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(54) **BUILDER SYSTEM FOR EFFECT ON BOOSTING PROTEIN SOIL REMOVAL**

(57) The present invention relates to cleaning compositions for hard surfaces, particularly dishwashing detergents, more particularly automatic dishwashing detergents, comprising two distinct liquid compositions A and B, wherein the cleaning composition comprises citrate in an amount of from 0 to 10 wt.-%, MGDA in an amount of from 5 to 40 wt.-%, and HEDP in an amount of from 1 to 8 wt.-%, each based on the total weight of the cleaning composition. The present invention further relates to a method for cleaning hard surfaces, particularly dishes, comprising application of such a cleaning composition, as well as to the use thereof.

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Description

[0001] The present invention relates to cleaning compositions for hard surfaces, particularly dishwashing detergents, more particularly automatic dishwashing detergents, comprising two distinct liquid compositions A and B, wherein the cleaning composition comprises citrate in an amount of from 0 to 10 wt.-%, MGDA in an amount of from 5 to 40 wt.-%, and HEDP in an amount of from 1 to 8 wt.-%, each based on the total weight of the cleaning composition. The present invention further relates to a method for cleaning hard surfaces, particularly dishes, comprising application of such a cleaning composition, as well as to the use thereof.

[0002] The most important criterion in automatic dishwashing is the cleaning performance on a wide variety of soiling, which are introduced into the dishwasher in the form of food residues. In this respect, there is generally a need for dishwashing detergents with increased cleaning performance. In addition, a general trend for reasons of environmental protection in machine dishwashing to dispense with phosphates is observed. The problem thus arises of providing phosphate-free automatic dishwashing detergents without the cleaning performance or stability being impaired.

[0003] Particularly protein-based soils require both alkalinity and enzymes, such as amylases and proteases. However, there is the problem that alkalinity and enzymes together cannot be stably formulated, and further the problem that protein-based soils are rather persistent and hard to remove, even in the presence of active enzymes.

[0004] There is thus still a need for a stable, environmentally friendly and effective detergent exhibiting improved protein-based soil removal.

[0005] This objective has been solved by the present invention.

[0006] Therefore, in a first aspect, the present invention relates to a cleaning composition for hard surfaces, in particular a dishwashing detergent, preferably an automatic dishwashing detergent, characterized in that it comprises two distinct liquid compositions A and B, wherein composition A comprises at least one enzyme and composition B is free from enzymes, wherein the cleaning composition comprises

a) citrate in an amount of from 0 to 10 wt.-%, based on the total weight of the cleaning composition;
b) MGDA in an amount of from 5 to 40 wt.-%, based on the total weight of the cleaning composition; and
c) HEDP in an amount of from 1 to 8 wt.-%, based on the total weight of the cleaning composition.

[0007] The present invention further relates to the use of a cleaning composition as disclosed herein for cleaning hard surfaces, particularly dishes.

[0008] In yet another aspect, the present inventio also relates to a method of cleaning hard surfaces, preferably dishes, preferably in an automatic dishwashing machine, characterized in that in at least one method step at least one cleaning composition as disclosed herein is used.

[0009] Preferred embodiments are set out in the dependent claims.

[0010] When wt.-% 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.

[0011] "About", as used herein in relation to a numerical value, means said value ±10%, preferably ±5%.

[0012] The term "liquid", as used herein, refers to compounds or mixtures of compounds that are flowable and pourable at room temperature (about 15 °C to about 25 °C).

[0013] 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.

[0014] "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.

[0015] The expression "essentially free from" 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.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] INCI means that the following or preceding name is a name according to the International Dictionary of Cosmetic Ingredients of The Cosmetic, Toiletry, and Fragrance Association (CTFA). The indication CAS means that the following sequence of numbers is a designation of the Chemical Abstracts Service.

[0020] The cleaning composition for hard surfaces of the present invention, which is in particular a dishwashing detergent, preferably an automatic dishwashing detergent, is characterized in that it comprises two distinct liquid compositions A and B. Composition A comprises at least one enzyme and composition B is free from enzymes. The cleaning composition is furthermore characterized in that it comprises

a) citrate in an amount of from 0 to 10 wt.-%, based on the total weight of the cleaning composition;
b) MGDA in an amount of from 5 to 40 wt.-%, based on the total weight of the cleaning composition; and
c) HEDP in an amount of from 1 to 8 wt.-%, based on the total weight of the cleaning composition.

[0021] According to 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.

[0022] 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.

[0023] 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.

[0024] Composition A comprises at least one enzyme and composition B is free from enzymes.

[0025] Enzymes suitable for incorporation in compositions of the present invention include, in particular, proteases, amylases, lipases, hemicellulases, cellulases, perhydrolases, and oxidoreductases, as well as mixtures thereof. Said enzymes are in principle of natural origin; proceeding from the natural molecules, improved variants for use in cleaning agents are available which are preferably used accordingly. 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.

[0026] 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.

[0027] 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).

[0028] Furthermore, lipases or cutinases can be used according to the invention, in particular due to their triglyceride-cleaving activities, but also in order to produce peracids in situ from suitable precursors. These include, for example, the lipases that could originally be obtained from Humicola lanuginosa (Thermomyces lanuginosus) and those that have been further developed, particularly those with the amino acid exchange in positions D96LT213R and/or N233R, particularly preferably all of the exchanges D96L, T213R, and N233R.

[0029] Moreover, enzymes can be used which can be grouped together under the term "hemicellulases." These include, for example, mannanases, xanthan lyases, pectin lyases (=pectinases), pectinesterases, pectate lyases, xyloglucanases (=xylases), pullulanases, and β-glucanases.

[0030] In order to increase the bleaching effect, oxidoreductases such as oxidases, oxygenases, catalases, peroxidases such as halo-, chloro-, bromo-, lignin, glucose, or manganese peroxidases, dioxygenases or laccases (phenoloxidases, polyphenoloxidases) can be used according to the invention.

[0031] Advantageously, organic, particularly preferably aromatic compounds that interact with the enzymes are additionally added in order to potentiate the activity of the relevant oxidoreductases (enhancers) or, in the event of greatly differing redox potentials, to ensure the flow of electrons between the oxidizing enzymes and the contaminants (mediators). A protein and/or enzyme can be protected, especially during storage, against damage such as inactivation, denaturing, or decomposition caused for example by physical influences, oxidation or proteolytic cleavage. When the proteins and/or enzymes are obtained microbially, it is particularly preferable for proteolysis to be inhibited, particularly if the agents also contain proteases. Cleaning agents may contain stabilizers for this purpose; the provision of such agents constitutes a preferred embodiment of the present invention.

[0032] 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.

[0033] 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, bleaching agents, 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.

[0034] Moreover, it is possible to formulate two or more enzymes together, so that a single granule exhibits a plurality of enzyme activities.

[0035] 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.

[0036] The cleaning composition is furthermore characterized in that it comprises

a) citrate in an amount of from 0 to 10 wt.-%, based on the total weight of the cleaning composition;
b) MGDA in an amount of from 5 to 40 wt.-%, based on the total weight of the cleaning composition; and
c) HEDP in an amount of from 1 to 8 wt.-%, based on the total weight of the cleaning composition.

[0037] According to the present invention, the cleaning composition comprises citric acid, its salts or derivatives thereof, more particularly the sodium and potassium citrates, for example trisodium citrate *2 H_2O and tripotassium citrate *H_2O, in an amount of from 0 to 10 wt.-%, for instance in an amount of from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 wt.-%, based on the total weight of the cleaning composition. In various embodiments, the cleaning composition comprises citric acid, its salts or derivatives thereof, in an amount of from 0 to 5 wt.-%, for instance in an amount of from 0, 1, 2, 3, 4 or 5 wt.-%, based on the total weight of the cleaning composition.

