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(54) **TWO-PHASE CLEANING COMPOSITION WITH VISIBLY DISTINCT DETERGENT PARTICLES**

(57) The present invention generally relates to two-phase cleaning compositions with visibly distinct detergent particles. In particular, the present invention relates to a two-phase cleaning composition comprising a liquid phase and visibly distinct detergent particles dis-

persed in the liquid phase, the use of said cleaning composition in automatic dishwashing, an automatic dishwashing method using said cleaning composition and a container containing said cleaning composition.

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Description

[0001] The present invention generally relates to two-phase cleaning compositions with visibly distinct detergent particles. In particular, the present invention relates to a two-phase cleaning composition comprising a liquid phase and visibly distinct detergent particles dispersed in the liquid phase, the use of said cleaning composition in automatic dishwashing, an automatic dishwashing method using said cleaning composition and a container containing said cleaning composition.

[0002] Cleaning compositions are available in a variety of forms such as liquids, powders, sprays or solids and are generally used to remove dirt, including dust, stains and bad smells. One class of cleaning compositions are automatic dishwashing (ADW) compositions which are expected to yield spot-less and film-free dishes and glasses. In general, ADW compositions are mixtures of ingredients whose purpose, in combination, is to break down and remove food solids, to inhibit foaming caused by certain food soils, and to remove stains which can be caused by beverages such as coffee or tea.

[0003] Although the cleaning properties are the chief criteria by which the performance of a cleaning composition is judged, consumers of liquid cleaning products, in particular ADW and laundry products, have a preference for products having a certain optical appearance. The addition of solid particles suspended in a liquid cleaning composition can improve the aesthetic acceptance of the product by simply improving the physical appearance of the product. Such solid particles can also serve to visualize the cleaning performance of the product and serve as general support for customer satisfaction.

[0004] Previously used particles in liquid ADW compositions have had the major disadvantage of contributing negatively to unwanted filming, particular on glass, stainless steel and plastic surfaces as the particles used were usually coated with water-insoluble coatings such as waxes which melt and are released into the wash solution due to the high temperatures encountered during ADW processes. Further, not all particles were compatible with the other ingredients of the composition and liquid compositions containing such particles usually showed poor storage stability due to sedimentation of the particles.

[0005] While the problem has been solved for laundry detergents which usually perform at lower temperatures, no satisfactory solution has been presented for ADW applications.

[0006] US 6,730,652 provides non-staining colored composite particles suitable for incorporation in a bleach-containing liquid detergent composition as well as a liquid automatic dishwashing detergent containing said particles. The particles are formed by a process comprising the steps of a) forming a colored liquid dispersion of pigment particles in a first liquid medium, wherein the size of said pigment particles in said colored liquid dispersion is no greater than about 5 μm ; b) mixing said colored liquid dispersion with a polymeric material and a second liquid medium to form a sprayable colored polymeric material, said polymeric material being selected from the group consisting of alkyl cellulose ethers and polyvinyl alcohol; and c) spraying said colored polymeric material on a composite particle and forming a colored polymeric coating on said composite particle.

[0007] US 7,357,755 discloses a liquid detergent composition comprising a liquid matrix having dispersed therein a plurality of visibly distinct beads, wherein the liquid matrix comprises a stripping agent, selected from the group consisting of enzymes, zwitterionic polymers, non-ionic deterative surfactants, transition metal catalysts, per-acid/organic catalysts, alternative singlet oxygen generators and mixtures thereof; the visibly distinct beads have a diameter of 0.2 to 8 mm, are in the form of polyelectrolyte complex microcapsules comprising alginate and chitosan, and the complex microcapsules comprise a hueing agent; and the hueing agent is a dye conjugate selected from the group consisting of dye-polymer conjugates, dye-clay conjugates and combinations thereof.

[0008] In light of customer satisfaction, it would be desirable to provide liquid cleaning compositions, in particular for automatic dishwashing, in which the cleaning performance can be visualized by visibly displaying the active component.

