic acid and/or an amino acid (apart from aspartic acid). Such carboxylic acids or hydroxycarboxylic acids are preferably polybasic. In this connection, polybasic carboxylic acids can thus be used in the preparation of the polyaspartic acid to be used according to the invention, e.g. oxalic acid, adipic acid, fumaric acid, maleic acid, itaconic acid, aconitic acid, succinic acid, malonic acid, suberic acid, azelaic acid, diglycolic acid, glutaric acid, C1-C26 alkylsuccinic acids (e.g. octylsuccinic acid), C2-C26 alkenylsuccinic acids (e.g. octenylsuccinic acid), 1,2,3-propanetricarboxylic acid, 1,1,3,3,3-pentanetricarboxylic acid, 1,1,1,2,2,2-hexanetricarboxylic acid, 1,1,1,2,2,3,3,3-octanetricarboxylic acid, 1,1,1,2,2,3,3,3,4,4,4-nonanetricarboxylic acid, 1,1,1,2,2,3,3,3,4,4,4,5,5,5-decanetricarboxylic acid, or 1,1,1,3,3,3,5-pentanetricarboxylic acid. Furthermore, in this connection it is also possible to use polybasic hydroxycarboxylic acids, e.g. citric acid, isocitric acid, mucic acid, tartaric acid, tartronic acid, or malic acid. Amino acids that can be used in this connection are, inter alia, aminocarboxylic acids (e.g. glutamic acid, cysteine), basic diaminocarboxylic acids (e.g. lysine, arginine, histidine, aminocaprolactam), neutral amino acids (e.g. glycine, alanine, valine, leucine, isoleucine, methionine, cysteine, norleucine, caprolactam, asparagine, iso-asparagine, glutamine, isoglutamine), aminosulfonic acids (e.g. taurine), hydroxylamino acids (e.g. hydroxyproline, serine, threonine), iminocarboxylic acids (e.g. proline, iminodiacetic acid), or aromatic and heterocyclic amino acids (e.g. anthranilic acid, tryptophan, tyrosine, histidine), but not aspartic acid. Preferred carboxyl-containing compounds (a2) in connection with the preparation of the modified polyaspartic acids to be used according to the invention are 1,2,3,4-butanetetracarboxylic acid, citric acid, glycine, glutamic acid, itaconic acid, succinic acid, taurine, maleic acid and glutaric acid, particularly preferably 1,2,3,4-butanetetracarboxylic acid, citric acid, glycine and glutamic acid.

[0026] The molecular weight (Mw) of the (modified) polyaspartic acid can easily be tuned by varying the reaction conditions. Molecular weights between 1000 g/mol and 100 000 g/mol can be achieved by simple adjustment of the process parameters (temperature, catalyst, reaction time).

[0027] The preferred molecular weight of the (modified) polyaspartic acid used according to the present invention lies in the range between 1000 g/mol and 20 000 g/mol, preferably between 1500 and 15 000 g/mol and particularly preferably between 2000 and 10 000 g/mol.

[0028] The aspartic acid used in connection with the preparation of the (modified) polyaspartic acid to be used according to the invention can either be L- or D- and DL-aspartic acid. Preference is given to using L-aspartic acid.

[0029] In a preferred embodiment the dishwashing detergent formulation contains polyaspartic acid as homopolymer in amounts and molecular weight as preferred above.

[0030] The preparation of the (modified) polyaspartic acids to be used according to the invention takes place generally via a poly(co)condensation of aspartic acid, optionally with at least one carboxyl-containing compound (not aspartic acid) and subsequent hydrolysis of the obtained (co)condensates with the addition of a base as illustrated and described above and below. The preparation of such (modified) polyaspartic acids is also described, by way of example in DE 4221875.6 or WO 2019/211231 A1, the disclosure of these is hereby referred to in its entirety.

[0031] In the case of the treatment with bases, neutralized (modified) polyaspartic acid are obtained in the form of the salts corresponding to the bases. The (modified) polyaspartic acids to be used according to the invention and/or their salts can be used as aqueous solution or in solid form, e.g. in powder or granule form. As is known to the person skilled in the art, the powder or granule form can be obtained for example by spray drying, spray granulation, fluidized-bed spray granulation, roller drying or freeze drying of the aqueous solution of the polyaspartic acids or their salts.

[0032] The composition according to the invention contains (b) at least one graft copolymer composed of

- (b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of
- (b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and
- (b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge.

[0033] In the context of the present invention, oligosaccharides that may be mentioned are carbohydrates with three to ten monosaccharide units per molecule, for example glycans. In the context of the present invention, polysaccharides is the term used to refer to carbohydrates with more than ten monosaccharide units per molecule. Oligo- and polysaccharides may be for example linear, cyclic or branched.

[0034] Polysaccharides to be mentioned by way of example are biopolymers such as starch and glycogen, and cellulose, dextran and tunicin. Furthermore, mention is to be made of inulin as polycondensate of D-fructose (fructans), chitin and alginic acid. Further examples of polysaccharides are starch degradation products, for example products which can be obtained by enzymatic or so-called chemical degradation of starch. Examples of the so-called chemical degradation of starch are oxidative degradation and acid-catalyzed hydrolysis.

[0035] Preferred examples of starch degradation products are maltodextrins and glucose syrup. In the context of the present invention, maltodextrin is the term used to refer to mixtures of monomers, dimers, oligomers and polymers of glucose. The percentage composition differs depending on the degree of hydrolysis. This is described by the dextrose equivalent, which in the case of maltodextrin is between 3 and 40.

[0036] Preferably, the graft base (b1) is selected from polysaccharides, in particular from starch, which is preferably not chemically modified. In one embodiment of the present invention, starch is selected from those polysaccharides which have in the range from 20 to 30% by weight amylose and in the range from 70 to 80% amylopectin. Examples are corn starch, rice starch, potato starch and wheat starch. Side chains are grafted on to the graft base (b1). Per molecule of graft copolymer (b), preferably on average one to ten side chains can be grafted on. Preferably, in this connection, a side chain is linked with the anomeric carbon atom of a monosaccharide or with an anomeric carbon atom of the chain end of an oligo- or polysaccharide. The number of side chains is limited upwards by the number of carbon atoms with hydroxyl groups of the graft base (b1) in question.

[0037] Examples of monocarboxylic acids (b2) are ethylenically unsaturated C₃-C₁₀-monocarboxylic acids and the alkali metal or ammonium salts thereof, in particular the potassium and the sodium salts. Preferred monocarboxylic acids (b2) are acrylic acid and methacrylic acid, and also sodium (meth)acrylate. Mixtures of ethylenically unsaturated C₃-C₁₀ monocarboxylic acids and in particular mixtures of acrylic acid and methacrylic acid are also preferred components (b2).

[0038] Examples of dicarboxylic acids (b2) are ethylenically unsaturated C₄-C₁₀-dicarboxylic acids and their mono- and in particular dialkali metal or ammonium salts, in particular the dipotassium and the disodium salts, and also anhydrides of ethylenically unsaturated C₄-C₁₀-dicarboxylic acids. Preferred dicarboxylic acids (b2) are maleic acid, fumaric acid, itaconic acid, and also maleic anhydride and itaconic anhydride.

[0039] In one embodiment, graft copolymer (b) comprises in at least one side chain, besides monomer (b3) at least one monocarboxylic acid (b2) and at least one dicarboxylic acid (b2). In a preferred embodiment of the present invention, graft copolymer (b) comprises in polymerized- in form in the side chains, besides monomer (b3), exclusively monocarboxylic acid (b2), but no dicarboxylic acid (b2).

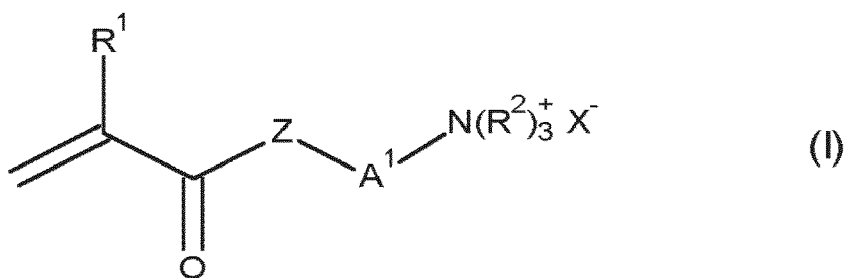
[0040] Examples of monomers (b3) are ethylenically unsaturated N-containing compounds with a permanent cationic charge, i.e. those ethylenically unsaturated N-containing compounds which form ammonium salts with anions such as sulfate, C₁-C₄-alkyl sulfates and halides, in particular with chloride, and independently of the pH. Any desired mixtures of two or more monomers (b3) are also suitable.

[0041] Examples of suitable monomers (b3) are the correspondingly quaternized derivatives of vinyl- and allyl-substituted nitrogen heterocycles such as 2-vinylpyridine and 4-vinylpyridine, 2-allylpyridine and 4-allylpyridine, and also N-vinylimidazole, e.g. 1-vinyl-3-methylimidazolium chloride. Also of suitability are the correspondingly quaternized derivatives of N,N-diallyl amines and N,N-diallyl-N-alkyl amines, such as e.g. N,N-diallyl-N,N-dimethylammonium chloride (DADMAC).

[0042] In one embodiment of the present invention, monomer (b3) is selected from correspondingly quaternized, ethylenically unsaturated amides of mono- and dicarboxylic acids with diamines which have at least one primary or secondary amino group. Preference is given here to those diamines which have one tertiary and one primary or secondary amino group. In another embodiment of the present invention, monomer (b3) is selected from correspondingly quaternized, ethylenically unsaturated esters of mono- and dicarboxylic acids with C₂-C₁₂- amino alcohols which are mono- or dialkylated on the amine nitrogen.