[0038] According to the present invention, the cleaning composition comprises methyl-glycine-diacetic acid (MGDA), its salts or derivatives thereof, in an amount of from 5 to 40 wt.-%, for instance in an amount of from 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, or 40 wt.-%, based on the total weight of the cleaning composition. In various embodiments, the cleaning composition comprises MGDA, its salts or derivatives thereof, in an amount of from 10 to 30 wt.-%, for instance in an amount of from 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29 or 30 wt.-%, based on the total weight of the cleaning composition.

[0039] According to the present invention, the cleaning composition comprises 1-hydroxyethylidene 1,1-diphosphonic acid (HEDP), its salts or derivatives thereof, in an amount of from 1 to 8 wt.-%, for instance in an amount of from 1, 2, 3, 4, 5, 6, 7 or 8 wt.-%, based on the total weight of the cleaning composition. In various embodiments, the cleaning composition comprises HEDP, its salts or derivatives thereof, in an amount of from 2 to 6 wt.-%, for instance in an amount of from 2, 3, 4, 5 or 6 wt.-%, based on the total weight of the cleaning composition.

[0040] In various embodiments, the cleaning composition of the present invention comprises

a) citrate in an amount of from 0 to 5 wt.-%, based on the total weight of the cleaning composition; and/or
b) MGDA in an amount of from 10 to 30 wt.-%, based on the total weight of the cleaning composition; and/or

c) HEDP in an amount of from 2 to 6 wt.-%, based on the total weight of the cleaning composition.

[0041] In various embodiments, the cleaning composition of the present invention comprises

a) citrate in an amount of from 0 to 5 wt.-%, based on the total weight of the cleaning composition;
b) MGDA in an amount of from 10 to 30 wt.-%, based on the total weight of the cleaning composition; and
c) HEDP in an amount of from 2 to 6 wt.-%, based on the total weight of the cleaning composition.

[0042] In various embodiments, the cleaning composition of the present invention comprises

a) citrate in an amount of from 0 to 10 wt.-%, based on the total weight of composition B; and/or
b) MGDA in an amount of from 5 to 40 wt.-%, based on the total weight of composition B; and/or
c) HEDP in an amount of from 1 to 8 wt.-%, based on the total weight of composition B.

[0043] In various other embodiments, the cleaning composition of the present invention comprises

a) citrate in an amount of from 0 to 10 wt.-%, based on the total weight of composition B;
b) MGDA in an amount of from 5 to 40 wt.-%, based on the total weight of composition B; and
c) HEDP in an amount of from 1 to 8 wt.-%, based on the total weight of composition B.

[0044] In various embodiments, the cleaning composition of the present invention comprises

a) citrate in an amount of from 0 to 5 wt.-%, based on the total weight of composition B; and/or
b) MGDA in an amount of from 10 to 30 wt.-%, based on the total weight of composition B; and/or
c) HEDP in an amount of from 2 to 6 wt.-%, based on the total weight of composition B.

[0045] In various embodiments, the cleaning composition of the present invention comprises

a) citrate in an amount of from 0 to 5 wt.-%, based on the total weight of composition B;
b) MGDA in an amount of from 10 to 30 wt.-%, based on the total weight of composition B; and
c) HEDP in an amount of from 2 to 6 wt.-%, based on the total weight of composition B.

[0046] In various embodiments, the cleaning composition is essentially free of phosphates, preferably free of phosphates.

[0047] "Phosphate-free," as used herein, means that the composition in question is essentially free of phosphates, which is to say in particular comprises phosphates in amounts of less than 0.1 wt. %, preferably less than 0.01 wt. %, based on the total composition. If phosphates are nonetheless present, these are preferably used in amounts that correspond to no more than 0.3 g/job. The expression g per job (g/job) or g/application refers to the amount of active substance used in relation to the total weight of the agent used for a complete cleaning cycle (which is to say in the case of automatic dishwashing agents, the total amount of the cleaning agent used in a complete cleaning cycle of a dishwasher). In the case of preportioned cleaning agents (preferably automatic dishwashing agents), this information is the amount of the active substance in g based on the total weight of the preportioned cleaning agent. The expression "phosphates", as used in this context, does not include the phosphonates.

[0048] 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.

[0049] In various embodiments, composition A comprises at least one surfactant. In various such embodiments, composition B is essentially free of surfactants. In various embodiments, composition A comprises the at least one surfactant in an amount of up to 20 wt.-%, for instance in an amount of about 0.1 to 20 wt.-%, such as in an amount of about 1 to 15 wt.-%, for instance in an amount of about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13,14, 15, 16, 17, 18, 19 or 20 wt.-%, based on the total weight of composition A; and/or composition B is essentially free of surfactants.

Nonionic Surfactants

[0050] 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

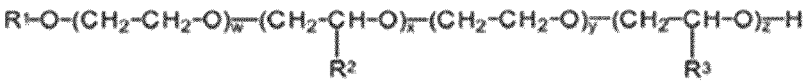
in greater detail below.

[0051] 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.

[0052] Ethoxylated non-ionic surfactants are particularly preferably used which were obtained from C_{6-20} monohydroxy alkanols or C_{6-20} alkyl phenols or C_{16-20} 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 (C_{16-20} alcohol), preferably from a C_{18} 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.

[0053] 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.

[0054] 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 R^1 represents a straight-chain or branched, saturated or mono- or polyunsaturated C_{6-24}-alkyl or alkenyl functional group; each R_2 and R_3 group is selected, independently of one another, from $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2-CH_3$, $-CH(CH_3)_2$; and the indices w, x, y and z represent, independently of one another, integers from 1 to 6.

[0055] Preferred non-ionic surfactants of the above formula can be prepared using known methods, from the corresponding alcohols R^1-OH and ethylene or alkylene oxide. The R^1 functional group in the above formula can vary depending on the origin of the alcohol. If native sources are used, the R^1 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 R^1 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.

[0056] 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 R^2 and R^3 are selected, independently of one another, from - $CH_2CH_2-CH_3$ and $-CH(CH_3)_2$ 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.

[0057] Further preferably used non-ionic surfactants of the solid phase are non-ionic surfactants of general formula

$$R^1O(AlkO)_xM(OAlk)_yOR^2,$$

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.

[0058] Preferred in this case are non-ionic surfactants of general formula

$$R^1\text{-}CH(OH)CH_2\text{-}O(CH_2CH_2O)_xCH_2CHR(OCH_2CH_2)_y\text{-}CH_2CH(OH)\text{-}R^2,$$

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.

[0059] Preferred in this case are, in particular, compounds of general formula

$$R^1\text{-}CH(OH)CH_2\text{-}O(CH_2CH_2O)_xCH_2CHR(OCH_2CH_2)_yO\text{-}CH_2CH(OH)\text{-}R^2,$$

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.

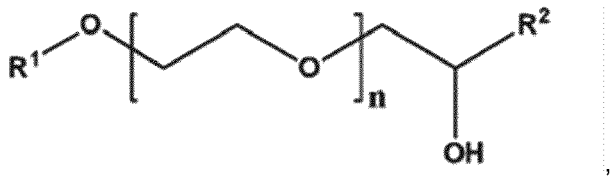
[0060] In this case, preferred non-ionic surfactants are those of general formula $R^1\text{-}CH(OH)CH_2O\text{-}(AO)_w\text{-}(AO)_x\text{-}(A"O)_y\text{-}(A‴O)_z\text{-}R^2$, in which

- R^1 represents a straight-chain or branched, saturated or mono- or polyunsaturated $C_{6\text{-}24}$ 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.

[0061] By adding the above-mentioned non-ionic surfactants of general formula $R^1\text{-}CH(OH)CH_2O\text{-}(AO)_w\text{-}(A'O)_x\text{-}(A"O)_y\text{-}(A‴O)_z\text{-}R^2$, 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.

[0062] 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.

[0063] In particular, those end-capped poly(oxyalkylated) non-ionic surfactants are preferred which, according to the following formula,



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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. 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}.