[0009] It was surprisingly found that this objective can be solved by a cleaning composition comprising at least one of the active cleaning components in form of visible particles which are solid under storage conditions but easily dissolve during the washing process. Therefore, a first aspect of the present invention is a two-phase cleaning composition for automatic dishwashing comprising a liquid phase and visibly distinct detergent particles dispersed in the liquid phase, characterized in that the detergent particles comprise one or more surfactants having a Krafft temperature of 30 to 55 °C, determined according to DIN 53918.

[0010] The Krafft temperature within the meaning of the present invention defines the minimum temperature from which micelle formation takes place, i.e. the surfactant becomes soluble in the liquid phase. The Krafft temperature, in some cases also referred to as Krafft point, can be determined as set out in DIN 53918.

[0011] Dispersed within the meaning of the present invention is to be understood as at least 70%, preferably at least 80%, especially at least 90% and in particular at least 95% of the detergent particles, based on the total amount of detergent particles present, being homogeneously suspended and floating in the liquid phase.

[0012] Most dispersions suffer from the drawback that they appear to be milky due to the solid particles suspended therein or in that the dispersions only show poor stability resulting in sedimentation of the solid phase. In contrast thereto,

the inventive cleaning composition shows a high transparency of the liquid phase and a low level of sedimentation of the detergent particles. Therefore, preference is given to an embodiment of the present invention wherein the liquid phase of the cleaning composition is transparent or translucent. Preferably, the transmittance of the liquid phase (without detergent particles) is in a range between 100% and 20%, preferably between 100% and 30%, in particular between 100% and 40%. To measure the light transmission (transmittance), the transmittance in % at 600 nm was determined against water as reference at 20 °C. For this purpose, the composition (without the particles) was poured into a 11 mm round cuvette and measured after 12 h storage time at room temperature in a LICO 300 colorimetric system according to Lange. In a further preferred embodiment, the inventive cleaning composition is free of any sediment, preferably the amount of sedimented detergent particles is less than 10%, preferably less than 5% and in particular less than 1%, based on the total amount of detergent particles.

[0013] Within the course of the present invention, it was found that carefully selecting a surfactant according to their Krafft temperature allowed the provision of a cleaning composition wherein the active component was actually visible under storage conditions but easily dissolved during the washing process. Thus, in a preferred embodiment of the present invention, the Krafft temperature of the one or more surfactant comprised in the detergent particles is 35 to 50 °C, preferably 40 to 45 °C, determined according to DIN 53918. By adapting the Krafft temperature of the one or more surfactant to be within the claimed range, sufficient solubility of the detergent particles is given to reach optimal cleaning performance and any solid residues which might negatively affect the overall outcome can be avoided.

[0014] The one or more surfactant employed in the present invention is preferably an ionic surfactant, in particular one selected from the group of anionic surfactants and cationic surfactants. In an especially preferred embodiment, the one or more surfactant is selected from the group consisting of alkyl sulfonates with $\geq$ C14, alkyl sulfates with $\geq$ C16 and alkyl benzenesulfonates with $\geq$ C12, C depicting the number of carbon atoms.

[0015] In an even more preferred embodiment, the one or more surfactant is selected from the group consisting of alkyl sulfonates with $\geq$ C14, C depicting the number of carbon atoms.

[0016] In this embodiment it is preferred that at least 50 wt.%, preferably at least 60 wt.%, more preferably at least 70 wt.%, most preferred at least 80 wt% of the surfactant comprised in the particles, based on the weight of the surfactant contained in the particles, is selected from alkyl sulfonates with $\geq$ C14, C depicting the number of carbon atoms. Especially preferred are C14 alkyl sulfonates, C16 alkyl sulfonates and/or C18 alkyl sulfonates.

[0017] Surfactants exhibiting a suitable Krafft temperature to be employed in the present invention can be easily identified by the person skilled in the art and are, for example, listed in Milton J. Rosen, Surfactants and Interfacial Phenomena, 3rd Edition, Wiley-Interscience, A John Wiley & Sons, Inc., Publication, USA, 2004.