[0043] Of suitability as acid component of the aforementioned esters and amides are e.g. acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, crotonic acid, maleic anhydride, monobutyl maleate and mixtures thereof. As acid component, preference is given to using acrylic acid, methacrylic acid and mixtures thereof.

[0044] Preferred monomers (b3) have the general formula (I),



wherein the variables are defined as follows:

Z is O or NR¹,

R¹ is selected from methyl and hydrogen,

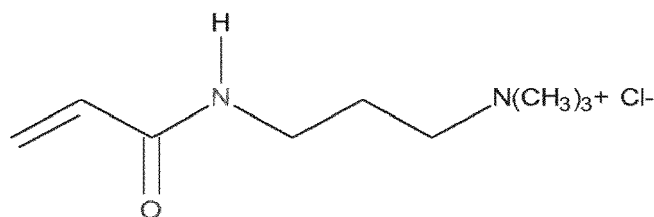
A¹ is selected from C₂-C₄-alkylene,

R² are identical or different and selected from C₁-C₄-alkyl,

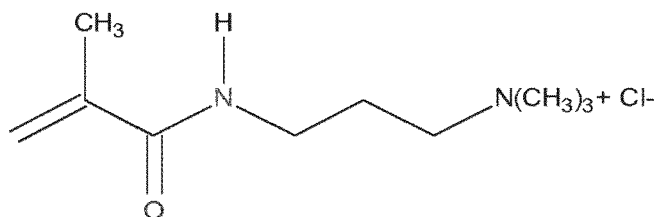
X is selected from halide, mono-C₁-C₄-alkyl sulfate and sulfate.

[0045] Particular preferred monomers (b3) are trialkylaminoethyl (meth)acrylatochloride or alkyl sulfate and trialkylaminopropyl (meth)acrylatochloride or alkyl sulfate, and also (meth)acryl-amidoethyltrialkylammonium chloride or alkyl sulfate and (meth)acrylamidopropyltrialkyl-ammonium chloride or alkyl sulfate, where the respective alkyl radical is preferably methyl or ethyl or mixtures thereof.

[0046] Very particular preference is given to (meth)acrylamidopropyltrimethylammonium halide, in particular acrylamidopropyltrimethylammonium chloride ("APTAC") or methacrylamidopropyl-trimethylammonium chloride ("MAPTAC").

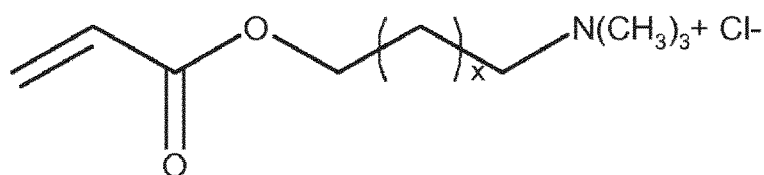


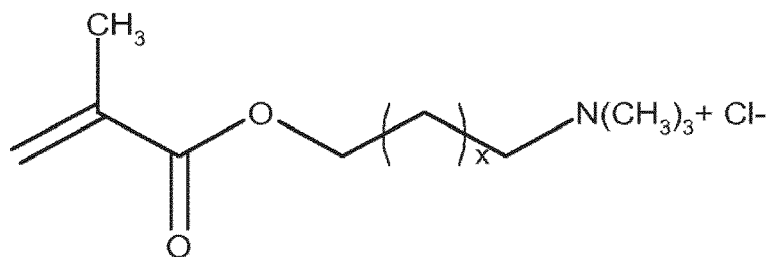
APTAC



MAPTAC

[0047] In another preferred embodiment of the present invention, monomer (b3) is selected from trimethylammonium C₂-C₃-alkyl(meth)acrylatohalide, in particular 2-(trimethylamino)ethyl(meth)-acrylatochloride and 3-(trimethylamino)propyl(meth)acrylatochloride.





$x = 0 \text{ or } 1$

[0048] In the most preferred embodiment of the present invention, monomer (b3) is trimethylaminoethyl (meth)acrylate or methacrylamidopropyl trimethyl ammonium Chloride, preferably ω -trimethylaminoethyl (meth)acrylate or methacrylamidopropyl trimethyl ammonium Chloride.

[0049] Graft copolymer (b) can comprise, in polymerized-in form, in one or more side chains at least one further comonomer (b4), for example hydroxyalkyl esters such as 2-hydroxyethyl (meth)acrylate or 3-hydroxypropyl (meth)acrylate, or esters of alkoxylated fatty alcohols, or comonomers containing sulfonic acid groups, for example 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and its alkali metal salts. Preferably, graft copolymer (b) comprises no further comonomers (b4) in one or more side chains apart from monomer (b3) and monocarboxylic acid (b2) or dicarboxylic acid (b2).

[0050] In one embodiment of the present invention, the fraction of graft base (b1) in graft copolymer (b) is in the range from 40 to 95% by weight, preferably from 50 to 90% by weight, in each case based on total graft copolymer (b). In one embodiment of the present invention, the fraction of monocarboxylic acid (b2) or dicarboxylic acid (b2) is in the range from 2 to 40% by weight, preferably from 5 to 30% by weight and in particular from 5 to 25% by weight, in each case based on total graft copolymer (b).

[0051] The monomers of type (b3) are polymerized in amounts of from 5 to 50% by weight, preferably from 5 to 40% by weight and particularly preferably from 5 to 30% by weight, in each case based on total graft copolymer (b).

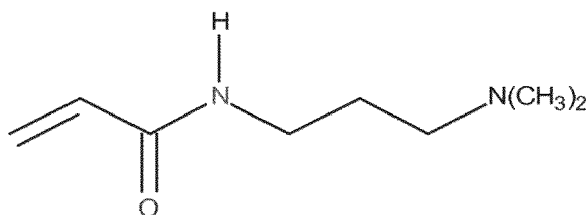
[0052] It is preferred if graft copolymer (b) comprises, in polymerized-in form, more monocarboxylic acid (b2) than compound (b3), and specifically based on the molar fractions, for example in the range from 1.1 :1 to 5:1, preferably 2:1 to 4:1.

[0053] In one embodiment of the present invention, the average molecular weight (M_w) of graft copolymer (b) is in the range from 2000 to 200 000 g/mol, preferably from 5000 to 150 000 and in particular in the range from 8000 to 100 000 g/mol. The average molecular weight M_w is measured preferably by gel permeation chromatography in aqueous KCl/formic acid solution.

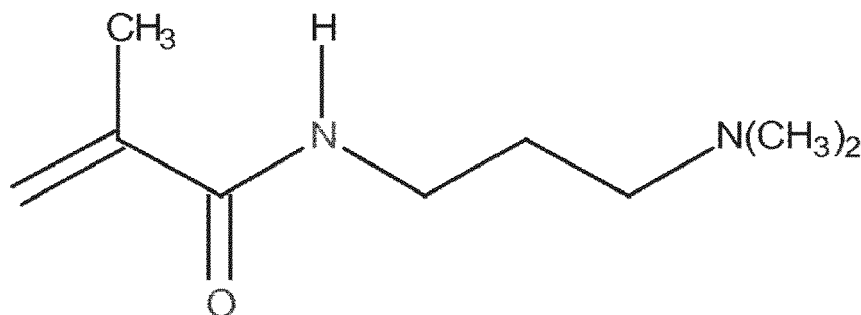
[0054] Graft copolymer (b) can preferably be obtained as aqueous solution from which it can be isolated, e.g. by spray drying, spray granulation or freeze drying.

[0055] If desired, solution of graft copolymer (b) or dried graft copolymer (b) can be used for producing the formulations according to the invention.

[0056] Monomer (b3) per se can be polymerized in graft copolymer (b) or a non quaternized equivalent, in the case of APT AC for example

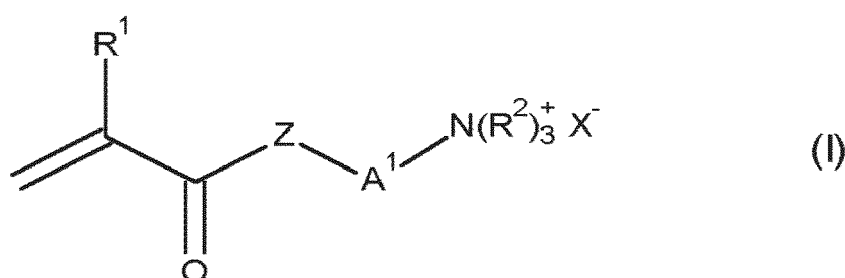


and in the case of MAPTAC with



and the copolymerization can be followed by alkylation, for example with C₁-C₈-alkyl halide or di-C₁-C₄-alkyl sulfate, for example with ethyl chloride, ethyl bromide, methyl chloride, methyl bromide, dimethyl sulfate or diethyl sulfate.

[0057] A preferred embodiment of the dishwashing detergent formulation according to the invention is, wherein the monomer (b3) is at least one compound of the general formula (I),



wherein the variables are defined as follows:

- Z is O or NR₁, preferably Z is O,
- R₁ is selected from methyl and hydrogen,
- A₁ is selected from C₂-C₄-alkylene,
- R₂ are identical or different and selected from C₁-C₄-alkyl,
- X⁻ is selected from halide, mono-C₁-C₄-alkyl sulfate and sulfates.

[0058] Especially preferred are monomers (b3) according to the foregoing formula (I) wherein R² are identical and methyl, A₁ is CH₂CH₂, and X⁻ is chloride.

[0059] The composition according to the invention comprising polyaspartic acid or modified polyaspartic acid (a) and graft copolymer (b) as described herein and to be used according to the invention can be used particularly advantageously in machine dishwashing detergents. They are characterized here in particular by their film-inhibiting effect both towards inorganic and organic films. In particular, they inhibit films made of calcium and magnesium carbonate and calcium and magnesium phosphates and phosphonates. Additionally, they prevent deposits which originate from the soil constituents of the wash liquor, such as grease, protein and starch films.