[0064] 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 $C_{2\text{-}26}$ fatty alcohol $(PO)_1\text{-}(EO)_{15\text{-}40}$-2-hydroxyalkyl ethers, in particular including the $C_{8\text{-}10}$ fatty alcohol $(PO)_1\text{-}(EO)_{22}$-2-hydroxydecyl ethers.

[0065] 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.

[0066] 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.

[0067] 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.

[0068] 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 C6-24 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.

[0069] 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.

[0070] 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 und R^2, independently of one another, represent an alkyl functional group or alkenyl functional group having 4 to 22 carbon atoms; R^3 und 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.

[0071] 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.

[0072] 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.

[0073] 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.

[0074] 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.

[0075] 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.

[0076] 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.

[0077] 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.

[0078] 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.

Anionic Surfactants

[0079] The anionic surfactants, which may be used in accordance with the invention, include, fatty alcohol ether sulfates, other aliphatic sulfates, such as fatty alcohol sulfates, dialkyl ether sulfates, monoglyceride sulfates and aliphatic sulfonates such as alkane sulfonates, olefin sulfonates, ether sulfonates, n-alkyl ether sulfonates, ester sulfonates and lignin sulfonates. Also useful in the context of the present invention are alkyl benzene sulfonates, fatty acid cyanamides, sulfosuccinic acid esters, fatty acid isethionates, acylaminoalkane sulfonates (fatty acid taurides), fatty acid sarcosinates, ether carboxylic acids and alkyl (ether) phosphates.

[0080] In preferred embodiments, the cleaning composition comprises anionic surfactants in an amount of < 1 wt.-%, based on the total weight of the cleaning composition.

Sugar Surfactants

[0081] Sugar surfactants are known surface-active compounds which include, for example, the sugar surfactant classes of alkyl glucose esters, aldobionamides, gluconamides (sugar acid amides), glycerol amides, glycerol glycolipids, polyhydroxyfatty acid amide sugar surfactants (sugar amides) and alkyl polyglycosides described, for example, in WO 97/00609 A1 (Henkel Corporation) and the publications cited therein (pages 4 to 12) to which reference is explicitly made in this regard and of which the disclosure is hereby included in the present application. According to the invention, preferred sugar surfactants are the alkyl polyglycosides and the sugar amides and their derivatives, more particularly their ethers and esters. The ethers are the products of the reaction of one or more, preferably one, sugar hydroxy group with a compound containing one or more hydroxy groups, for example C_{1-22} alcohols or glycols, such as ethylene and/or propylene glycol; the sugar hydroxy group may also carry polyethylene glycol and/or propylene glycol residues. The esters are the reaction products of one or more, preferably one, sugar hydroxy group with a carboxylic acid, more particularly a C_{6-22} fatty acid.

Alkyl Polyglycosides

[0082] The alkyl polyglycosides (APGs) are particularly preferred sugar surfactants for the purposes of the present invention and preferably correspond to the general formula $R^1O(AO)_a[G]_x$, where R^1 is a linear or branched, saturated or unsaturated alkyl group containing 6 to 22, preferably 6 to 18 and more preferably 8 to 14 carbon atoms, [G] is a glycosidic sugar unit and x is a number of 1 to 10 and AO stands for an alkyleneoxy group, for example an ethyleneoxy or propyleneoxy group, and a stands for the mean degree of alkoxylation of 0 to 20. The group $(AO)_a$ may also contain various alkyleneoxy units, for example ethyleneoxy or propyleneoxy units, in which case a stands for the mean total degree of alkoxylation, i.e. the sum of the degree of ethoxylation and the degree of propoxylation. Unless indicated in detail or indicated otherwise in the following, the alkyl groups R^1 of the APGs are linear unsaturated groups with the indicated number of carbon atoms.

[0083] APGs are nonionic surfactants and represent known substances which may be obtained by the relevant methods of preparative organic chemistry. The index x indicates the degree of oligomerization (DP degree), i.e. distribution of mono- and oligoglycosides, and is a number of 1 to 10. Whereas x in a given compound must always be an integer and, above all, may assume a value of 1 to 6, the value x for a certain alkyl oligoglycoside is an analytically determined calculated quantity which is generally a broken number. Alkyl glycosides having an average degree of oligomerization x of 1.1 to 3.0 are preferably used. Alkyl glycosides having a degree of oligomerization of less than 1.7 and, more particularly, between 1.2 and 1.6 are preferred from the applicational point of view. The glycosidic sugar used is preferably

xylose but especially glucose.

[0084] The alkyl or alkenyl radical R^1 may be derived from primary alcohols containing 8 to 18 and preferably 8 to 14 carbon atoms. Typical examples are caproic alcohol, caprylic alcohol, capric alcohol and undecyl alcohol and the technical mixtures thereof obtained, for example, in the hydrogenation of technical fatty acid methyl esters or in the hydrogenation of aldehydes from Roelen's oxosynthesis.

[0085] However, the alkyl or alkenyl radical R^1 is preferably derived from lauryl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol or oleyl alcohol and may also be derived from elaidyl alcohol, petroselinyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and technical mixtures thereof.

[0086] Particularly preferred APGs are not alkoxylated (a=0) and correspond to the formula $RO[G]_x$, in which R again stands for a linear or branched, saturated or unsaturated alkyl group containing 4 to 22 carbon atoms, [G] is a glycosidic sugar, preferably glucose, and x is a number of 1 to 10, preferably 1.1 to 3 and more preferably 1.2 to 1.6. Accordingly, preferred alkyl polyglycosides are, for example, C_{8-10} and a C_{12-14} alkyl polyglucoside with a DP degree of 1.4 or 1.5, more particularly C_{8-10} alkyl-1 ,5-glucoside and C_{12-14} alkyl-1,4-glucoside.

Cationic surfactants

[0087] Cationic surfactants are generally known in the art. In particularly preferred embodiments of the invention, no cationic surfactants are present in the cleaning compositions.

[0088] In various embodiments, composition A comprises at least one thickener.

[0089] While any kind of thickener generally known in the art for incorporation into cleaning compositions, such as dishwashing detergent compositions, may be used in the context of the present invention, particular preference is given to polymeric thickeners.

Polymeric Thickeners

[0090] Polymeric thickeners in the context of the present invention are the polycarboxylates with a thickening effect as polyelectrolytes, preferably homopolymers and copolymers of acrylic acid, more particularly acrylic acid copolymers, such as acrylic acid/methacrylic acid copolymers, and the polysaccharides, more particularly heteropolysaccharides, and other typical thickening polymers.

[0091] Suitable polysaccharides or heteropolysaccharides are the polysaccharide gums, for example gum arabic, agar, alginates, carrageenans and their salts, guar, guaran, tragacanth, geilan, ramsan, dextran or xanthan and their derivatives, e.g., propoxylated guar, as well as their mixtures. Other polysaccharide thickeners, such as starches or celluose derivatives, can be used alternatively, but preferably in addition to a polysaccharide gum, for example starches of various origins and starch derivatives, e.g. hydroxyethyl starch, starch phosphate esters or starch acetates, or carboxymethyl cellulose or its sodium salt, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose or hydroxyethyl methyl cellulose or cellulose acetate.

[0092] A particularly preferred polymeric thickener is the microbial anionic heteropolysaccharide xanthan gum which is produced by *Xanthomonas campestris* and a few other species under aerobic conditions and which has a molecular weight of 2 to 15×10^6. This polymer is obtainable from Kelco, for example, under the name of Keltrol®, for example as the cream-colored powder Keltrol® T (transparent) or the white granules Keltrol® RD (readily dispersible).