[0018] The cleaning composition according to the invention is distinguished by the visibly distinct detergent particles dispersed in the liquid phase which allow visualization of the active cleaning agent to improve customer satisfaction. In order to be clearly visible, the particle size of the detergent particles should not be too small, also to avoid clouding of the liquid phase. On the other hand, the particles should not be too large to ensure sufficient pourability of the cleaning composition. Therefore, in a preferred embodiment, detergent particles with an average particle size of 0.1 to 4 mm, preferably 0.25 to 3 mm, in particular 0.5 to 2 mm, determined by a sieving column, are chosen. Appropriate methods for determining the particle size can, for example, be found in ASTM C 136.

[0019] Preferably at least 80 % of the particles should have a particle size that is from 0.5 to 2 mm.

[0020] The cleaning composition according to the invention combines appealing aesthetic as well as excellent cleaning properties. In this regard, it was found to be advantageous to keep the amount of detergents particles within certain limits to ensure good pourability of the composition. Preference is therefore given to a cleaning composition according to the invention which comprises the detergent particles in an amount of 0.05 to 5 wt.%, preferably 0.1 to 3.5 wt.%, in particular 0.2 to 2 wt.%, based on the total weight of the cleaning composition, respectively.

[0021] The detergent particles comprised in the inventive cleaning composition are designed to dissolve under washing conditions thus releasing the one or more surfactant. In order to ensure complete dissolution of the detergent particles, an embodiment of the present invention is preferred wherein each detergent particle comprises at least 50 wt.%, preferably at least 60 wt.%, in particular at least 70 wt.% of the one or more surfactant, based on the total weight of the particle, respectively. In a preferred embodiment, the detergent particles do not comprise further additives such as dyes and hueing agents or bleach catalysts. Rather, embodiments are preferred wherein the presence of such additives is limited to the liquid phase.

[0022] The cleaning composition according to the invention is provided in form of a liquid. The term "liquid" as used herein includes liquids and gels, both being in particular characterized by their yield point. Within the disclosure of the present invention, "gel" is used for a composition which acts as a solid body below its yield strength while "liquid" refers to compositions which exhibit a fluid behavior below their yield strength.

[0023] The provision of the cleaning composition according to the invention in the form of a liquid entails that the composition also needs to exhibit a good pourability, despite the presence of the solid detergent particles. It was surprisingly found that excellent pourability could be achieved, while at the same time maintaining suitable stability to suspend the solid detergent particles, by carefully adapting the rheological yield strength of the liquid phase of the

cleaning composition according to the invention. In a preferred embodiment, the liquid phase thus has a rheological yield strength of at least 0.1 Pa. In further preferred embodiments, the liquid phase exhibits a rheological yield strength of 0.1 to 10 Pa, preferably 0.5 to 7.5 Pa, in particular 1 to 5 Pa. It was surprisingly found that the inventive cleaning composition also showed an excellent long-term stability if the yield strength was controlled to be within the claimed ranges. The sedimentation of particles from the liquid phase is reduced.

[0024] The determination of the yield strength for the purpose of the present invention can be carried out by means of a shear stress controlled Rheometer, e.g. AR G2 from TA Instruments or Malvern Kinexus, at a temperature of 25 °C with a cone-plate measuring system 40 mm in diameter and 2° cone angle. The samples were measured in the rheometer with a shear stress s increasing with time t within 60 minutes from the lowest possible value to a value above the expected yield strength. The deformation γ of the sample was measured and plotted as a function of the shear stress $s(t)$ in a double logarithmic plot. If the sample has a yield point, two different regions can be distinguished in this graph. Below a certain shear stress a purely elastic deformation can be found. The slope of the curve $\gamma(\sigma)$ (log-log Plot) in this region is equal to unity. Above this shear stress the flow area begins and the slope of the curve is abruptly higher. This shear stress in which the bending of the curve occurs is the transition from elastic to plastic deformation and it indicates the yield point and thus the yield strength. A convenient determination of the bending point is possible by the application of tangents to the two parts of the curve. Samples without yield point do not have this characteristic bend in the function $\gamma(\sigma)$.

