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(54) **MANGANESE-AMINO ACID COMPOUNDS IN CLEANING COMPOSITIONS**

(57) The present invention relates to co-granulated and/or coated manganese-amino acid compounds, cleaning compositions comprising co-granulated and/or coated manganese-amino acid compounds, particularly to automatic machine dishwashing cleaning composi-

tions, to the use of such manganese-amino acid compounds for cleaning, in particular for cleaning dishware, and for corrosion protection, in particular for silver corrosion protection; and to methods for preparing co-granulated and/or coated manganese-amino acid compounds.

EP 3 075 832 A1

Description

5 [0001] The present invention relates to co-granulated and/or coated manganese-amino acid compounds, cleaning compositions comprising co-granulated and/or coated manganese-amino acid compounds, particularly to automatic machine dishwashing cleaning compositions (ADCC), to the use of such manganese-amino acid compounds for cleaning, in particular for cleaning dishware, and for corrosion protection, in particular silver corrosion protection; and to methods for preparing co-granulated and/or coated manganese-amino acid compounds.

10 [0002] It is generally well-known that silver surfaces even when not in use get tarnished in course of time due to corrosive reactions. The same phenomenon can be observed when silverware is washed in machine dishwashers. This is due to several chemical reactions which can occur when the silver gets into contact with sulfur, oxygen and chlorine containing compounds under the high temperature and alkalinity conditions in a machine dishwasher. The sulfur containing compounds result from food residues, e.g. egg yolk which are solved in the dishwashing water. The oxygen containing compounds reactive with the silver surfaces, e.g. peracetic acid, can be formed when bleach activators are used in the dishwasher cleaning composition. A high amount of salt in dishwashing water can result in chlorine containing plaques on the silver surfaces.

15 [0003] Several silver corrosion protection agents have been described in the patent literature. The British patent GB 1131738 discloses dishwashing agents which use benzotriazoles as a corrosion inhibitor for silver. Benzotriazoles in the context of silver corrosion protection are also disclosed in the U.S. patent 2,549,539 and the European patents EP 135 226 and EP 135 227.

20 [0004] Another group of compounds used as silver corrosion protection agents comprises manganese salts or manganese complex compounds. The German patent number DE 4315397 discloses organic and anorganic redox compounds containing manganese (II) compounds, e.g. manganese (II) sulfate, manganese (II) acetoacetate and manganese (II) acetylacetonate. These low valent manganese compounds have to be coated prior to their use in cleaning compositions containing bleaching agents in order to avoid their oxidation or decomposition during storage. EP 530 870 A1 discloses dinuclear manganese complexes in machine dishwashing compositions, wherein the manganese is in the III or IV oxidation state. EP 697 035 A1 describes ADCCs comprising at least partially water-soluble metal salts and/or metal complexes comprising manganese salts or complexes, but nowhere the salt building counterion or the complexing agent is an amino acid.

25 [0005] WO2005/095570 describes a non-coated, non-co-granulated manganese-proteinate for use in an ADCCs for silver protection, but again single amino acids do not represent the salt building counterions or complexing agents according to the disclosure.

30 [0006] It is an object of the present invention to provide an agent imparting increased (silver) corrosion protection properties to cleaning compositions, preferably to ADCCs, whereby the agent is easy to handle, biodegradable and has good storage stability. Another object of the invention is to provide cleaning compositions comprising such agent.

35 [0007] This object can be achieved by the compound, composition and methods of the present invention. The inventive agent is a manganese-amino acid compound co-granulated and/or coated with at least one polymer wherein the manganese in the manganese-amino acid compound is bound to, associated with or complexed with at least one single amino acid or at least one amino acid residue being part of a protein.

40 [0008] The present invention thus concerns a manganese-amino acid compound co-granulated with at least one polymer, wherein the manganese in the manganese-amino acid compound is bound to, associated with or complexed with at least one single amino acid or at least one amino acid residue being part of a peptide or protein.

[0009] Furthermore, the invention relates to a manganese-amino acid compound coated with at least one polymer, wherein the manganese in the manganese-amino acid compound is bound to, associated with or complexed with at least one single amino acid or at least one amino acid residue being part of a peptide or protein.