[0093] Acrylic acid polymers suitable as polymeric thickeners are, for example, the high molecular weight homopolymers of acrylic acid crosslinked with a polyalkenyl polyether, more particularly an allyl ether of sucrose, pentaerythritol or propylene (INCI Carbomer), which are also known as carboxyvinyl polymers. Polyacrylic acids such as these are obtainable inter alia from B.F. Goodrich under the name of Carbopol®, for example Carbopol® 940 (molecular weight ca. 4,000,000 g/mol), Carbopol® 941 (molecular weight ca. 1,250,000 g/mol) or Carbopol® 934 (molecular weight ca. 3,000,000 g/mol).

[0094] However, particularly suitable polymeric thickeners are the following acrylic acid copolymers: (i) copolymers of two or more monomers from the group of acrylic acid, methacrylic acid and their simple esters preferably formed with C_{1-4} alkanols (INCI Acrylates Copolymer), which include for example the copolymers of methacrylic acid, butyl acrylate and methyl methacrylate (CAS 250235-69-2) or of butyl acrylate and methyl methacrylate (CAS 25852-37-3) and which are obtainable, for example, from Rohm & Haas under the names of Aculyn® and Acusol®, for example the anionic non-associative polymers Aculyn® 33 (crosslinked), Acusol® 810 and Acusol® 830 (CAS 25852-37-3); (ii) crosslinked high molecular weight acrylic acid copolymers which include, for example, the copolymers of C_{10-30} alkyl acrylates-crosslinked with an allyl ether of sucrose or pentaerythritol-with one or more monomers from the group of acrylic acid, methacrylic acid and their simple esters preferably formed with C_{1-4} alkanols (INCI Acrylates/C10-30 Alkyl Acrylate Crosspolymer) and which are obtainable, for example, from B.F. Goodrich under the name of Carbopol®, for example the hydrophobicized Carbopol® ETD 2623 and Carbopol® 1382 (INCI Acrylates/C10-30 Alkyl Acrylate Crosspolymer) and Carbopol® AQUA 30 (formerly Carbopol® EX 473).

[0095] The polymeric thickener content is normally not more than 8% by weight, preferably between 0.1 and 7% by weight, more preferably between 0.5 and 6% by weight, most preferably between 1 and 5% by weight and, in one most particularly preferred embodiment, between 1.5 and 4% by weight, for example between 2 and 2.5% by weight.

[0096] In various embodiments, composition A comprises at least one of xanthan and polyacrylates.

[0097] In various embodiments, composition A comprises at least one sulfopolymer, preferably a copolymeric polysulfonate, preferably a hydrophobically modified copolymeric polysulfonate.

[0098] The copolymers can have two, three, four, or more different monomer units. Preferred copolymeric polysulfonates contain, besides sulfonic acid group-containing monomer(s), at least one monomer from the group of unsaturated carboxylic acids.

[0099] According to a particularly preferred embodiment, composition A contains a polymer comprising at least one sulfonic acid group-containing monomer.

[0100] As unsaturated carboxylic acid(s), unsaturated carboxylic acids of formula $R^1(R^2)C=C(R^3)COOH$ are particularly preferably used, in which R^1 to R^3 represent, independently of one another, -H, $-CH_3$, a straight-chain or branched saturated alkyl functional group having 2 to 12 carbon atoms, a straight-chain or branched, mono- or polyunsaturated alkenyl functional group having 2 to 12 carbon atoms, - NH2, -OH, or -COOH-substituted alkyl or alkenyl functional groups as defined above, or represent - COOH or $-COOR^4$, where R^4 is a saturated or unsaturated, straight-chain or branched hydrocarbon functional group having 1 to 12 carbon atoms.

[0101] Particularly preferred unsaturated carboxylic acids are acrylic acid, methacrylic acid, ethacrylic acid, α-chloroacrylic acid, α-cyanoacrylic acid, crotonic acid, α-phenylacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, citraconic acid, methylene malonic acid, sorbic acid, cinnamic acid, or mixtures thereof. Unsaturated dicarboxylic acids can of course also be used.

[0102] For sulfonic acid group-containing monomers, those of the formula $R^5(R^6)C=C(R^7)\text{-}X\text{-}SO_3H$ are preferred, in which R^5 to R^7, independently of one another, represent -H, $-CH_3$, a straight-chain or branched saturated alkyl functional group having 2 to 12 carbon atoms, a straight-chain or branched, mono- or polyunsaturated alkenyl functional group having 2 to 12 carbon atoms, $-NH_2$, -OH, or - COOH-substituted alkyl or alkenyl functional groups, or represent -COOH or $-COOR^4$, where R^4 is a saturated or unsaturated, straight-chain or branched hydrocarbon functional group having 1 to 12 carbon atoms, and X represents an optionally present spacer group that is selected from $-(CH_2)_n-$, where n = 0 to 4, $-COO-(CH_2)_k-$, where k = 1 to 6, $-C(O)-NH-C(CH_3)_2-$, $-C(O)-NH-C(CH_3)_2-CH_2-$ and - $C(O)-NH-CH(CH_2CH_3)-CH_2-$.

[0103] Among these monomers, those of formulas $H_2C=CH\text{-}X\text{-}SO_3H$, $H_2C=C(CH_3)\text{-}X\text{-}SO_3H$ or $HO_3S\text{-}X\text{-}(R^6)C=C(R^7)\text{-}X\text{-}SO_3H$ are preferred, in which R^6 and R^7, independently of one another, are selected from -H, $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$ and $-CH(CH_3)_2$, and X represents an optionally present spacer group that is selected from $-(CH_2)_n-$, where n = 0 to 4, $-COO-(CH_2)_k-$, where k = 1 to 6, $-C(O)-NH-C(CH_3)_2-$, $-C(O)-NH-C(CH_3)_2-CH_2-$ and $-C(O)-NH-CH(CH_3)-CH_2-$.

[0104] According to a particularly preferred embodiment, composition A comprises a polymer comprising, as a sulfonic acid group-containing monomer, acrylamidopropanesulfonic acids, methacrylamidomethylpropanesulfonic acids or acrylamidomethylpropanesulfonic acid.

[0105] Particularly preferred sulfonic acid group-containing monomers are 1-acrylamido-1-propanesulfonic acid, 2-acrylamido-2-propanesulfonic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid, 2-methacrylamido-2-methyl-1-propanesulfonic acid, 3-methacrylamido-2-hydroxy-propanesulfonic acid, allyl sulfonic acid, methallyl sulfonic acid, allyloxybenzene sulfonic acid, methallyloxybenzene sulfonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulfonic acid, 2-methyl-2-propene-1-sulfonic acid, styrene sulfonic acid, vinylsulfonic acid, 3-sulfopropylacrylate, 3-sulfopropylmethacrylate, sulfomethacrylamide, sulfomethylmethacrylamide, as well as mixtures of the above acids or water-soluble salts thereof. The sulfonic acid groups can be present in the polymers in a fully or partially neutralized form, i.e., the acidic hydrogen atom of the sulfonic acid group can be replaced in some or all of the sulfonic acid groups with metal ions, preferably alkali metal ions, and in particular with sodium ions. The use of partially or fully neutralized sulfonic acid group-containing copolymers is preferred according to the invention.

[0106] In copolymers that contain only carboxylic acid group-containing monomers and sulfonic acid group-containing monomers, the monomer distribution of the copolymers that are preferably used according to the invention is preferably 5 to 95 wt.% in each case; particularly preferably, the proportion of the sulfonic acid group-containing monomer is 50 to 90 wt.%, and the proportion of the carboxylic acid group-containing monomer is 10 to 50 wt.%, with the monomers preferably being selected from those mentioned above. The molar mass of the sulfo-copolymers that are preferably used according to the invention can be varied in order to adapt the properties of the polymers to the desired intended use. Preferred cleaning agents are characterized in that the copolymers have molar masses of from 2,000 to 200,000 $gmol^{-1}$, preferably 4,000 to 25,000 $gmol^{-1}$, and in particular 5,000 to 15,000 $gmol^{-1}$.