[0060] The dishwashing detergent formulation according to the invention comprises from 3 to 25% by weight of the total composition of complexing agent selected from the group of citric acid or salts thereof, methylglycinediacetic acid (MGDA) or salts thereof and glutamic acid diacetic acid (GLDA) or salts thereof.

[0061] Particularly preferred representatives of this class are the alkali metal salts thereof, especially the trisodium salt of methylglycinediacetic acid (MGDA) or the tetrasodium salt of glutamic diacetic acid (GLDA) and/or trisodium citrate, in particular anhydrous trisodium citrate or trisodium citrate dihydrate.

[0062] Preferred are also combinations of citric acid or salts thereof with methylglycinediacetic acid (MGDA) or salts thereof. Especially preferred is the combination of trisodium salt of methylglycinediacetic acid (MGDA) and trisodium citrate.

[0063] In a preferred embodiment of the composition the dishwashing detergent formulation is characterized in that the amount of methylglycinediacetic acid (MGDA) and its salts, is from 4.5 to 20 % by weight of the total composition.

[0064] In another preferred embodiment of the composition the dishwashing detergent formulation is characterized in that the amount of citric acid and its salts, is from 0.5 to 15 % by weight of the total composition.

[0065] In a preferred embodiment of the composition the dishwashing detergent formulation is characterized in that the amount of methylglycinediacetic acid (MGDA) and its salts, is from 4.5 to 20 % by weight of the total composition

and the amount of citric acid and its salts, is from 0.5 to 15 % by weight of the total composition.

[0066] The compositions according to the invention comprise from 0.2 to 6 % by weight of the total composition of thickener. Preferably, the thickener is selected from the group consisting of polysaccharide gums such as xanthan gum, guar, carageenan, pectin, alginate, and succinoglycan gum; synthetic rheology modifiers based on acrylates (such as Carbopol® Aqua 30, Acusol® 810, Acusol® 830, Acusol® 835 or Acusol® 842) or urethanes (such as Acusol® 880 and Acusol® 882); "low-molecular-weight gelators" "LMWG", such as dibenzylidene sorbitol (DBS), hydrogenated castor oil (HCO), urea derivatives (such as Rheobyk® 7420) or cyclic dipeptides.

[0067] Especially preferred are cleaning compositions that contain from 0.2 to 5.0 wt.%, preferably from 0.20 to 2.5 wt.%, more preferably to 0.25 to 1.5 wt.% of thickeners, most preferred from 0.3 to 1.0 wt.%, based on the weight of the liquid phase.

[0068] Preferred thickeners are selected from the group of xanthan gum, crosslinked polyacrylate and urea derivatives.

[0069] Xanthan gum, urea derivatives, such as Rheobyk® 7420, and/or crosslinked polyacrylate, such as Acusol® 810, are able to stabilize the liquid phase and minimize disintegration of this mixture. Especially, they reduce sedimentation of the detergent ingredients.

[0070] In a preferred embodiment the dishwashing detergent formulation according to the inventions comprises xanthan gum as a thickener, preferably in an amount from 0.25 to 0.8 % by weight of the total composition.

[0071] In a preferred embodiment the dishwashing detergent formulation according to the inventions comprises a thickener selected from crosslinked polyacrylic acids, preferably in an amount from 0.5 to 1.0 % by weight of the total composition.

[0072] The cleaning composition according to the present invention comprises a significant amount of water. In a preferred embodiment of the invention the amount of water is at least 30 % by weight of the total composition, preferably from 40 to 70 % by weight of the total composition, most preferred from 40 to 60 % by weight of the total composition.

[0073] In a preferred embodiment of the invention the cleaning composition contains 45 to 75 wt.% water and 0.2 to 2.5 wt.% of thickeners, each based on the weight of the composition. More preferably it contains 50 to 70 wt.% water and 0.25 to 1.5 wt.% of thickener, selected from xanthan gum or crosslinked polyacrylates or urea derivatives, each based on the weight of the composition.

[0074] Builders and/or cobuilders according to the invention (mentioned as components (v) in the main claim) that can be used are, in particular, water-soluble or water-insoluble substances, the main task of which consists in the binding of calcium and magnesium ions. These expressions "builders" and "cobuilders" according to the invention do not include citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) and/or salts thereof. Builders and/or cobuilders may be low molecular weight carboxylic acids, and salts thereof such as alkali metal malonates, fatty acid sulfonates, gluconic acids, oxadiacetates, carboxymethyloxysuccinates, tartrate monoacetate, tartrate diacetate and α-hydroxypropionic acid.

[0075] Furthermore, builders which can be used in connection with the dishwashing detergent formulations according to the invention are carbonates and hydrocarbonates, among which the alkali metal salts, in particular sodium salts, are preferred.

[0076] In a preferred embodiment the dishwashing detergent formulation is characterized in that the composition comprises as builder (a component according to (v) of the main claim) from 5 to 12% by weight, preferably 7 to 10 % by weight of the total composition an alkali metal carbonate.

[0077] Another cobuilder which can be present in some embodiments of the cleaning composition to the invention are phosphonates. These are in particular hydroxylalkane- and aminoalkanephosphonates. Among the hydroxylalkanephosphonates, 1-hydroxyethane-1,1-diphosphonate (HEDP) is of particular importance as cobuilder. It is preferably used as sodium salt, with the disodium salt giving a neutral reaction and the tetrasodium salt an alkaline reaction (pH 9). Suitable aminoalkanephosphonates are preferably ethylenediaminetetramethylene-phosphonate (EDTMP), diethylenetriaminepentamethylenephosphonate (DTPMP), and higher homologs thereof. They are preferably used in the form of the neutrally reacting sodium salts, e.g. as hexasodium salt of EDTMP or as hepta- and octasodium salt of DTPMP. The builder used here from the class of phosphonates is preferably HEDP. Moreover, the aminoalkane-phosphonates have a marked heavy metal binding capacity.

[0078] In a highly preferred embodiment, the composition comprises less than 0.1 %, preferably less than 0.01 % by weight of phosphonates. Preferably the composition comprises less than 0.01 % by weight of phosphorous containing compounds. Phosphonate free compositions show better biodegradability and/or are improved from an ecological point of view. Therefore, these embodiments are most preferred.

[0079] In a preferred embodiment of the invention the formulations are essentially free of silicate. Preferably the total weight of silicates is less than 0.1 % by weight, more preferably less than 0.001 % by weight, in particular free of it, based on the total weight of the composition.

[0080] Copolymers of acrylic acid or of methacrylic acid might be used. Suitable comonomers are, in particular, monoethylenically unsaturated dicarboxylic acids such as maleic acid, fumaric acid and itaconic acid, and anhydrides thereof such as maleic anhydride. Comonomers containing sulfonic acid groups, such as 2-acrylamido-2-methylpropanesulfonic

acid, allylsulfonic acid and vinylsulfonic acid, are also suitable. Hydrophobic comonomers are also suitable, such as, for example, isobutene, diisobutene, styrene, alpha-olefins with 10 or more carbon atoms. Hydrophilic monomers with hydroxy function or alkylene oxide groups can likewise be used as comonomers. For example, mention may be made of: allyl alcohol and isoprenol, and alkoxylates thereof and methoxypolyethylene glycol (meth)acrylate. In addition, graft polymers based on degraded starch and the aforementioned monomers such as (meth)acrylic acid, maleic acid, fumaric acid and 2-acrylamido-2-methylpropanesulfonic acid can be used as cobuilder.

[0081] As these kind of components, in contrast to the graft polymers according to (b) as described above, are in general not easily biodegradable it is a preferred embodiment of the invention that these homopolymers and copolymers of acrylic acid or of methacrylic acid which preferably have a weight-average molar mass of 2000 to 50 000 g/mol are not comprised in the formulations according to the invention.

[0082] Cleaning compositions formulations, as contemplated herein, may contain one or more surfactants selected from the group consisting of anionic surfactants, nonionic surfactants cationic, zwitterionic, and amphoteric surfactants. Combinations of the aforementioned types of surfactants are also anticipated.

[0083] The dishwashing detergent formulation according to any one of points 1 to 20, characterized in that the composition comprises from 0.5 to 6% by weight, preferably 1 to 4 % by weight of the total composition of nonionic surfactants.

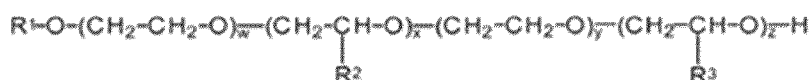
[0084] All non-ionic surfactants that are known to a person skilled in the art can be used as non-ionic surfactants. Low foaming non-ionic surfactants are preferably used, in particular alkoxylated, especially ethoxylated, low-foaming non-ionic surfactants such as alkyl glycosides, alkoxylated, preferably ethoxylated or ethoxylated and propoxylated fatty acid alkyl esters, polyhydroxy fatty acid amides, or amine oxides. Particularly preferred non-ionic surfactants are specified in greater detail below.

[0085] Preferred alcohol ethoxylates have a narrowed homolog distribution (narrow range ethoxylates, NRE). In addition to these non-ionic surfactants, fatty alcohols having more than 12 EO can also be used. Examples of these are tallow fatty alcohols having 14 EO, 25 EO, 30 EO, or 40 EO.