[0025] It was surprisingly found that pourability of the inventive cleaning composition could be further improved by carefully controlling the viscosity of the liquid phase. In this regard, an embodiment of the cleaning composition according to the invention is preferred, wherein the liquid phase has a viscosity at a shear rate of 10 s⁻¹ of less than 2000 mPas, preferably less than 1000 mPas. In a further preferred embodiment, the viscosity at a shear rate of 10 s⁻¹ of the liquid phase is at least 100 mPas. The viscosity can be determined under the following conditions: Malvern Kinexus, KP 40 mm, 1°, 25°C.

[0026] In order to achieve suitable conditions to stabilize the detergent particles, the liquid phase preferably comprises at least one rheological modifier. Preferably, the rheological modifier 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.

[0027] Especially preferred are cleaning composition wherein the liquid phase contains from 0.15 to 5.0 wt.%, preferably from 0.20 to 2.5 wt.%, more preferably to 0.25 to 1.5 wt.% of rheological modifier, most preferred from 0.3 to 1.0 wt.%, based on the weight of the liquid phase.

[0028] Preferred rheological modifiers are selected from the group of xanthan gum, crosslinked polyacrylate and urea derivatives.

[0029] Xanthan gum, urea derivatives, such as Rheobyk® 7420, and/or crosslinked polyacrylate, such as Acusol® 810, are able to stabilize the dispersion of the detergent particles in the liquid phase and minimize disintegration of this mixture. Especially, they reduce sedimentation of the detergent particles and also aggregation of the particles. A floating up of a larger portion of the particles contained in the liquid phase to the upper surface of the liquid phase is reduced or even inhibited.

[0030] The liquid phase of the cleaning composition according to the present invention comprises a significant amount of water. Organic solvents might be present as well but are preferably limited to an amount of up to 15 wt.%, based on the weight of the liquid phase. More preferably the organic solvent content is limited up to 10 wt.%, based on the weight of the liquid phase. Especially preferred organic solvents are propane diol, glycerol and/or sorbitol. These amount of organic solvents add to the pourability as well as to the stabilization of active ingredients and also to the stabilization of the gel, especially via reduction of particle sedimentation.

[0031] Due to a preferred embodiment of the present invention the amount of water is at least 20 wt.%, based on the weight of the liquid phase. Especially preferred are cleaning composition wherein the liquid phase contains from 40 to 80 wt.%, preferably from 45 to 75 wt.%, more preferably from 50 to 70 wt.% of water, based on the weight of the liquid phase.

[0032] In a preferred embodiment of the invention the liquid phase of the cleaning composition contains 45 to 75 wt.% water and 0.2 to 2.5 wt.% of rheological modifiers, each based on the weight of the liquid phase. More preferably the liquid phase contains 50 to 70 wt.% water and 0.25 to 1.5 wt.% of rheological modifier, selected from xanthan gum or crosslinked polyacrylates or urea derivatives, each based on the weight of the liquid phase.

[0033] The cleaning composition according to the present invention may further comprise a variety of detergent ingredients such as builders. Builder materials are used to provide alkalinity and buffering capacity, maintain ionic strength, extract metals from soils and/or remove alkaline earth metals from washing solutions. Preferably, the builder is selected from the group consisting of aminocarboxylic acids and their salts, carbonates, organic cobuilders and silicates.

[0034] Amino carboxylic acids and/or the salts thereof represent another important class of builders. Particularly preferred representatives of this class are methylglycinediacetic acid (MGDA) or the salts thereof, and glutamic diacetic acid (GLDA) or the salts thereof or ethylenediaminediacetic acid or the salts thereof (EDDS). Iminodisuccinic acid (IDS)

and iminodiacetic acid (IDA) are also suitable. The content of these amino carboxylic acids or the salts thereof can, for example, be between 0.1 and 25 wt.%, preferably between 0.5 and 20.0 wt.%, and in particular between 0.5 and 17 wt.%, based in the total weight of the liquid phase. Amino carboxylic acids and the salts thereof can be used together with the aforementioned builders, in particular also with phosphate-free builders.