[0107] In another preferred embodiment, the copolymers comprise not only a carboxyl group-containing monomer and sulfonic acid group-containing monomer but also at least one non-ionic, preferably hydrophobic monomer. In particular, the rinsing performance of dishwasher detergents according to the invention was able to be improved through the use of these hydrophobically modified polymers.

[0108] Particularly preferably, composition A further comprises an anionic copolymer, a copolymer comprising

i) carboxylic acid group-containing monomers
ii) sulfonic acid group-containing monomers
iii) non-ionic monomers, in particular hydrophobic monomers, being used as the anionic copolymer.

[0109] As non-ionic monomers, monomers of general formula $R^1(R^2)C=C(R^3)$-X-R^4 are preferably used, in which R^1 to R^3 represent, independently of one another, -H, $-CH_3$ or $-C_2H_5$, X represents an optionally present spacer group selected from $-CH_2-$, -C(O)O- and -C(O)-NH-, and R^4 represents a straight-chain or branched saturated alkyl functional group having 2 to 22 carbon atoms or an unsaturated, preferably aromatic functional group having 6 to 22 carbon atoms.

[0110] Particularly preferred non-ionic monomers are butene, isobutene, pentene, 3-methylbutene, 2-methylbutene, cyclopentene, hexene, hexene-1, 2-methlypentene-1, 3-methlypentene-1, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, 2,4,4-trimethylpentene-1, 2,4,4-trimethylpentene-2,2,3-dimethylhexene-1, 2,4-dimethylhexene-1, 2,5-dimethylhexene-1, 3,5-dimethylhexene-1, 4,4-dimethylhexane-1, ethylcyclohexene, 1-octene, α-olefins having 10 or more carbon atoms such as 1-decene, 1-dodecene, 1-hexadecene, 1-octadecene and C_{22} α-olefin, 2-styrene, α-methylstyrene, 3-methylstyrene, 4-propylstyrene, 4-cyclohexylstyrene, 4-dodecylstyrene, 2-ethyl-4-benzylstyrene, 1-vinyl naphthalene, 2-vinyl naphthalene, acrylic acid methyl ester, acrylic acid ethyl ester, acrylic acid propyl ester, acrylic acid butyl ester, acrylic acid pentyl ester, acrylic acid hexyl ester, methacrylic acid methyl ester, *N*-(methyl)acrylamide, acrylic acid-2-ethylhexyl ester, methacrylic acid-2-ethylhexyl ester, *N*-(2-ethylhexyl)acrylamide, acrylic acid octyl ester, methacrylic acid octyl ester, *N*-(octyl)acrylamide, acrylic acid lauryl ester, methacrylic acid lauryl ester, *N*-(lauryl)acrylamide, acrylic acid stearyl ester, methacrylic acid stearyl ester, *N*-(stearyl)acrylamide, acrylic acid behenyl ester, methacrylic acid behenyl ester, and *N*-(behenyl)acrylamide or mixtures thereof, in particular acrylic acid, ethyl acrylate, 2-acrylamido-2-methylpropanesulfonic acid (AMPS) as well as mixtures thereof.

[0111] The proportion of the anionic polymer is preferably 1 wt.% to 35 wt.%, in particular 3 wt.% to 30 wt.%, in particular 4 wt.% to 25 wt.%, preferably 5 wt.% to 20 wt.%, for example 10 wt.%, based on the total weight of the cleaning composition. Sulfopolymers, in particular the preferred copolymeric polysulfonates, which, in addition to sulfonic acid group-containing monomer(s), also contain at least one monomer from the group of unsaturated carboxylic acids, in particular acrylic acid, also provide an excellent shine on the surface. What is more, fingerprints are not left behind. Therefore, the proportion of sulfopolymers, in particular the preferred copolymeric polysulfonates which contain not only sulfonic acid group-containing monomer(s) but also at least one monomer from the group of unsaturated carboxylic acids, in particular acrylic acid, in particular the proportion of said sulfopolymers having AMPS as a sulfonic acid group-containing monomer, for example Acusol 590, Acusol 588 or Sokalan CP50, is preferably 1 wt.% to 25 wt.%, in particular 3 wt.% to 18 wt.%, particularly 4 wt.% to 15 wt.%, preferably 5 wt.% to 12 wt.%, based on the weight of the cleaning composition.

[0112] In various embodiments, the at least one sulfopolymer, as herein defined above, is present in composition A in an amount of up top 10 wt.-%, based on the total weight of composition A.

[0113] In various embodiments, composition A comprises

i) at least one surfactant, preferably in an amount of up to 20 wt.-% based on the total weight of composition A; and/or
ii) at least one of xanthan or a polyacrylate; and/or
iii) at least one sulfopolymer, preferably in an amount of up to 10 wt.-%, based on the total weight of composition A.

[0114] In various embodiments, composition A comprises

i) at least one surfactant, preferably in an amount of up to 20 wt.-% based on the total weight of composition A; and
ii) at least one of xanthan or a polyacrylate; and optionally
iii) at least one sulfopolymer, preferably in an amount of up to 10 wt.-%, based on the total weight of composition A.

Solvents

[0115] The water content of the cleaning composition according to the invention may be in the range of about 10 to 95 wt.-%, preferably 20 to 85 wt.-%, more preferably 30 to 75 wt.-% and most preferably 30 to 70 wt.-%, based on the total weight of the cleaning composition. The composition according to the invention may advantageously contain one or more water-soluble organic solvents in a quantity of typically 0.1 to 30% by weight, preferably 1 to 20% by weight, more preferably 2 to 15% by weight, most preferably 4 to 12% by weight and, in one most particularly preferred embodiment, 6 to 10% by weight.

[0116] In the context of the teaching according to the invention, the solvent is used in particular as a hydrotropic agent, a viscosity adjuster and/or low-temperature stabilizer according to requirements. It has a solubilizing effect, particularly

on surfactants and electrolytes, perfumes and dyes, and thus contributes to their incorporation, prevents the formation of liquid crystalline phases and contributes to the formation of clear products. The viscosity of the composition according to the invention decreases with increasing solvent content. However, too much solvent can produce a fall in viscosity. Finally, the cold cloud and clear point of the composition according to the invention decreases with increasing solvent content. Suitable solvents are, for example, saturated or unsaturated, preferably saturated, branched or unbranched C_{1-20} hydrocarbons, preferably C_{2-15} hydrocarbons, containing at least one hydroxy group and optionally one or more ether functions C-O-C, i.e. oxygen atoms interrupting the carbon atom chain.

[0117] Preferred solvents are the C_{2-6} alkylene glycols and poly-C_{2-3}-alkylene glycol ethers, optionally etherified on one side with a C_{1-6} alkanol, containing on average 1 to 9 identical or different, preferably identical, alkylene glycol groups per molecule and the C_{1-6} alcohols, preferably ethanol, n-propanol or isopropanol, more particularly ethanol.

[0118] Examples of solvents are the following compounds identified by their INCI names: Alcohol (Ethanol), Buteth-3, Butoxydiglycol, Butoxyethanol, Butoxyisopropanol, Butoxypropanol, n-Butyl Alcohol, t-Butyl Alcohol, Butylene Glycol, Butyloctanol, Diethylene Glycol, Dimethoxydiglycol, Dimethyl Ether, Dipropylene Glycol, Ethoxydiglycol, Ethoxyethanol, Ethyl Hexanediol, Glycol, Hexanediol, 1,2,6-Hexanetriol, Hexyl Alcohol, Hexylene Glycol, Isobutoxypropanol, Isopentyldiol, Isopropyl Alcohol (isoPropanol), 3-Methoxybutanol, Methoxydiglycol, Methoxyethanol, Methoxyisopropanol, Methoxymethylbutanol, Methoxy PEG-10, Methylal, Methyl Alcohol, Methyl Hexyl Ether, Methylpropanediol, Neopentyl Glycol, PEG-4, PEG-6, PEG-7, PEG-8, PEG-9, PEG-6 Methyl Ether, Pentylene Glycol, PPG-7, PPG-2-Buteth-3, PPG-2 Butyl Ether, PPG-3 Butyl Ether, PPG-2 Methyl Ether, PPG-3 Methyl Ether, PPG-2 Propyl Ether, Propanediol, Propyl Alcohol (n-Propanol), Propylene Glycol, Propylene Glycol Butyl Ether, Propylene Glycol Propyl Ether, Tetrahydrofurfuryl Alcohol, Trimethylhexanol.