45 [0010] Also, the present invention relates to a manganese-amino acid compound co-granulated and coated with at least one polymer, wherein the manganese in the manganese-amino acid compound is bound to, associated with or complexed with at least one single amino acid or at least one amino acid residue being part of a protein.

50 [0011] Additionally, the present invention relates to the use of said manganese-amino acid compound in cleaning compositions, in particular, automatic dishwashing detergent (ADD) compositions or ADCCs, for improved cleaning performance and for improved corrosion protection, in particular improved silver protection, and to methods for preparing said compound.

[0012] The present invention covers every possible combination of the herein above mentioned features and aspects with the features and aspects mentioned herein below.

55 **MANGANESE-AMINO ACID COMPOUND**

[0013] By manganese-amino acid compound, a compound is meant that comprises or consists of a manganese, preferably a manganese ion such as, for example, Mn (II), is meant, that is bound to, associated with or complexed with

at least one single amino acid or at least one amino acid residue being part of a protein.

[0014] The manganese-amino acid compound of the present invention preferably comprises manganese sulfate, preferably a manganese(II)sulfate monohydrate that is bound to, associated with or surrounded by an amino acid residue being part of a protein.

[0015] The term "bound to" refers to any kind of chemical bonding between the manganese and the amino acid or amino acid residue. In particular it refers to ionic interactions between ionic forms of the manganese and the amino acid or amino acid residue. The term "associated with" refers to non-covalent interactions between the manganese and the amino acid or amino acid residue; in particular to interactions based on van der Waals interactions, H-bonds and the like. The term "complexed with" refers to any kind of ligandization or chelation of the manganese or manganese ion by the amino acid or amino acid residue.

[0016] By "single amino acid" a monomeric amino acid that is not part of a protein is meant. With "at least one single amino acid" it is meant that more than one amino acid can be bound to or complexed with the manganese, however, the amino acid(s) is/are (a) single amino acid(s), monomers not being part of a protein. Preferred single amino acids are low molecular weight aliphatic amino acids, like e.g. glycine, alanine, valine, leucine or isoleucine or more hydrophilic amino acids like e.g. serine or threonine. Further, as well charged (chargeable) amino acids can be used, like lysine, arginine and histidine and in particular due to their negative charge aspartate and glutamate. Asparagine or glutamine, however, are also suitable. The sulfur-comprising amino acids cysteine and methionine and the sterically restricted (proline) and/or aromatic amino acids (phenylalanine, tyrosine and tryptophane) can be used, however, are less preferred. A particular preferred amino acid is glycine.

[0017] By "manganese-single amino acid compound" it is referred to a compound comprising a manganese that is bound to, associate with or complexed with a single amino acid as specified above.

[0018] In a preferred embodiment of the invention, the manganese in the manganese-single amino acid compound is bound to, associated with or complexed with at least one single amino acid, whereas - if more than one amino acid is involved - the amino acids can differ from each other. E.g. one manganese in a manganese-single amino acid compound might be bound to, associated with or complexed with glycine forming manganese glycinate, whereas a further manganese in the manganese-single amino acid compound is bound to, associated with or complexed with another amino acid, e.g. aspartate, forming manganese aspartate. Such a mixture of manganese-single amino acid compounds can be used according to the present invention.

[0019] Preferably, at least one manganese ion, atom or compound is bound, associated with, or complexed by at least one single amino acid. Preferred manganese compounds are manganese (II) salts.

[0020] In a particularly preferred embodiment the manganese-single amino acid compound is provided in a form of a "manganese glycinate", wherein preferably a manganese sulfate, particularly preferred a manganese(II)sulfate is bound to, associated with or complexed with a glycine. Such manganese glycinate up to now are known as dietary supplements or ingredients in food, particularly in food for animals and as fertilizers.

[0021] By "amino acid residue", a polymeric amino acid is meant, i.e. an amino acid that is part of a protein, thus being engaged by a peptide bond to at least one other amino acid.

[0022] As meant in the present application "protein" defines an amino acid sequence having more than one amino acid, like a peptide having at least 2, at least 4, at least 6, at least 10, at least 20, at least 50, or at least 100 amino acids, or proteins having more than 100 amino acids, more than 150, more than 200, or more than 300 amino acids, or a mixture of said peptides and proteins. The term "protein" means any type of proteins like for example protein clusters with several subunits, proteins with a single amino acid sequence chain and protein fragments or peptides, however, no single i.e. monomeric amino acids. It might be, but is not necessary that the protein has any catalytic activity.