[0086] Ethoxylated non-ionic surfactants are particularly preferably used which were obtained from C₆₋₂₀ monohydroxy alkanols or C₆₋₂₀ alkyl phenols or C₁₆₋₂₀ fatty alcohols and more than 12 mol, preferably more than 15 mol, and in particular more than 20 mol, ethylene oxide per mol of alcohol. A particularly preferred non-ionic surfactant is obtained from a straight-chain fatty alcohol having 16 to 20 carbon atoms (C₁₆₋₂₀ alcohol), preferably from a C₁₈ alcohol and at least 12 mol, preferably at least 15 mol and in particular at least 20 mol of ethylene oxide. Of these, what are referred to as "narrow range ethoxylates" are particularly preferred.

[0087] Surfactants that are preferably used come from the group of the alkoxylated non-ionic surfactants, in particular the ethoxylated primary alcohols and mixtures of these surfactants with structurally complex surfactants such as polyoxypropylene/polyoxyethylene/polyoxypropylene ((PO/EO/PO) surfactants). Such (PO/EO/PO) non-ionic surfactants are also characterized by good foam control.

[0088] In the context of the present invention, low-foaming non-ionic surfactants which have alternating ethylene oxide and alkylene oxide units have proven to be particularly preferred. Among these, in turn, surfactants having EO-AO-EO-AO blocks are preferred, with one to ten EO groups or AO groups being bonded to one another before a block of the other group follows. Here, non-ionic surfactants of the general formula



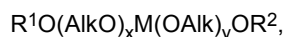
are preferred, in which R¹ represents a straight-chain or branched, saturated or mono- or polyunsaturated C₆₋₂₄-alkyl or alkenyl functional group; each R₂ and R₃ group is selected, independently of one another, from -CH₃, -CH₂CH₃, -CH₂CH₂-CH₃, -CH(CH₃)₂; and the indices w, x, y and z represent, independently of one another, integers from 1 to 6.

[0089] Preferred non-ionic surfactants of the above formula can be prepared using known methods, from the corresponding alcohols R¹-OH and ethylene or alkylene oxide. The R¹ functional group in the above formula can vary depending on the origin of the alcohol. If native sources are used, the R¹ functional group has an even number of carbon atoms and is generally unbranched, with the linear functional groups of alcohols of native origin having 12 to 18 C atoms, such as coconut, palm, tallow fatty or oleyl alcohol, for example, being preferred. Some examples of alcohols that are available from synthetic sources are the Guerbet alcohols or functional groups that are methyl-branched or linear and methyl-branched in the 2 position in admixture, such as those usually present in oxo alcohol functional groups. Irrespective of the type of alcohol used to prepare the non-ionic surfactants contained in the agents, non-ionic surfactants are preferred in which R¹ represents an alkyl functional group having 6 to 24, preferably 8 to 20, particularly preferably 9 to 15, and in particular 9 to 11, carbon atoms in the above formula.

[0090] Besides propylene oxide, butylene oxide in particular is worthy of consideration as an alkylene oxide unit that is contained alternately with the ethylene oxide unit in the preferred non-ionic surfactants. However, other alkylene oxides in which R² and R³ are selected, independently of one another, from -CH₂CH₂-CH₃ and -CH(CH₃)₂ are also suitable.

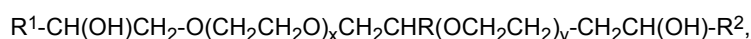
Preferably, non-ionic surfactants of the above formula are used in which R^2 and R^3 represent a $-CH_3$ functional group; w and x represent, independently of one another, values of 3 or 4; and y and z represent, independently of one another, values of 1 or 2.

[0091] Further preferably used non-ionic surfactants of the solid phase are non-ionic surfactants of general formula



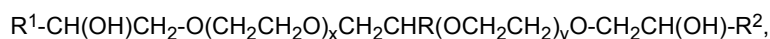
in which R^1 and R^2 represent, independently of one another, a branched or unbranched, saturated or unsaturated, optionally hydroxylated alkyl functional group having 4 to 22 carbon atoms; Alk represents a branched or unbranched alkyl functional group having 2 to 4 carbon atoms; x and y represent, independently of one another, values of between 1 and 70; and M represents an alkyl functional group from the group CH_2 , CHR^3 , CR^3R^4 , CH_2CHR^3 and CHR^3CHR^4 , R^3 and R^4 representing, independently of one another, a branched or unbranched, saturated or unsaturated alkyl functional group having 1 to 18 carbon atoms.

[0092] Preferred in this case are non-ionic surfactants of general formula



in which R, R^1 and R^2 represent, independently of one another, an alkyl functional group or alkenyl functional group having 6 to 22 carbon atoms; x and y represent, independently of one another, values between 1 and 40.

[0093] Preferred in this case are, in particular, compounds of general formula



in which R represents a linear, saturated alkyl functional group having 8 to 16 carbon atoms, preferably 10 to 14 carbon atoms, and n and m represent, independently of one another, values of from 20 to 30. Such compounds can be obtained, for example, by reacting alkyl diols $HO-CHR-CH_2-OH$ with ethylene oxide, a reaction with an alkyl epoxide being performed subsequently in order to close the free OH functions during formation of a dihydroxy ether.

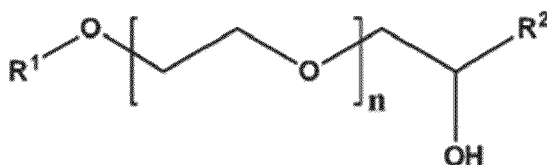
[0094] In this case, preferred non-ionic surfactants are those of general formula $R^1-CH(OH)CH_2O-(AO)_w-(A'O)_x-(A''O)_y-(A'''O)_z-R^2$, in which

- R^1 represents a straight-chain or branched, saturated or mono- or polyunsaturated C_{6-24} alkyl or alkenyl functional group;
- R^2 represents hydrogen or a linear or branched hydrocarbon functional group having 2 to 26 carbon atoms;
- A, A', A'' and A''' represent, independently of one another, a functional group from the group $-CH_2CH_2$, $-CH_2CH_2-CH_2$, $-CH_2-CH(CH_3)$, $-CH_2-CH_2-CH_2-CH_2$, $-CH_2-CH(CH_3)-CH_2$, $-CH_2-CH(CH_2-CH_3)$;
- w, x, y and z represent values of between 0.5 and 120, where x, y and/or z can also be 0.

[0095] By adding the above-mentioned non-ionic surfactants of general formula $R^1-CH(OH)CH_2O-(AO)_w-(A'O)_x-(A''O)_y-(A'''O)_z-R^2$, subsequently also referred to as "hydroxy mixed ethers," surprisingly, the cleaning performance of preparations according to the invention can be significantly improved, both in comparison with surfactant-free systems and in comparison with systems containing alternative non-ionic surfactants, for example from the group of polyalkoxylated fatty alcohols.

[0096] By using these non-ionic surfactants having one or more free hydroxyl groups on one or both terminal alkyl functional groups, the stability of the enzymes contained in the cleaning agent preparations according to the invention can be improved substantially.

[0097] In particular, those end-capped poly(oxyalkylated) non-ionic surfactants are preferred which, according to the following formula,



besides a functional group R^1 , which represents linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon functional groups having 2 to 30 carbon atoms, preferably having 4 to 22 carbon atoms, also have a linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon functional group R^2 having 1 to 30 carbon

atoms, where n represents values of between 1 and 90, preferably values of between 10 and 80, and in particular values of between 20 and 60.

[0098] Surfactants of the above formula are in particular preferred in which R^1 represents C_7 to C_{13} , n represents a whole natural number from 16 to 28 and R^2 represents C_8 to C_{12} .

[0099] Surfactants of formula $R^1O[CH_2CH(CH_3)O]_x[CH_2CH_2O]_yCH_2CH(OH)R^2$ are particularly preferred, in which R^1 represents a linear or branched aliphatic hydrocarbon functional group having 4 to 18 carbon atoms or mixtures thereof, R^2 denotes a linear or branched hydrocarbon functional group having 2 to 26 carbon atoms or mixtures thereof, x represents values between 0.5 and 1.5, and y represents a value of at least 15. The group of these non-ionic surfactants includes for example the C_{2-26} fatty alcohol $(PO)_{1-}(EO)_{15-40}$ -2-hydroxyalkyl ethers, in particular including the C_{8-10} fatty alcohol $(PO)_1-(EO)_{22}$ -2-hydroxydecyl ethers.

[0100] In particular, the end-capped poly(oxyalkylated) non-ionic surfactants of formula $R^1O[CH_2CH_2O]_x[CH_2CH(R^3)O]_yCH_2CH(OH)R^2$ are preferred, in which R^1 and R^2 represent, independently of one another, a linear or branched, saturated or mono- or polyunsaturated hydrocarbon functional group having 2 to 26 carbon atoms, R^3 is selected, independently of one another, from $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2-CH_3$, $-CH(CH_3)_2$, but preferably represents $-CH_3$, and x and y represent, independently of one another, values of between 1 and 32, with non-ionic surfactants where $R^3 = -CH_3$ and having values for x of from 15 to 32 and for y of 0.5 and 1.5 being very particularly preferred.

[0101] Further non-ionic surfactants that can preferably be used are the end-capped poly(oxyalkylated) non-ionic surfactants of the formula $R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$, in which R^1 and R^2 represent linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon functional groups having 1 to 30 carbon atoms, R^3 represents H or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl or 2-methyl-2-butyl functional group, x represents values between 1 and 30, and k and j represent values between 1 and 12, preferably between 1 and 5. If the value x is > 2, each R^3 in the above formula $R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$ can be different. R^1 and R^2 are preferably linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon functional groups having 6 to 22 carbon atoms, with functional groups having 8 to 18 C atoms being particularly preferred. For the functional group R^3 , H, $-CH_3$ or $-CH_2CH_3$ are particularly preferred. Particularly preferred values for x are in the range of from 1 to 20, in particular from 6 to 15.