[0119] In various embodiments, the cleaning composition according to the present invention is characterized in that

i) composition A comprises water in an amount of from 6 to 70 wt.-%, preferably in an amount of from 10 to 55 wt.-%, more preferably in an amount of from 15 to 50 wt.-%, based on the total weight of composition A; and/or
ii) composition B comprises water in an amount of from 6 to 70 wt.-%, preferably in an amount of from 10 to 55 wt.-%, more preferably in an amount of from 15 to 50 wt.-%, based on the total weight of composition B.

[0120] It is further preferable that the cleaning composition comprises, in addition to any of the aforementioned ingredients, at least one further ingredient, which may improve cleaning performance, stability, aesthetics or other attributes and characteristics of the cleaning composition. In various embodiments, the cleaning composition further comprises at least one additive selected from the group consisting of water-soluble salts, acids, perfumes, dyes, opacifiers, corrosion inhibitors, pH-value adjuster, bleaching agents, bleach catalysts, bleach activators, preservatives, or mixtures thereof

[0121] A change in the content of dicarboxylic acid (salt), more particularly in quantities above 2% by weight, can contribute to a clear solution of the ingredients. The viscosity of the mixture can also be influenced within certain limits by this component. In addition, this component influences the solubility of the mixture. In a particularly preferred embodiment, the component in question is used where the surfactant content is high, more particularly above 30% by weight. However, if their presence is not essential, the composition according to the invention is preferably free from dicarboxylic acids (salts).

[0122] According to various preferred embodiments, the cleaning composition comprises at least one perfume.

[0123] Suitable perfume oils may comprise individual fragrant compounds, for example synthetic products of the ester, ether, aldehyde, ketone, alcohol, and hydrocarbon type. Fragrant compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butylcyclohexyl acetate, linalyl acetate, dimethylbenzyl carbinyl acetate (DMBCA), phenylethyl acetate, benzyl acetate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styrallyl propionate, benzyl salicylate, cyclohexyl salicylate, floramate, melusate and jasmecyclate. The ethers include, for example, benzyl ethyl ether and ambroxan; the aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, lilial and bourgeonal; the ketones include, for example, the ionones, isomethyl ionone and methyl cedryl ketone; the alcohols include anethol, citronellol, eugenol, geraniol, linalool, phenylethyl alcohol and terpineol and the hydrocarbons include, for example the terpenes, such as limonene and pinene. However, mixtures of various fragrances, which together produce an attractive fragrant note of the resulting perfume oil, are preferably used.

[0124] The perfume oils may also contain natural mixtures of fragrances, as are obtainable from vegetal sources, for example pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. Also suitable are e.g. muscatel sage oil, chamomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime blossom oil, juniper berry oil, vetivert oil, olibanum oil, galbanum oil and laudanum oil and orange blossom oil, neroli oil, orange peel oil and sandalwood oil.

[0125] Exemplary long-lasting fragrances may be selected from essential oils, such as angelica root oil, aniseed oil, arnica flowers oil, basil oil, bay oil, bergamot oil, champax blossom oil, silver fir oil, silver fir cone oil, elemi oil, eucalyptus oil, fennel oil, pine needle oil, galbanum oil, geranium oil, ginger grass oil, guaiacum wood oil, Indian wood oil, helichrysum oil, ho oil, ginger oil, iris oil, cajuput oil, sweet flag oil, chamomile oil, camphor oil, Canoga oil, cardamom oil, cassia oil,

Scotch fir oil, copaiba balsam oil, coriander oil, spearmint oil, caraway oil, cumin oil, lavender oil, lemon grass oil, limette oil, mandarin oil, melissa oil, amber seed oil, myrrh oil, clove oil, neroli oil, niaouli oil, olibanum oil, orange oil, origanum oil, Palma Rosa oil, patchouli oil, Peru balsam oil, petit grain oil, pepper oil, peppermint oil, pimento oil, pine oil, rose oil, rosemary oil, sandalwood oil, celery seed oil, lavender spike oil, Japanese anise oil, turpentine oil, thuja oil, thyme oil, verbena oil, vetiver oil, juniper berry oil, wormwood oil, wintergreen oil, ylang-ylang oil, ysop oil, cinnamon oil, cinnamon leaf oil and cypress oil. However, in the context of the present invention, the higher boiling or solid fragrances of natural or synthetic origin can be advantageously used as long-lasting fragrances or mixtures of fragrances. These compounds include for example the following compounds and their mixtures: ambrettolide, amyl cinnamaldehyde, anethol, anisaldehyde, anis alcohol, anisole, methyl anthranilate, acetophenone, benzyl acetone, benzaldehyde, ethyl benzoate, benzophenone, benzyl alcohol, borneol, bornyl acetate, bromostyrene, n-decyl aldehyde, n-dodecyl aldehyde, eugenol, eugenol methyl ether, eucalyptol, farnesol, fenchone, fenchyl acetate, geranyl acetate, geranyl formate, heliotropin, methyl heptyne carboxylate, heptaldehyde, hydroquinone dimethyl ether, hydroxycinnamaldehyde, hydroxycinnamyl alcohol, indole, irone, isoeugenol, isoeugenol methyl ether, isosafrol, jasmone, camphor, carvacrol, carvone, p-cresol methyl ether, coumarone, p-methoxyacetophenone, methyl n-amyl ketone, methyl anthranilic acid methyl ester, p-methylacetophenone, methyl chavicol, p-methylquinoline, methyl naphthyl ketone, methyl n-nonyl acetaldehyde, methyl n-nonyl ketone, muscone, naphthol ethyl ether, naphthol methyl ether, nerol, nitrobenzene, n-nonyl aldehyde, nonyl alcohol, n-octyl aldehyde, p-oxyacetophenone, pentadecanolide, phenyl ethyl alcohol, phenyl acetaldehyde dimethyl acetal, phenylacetic acid, pulegone, safrol, isoamyl salicylate, methyl salicylate, hexyl salicylate, cyclohexyl salicylate, santalol, scatol, terpineol, thymine, thymol, undecalactone, vanillin, veratrum aldehyde, cinnamaldehyde, cinnamyl alcohol, cinnamic acid, ethyl cinnamate, benzyl cinnamate. In the context of the present invention, the advantageously utilizable fragrances of higher volatility particularly include the lower boiling fragrances of natural or synthetic origin that can be used alone or in mixtures. Exemplary fragrances of higher volatility are alkyl isothiocyanates (alkyl mustard oils), butanedione, limonene, linalool, linalyl acetate and linalyl propionate, menthol, menthone, phellandrene, phenylacetaldehyde, terpinyl acetate, citral, citronellal.

Glass corrosion inhibitors

[0126] Glass corrosion inhibitors prevent the appearance of clouding, streaking, and scratching, but also iridescence of the glass surface of automatically cleaned glassware. Preferred glass corrosion inhibitors come from the group of magnesium and zinc salts and of the magnesium and zinc complexes. Within the scope of the present disclosure, the content of zinc salt in cleaning agents, preferably dishwashing agents, in particular automatic dishwashing agents, is especially between about 0.1 and about 5 wt. %, preferably between about 0.2 and about 4 wt. %, and in particular between about 0.4 and about 3 wt. %, or the content of zinc in oxidized formed (calculated as Zn^{2+}) is between about 0.01 and about 1 wt. %, especially between about 0.02 and about 0.5 wt. %, and in particular between about 0.04 and about 0.2 wt. %, in each case based on the total weight of the cleaning agent.

pH-value

[0127] The pH-value of the of the compositions according to the invention may be adjusted with typical pH adjusters, for example acids, such as mineral acids or citric acid, and/or alkalis, such as sodium or potassium hydroxide. In various embodiments, the pH of composition A is in the range from 7.0 to 10, preferably in the range from 7.1 to 8.5 and more particularly in the range from 7.2 to 7.9, and/or the pH of composition B is in the range from 10.0 to 14, preferably in the range from 10.5 to 13 and more particularly in the range from 11 to 12.