[0035] Especially preferred are cleaning composition wherein the liquid phase contains between 0.1 to 20 wt.%, preferably between 0.5 to 17.0 wt.%, more preferably between 1.0 to 15 wt.% of methylglycine diacetic acid (MGDA) or the salts thereof, based on the weight of the liquid phase. An advantage of these lower amounts of amino carboxylate, especially MGDA tri sodium salt is, that it does not cause severe damages to glassware due to reduced glass corrosion.

[0036] Polycarboxylates/polycarboxylic acids, polymeric carboxylates, aspartic acid, polyacetals and dextrans are particularly noteworthy as organic cobuilders.

[0037] Suitable organic builders are polycarboxylic acids that can be used in the form of the free acids and/or the sodium salts thereof, with polycarboxylic acids being understood to mean those carboxylic acids which carry more than one acid function. These include, for example, citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, saccharic acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), provided that the use of NTA is not objectionable for ecological reasons, and mixtures thereof.

[0038] It is also possible, for example, to use carbonate(s) and/or hydrogen carbonate(s), preferably alkali carbonate(s), particularly preferably sodium carbonate. Alkali carbonates, in particular sodium carbonate, can also be used as pH adjusters, and in various embodiments of the invention are preferably contained in an amount of 5 to 40 wt.%, more preferably 10 to 30 wt.%, based on the total weight of the liquid phase.

[0039] Polymeric polycarboxylates are also suitable as builders. These are, for example, the alkali metal salts of polyacrylic acid or polymethacrylic acid, for example those having a weight-average molecular weight of 500 to 70,000 g/mol.

[0040] Suitable polymers are in particular polyacrylates which preferably have a weight-average molecular weight of 2,000 to 20,000 g/mol. Due to their superior solubility, the short-chain polyacrylates which have a weight-average molecular weight of 2,000 to 10,000 g/mol, and particularly preferably 3,000 to 5,000 g/mol, can be preferred from this group.

[0041] A copolymeric polyacrylate, preferably a sulfopolymer, preferably a copolymeric polysulfonate, preferably a hydrophobically modified copolymeric polysulfonate, is preferably used as the polycarboxylate. 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.

[0042] 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, -CH₃, 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 -COOR⁴, wherein R^4 is a saturated or unsaturated, straight-chain or branched hydrocarbon functional group having 1 to 12 carbon atoms.

[0043] 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.

[0044] For sulfonic acid group-containing monomers, those of the formula $R^5(R^6)C=C(R^7)-X-SO_3H$ are preferred, in which R^5 to R^7 , independently of one another, represent -H, -CH₃, 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, or represent -COOH or -COOR⁴, 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 $-(CH_2)_n-$, with $n = 0$ to 4, $-COO-(CH_2)_k-$, with $k = 1$ to 6, $-C(O)-NH-C(CH_3)_2-$, $-C(O)-NH-C(CH_3)_2-CH_2-$ and $-C(O)-NH-CH(CH_2CH_3)-CH_2-$.

[0045] Among these monomers, those of formulas $H_2C=CH-X-SO_3H$, $H_2C=C(CH_3)-X-SO_3H$ or $HO_3S-X-(R^6)C=C(R^7)-X-SO_3H$ are preferred, in which R^6 and R^7 , independently of one another, are selected from -H, -CH₃, -CH₂CH₃, -CH₂CH₂CH₃ and -CH(CH₃)₂, and X represents an optionally present spacer group that is selected from $-(CH_2)_n-$, with $n = 0$ to 4, $-COO-(CH_2)_k-$, with $k = 1$ to 6, $-C(O)-NH-C(CH_3)_2-$, $-C(O)-NH-C(CH_3)_2-CH_2-$ and $-C(O)-NH-CH(CH_3)-CH_2-$.

[0046] According to a particularly preferred embodiment, the liquid phase contains a polymer comprising at least one sulfonic acid group-containing monomer.