[0023] Preferably, the co-granulated and/or coated manganese-amino acid compound is a manganese-proteinate, wherein the manganese-proteinate compound comprises a manganese bound to, associated with or complexed with at least one single amino acid residue that is part of a protein, e.g. such manganese proteinates as described in WO 2005/095570.

[0024] Preferably, the term "protein" within the proteinate does not refer to catalytic proteins depending on manganese for their activity such as dehydrogenases, oxidases, reductases, transferases, synthases, isomerases, kinases, lyases, ligases, cyclases, peptidases, hydrolases, phosphatases, phosphodiesterases, carboxylases, decarboxylases, catalases, and super oxide dismutases that carry a manganese ion in their active site. More preferably the term "protein" with respect to the proteinate does not comprise any functional enzymes. The protein can comprise any three dimensional structure or can be a random coil.

[0025] Preferably, in the manganese-proteinate at least one manganese ion, atom or compound is bound to, associated with, contained in or surrounded by the protein. More preferred at least two, particularly preferred at least four manganese ions, atoms or compounds are contained. Preferred manganese compounds are manganese (II) salts.

[0026] A particularly preferred Manganese-proteinate is a product called "Proteinato di Manganese", available from SICIT 2000 S.p.A., Chiampo, Italy. Such manganese proteinates up to now are known as ingredients in animal food, particularly in food for cattle, and for use as fertilizer.

[0027] A particularly preferred manganese proteinate according to the present invention comprises for example: 6.4 wt.-% organic nitrogen, 6.8 wt.-% total nitrogen, 0.4 wt.-% ammonium nitrogen, 21 wt.-% organic carbon, 14 wt.-% manganese, 0.2 wt.-% calcium, 3.5 wt.-% sodium, 4.4 wt.-% chloride, 25.4 wt.-% sulfate.

[0028] The amino acid profile is of a particularly preferred manganese proteinate according to the present invention comprises for example (per 100 g total amount of amino acid): 9.0 g alanine, 6.3 g arginine, 5.6 g aspartic acid, 0.3 g cysteine, 10.4 g glutamic acid, 25.0 g glycine, 8.2 g hydroxyproline, 1.2 g histidine, 1.5 g isoleucine, 3.5 g leucine, 4.4 g lysine, 0.8 g methionine, 2.3 g phenylalanine, 13.7 g proline, 1.7 g serine, 1.0 g threonine, 0.3 g tryptophan, 1.3 g tyrosine and 2.6 g valine.

[0029] In addition, the cleaning compositions according to the present invention may optionally comprise other known manganese compounds commonly used in ADCCs, e.g. as silver/corrosion protecting agents or as bleach catalysts. Such compounds are described below in detail.

[0030] The manganese-amino acid compound according to the present invention preferably may be co-granulated with at least one polymer as specified herein below. In the context of the present invention the term "co-granulation" refers to the formation of particles comprising the manganese-amino acid compound according to the present invention and at least one polymer as specified below in a process specified below. In this context the term "particle" refers to any solid form or shape, for example including spheres, fragments, cones, egg-like bodies, rods, crystals, pyramids, cubes and the like. The term "particle" refers to particles of any shape as specified above, preferably with an average particle size from 10 to 5000 μm , preferably from 50 to 3500 μm , more preferably from 50 to 2500 μm , even more preferably from 80 to 2200 μm , most preferably from 100 to 2000 μm . The particle size can be determined by sieving and / or laser diffraction.

[0031] The manganese-amino acid compound according to the present invention preferably may be coated. In the context of the present invention, the term "coating" refers to a complete and closed overlay or layer on the surface of the manganese-amino acid compound or a particle comprising it, said overlay or layer comprising at least one polymer and/or at least one surfactant, wherein the core of the coated compound comprises or consists of a manganese-amino acid compound selected from a manganese-single amino acid compound and/or a manganese-proteinate. As disclosed above the manganese-single amino acid compound comprises a manganese bound to, associated with or complexed with at least one single amino acid. The overlay or layer surrounding the above described core comprises at least one polymer, wherein the at least one polymer is not a protein cluster, protein, proteinate, protein fragment or peptide.