Viscosity

[0128] The viscosity favorable for the cleaning composition according to the invention (at 20° C and at a shear rate of 30 s^{-1}, as measured with a Brookfield LV DV 11 viscosimeter, spindle 25) is in the range from about 10 to about 1,000 mPa·s, preferably about 50 to about 500 mPa·s, in particular about 100 to about 400 mPa·s, more preferably about 150 to about 300 mPa·s.

[0129] Accordingly, in various embodiments, at 20 °C and a shear rate of 30 s^{-1}, composition A and/or composition B has a viscosity of about 10 to about 1,000 mPa·s, preferably about 50 to about 500 mPa·s, in particular about 100 to about 400 mPa·s, more preferably about 150 to about 300 mPa·s.

[0130] The cleaning compositions described herein are preferably packaged in a multi-chamber bottle, in particular in a two-chamber bottle, and dosed out said bottle, preferably into the dosing chamber of the dishwasher. The cleaning composition of the present invention comprises at least one composition A and at least one composition B, as herein described above. Consequently, in the case of the cleaning composition of the present invention being in the form of a unit dose article, said article comprises at least two, three or more chambers and be filled with the respective liquid

compositions. For example, it is possible to close the chambers on the open side with either a second molded body or with one or more water-soluble films (in particular as described herein). In this way, the release of the compositions present in the chambers can be arbitrarily controlled based on the desired release point in time. It is possible to either release the entire agent at once (either directly at the beginning of the cleaning cycle or at a certain point in time during the course of the cleaning cycle) or, by varying the film composition, at certain points in time that are different from each other within the cycle of the dishwasher (for example, as a function of the temperature of the dishwater).

[0131] Suitable water-soluble films for producing the water-soluble wrapping are preferably based on a polyvinyl alcohol, or a polyvinyl alcohol copolymer, having a relative molar mass in the range from about 10,000 to about 1,000,000 g/mol, preferably from about 20,000 to about 500,000 g/mol, particularly preferably from about 30,000 to about 100,000 g/mol, and in particular from about 40,000 to about 80,000 g/mol.

[0132] The polyvinyl alcohol is typically produced by the hydrolysis of polyvinyl acetate since the direct synthesis pathway is not possible. The same applies to polyvinyl alcohol copolymers produced accordingly from polyvinyl acetate copolymers. It is preferred if at least one layer of the water-soluble wrapping comprises a polyvinyl alcohol having a degree of hydrolysis of about 70 to about 100 mole %, preferably about 80 to about 90 mole %, particularly preferably about 81 to about 89 mole %, and in particular about 82 to about 88 mole %.

[0133] Additionally, a polymer selected from the group consisting of (meth)acrylic acid-containing (co)polymers, polyacrylamides, oxazoline polymers, polystyrene sulfonates, polyurethanes, polyesters, polyethers, polylactic acid or mixtures of the above polymers can be added to a polyvinyl alcohol-containing film material that is suitable for producing the water-soluble wrapping. A preferred additional polymer is polylactic acids.

[0134] In addition to vinyl alcohol, preferred polyvinyl alcohol copolymers comprise dicarboxylic acids as further monomers. Suitable dicarboxylic acids are itaconic acid, malonic acid, succinic acid and mixtures thereof, itaconic acid being preferred.

[0135] Likewise preferred polyvinyl alcohol copolymers include an ethylenically unsaturated carboxylic acid, the salt thereof, or the ester thereof, in addition to vinyl alcohol. In addition to vinyl alcohol, such polyvinyl alcohol copolymers particularly preferably comprise acrylic acid, methacrylic acid, acrylic acid esters, methacrylic acid esters or mixtures thereof.

[0136] It may be preferred for the film material to contain further additives. For example, the film material may contain plastizicers such as dipropylene glycol, ethylene glycol, diethylene glycol, propylene glycol, glycerol, sorbitol, mannitol or mixtures thereof. Examples of further additives include release aids, fillers, cross-linking agents, surfactants, antioxidants, UV absorbers, anti-blocking agents, non-stick agents or mixtures thereof.

[0137] Suitable water-soluble films for use in the water-soluble wrappings of the water-soluble packaging according to the disclosure are films sold by MonoSol LLC, for example, by the designation M8630, C8400 or M8900. Other suitable films include films by the designation Solublon® PT, Solublon® GA, Solublon® KC or Solublon® KL from Aicello Chemical Europe GmbH, or the VF-HP films from Kuraray.

[0138] In a further aspect, the present invention relates to the use of a cleaning composition, as herein described above, for the cleaning of hard surfaces, particularly dishes, preferably dishware. "Dishware", in the context of the present invention, includes dishes, cups, cutlery, glassware, food storage containers, cooking utensils (cookware) and the like.

[0139] Furthermore, the present invention relates to a method of cleaning hard surfaces, preferably 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.

[0140] All embodiments disclosed herein in relation to the liquid compositions apply similarly to the methods and uses of the invention and *vice versa.*

[0141] The following examples are given to illustrate the present invention. Because these examples are given for illustrative purposes only, the invention should not be deemed limited thereto.

Examples

Example 1: Composition formulations

[0142]

Table 1

Ingredients	Active substances [wt.-%]
Composition A	
Thickener (acrylate based)	0.9
Sorbitol	8.5
Acrylic acid terpolymer containing sulfonated monomers (Sulfopolymer)	5
MGDA - trisodium salt	10
Citric acid (waterfree)	0.35
Calcium chloride	0.27
Nonionic surfactant FA EO end capped	3.5
Protease according to Seq ID No. 2 of WO2013/060621 (active enzyme protein)	0.2
Amylase (active enzyme protein)	0.02
Miscellaneous (preservative, perfume, colorants)	0.1
Water	Add 100
Composition B	
Thickener (acrylate based)	0.9
HEDP sodium salt (phosphonate)	4.5
Sodium citrate dihydrate	4.0
MGDA trisodium salt	10
Sodium carbonate	9.0
cationic polymer	0.2
Miscellaneous (alkaline pH control agent, preservative, perfume, colorants)	6
Water	Add 100

[0143] Composition A has a pH of 7.2 - 7.8 and a viscosity of 150-240 mPa·s (measured at 20 °C, 3 rpm, Spindle 31, Brookfield DV2T). Composition B has a pH of 11.0 - 11.4 and a viscosity of 150-240 mPa·s (measured at 20 °C, 3 rpm, Spindle 31, Brookfield DV2T). Dosing scheme: 16 g of A and 18 g B mixed.