[0102] As described above, each R^3 in the above formula can be different if $x > 2$. In this way, the alkylene oxide unit in square brackets can be varied. For example, if x represents 3, the functional group R^3 can be selected in order to form ethylene oxide ($R^3 = H$) or propylene oxide ($R^3 = CH_3$) units, which can be joined together in any sequence, for example $(EO)(PO)(EO)$, $(EO)(EO)(PO)$, $(EO)(EO)(EO)$, $(PO)(EO)(PO)$, $(PO)(PO)(EO)$ and $(PO)(PO)(PO)$. The value 3 for x has been selected here by way of example and can by all means be greater, in which case the range of variation increases as the values for x increase and includes a large number of (EO) groups combined with a small number of (PO) groups, for example, or vice versa.

[0103] Particularly preferred end-capped poly(oxyalkylated) alcohols of the above formula have values of k = 1 and j = 1, and therefore the previous formula is simplified to $R^1O[CH_2CH(R^3)O]_xCH_2CH(OH)CH_2OR^2$. In the formula mentioned last, R^1 , R^2 and R^3 are as defined above and x represents numbers from 1 to 30, preferably from 1 to 20, and in particular from 6 to 18. Surfactants in which the functional groups R^1 and R^2 have 9 to 14 C atoms, R^3 represents H, and x assumes values from 6 to 15 are particularly preferred. Finally, the non-ionic surfactants of general formula $R^1-CH(OH)CH_2O-(AO)_w-R^2$ have been found to be particularly effective, in which

- R^1 represents a straight-chain or branched, saturated or mono- or polyunsaturated C_6 -24 alkyl or alkenyl functional group;
- R^2 represents a linear or branched hydrocarbon functional group having 2 to 26 carbon atoms;
- A represents a functional group from the group CH_2CH_2 , $CH_2CH_2CH_2$, $CH_2CH(CH_3)$, preferably represents CH_2CH_2 , and
- w represents values of between 1 and 120, preferably 10 to 80, in particular 20 to 40.

[0104] The group of these non-ionic surfactants includes, for example, the C_{4-22} fatty alcohol- $(EO)_{10-80}$ -2-hydroxyalkyl ethers, in particular including the C_{8-12} fatty alcohol- $(EO)_{22}$ -2-hydroxydecyl ethers and the C_{4-22} fatty alcohol- $(EO)_{40-80}$ -2-hydroxyalkyl ethers.

[0105] In various embodiments, the non-ionic surfactant of is selected from non-ionic surfactants of general formula $R^1-O(CH_2CH_2O)_xCR^3R^4(OCH_2CH_2)_yO-R^2$, in which R^1 and R^2 , independently of one another, represent an alkyl functional group or alkenyl functional group having 4 to 22 carbon atoms; R^3 and R^4 represent, independently of one another, H or an alkyl functional group of alkenyl functional group having 1 to 18 carbon atoms, and x and y represent, independently of one another, values between 1 and 40.

[0106] In particular, compounds of general formula $R^1-O(CH_2CH_2O)_xCR^3R^4(OCH_2CH_2)_yO-R^2$ are preferred, in which R^3 and R^4 represent H and the indices x and y, independently of one another, assume values from 1 to 40, preferably from 1 to 15.

[0107] In particular, compounds of general formula $R^1-O(CH_2CH_2O)_xCR^3R^4(OCH_2CH_2)_yO-R^2$ are particularly preferred, in which the functional groups R^1 and R^2 , independently of one another, represent saturated alkyl functional groups having 4 to 14 carbon atoms and the indices x and y , independently of one another, assume values from 1 to 15 and in particular from 1 to 12.

[0108] In addition, such compounds of general formula $R^1-O(CH_2CH_2O)_xCR^3R^4(OCH_2CH_2)_yO-R^2$ are preferred in which one of the functional groups R^1 and R^2 is branched.

[0109] Most particularly preferred are compounds of general formula $R^1-O(CH_2CH_2O)_xCR^3R^4(OCH_2CH_2)_yO-R^2$, in which the indices x and y , independently of one another, assume values from 8 to 12.

[0110] The indicated C chain lengths and degrees of ethoxylation or degrees of alkoxylation of the non-ionic surfactants represent statistical averages that can be an integer or a fraction for a given product. Owing to the manufacturing methods, commercial products of the above-mentioned formulas generally do not consist of an individual representative, but of mixtures, for which reason average values and, resulting from those, fractional numbers can arise both for the C chain lengths and for the degrees of ethoxylation and degrees of alkoxylation.

[0111] Naturally, the above-mentioned non-ionic surfactants can be used not only as individual substances but also as surfactant mixtures of two, three, four, or more surfactants.

[0112] Non-ionic surfactants having a melting point above room temperature are particularly preferred. Non-ionic surfactant(s) having a melting point above 20 °C, preferably above 25 °C, particularly preferably between 25 and 60 °C, and particularly between 26.6 and 43.3 °C, is/are particularly preferred.

[0113] The non-ionic surfactant that is solid at room temperature preferably has propylene oxide (PO) units in the molecule. Preferably, such PO units constitute up to 25 wt.%, particularly preferably up to 20 wt.%, and in particular up to 15 wt.% of the total molar mass of the non-ionic surfactant. Particularly preferred non-ionic surfactants are ethoxylated monohydroxy alkanols or alkyl phenols that additionally have polyoxyethylene-polyoxypropylene block copolymer units. The alcohol or alkyl phenol fraction of such non-ionic surfactant molecules preferably constitutes greater than 30 wt.%, particularly preferably greater than 50 wt.%, and in particular greater than 70 wt.% of the total molar mass of such non-ionic surfactants. Preferred agents are characterized in that they contain ethoxylated and propoxylated non-ionic surfactants in which the propylene oxide units in the molecule constitute up to 25 wt.%, preferably up to 20 wt.%, and particularly up to 15 wt.% of the total molar mass of the non-ionic surfactant.

[0114] As further additives, in connection with the dishwashing detergent formulations according to the invention, for example anionic or zwitterionic surfactants, alkali carriers, polymeric dispersants, corrosion inhibitors, antifoams, dyes, fragrances, fillers, solubility promoters, or water can be used. Alkali carriers that can be used are, for example, besides the ammonium or alkali metal carbonates, ammonium or alkali metal hydrogencarbonates and ammonium or alkali metal sesquicarbonates already specified for the builder substances, also ammonium or alkali metal hydroxides, and mixtures of the aforementioned substances.

[0115] To prevent glass corrosion, which is evident from clouding, iridescence, streaking and lines on the glassware, preference is given to using glass corrosion inhibitors. Preferred glass corrosion inhibitors are for example, magnesium, zinc and bismuth salts and complexes and polyethyleneimine.

[0116] As corrosion inhibitors, it is possible to use, inter alia, silver protectors from the group of triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, alkylaminotriazoles and the transition metal salts or complexes, if ecologically compliant.

[0117] The dishwashing detergent formulations according to the invention can comprise 0 to 5 % by weight of enzymes.

[0118] Enzymes can be added to the dishwashing detergent in order to increase the cleaning performance or, under more mild conditions (e.g. at lower temperatures), to ensure the cleaning performance in identical quality. The enzymes can be used in free form or chemically or physically immobilized form on a support, or in encapsulated form.

[0119] Cleaning agents according to the invention preferably contain enzymes in total quantities of from 1×10^{-6} wt.% to 5 wt.% based on active protein. The protein concentration can be determined with the aid of known methods, for example the BCA method or the Biuret method.

[0120] Among the proteases, the subtilisin-type proteases are preferred. Examples of these are the subtilisins BPN' and Carlsberg, as well as the further-developed forms thereof, protease PB92, subtilisins 147 and 309, the alkaline protease from *Bacillus lentus*, subtilisin DY, and the enzymes thermitase, proteinase K and proteases TW3 and TW7, which belong to the subtilases but no longer to the subtilisins in the narrower sense.

[0121] Examples of amylases that can be used according to the invention are α -amylases from *Bacillus licheniformis*, from *B. amyloliquefaciens*, from *B. stearothermophilus*, from *Aspergillus niger*, and *A. oryzae*, as well as the further developments of the above-mentioned amylases that have been improved for use in cleaning agents. Others that are particularly noteworthy for this purpose are the α -amylases from *Bacillus* sp. A 7-7 (DSM 12368) and cyclodextrin glucanotransferase (CGTase) from *B. agaradherens* (DSM 9948).

[0122] Cleaning-active proteases and amylases are generally not made available in the form of the pure protein, but rather in the form of stabilized, storable and transportable preparations. These ready-made preparations include, for

example, the solid preparations obtained through granulation, extrusion, or lyophilization or, particularly in the case of liquid or gel agents, solutions of the enzymes, advantageously maximally concentrated, low-water, and/or supplemented with stabilizers or other auxiliaries.

[0123] Alternatively, the enzymes can also be encapsulated, for example by spray-drying or extrusion of the enzyme solution together with a preferably natural polymer or in the form of capsules, for example those in which the enzymes are enclosed in a set gel, or in those of the core-shell type in which an enzyme-containing core is coated with a water-, air-, and/or chemical-impermeable protective layer. In the case of overlaid layers, other active substances, such as stabilizers, emulsifiers, pigments, or dyes, can be additionally applied. Such capsules are applied using inherently known methods, for example by shaking or roll granulation or in fluidized bed processes. Such granular materials are advantageously low in dust, for example due to the application of polymeric film-formers, and stable in storage due to the coating.

[0124] As is clear from the preceding remarks, the enzyme protein forms only a fraction of the total weight of conventional enzyme preparations. Protease and amylase preparations used according to the invention contain between 1 and 40 wt.%, preferably between 2 and 30 wt.%, particularly preferably between 3 and 25 wt.% of the enzyme protein. In particular, those cleaning agents are preferred which contain, based on their total weight, 0.1 to 12 wt.%, preferably 0.2 to 10 wt.%, and in particular 0.5 to 8 wt.% of the respective enzyme preparations.