POLYMERS

[0032] The co-granulation and/or coating material of the present invention comprises one or more polymers. Polymers suitable for co-granulation and coating of the manganese-amino acid compound or the composition comprising such compound are described herein below. Particularly suitable are dispersant polymers and film forming polymers, wherein copolymers comprising at least one anionic group are preferred, in particular copolymers comprising a sulfate or sulfonate group.

[0033] Preferred polymers have dispersing properties and/or film forming properties. Polymers consisting of an amino acid sequence like peptides, protein fragments, proteins, proteinates or protein clusters are not used as coating or co-granulating material according to the invention.

[0034] Preferred polymers include, but are not limited to, homo-polymers or co-polymers comprising or consisting of two, three, four or more different types of monomers (including alternating, periodic, statistical, block and graft-copolymers).

[0035] Polymers can be provided in acidic, fully neutralized or partly neutralized form. The molar weight of the polymers can vary between 150 and 500.000. The polymers can be linear, branched or cross-linked (including star-, comb-, brush-, dendronized-, ladders- and dendrimer-polymers). The polymers can be fully saturated or partially unsaturated.

[0036] Monomers that can be present in preferred polymers include, but are not limited to, acetic acid, N-Acetylglucosamine, acrylamide (AM), acrylic acid, alkylene oxides, (e.g. ethylene oxide (EO), propylene oxide (PO)) alpha-olefins (e.g. ethylene, 1-butene, 1-hexene, 1-octene, 1-decene), 2-acrylamido-2-methyl propane sulfonic acid (AMPS), citraconic acid, itaconic acid, fumaric acid, lactic acid, maleic acid, methylenemalononic acid, mesaconic acid, methacrylic acid, methallyl sulphonic acid, methyl methacrylic acid, monosaccharides (e.g. D-glucose, fructose, galactose, xylose, ribose), styrene, sulphonated styrene, sucrose, cationic monomers, amphoteric monomers, sulfonic acid based monomers, phosphoric based monomers, vinyl acetate (VAc), vinyl alcohol (VOH), vinyl imidazole (VI), vinyl pyrrolidone (VP), diallyl dimethyl ammonium chloride (DADMAC), methacryloyloxethyl trimethyl ammonium methylsulfate (METAMS), methacrylamidopropyl trimethyl ammonium chloride (MAPTAC), dimethyl acrylamide (DMAA).

[0037] Preferred polymers that can be used in the present invention are homo- or co-polymers comprising or consisting of two, three, four or more different types of monomers and include, but are not limited to polyvinylpyrrolidone, polyvinylpyrrolidone - vinyl imidazole copolymer, polyvinyl alcohol, polyvinyl alcohol - vinylacetate co-polymer, polyvinyl alcohol - alkene-oxide co-polymer (e.g. polyvinyl alcohol - ethylene oxide copolymer), polyvinyl alcohol - vinylacetate - alkene-

oxide co-polymer (e.g. polyvinyl alcohol-vinylacetate - ethylene oxide co-polymer), poly epoxy succinic acid, poly acrylic acid, poly acrylic acid - maleic acid co-polymer, poly acrylic acid - poly saccharide co-polymer, poly methacrylic acid, poly acrylic acid with a phosphine end-group, poly maleic acid - alpha olefin co-polymer (e.g. poly maleic acid - 1-butene co-polymer, poly maleic acid - 1-hexene co-polymer), poly acrylic acid with (poly) ethylene oxide side-chains, poly vinylpyrrolidone, poly vinyl poly pyrrolidone, poly vinylpyrrolidone - vinylimidazole co-polymer, poly acrylic acid - cationic co-polymer, poly acrylic acid - amphoteric co-polymer, poly acrylic acid - diallyl dimethyl ammonium chloride co-polymer, poly acryl amide - diallyl dimethyl ammonium chloride co-polymer, poly acrylic acid - diallyl dimethyl ammonium chloride - acryl amide co-polymer, poly ethylene oxide - ethylene terephthalate co-polymer, poly methylvinylether- maleic acid co-polymer, poly acrylic acid - 2-acrylamido-2-methyl propane sulfonic acid co-polymer, poly acrylic acid - maleic acid - 2-acrylamido-2-methyl propane sulfonic acid co-polymer, poly acrylic acid - maleic acid - methyl methacrylic acid - 2-acrylamido-2-methyl propane sulfonic acid - copolymer, poly acrylic acid - 2-acrylamido-2-methyl propane sulfonic acid - maltodextrin co-polymer, poly acrylic acid - 2-acrylamido-2-methyl propane sulfonic acid - styrene co-polymer, poly maleic acid - sulphonated styrene co-polymer, poly maleic acid - styrene - sulphonated styrene co-polymer, poly acrylic acid - sulphonated styrene co-polymer, poly acrylic acid - styrene - sulphonated styrene copolymer, poly acrylic acid with a sulphono end group, poly acrylic acid - 2-acrylamido-2-methyl propane sulfonic acid - alpha-olefin co-polymer (e.g. poly acrylic acid - 2-acrylamido-2-methyl propane sulfonic acid - 1-butene co-polymer), poly acrylic acid - methallyl sulphonated acid co-polymer, sulphonated polysaccharides, carboxylated polysaccharides.