[0047] According to a particularly preferred embodiment, the liquid phase comprises a polymer comprising, as a sulfonic acid group-containing monomer, acrylamidopropanesulfonic acids, methacrylamidomethylpropanesulfonic acids or acrylamidomethylpropanesulfonic acid.

[0048] 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-pro-

panesulfonic 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 watersoluble 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.

[0049] 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 compositions 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} .

[0050] 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.

[0051] Particularly preferably, the liquid phase of the cleaning composition according to the invention further comprises an anionic copolymer, the copolymer comprising

i) carboxylic acid group-containing monomers

ii) sulfonic acid group-containing monomers

iii) non-ionic monomers, in particular hydrophobic monomers.

[0052] 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.

[0053] Particularly preferred non-ionic monomers are butene, isobutene, pentene, 3-methylbutene, 2-methylbutene, cyclopentene, hexene, hexene-1, 2-methylpentene-1, 3-methylpentene-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.

[0054] 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 liquid phase. 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 liquid phase.

[0055] Any molecular weight given herein refers to the number average molecular weight M_n , unless explicitly stated otherwise. The number average molecular weight can, for example, be determined by means of gel permeation chro-

matography (GPC) according to DIN 55672-1:2007-08 with THF as eluent.

[0056] The liquid phase of the inventive cleaning composition can also contain, as a builder, crystalline layered silicates of general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot y \text{H}_2\text{O}$, where M represents sodium or hydrogen, x is a number from 1.9 to 22, preferably from 1.9 to 4, with 2, 3 or 4 being particularly preferred values for x, and y represents a number from 0 to 33, preferably from 0 to 20. Amorphous sodium silicates with an $\text{Na}_2\text{O} : \text{SiO}_2$ modulus of 1:2 to 1:3.3, preferably 1:2 to 1:2.8, and in particular 1:2 to 1:2.6, can also be used which preferably exhibit retarded dissolution and secondary washing properties.

[0057] In alternatively preferred embodiments, the silicate and/or silica content is limited to amounts below 10 wt.%, preferably below 5 wt.%, and in particular below 2 wt.%, based on the total weight of the liquid phase. In particularly preferred embodiments, the liquid phase is silicate-free and/or silica free. These compositions, especially the silica free compositions, deliver a better shine of the washed dishware due to reduced scaling.

[0058] In a preferred embodiment, the cleaning composition according to the invention further contains at least one additive selected from the group consisting of alkali and alkaline-earth metal salts, such as sodium sulfate, fillers, corrosion inhibitors, foam inhibitors, surfactants, bitterns, sequestering agents, electrolytes, fragrances, antimicrobial active ingredients and dyes.

[0059] As an additional component, cleaning compositions according to the invention preferably contain enzyme(s) in the liquid phase. Suitable enzymes include, in particular, proteases, amylases, lipases, hemicellulases, cellulases, perhydrolases, or oxidoreductases, as well as preferably 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.

[0060] 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.

[0061] 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). Especially preferred are amylases commercially available from Novozymes (i.e. Stainzyme®, Stainzyme® Plus, Achieve®) and IFF (i.e. Excellenz® S1000 and S3300). All amylases are preferably added in liquid enzyme preparations.

[0062] 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.

[0063] 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.

[0064] 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. 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.

[0065] 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.

[0066] 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.

[0067] Moreover, it is possible to formulate two or more enzymes together, so that a single granule exhibits a plurality of enzyme activities.

[0068] 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, based on the weight of the liquid phase.

[0069] Individual odorant compounds, such as the synthetic products of the ester, ether, aldehyde, ketone, alcohol, and hydrocarbon types, can be used as perfume oils or fragrances within the scope of the present invention. However, mixtures of different odorants are preferably used which together produce an appealing fragrance note. Perfume oils of this kind can also contain natural odorant mixtures, as are obtainable from plant sources, e.g. pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. The fragrances/perfume oils can be encapsulated, for example in microcapsules, or used in free form or both.