[0125] If the dishwashing detergent formulations comprise enzymes, they preferably comprise these in amounts of from 0.001 to 3.0 % of active enzyme protein by weight of the total composition. The wt % of enzymes are calculated by mass of the active enzyme protein per weight of the total composition.

[0126] In a preferred embodiment the dishwashing detergent formulation is characterized in that the composition comprises amylases in an amount of 0.05 to 20 mg active enzyme protein per gram of the total composition, preferably 0.10 to 10 mg active enzyme protein per gram of the total composition, most preferred 0.15 to 2 mg active enzyme protein per gram of the total composition.

[0127] Furthermore, in a preferred embodiment the dishwashing detergent formulation is characterized in that the composition comprises proteases in an amount of 0.1 to 50 mg active enzyme protein per gram of the total composition, preferably 0.2 to 25 mg active enzyme protein per gram of the total composition, 0.5 to 10 mg active enzyme protein per gram of the total composition.

[0128] According to the invention, preference is given to using amylases and proteases.

[0129] Formulations according to the invention can comprise one or more enzyme stabilizers. Enzyme stabilizers serve to protect enzyme - particularly during storage - against damage such as, for example, inactivation, denaturation or decomposition for example as a result of physical influences, oxidation or proteolytic cleavage.

[0130] Examples of enzyme stabilizers are reversible protease inhibitors, for example benzamidine hydrochloride, borax, boric acid, boronic acids or salts or esters thereof, including in particular derivatives with aromatic groups, for example ortho-, meta- or para-substituted phenyl boronic acids, in particular 4-formylphenyl boronic acid, or the salts or esters of the aforementioned compounds. Peptide aldehydes, i.e. oligopeptides with a reduced carbon terminus, in particular those made of 2 to 50 monomers, are also used for this purpose. Peptidic reversible protease inhibitors include inter alia ovomucoid and leupeptin. Specific, reversible peptide inhibitors for the protease subtilisin, as well as fusion proteins of proteases and specific peptide inhibitors are also suitable for this purpose. Further examples of enzyme stabilizers are amino alcohols such as mono-, di-, triethanol- and - propanolamine and mixtures thereof, aliphatic mono- and dicarboxylic acids up to C12-carboxylic acids, such as for example succinic acid. Terminally capped fatty acid amide alkoxylates are also suitable enzyme stabilizers.

[0131] Other examples of enzyme stabilizers are sodium sulfite, reducing sugars and potassium sulfate. A further example of a suitable enzyme stabilizer is sorbitol.

[0132] Organic solvents might be present as well but are preferably limited to an amount of up to 30 wt.%, based on the weight of the composition. Especially preferred organic solvents are propane diol, glycerol and/or sorbitol. These amounts of organic solvents add to the pourability as well as to the stabilization of active ingredients.

[0133] In a preferred embodiment of the present invention the dishwashing detergent composition comprises one or more organic solvent selected from the group of sorbitol, glycerol and/or propane diol. More preferably, the composition comprises from 1 to 25% by weight, preferably 2 to 12 % by weight of the total composition from the group of sorbitol, glycerol and/or propane diol.

[0134] The dishwashing detergent formulation according to the invention is preferably characterized in that the composition has a pH of 7.0 to 11.5 at 20 °C. The pH is measured in the product itself. A suitable instrument is e. g. a conventional pH-electrode.

[0135] According to a preferred embodiment of the present invention the composition comprises

(i) 1 - 4 % by weight of the total composition of

(a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid

and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,

(b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

(b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and

(b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 5 - 20 % by weight of the total composition of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts thereof;

(iii) 0.3 - 0.8 % by weight of the total composition of xanthan;

(iv) at least 20 % by weight of the total composition of water;

(v) 1 - 5 % by weight of the total composition of nonionic surfactants and

(vi) 0.001 - 3% by weight of the total composition of enzymes.

[0136] Preferably, the composition has a pH of 7.0 to 8.5, preferably 7.5 to 8.0 at 20 °C.

The enzyme stability is enhanced due to the pH. These compositions are surprisingly good to clean delicate dishware, without damages to glass or decors on glass or porcelain.

[0137] In another embodiment of the dishwashing detergent formulation according to the invention the composition comprises

(i) 1 - 4 % by weight of the total composition of

(a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof,

wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,

(b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

(b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and

(b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 5 - 20 % by weight of the total composition of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts;

(iii) 0.5 - 1.5 % by weight of the total composition of a crosslinked polyacrylate comprising thickener;

(iv) at least 20 % by weight of the total composition of water;

(v) 1 - 10 % by weight of the total composition of nonionic surfactants and

(vi) 0.001 - 3% by weight of the total composition of enzymes and

(vii) from 4 to 15 wt% of the total composition of organic solvents selected from the group the group of sorbitol, glycerol and/or propane diol.

[0138] These compositions might also be used alone or as enzyme containing component (A) of a multicomponent system. Preferably, the composition has a pH of 7.0 to 8.5, preferably 7.5 to 8.0 at 20 °C. The enzyme stability is enhanced due to the pH.

[0139] Another preferred embodiment of the invention is a dishwashing detergent formulation characterized in that the composition comprises

(i) 1 - 4 % by weight of the total composition of

(a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,

(b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

(b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and

(b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 5 - 20 % by weight of the total composition of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts;

(iii) 0.5 - 1.5 % by weight of the total composition of a crosslinked polyacrylate comprising thickener;

(iv) at least 20 % by weight of the total composition of water and

(v) from to 4 to 15 % by weight of the total composition of alkali metal carbonate.

[0140] The dishwashing detergent formulation is preferably characterized in that the composition has a pH of 9 to 11.5 at 20 °C. These compositions may be used alone or as alkaline compositions (B) of a multicomponent system.

[0141] In preferred embodiments the composition comprises from 1 to 7% by weight, preferably 2 to 5 % by weight of the total composition as builder (component according to (v) of claim 1) a phosphonate or its salts, preferably HEDP or its salts.

[0142] A preferred embodiment of the invention is that the cleaning composition is characterized in that it comprises two distinct liquid compositions A and B. Composition A comprises at least one enzyme and composition B is preferably free from enzymes. According to this embodiment of the present invention, composition A and composition B are distinct from one another. In the context of the present invention, this means that composition A and B differ in terms of formulation and are further spatially separated from one another.

[0143] In a preferred composition A comprises at least one enzyme and composition B is free from enzymes.

[0144] The term "spatially separated", as used herein with respect to compositions A and B of the cleaning composition of the present invention, means that the individual components of compositions A cannot come into contact with the components of composition B. Typically, to this end, the cleaning composition of the present invention may be provided in the form of a multi-chambered package, such as a bottle, tube or pouch, in particular a dual-chambered bottle or pouch, wherein compositions A and B are located separately from one another in separate, distinct chambers.

[0145] By spatially separating individual components of the agent, it is possible, on the one hand, to separate incompatible ingredients from one another and, on the other hand, to provide several different components of the agent in combination, which may be used/released at different times during application of the cleaning composition of the present invention.

[0146] In a further aspect, the present invention relates to the use of a cleaning composition, as herein described above, for the cleaning of dishes, preferably dishware. The compositions are preferably used in automatic dishwashing and/or automatic dishwashing machines. "Dishware", in the context of the present invention, includes dishes, cups,

cutlery, glassware, food storage containers, cooking utensils (cookware) and the like.

[0147] Furthermore, the present invention relates to a method of cleaning dishes, preferably in an automatic dishwashing machine, characterized in that in at least one method step at least one cleaning composition according to the invention, as herein disclosed, is used. Particularly, the present invention relates to a method for cleaning dishes in an automatic dishwasher, in which the agent is dispensed into the interior of an automatic dishwasher while a dishwashing program is being executed, before the main washing cycle begins, or in the course of the main washing cycle. Dispensing or introduction of the agent into the interior of the automatic dishwasher can take place manually, but preferably the agent is dispensed into the interior of the automatic dishwasher by means of the dosing chamber. In various embodiments of the disclosure, the (washing) temperature in such dishwashing methods is preferably 50°C or lower, particularly preferably 45°C or lower, still more preferably 40°C or lower.

[0148] All embodiments disclosed herein in relation to the liquid compositions apply similarly to the methods and uses of the invention and *vice versa*.

[0149] Preferred embodiments of the present invention are further described by the following points.

1. A phosphate free, dishwashing detergent formulation, liquid at 20 °C, that is essentially free of bleach, comprising

(i) 1 - 5 % by weight of the total composition of

(a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,

(b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

(b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and

(b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 3 to 25% by weight of the total composition of complexing agent selected from the group of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts thereof;

(iii) from 0.2 to 6 % by weight of the total composition of thickener;

(iv) at least 20 % by weight of the total composition of water and

(v) optionally from 4 to 15% by weight of the total composition of builders and/or cobuilders;

(vi) optionally from 1 to 8% by weight of the total composition of nonionic surfactants;

(vii) optionally from 0.001 to 3% by weight of the total composition of enzymes;

(viii) optionally from 2 to 30 wt% of the total composition of organic solvents.

2. The dishwashing detergent formulation according to point 1, characterized in that the weight ratio of (a): (b) is from 11: 1 to 8 : 1.

3. The dishwashing detergent formulation according to any one of points 1 or 2, characterized in that the weight ratio of (a): (b) is from 11: 1 to 9 : 1.

4. The dishwashing detergent formulation according to any one of points 1 to 3 characterized in that the amount of the component according to (i) is from 1.2 % to 4.5%, preferably from 1.5 % to 4.0 % by weight of the total composition.