Example 2: Composition formulations

[0144]

Table 2

Ingredients	Active substances [wt.-%]
Composition A	
Thickener (acrylate based)	0.85
Sorbitol	8.5
Acrylic acid terpolymer containing sulfonated monomers (Sulfopolymer)	4,5
MGDA - trisodium salt	10
Citric acid (waterfree)	0
Calcium chloride	0.2
Nonionic surfactant FA EO end capped	3.7

(continued)

Ingredients	Active substances [wt.-%]
Composition A	
Protease according to Seq ID No. 2 of WO2013/060621 (active enzyme protein)	0.2
Amylase (active enzyme protein)	0.02
Miscellaneous (preservative, perfume, colorants)	0.1
Water	Add 100
Composition B	
Thickener (acrylate based)	0.85
HEDP sodium salt (phosphonate)	4.5
Sodium citrate dihydrate	4.2
MGDA trisodium salt	10
Sodium carbonate	10
cationic polymer	0.2
Miscellaneous (alkaline pH control agent, preservative, perfume, colorants)	6
Water	Add 100

[0145] Composition A has a pH of 7.2 - 7.8 and a viscosity of 150-240 mPa·s (measured at 20 °C, 30 rpm, Spindle 31, Brookfield DV2T). Composition B has a pH of 11.0 - 11.4 and a viscosity of 150-240 mPa·s (measured at 20 °C, 30 rpm, Spindle 31, Brookfield DV2T). Dosing scheme: 16 g of A and 18 g B mixed.

Claims

1. A cleaning composition for hard surfaces, in particular a dishwashing detergent, preferably an automatic dishwashing detergent, **characterized in that** it comprises two distinct liquid compositions A and B, wherein composition A comprises at least one enzyme and composition B is free from enzymes, wherein the cleaning composition comprises

   a) citrate in an amount of from 0 to 10 wt.-%, based on the total weight of the cleaning composition;
   b) MGDA in an amount of from 5 to 40 wt.-%, based on the total weight of the cleaning composition; and
   c) HEDP in an amount of from 1 to 8 wt.-%, based on the total weight of the cleaning composition.

2. The cleaning composition according to claim 1, wherein

   a) citrate is present in an amount of from 0 to 5 wt.-%, based on the total weight of the cleaning composition; and/or
   b) MGDA is present in an amount of from 10 to 30 wt.-%, based on the total weight of the cleaning composition; and/or
   c) HEDP is present in an amount of from 2 to 6 wt.-%, based on the total weight of the cleaning composition.

3. The cleaning composition according to claim 1 or claim 2, wherein

   a) citrate is present in an amount of from 0 to 10 wt.-%, based on the total weight of composition B; and/or
   b) MGDA is present in an amount of from 5 to 40 wt.-%, based on the total weight of composition B; and/or
   c) HEDP is present in an amount of from 1 to 8 wt.-%, based on the total weight of composition B.

4. The cleaning composition according to any one of claim 1 to 3, wherein

   a) citrate is present in an amount of from 0 to 5 wt.-%, based on the total weight of composition B; and/or
   b) MGDA is present in an amount of from 10 to 30 wt.-%, based on the total weight of composition B; and/or
   c) HEDP is present in an amount of from 2 to 6 wt.-%, based on the total weight of composition B.

5. The cleaning composition according to any one of claims 1 to 4, wherein composition A comprises at least one amylase and at least one protease and optionally at least one additional enzyme selected from the list consisting of lipases, hemicellulases, in particular pectinases and/or mannanases, cellulases, perhydrolases and oxidoreductases.

6. The cleaning composition according to any one of claims 1 to 5, wherein composition A comprises i) at least one surfactant, preferably in an amount of up to 20 wt.-% based on the total weight of composition A; and/or

ii) at least one thickener, preferably xanthan or a polyacrylate; and/or
iii) at least one sulfopolymer, preferably in an amount of up to 10 wt.-%, based on the total weight of composition A.

7. The cleaning composition according to any one of claims 1 to 6, comprising water in an amount of from 10 to 90 wt.-%, preferably in an amount of from 20 to 80 wt.-%, more preferably in an amount of from 30 to 75 wt.-%, based on the total weight of the cleaning composition.

8. The cleaning composition according to any one of claims 1 to 7, wherein

i) composition A comprises water in an amount of from 6 to 70 wt.-%, preferably in an amount of from 10 to 55 wt.-%, more preferably in an amount of from 15 to 50 wt.-%, based on the total weight of composition A; and/or
ii) composition B comprises water in an amount of from 6 to 70 wt.-%, preferably in an amount of from 10 to 55 wt.-%, more preferably in an amount of from 15 to 50 wt.-%, based on the total weight of composition B.

9. The cleaning composition according to any one of claims 1 to 8, wherein the cleaning composition is essentially free of phosphates, preferably free of phosphates.

10. The cleaning composition according to any one of claims 1 to 9, further comprising at least one additive selected from the group consisting of water-soluble salts, acids, perfumes, dyes, opacifiers, corrosion inhibitors, pH-value adjuster, preservatives, or mixtures thereof.

11. The cleaning composition according to any one of claims 1 to 10, wherein, at 20 °C and a shear rate of 30 s^{-1}, composition A and/or composition B has a viscosity of about 10 to about 1,000 mPa·s, preferably about 50 to about 500 mPa·s, in particular about 100 to about 400 mPa·s as measured with a Brookfield® DV2T viscosimeter, 30 rpm, Spindle 31.

12. Use of a cleaning composition according to any one of claims 1 to 12 for cleaning hard surfaces, particularly dishes, preferably dishware.

13. Method of cleaning hard surfaces, preferably dishes, preferably in an automatic dishwashing machine, **characterized in that** in at least one method step at least one cleaning composition according to any one of claims 1 to 12 is used.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 21 0097

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 10 2015 210828 A1 (HENKEL AG & CO KGAA [DE]) 15 December 2016 (2016-12-15) * Recept 1 combining stable liquid recepts 44 and 26; claims 1-10; examples 1-2; tables 1, 2 *	1,5-13	INV. C11D3/20 C11D3/33 C11D3/386 C11D17/04 C11D3/36
X	DE 10 2019 117742 A1 (HENKEL AG & CO KGAA [DE]) 7 January 2021 (2021-01-07) * examples *	1-6,8-13	
A	EP 3 325 597 B1 (HENKEL AG & CO KGAA [DE]) 1 July 2020 (2020-07-01) * example E1; tables 1, 2 *	1-13	
A	DE 10 2018 220187 A1 (HENKEL AG & CO KGAA [DE]) 28 May 2020 (2020-05-28) * recept 4; paragraphs [0043], [0044], [0046], [0048], [0079], [0102]; claims 1-15 *	1-13	
A	EP 3 656 839 A1 (HENKEL AG & CO KGAA [DE]) 27 May 2020 (2020-05-27) * paragraphs [0106] - [0108]; claim 1 *	1-13	TECHNICAL FIELDS SEARCHED (IPC) C11D
A	EP 3 080 242 B1 (HENKEL AG & CO KGAA [DE]) 22 August 2018 (2018-08-22) * paragraphs [0042], [0090]; claims 1, 6, 7, 9, 10 *	1-13	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	5 April 2024	Loiselet-Taisne, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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& : member of the same patent family, corresponding document

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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
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05-04-2024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102015210828 A1	15-12-2016	DE 102015210828 A1	15-12-2016
		WO 2016198446 A1	15-12-2016
DE 102019117742 A1	07-01-2021	DE 102019117742 A1	07-01-2021
		EP 3994241 A1	11-05-2022
		WO 2021001248 A1	07-01-2021
EP 3325597 B1	01-07-2020	DE 102015213940 A1	26-01-2017
		EP 3325597 A1	30-05-2018
		ES 2810750 T3	09-03-2021
		PL 3325597 T3	28-12-2020
		WO 2017013159 A1	26-01-2017
DE 102018220187 A1	28-05-2020	NONE	
EP 3656839 A1	27-05-2020	DE 102018220189 A1	28-05-2020
		EP 3656839 A1	27-05-2020
EP 3080242 B1	22-08-2018	DE 102013225920 A1	18-06-2015
		EP 3080242 A1	19-10-2016
		ES 2691557 T3	27-11-2018
		WO 2015086761 A1	18-06-2015

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 9700609 A1 **[0081]**
- WO 2013060621 A **[0142] [0144]**

Non-patent literature cited in the description

- *CHEMICAL ABSTRACTS,* 250235-69-2 **[0094]**
- *CHEMICAL ABSTRACTS,* 25852-37-3 **[0094]**