[0070] In a preferred embodiment, the cleaning composition according to the invention is phosphate-free. "Phosphate-free" or "phosphonate-free" as used herein is to be understood as the cleaning composition being substantially free of phosphate or phosphonates, in particular as comprising phosphates or phosphonates in an amount of less than 0.1 wt.%, preferably less than 0.01 wt.%, based on the total weight of the composition.

[0071] Recently, dual chamber systems for cleaning compositions have been introduced, allowing the provision of stable multi-functional products which employ the advantageous technology of enzymes and alkalinity, thus further improving cleaning performance. It was surprisingly found that the inventive cleaning composition may also be provided as such a dual-chamber system with the detergent particles being present in either chamber. The cleaning composition according to the present invention can thus be provided as a single-chamber system or a dual chamber system. In the single chamber system, the cleaning composition is provided in a all-in-one manner with all components combined in one chamber.

[0072] In an alternatively preferred embodiment, the cleaning composition is provided as dual-chamber system containing at least two mutually spatially separated liquid compositions A and B which differ with respect to their pH value. Preferably the pH of one of the compositions is less than 8.5, preferably less than 8, in particular from 7 to 8 and especially 7.5, whereas the pH of the other composition is preferably greater than 9, preferably greater 10, in particular from greater than 10 to less than 11.5. The pH value as used herein refers to the value measured with a standard electrode in the undiluted composition at 25 °C.

[0073] The term "spatially separated" as used herein is to be understood in that the compositions are not in contact with each other prior to use. For this purpose, the cleaning composition may be provided in a multi-chamber package, such as a bottle or pouch, wherein the respective compositions A and B are present in separate chambers.

[0074] Preferably, one of the compositions A and B comprises at least one enzyme, at least one stabilizer for said enzyme and at least one builder while the other composition is preferably enzyme-free and comprises at least one phosphonate and at least one builder. The enzyme is preferably selected from protease and amylase. The phosphonate is preferably 1-hydroxyethane-(1,1-diphosphonic acid). Suitable compositions for dual-chamber cleaning compositions are, for example, described in WO 2007/025665, WO 2015/086761, WO 2007/025666 and WO 2010/092066.

[0075] The cleaning composition according to the invention is in particular designed for automatic dishwashing. A further aspect of the present invention is therefore the use of the inventive cleaning composition in automatic dishwashing.

[0076] A further aspect of the present invention is an automatic dishwashing method employing the cleaning composition according to the invention. According to the method of the invention, the cleaning composition can be introduced directly into the washing compartment or the dishwasher.

[0077] All of the (preferred) embodiments described herein in connection with the cleaning composition according to the invention can also be used for the use according to the invention and corresponding methods, and vice versa.

[0078] Another aspect of the present invention is a container comprising a cleaning composition according to the invention, preferably a bottle or a pouch. The container may be a single chamber container or a multi-chamber container, in particular a dual-chamber container. Preferably, the container is made from recycled material, in particular recycled plastics and/or polymers.

[0079] The present invention will be explained in more detail with reference to the following examples which, by no means, are to be understood as limiting the spirit and scope of the invention.

Examples:

[0080] Exemplary liquid phases I and II were prepared using the components summarized in Table 1 with the amounts given in wt.% referring to the total weight of the liquid phase unless otherwise specified.

Table 1:

Component	I	II	III	IV
Xanthan Gum	0.4	0.4	0.4	0.4
1-hydroxy-1-phosphonoethyl) phosphonic acid (HEDP)	4.0	0.0	0.0	0.0
Acusol® 588 G (DOW Inc.)	1.0	0.0	0.0	0.0
Polyacrylate, Homopolymer	0.0	1.0	1.0	0.0
MGDA, tri sodium salt	11.00	15.00	5.0	6.0
Soda	6.00	6.00	0.0	0.0
cationic acrylic acid copolymer	0.5	0.5	0.1	0.1
Sodium Citrate	10.00	8.00	2.0	0.0
Low foaming nonionic surfactant (hydroxy mixed ether)	1.00	1.50	2.0	1.0
Stainzyme® 12 L (Amylase available from Novozymes)	1.5	1.5	1.5	1.0
Protease (amount in active enzyme protein in mg/100g composition)	0.25	0.25	0.25	0.25
Perfume	0.05	0.05	0.05	0.05
Dye	0.005	0.005	0.005	0.005
Preservatives	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
water	Ad 100	Ad 100	Ad 100	Ad 100