[0038] Some of these polymers with film-forming and/or dispersing properties are described e.g. in EP-A 1 363 986, EP-A 1 268 729, EP-A1 299 513 and EP-A 0 877 002. These polymers are known to artisans, thoroughly described in relevant literature and available at raw-material suppliers of the chemical industry.

[0039] Particularly preferred polymers according to the present invention are selected from copolymers having at least one sulfate or sulfonate comprising monomer. Such sulfate or sulfonate comprising co-polymers are known in the state of the art and are commonly used in ADDCs. Suitable copolymers are e.g. described in WO03/16444 A2, WO05/108540 A1 or several other applications.

[0040] Copolymers comprising, preferably consisting of the following monomers are preferred for co-granulation and/or coating according to the present invention:

(i) unsaturated carboxylic acid

(ii) monomers containing sulfonic acid group

(iii) optionally further ionic or nonionic monomers

[0041] Copolymers of

(i) unsaturated carboxylic acids corresponding to formula (I): $R^1(R^2)C=C(R^3)COOH$ (I) in which R^1 to R^3 independently represent -H, $-CH_3$, a linear or branched, saturated alkyl group containing 2 to 12 carbon atoms, a linear or branched, mono- or polyunsaturated alkenyl group containing 2 to 12 carbon atoms, $-NH_2$ -, $-OH$ - or $-COOH$ -substituted alkyl or alkenyl groups as defined above or $-COOH$ or $-COOR^4$, where R^4 is a saturated or unsaturated, linear or branched hydrocarbon radical containing 1 to 12 carbon atoms,

(ii) monomers containing sulfonic acid groups corresponding to formula (II): $R^5(R^6)C=C(R^7)-X-SO_3H$ (II) in which R^5 to R^7 independently of one another represent -H, $-CH_3$, a linear or branched, saturated alkyl group containing 2 to 12 carbon atoms, a linear or branched, mono- or polyunsaturated alkenyl group containing 2 to 12 carbon atoms, $-NH_2$ -, $-OH$ - or $-COOH$ -substituted alkyl or alkenyl groups as defined above or $-COOH$ or $-COOR^4$, where R^4 is a saturated or unsaturated, linear or branched hydrocarbon radical containing 1 to 12 carbon atoms, and X is an optionally present spacer group selected from $-(CH_2)_n-$ with $n=0$ to 4, $-COO-(CH_2)_k-$ with $k=1$ to 6, $-C(O)-NH-C(CH_3)_2-$ and $-C(O)-NH-CH(CH_2CH_3)-$,

(iii) optionally other ionic or nonionic monomers, are particularly preferred.

[0042] Suitable other ionic or nonionic monomers are, in particular, ethylenically unsaturated compounds. The polymers used in accordance with the invention preferably contain less than 20 percent by weight, based on polymer, of monomers belonging to group (iii). Particularly preferred polymers consist solely of monomers belonging to groups (i) and (ii).