5. The dishwashing detergent formulation according to any one of points 1 to 4, characterized in that the composition

comprises methylglycinediacetic acid (MGDA) or salts thereof as complexing agent.

6. The dishwashing detergent formulation according to any one of points 1 to 5, characterized in that the amount of methylglycinediacetic acid (MGDA) and its salts, is from 4.5 to 20 % by weight of the total composition.

7. The dishwashing detergent formulation according to any one of points 1 to 6, characterized in that the thickener is selected from polysaccharides, urea derivatives and crosslinked polyacrylic acids.

8. The dishwashing detergent formulation according to any one of points 1 to 7, characterized in that the thickener is xanthan gum, preferably in an amount from 0.25 to 0.8 % by weight of the total composition.

9. The dishwashing detergent formulation according to any one of points 1 to 7, characterized in that the thickener is selected from crosslinked polyacrylic acids, preferably in an amount from 0.5 to 1.0 % by weight of the total composition.

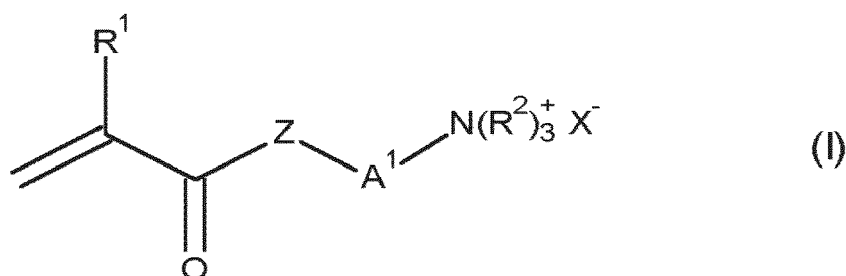
10. The dishwashing detergent formulation according to any one of points 1 to 9, wherein the amount of water is at least 30 % by weight of the total composition, preferably from 40 to 70 % by weight of the total composition, most preferred from 40 to 60 % by weight of the total composition.

11. The dishwashing detergent formulation according to any one of points 1 to 10, containing polyaspartic acid as homopolymer.

12. The dishwashing detergent formulation according to any one of points 1 to 11, containing a modified polyaspartic acid or salt thereof obtainable by polycondensation of (a1) is 80 to 95 mol% of aspartic acid and (a2) is 5 to 20 mol% of at least one carboxyl-containing compound different from aspartic acid.

13. The dishwashing detergent formulation of point 12, wherein the at least one carboxyl-containing compound (a2) is selected from the group consisting of 1,2,3,4-butanetetracarboxylic acid, citric acid, glycine and glutamic acid.

14. The dishwashing detergent formulation according to any one of points 1 to 13, wherein the monomer (b3) is at least one compound of the general formula (I),



wherein the variables are defined as follows:

Z is O or NR¹,

R¹ is selected from methyl and hydrogen,

A¹ is selected from C²-C⁴-alkylene,

R² are identical or different and selected from C¹-C⁴-alkyl,

X⁻ is selected from halide, mono-C¹-C⁴-alkyl sulfate and sulfate.

15. The dishwashing detergent formulation according to claim 14, wherein Z is O.

16. The dishwashing detergent formulation according to claim 13 to 15, wherein R² are identical and methyl, A¹ is CH₂CH₂, and X⁻ is chloride.

17. The dishwashing detergent formulation according to points 13 to 16, wherein monomer (b3) is trimethylaminoethyl (meth)acrylatochloride or methacrylamidopropyl trimethyl ammonium Chloride, preferably ω-trimethylaminoethyl (meth)acrylatochloride.

18. The dishwashing detergent formulation according to any one of points 1 to 17, characterized in that the composition comprises a builder from 5 to 12% by weight, preferably 7 to 10 % by weight of the total composition an alkali metal carbonate.

19. The dishwashing detergent formulation according to any one of points 1 to 18, characterized in that the composition comprises from 1 to 7% by weight, preferably 2 to 5 % by weight of the total composition as cobuilder a phosphonate or its salts, preferably HEDP or its salts.

20. The dishwashing detergent formulation according to any one of points 1 to 18, characterized in that the composition comprises less than 0.1 %, preferably less than 0.01 % by weight of phosphonates, preferably the composition comprises less than 0.01 % by weight of phosphorous containing compounds.

21. The dishwashing detergent formulation according to any one of points 1 to 20, characterized in that the composition comprises from 0.5 to 6% by weight, preferably 1 to 4 % by weight of the total composition of nonionic surfactants.

22. The dishwashing detergent formulation according to any one of points 1 to 21, characterized in that the composition comprises amylases in an amount from 0.05 to 20 mg active enzyme protein per gram of the total composition, preferably from 0.10 to 10 mg active enzyme protein per gram of the total composition, most preferred from 0.15 to 2 mg active enzyme protein per gram of the total composition.

23. The dishwashing detergent formulation according to any one of points 1 to 22, characterized in that the composition comprises proteases in an amount of 0.1 to 50 mg active enzyme protein per gram of the total composition, preferably 0.2 to 25 mg active enzyme protein per gram of the total composition, 0.5 to 10 mg active enzyme protein per gram of the total composition.

24. The dishwashing detergent formulation according to any one of points 1 to 23, characterized in that the composition comprises one or more organic solvent selected from the group of sorbitol, glycerol and/or propane diol.

25. The dishwashing detergent formulation according to point 24, characterized in that the composition comprises from 1 to 25% by weight, preferably 2 to 12 % by weight of the total composition from the group of sorbitol, glycerol and/or propane diol.

26. The dishwashing detergent formulation according to any one of points 1 to 25, characterized in that the composition has a pH of 7.0 to 11.5 at 20 °C.

27. The dishwashing detergent formulation according to any one of points 1 to 26, characterized in that the composition comprises

(i) 1 - 4 % by weight of the total composition of

(a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,

(b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

(b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and

(b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 5 - 20 % by weight of the total composition of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts;

(iii) 0.3 - 0.8 % by weight of the total composition of xanthan;

(iv) at least 20 % by weight of the total composition of water and

(v) 1 - 5 % by weight of the total composition of nonionic surfactants and

(vi) 0.001 - 3% by weight of the total composition of enzymes.

28. The dishwashing detergent formulation according to any one of points 1 to 26, characterized in that the composition comprises

(i) 1 - 4 % by weight of the total composition of

(a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,

(b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

(b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and

(b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 5 - 20 % by weight of the total composition of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts thereof;

(iii) 0.5 - 1.5 % by weight of the total composition of a crosslinked polyacrylate comprising thickener;

(iv) at least 20 % by weight of the total composition of water;

(v) 1 - 10 % by weight of the total composition of nonionic surfactants and

(vi) 0.001 - 3% by weight of the total composition of enzymes and

(viii) from 4 to 15 wt% of the total composition of organic solvents selected from the group the group of sorbitol, glycerol and/or propane diol.

29. The dishwashing detergent formulation according to claim 27 or 28, characterized in that the composition has a pH of 7.0 to 8.5, preferably 7.5 to 8.0 at 20 °C.

30. The dishwashing detergent formulation according to any one of points 1 to 26, characterized in that the composition comprises

(i) 1 - 4 % by weight of the total composition of

(a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,

(b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides,

and side chains obtainable by grafting on of
 (b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and
 (b3) at least one ethylenically unsaturated N-containing monomer with a
 permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 5 - 20 % by weight of the total composition of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts;

(iii) 0.5 - 1.5 % by weight of the total composition of a crosslinked polyacrylate comprising thickener;

(iv) at least 20 % by weight of the total composition of water and

(v) from to 4 to 15 % by weight of the total composition of alkali metal carbonate.

31. The dishwashing detergent formulation according to point 30, characterized in that the composition has a pH of 9 to 11.5 at 20 °C.

32. Use of a cleaning composition according to any of points 1 to 31 in automatic dishwashing.

33. An automatic dishwashing method characterized in that a cleaning composition according to any of points 1 to 31 is used.

Examples:

[0150] Exemplary compositions I to IV were prepared using the components summarized in Table 1 with the amounts of active ingredients given in wt.% referring to the total weight of the composition unless otherwise specified.

Table 1:

Component	Comparison example	I	II	III	IV
Xanthan Gum	0.5	0.5	0.5	0.5	0.5
1-hydroxy-1-phosphonoethyl) phosphonic acid (HEDP)	0.0	0.0	0.0	0.0	0.0
Acusol® 588 G (ex DOW Inc.)	0.0	0.0	0.0	0.0	0.0
Polyacrylate, Homopolymer	2.5	0.0	0.0	0.0	0.0
Polyaspartic acid, homopolymer	0.0	2.0	2.0	1.6	2.35
Graft polymer as described in WO2019/211231 as polymer P2	0.0	0.2	0.2	0.15	0.25
MGDA, tri sodium salt	11.00	11.00	15.00	8.0	9.0
Calcium chloride	0.2	0.2	0.2	0.2	0.2
Soda	0.00	0.00	6.00	2.0	0.0
cationic acrylic acid copolymer	0.0	0.0	0.0	0.0	0.0
Citric acid anhydrous	1.5	1.5	2.5	6.0	3.0
Sodium Citrate	8.00	8.00	6.00	2.0	0.0
Low foaming nonionic surfactant (hydroxy mixed ether)	2.00	2.00	1.50	2.5	1.0
Stainzyme® 12 L (Amylase available from Novozymes)	1.5	1.5	1.5	1.5	1.0

(continued)

Component	Comparison example	I	II	III	IV
Protease (amount given in active enzyme protein in mg per 100g composition)	150	150	150	150	150
Perfume	0.05	0.05	0.05	0.05	0.05
Dye	0.005	0.005	0.005	0.005	0.005
Preservatives	0.5	0.5	0.5	0.5	0.5
NaOH	To achieve pH given	To achieve pH given	To achieve pH given	To achieve pH given	To achieve pH given
water	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100

[0151] The pH of the undiluted liquid phase was adjusted to 7.8 at 20 °C. The compositions were tested for filming and spotting. The compositions I to IV according to the invention delivered significantly reduced spotting and filming results compared to the comparison example that showed heavy spotting and filming.