[0081] The pH of the undiluted liquid phase was adjusted to 7.8 at 20 °C. Solid detergent particles were made out of a mixture comprising 20 to 30 wt.% C12-14 fatty alcohol sulfonates and 70 to 80 wt.% C16-18 fatty alcohol sulfonates. The solid detergent particles in an amount of 0.1 to 2 wt.% were added to the liquid composition to obtain a stable dispersion which showed no deviation in their optical appearance such as sedimentation of the detergent particles even after prolonged storage time.

Claims

- Two-phase cleaning composition for automatic dishwashing comprising a liquid phase and visibly distinct detergent particles dispersed in the liquid phase, **characterized in that** the detergent particles comprise one or more surfactant having a Krafft temperature of 30 to 55 °C, determined according to DIN 53918.
- Cleaning composition according to claim 1, **characterized in that** the surfactant has a Krafft temperature of 35 to 50 °C, preferably 40 to 45 °C, determined according to DIN 53918.
- Cleaning composition according to any of the forgoing claims, **characterized in that** the surfactant is selected from the group consisting of anionic and cationic surfactants, especially from the group consisting of alkyl sulfonates with $\geq$ C14, alkyl sulfates with $\geq$ C16 and alkyl benzenesulfonates with $\geq$ C12.
- Cleaning composition according to any of the forgoing claims, **characterized in that** the surfactant is selected from

alkyl sulfonates with $\geq$ C14.

5. Cleaning composition according to any of the forgoing claims, **characterized in that** the detergent particles have an average particle size of 0.1 to 4 mm, preferably 0.25 to 3 mm, in particular 0.5 to 2 mm, determined by a sieving column.
6. Cleaning composition according to any of the forgoing claims, **characterized in that** the detergent particles are comprised in the composition in an amount of 0.05 to 5 wt.%, preferably 0.1 to 3.5 wt.%, in particular 0.2 to 2 wt.%, based on the total weight of the cleaning composition, respectively.
7. Cleaning composition according to any of the forgoing claims, **characterized in that** each detergent particle comprises at least 50 wt.% of the surfactant, based on the weight of the particle.
8. Cleaning composition according to any of the forgoing claims, **characterized in that** the liquid phase has a rheological yield strength of at least 0.1 Pa.
9. Cleaning composition according to any of the forgoing claims, **characterized in that** the liquid phase contains between 0.1 to 20 wt.%, preferably between 0.5 to 17.0 wt amino carboxylic acid or the salts thereof, based on the weight of the liquid phase.
10. Cleaning composition according to any of the forgoing claims, **characterized in that** the liquid phase contains between 0.1 to 20 wt.%, preferably between 0.5 to 17.0 wt.%, more preferably between 1.0 to 15 wt.% of methylglycinediacetic acid (MGDA) or the salts thereof, based on the weight of the liquid phase.
11. Cleaning composition according to any of the forgoing claims, **characterized in that** the liquid phase contains from 40 to 80 wt.%, preferably from 45 to 75 wt.%, more preferably from 50 to 70 wt.% of water, based on the weight of the liquid phase.
12. Cleaning composition according to any of the forgoing claims, **characterized in that** the liquid phase contains from 0.15 to 5.0 wt.%, preferably from 0.20 to 2.5 wt.%, more preferably to 0.25 to 1.5 wt.% of rheological modifier, most preferred from 0.3 to 1.0 wt.%, based on the weight of the liquid phase.
13. Use of a cleaning composition according to any of claims 1 to 12 in automatic dishwashing.
14. An automatic dishwashing method **characterized in that** a cleaning composition according to any of claims 1 to 12 is used.
15. Container containing a cleaning solution according to any of claims 1 to 12.



EUROPEAN SEARCH REPORT

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