Claims

1. A phosphate free, dishwashing detergent formulation, liquid at 20 °C, that is essentially free of bleach, comprising

(i) 1 - 5 % by weight of the total composition of

(a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,

(b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

(b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and

(b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 3 to 25% by weight of the total composition of complexing agent selected from the group of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts thereof;

(iii) from 0.2 to 6 % by weight of the total composition of thickener;

(iv) at least 20 % by weight of the total composition of water and

(v) optionally from 4 to 15% by weight of the total composition of builders and/or cobuilders;

(vi) optionally from 1 to 8% by weight of the total composition of nonionic surfactants;

(vii) optionally from 0.001 to 3% by weight of the total composition of enzymes;

(viii) optionally from 2 to 30 wt% of the total composition of organic solvents.

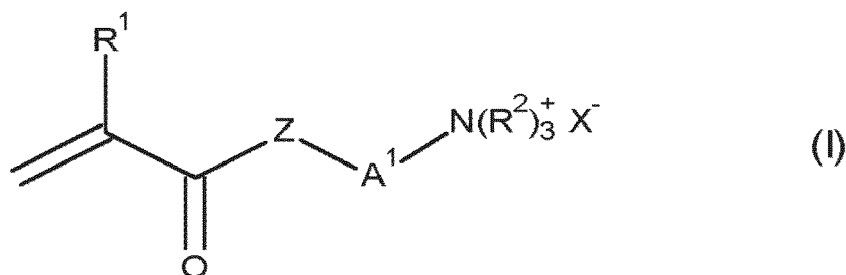
2. The dishwashing detergent formulation according to claim 1, **characterized in that** the weight ratio of (a): (b) is from 11: 1 to 8 : 1.

3. The dishwashing detergent formulation according to any one of claims 1 to 2 **characterized in that** the amount of the component according to (i) is from 1.2 % to 4.5%, preferably from 1.5 % to 4.0 % by weight of the total composition.

4. The dishwashing detergent formulation according to any one of claims 1 to 3, **characterized in that** the composition

comprises methylglycinediacetic acid (MGDA) or salts thereof as complexing agent, preferably wherein the amount of methylglycinediacetic acid (MGDA) and its salts, is from 4.5 to 20 % by weight of the total composition.

5. The dishwashing detergent formulation according to any one of claims 1 to 4, **characterized in that** the thickener is selected from polysaccharides, urea derivatives and crosslinked polyacrylic acids.
6. The dishwashing detergent formulation according to any one of claims 1 to 5, wherein the amount of water is at least 30 % by weight of the total composition, preferably from 40 to 70 % by weight of the total composition, most preferred from 40 to 60 % by weight of the total composition.
7. The dishwashing detergent formulation according to any one of claims 1 to 6, wherein the monomer (b3) is at least one compound of the general formula (I),



wherein the variables are defined as follows:

- Z is O or NR¹,
- R¹ is selected from methyl and hydrogen,
- A¹ is selected from C2-C4-alkylene,
- R² are identical or different and selected from C1-C4-alkyl,
- X⁻ is selected from halide, mono-C1-C4-alkyl sulfate and sulfate.

8. The dishwashing detergent formulation according to claim 7, wherein monomer (b3) is trimethylaminoethyl (meth)acrylatechloride or methacrylamidopropyl trimethyl ammonium Chloride, preferably ω-trimethylaminoethyl (meth)acrylatechloride.
9. The dishwashing detergent formulation according to any one of claims 1 to 8, **characterized in that** the composition has a pH of 7.0 to 11.5 at 20 °C.
10. The dishwashing detergent formulation according to any one of claims 1 to 9, **characterized in that** the composition comprises

(i) 1 - 4 % by weight of the total composition of

- (a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,
- (b) at least one graft copolymer composed of

- (b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of
- (b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and
- (b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

(ii) from 5 - 20 % by weight of the total composition of citric acid, methylglycinediacetic acid (MGDA), glutamic

- acid diacetic acid (GLDA) or salts;
- (iii) 0.3 - 0.8 % by weight of the total composition of xanthan;
- (iv) at least 20 % by weight of the total composition of water and
- (v) 1 - 5 % by weight of the total composition of nonionic surfactants and
- (vi) 0.001 - 3% by weight of the total composition of enzymes.

11. The dishwashing detergent formulation according to any one of claims 1 to 9, **characterized in that** the composition comprises

(i) 1 - 4 % by weight of the total composition of

- (a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,
- (b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

- (b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and
- (b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

- (ii) from 5 - 20 % by weight of the total composition of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts;
- (iii) 0.5 - 1.5 % by weight of the total composition of a crosslinked polyacrylate comprising thickener;
- (iv) at least 20 % by weight of the total composition of water;
- (v) 1 - 10 % by weight of the total composition of nonionic surfactants and
- (vi) 0.001 - 3.0 % by weight of the total composition of enzymes and
- (viii) from 4 to 15 wt% of the total composition of organic solvents selected from the group the group of sorbitol, glycerol and/or propane diol.

12. The dishwashing detergent formulation according to claim 10 or 11, **characterized in that** the composition has a pH of 7.0 to 8.5, preferably 7.5 to 8.0 at 20 °C.

13. The dishwashing detergent formulation according to any one of claims 1 to 9, **characterized in that** the composition comprises

(i) 1 - 4 % by weight of the total composition of

- (a) at least one of polyaspartic acid or modified polyaspartic acid or salts thereof, wherein the modified polyaspartic acid is obtainable by polycondensation of (a1) 50 to 99 mol% of aspartic acid and (a2) 1 to 50 mol% of at least one carboxyl-containing compound different from aspartic acid and subsequent hydrolysis of the cocondensates with the addition of a base,
- (b) at least one graft copolymer composed of

(b1) at least one graft base selected from oligosaccharides and polysaccharides, and side chains obtainable by grafting on of

- (b2) at least one ethylenically unsaturated mono- or dicarboxylic acid and
- (b3) at least one ethylenically unsaturated N-containing monomer with a permanent cationic charge,

wherein the weight ratio of (a) : (b) is from 18: 1 to 5:1;

- (ii) from 5 - 20 % by weight of the total composition of citric acid, methylglycinediacetic acid (MGDA), glutamic acid diacetic acid (GLDA) or salts;

EP 4 386 071 A1

- (iii) 0.5 - 1.5 % by weight of the total composition of a crosslinked polyacrylate comprising thickener;
 - (iv) at least 20 % by weight of the total composition of water and
 - (v) from 4 to 15 % by weight of the total composition of alkali metal carbonate,
- wherein the composition preferably has a pH of 9 to 11.5 at 20 °C.

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14. Use of a cleaning composition according to any of claims 1 to 13 in automatic dishwashing.
15. An automatic dishwashing method **characterized in that** a cleaning composition according to any of claims 1 to 13 is used.
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EUROPEAN SEARCH REPORT

Application Number

EP 22 21 3740

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EPO FORM 1503 03.82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y, D	WO 2019/211231 A1 (BASF SE [DE]) 7 November 2019 (2019-11-07) * page 21, line 9 - line 12; claims; example 4 * * page 22, line 7 - line 30 * -----	1-15	INV. C11D1/66 C11D3/22 C11D3/37 C11D11/00 C11D17/00
Y	US 2017/130168 A1 (TÜRK HOLGER [DE] ET AL) 11 May 2017 (2017-05-11) * paragraphs [0144], [0147] - [0150], [0170]; claims 1, 8 * -----	1-15	
A	US 2017/145352 A1 (TÜRK HOLGER [DE] ET AL) 25 May 2017 (2017-05-25) * paragraph [0130]; claims * -----	1-15	
			TECHNICAL FIELDS SEARCHED (IPC)
			C11D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 24 May 2023	Examiner Veefkind, Victor
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 22 21 3740

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2019211231 A1	A1	07-11-2019	BR 112020021882 A2	26-01-2021
			CN 112074589 A	11-12-2020
			EP 3788125 A1	10-03-2021
			JP 2021522393 A	30-08-2021
			KR 20210006389 A	18-01-2021
			US 2021238504 A1	05-08-2021
			WO 2019211231 A1	07-11-2019

US 2017130168 A1	A1	11-05-2017	BR 112016030224 B1	25-05-2021
			CA 2951074 A1	30-12-2015
			CN 106459840 A	22-02-2017
			EP 3157901 A1	26-04-2017
			ES 2672370 T3	14-06-2018
			JP 6628749 B2	15-01-2020
			JP 2017520653 A	27-07-2017
			KR 20170020509 A	22-02-2017
			PL 3157901 T3	31-08-2018
			TR 201808396 T4	23-07-2018
			US 2017130168 A1	11-05-2017
			WO 2015197379 A1	30-12-2015

US 2017145352 A1	A1	25-05-2017	BR 112016030284 A2	22-08-2017
			CA 2951589 A1	30-12-2015
			CN 106459849 A	22-02-2017
			EP 3157969 A1	26-04-2017
			ES 2670687 T3	31-05-2018
			JP 6595516 B2	23-10-2019
			JP 2017520655 A	27-07-2017
			KR 20170023947 A	06-03-2017
			PL 3157969 T3	31-08-2018
			US 2017145352 A1	25-05-2017
			WO 2015197378 A1	30-12-2015

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2019211231 A1 [0002] [0030]
- WO 2015197379 A1 [0003]
- DE 4221875 [0030]