[0043] Particularly preferred copolymers consist of:

(i) one or more unsaturated carboxylic acids from the group consisting of acrylic acid, methacrylic acid and/or maleic acid,

(ii) one or more monomers containing sulfonic acid groups corresponding to formulas $H_2C=CH-X-SO_3H$ (a) $H_2C=C(CH_3)-X-SO_3H$ (b) $HO_3S-X-(R^6)C=C(R^7)-X-SO_3H$ (c), in which R^6 and R^7 independently are selected from -H, -CH₃, -CH₂CH₃, -CH₂CH₂CH₃, -CH(CH₃)₂ and X is an optionally present spacer group selected from -(CH₂)_n- with n=0 to 4, -COO-(CH₂)_k- with k=1 to 6, -C(O)-NH-C(CH₃)₂-- and -C(O)-NH-CH(CH₂CH₃)-, (iii) optionally other ionic or nonionic monomers.

[0044] Particularly preferred monomers containing sulfonic acid groups 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-hydroxypropanesulfonic acid, allylsulfonic acid, methallylsulfonic acid, allyloxybenzenesulfonic acid, methallyloxybenzenesulfonic acid, 2-hydroxy-3-(2-propenyloxy)-propanesulfonic acid, 2-methyl-2-propene-1-sulfonic acid, styrenesulfonic acid, vinylsulfonic acid, 3-sulfopropylacrylate, 3-sulfopropylmethacrylate, sulfomethylacrylamide, sulfomethylmethacrylamide and water-soluble salts of the acids mentioned.

[0045] The co-granulated and/or coated manganese amino acid compounds can be used as reducing agents in cleaning compositions whereby the co-granulated and/or coated manganese amino acid-compound preferably may be a manganese-single amino acid compound and/or a manganese-protein compound. Said manganese-amino acid compound(s) can be used to improve corrosion inhibition, preferably silver protection, and cleaning performance of the cleaning composition.

[0046] The term "corrosion" herein refers to any visible change of a metal surface, preferably of a silver surface. For example, the visible change of a silver surface can result from chemical reactions of the silver with sulfur, oxygen or chlorine containing compounds under the conditions in a machine dishwasher during operation.

[0047] In a further aspect the invention provides a cleaning composition containing a manganese-single amino acid compound as a reducing agent whereby said manganese is bound to, associated with or complexed with at least one single amino acid. Also the manganese-single amino acid compound can be used to improve cleaning performance and corrosion inhibition, preferably silver protection, of the cleaning composition according to the present invention.

[0048] Surprisingly, it has been found that if a manganese-single amino acid compound is used no coating or co-granulation of said manganese-single amino acid compound is required. It has surprisingly been found that dishwashing cleaning compositions containing low valent manganese-single amino acid (compound(s)), preferably manganese glycinate, exhibit excellent silver corrosion protection properties.

[0049] Furthermore, it was found that the silver protecting performance of a commonly used silver protecting agent, like e.g. benzotriazole, can be considerably increased when it is combined with the manganese-amino acid compounds of the present invention.

[0050] Furthermore, it has been found that the cleaning performance of an ADCC, in particular tea soil removal, can be noticeably increased when the manganese-amino acid compound is co-granulated and/or coated with a film-forming polymer. The co-granulation and/or coating of the manganese-amino acid compound furthermore has an advantageous effect concerning the discoloration of the dishwashing composition.

[0051] For co-granulating or coating the manganese-amino acid with at least one polymer the manganese-amino acid is provided in solid form, preferably in granulated or powder form. The polymer is provided in liquid form, preferably as an aqueous solution or as a melt.

[0052] One example for a suitable co-granulation and/or coating process, without being limited to this is the following: while the manganese-amino acid compound is constantly moved the polymer in liquid form is sprayed onto the manganese-amino acid compound. During this process facilities are optionally available for lowering the temperature of the mixture and/or evaporation of the solvent. After applying the polymer, the material is solidified, e.g. by drying (evaporating the solvent like water) or by solidifying of the melt. During this process the manganese-amino acid compound particles become co-granulated as particles agglomerate to form larger particles. The process is continued if a coating of the manganese-amino acid compound particles is desired.

[0053] The ratio of manganese-amino acid compound to the polymer (solid, after drying) is preferably 1000:1 to 1:5, preferably 500:1 to 1:4, more preferred 250:1 to 1:3, even more preferred 100:1 to 1:2 and most preferred 50:1 to 1:1, wherein 30:1, 25:1, 20:1, 15:1, 10:1, 8:1, 6:1, 5:1, 4:1, 3:1 and 2:1 are included as well as all the ranges between the particularly mentioned ratios.

[0054] Co-granulated manganese-amino acid compound particles according to the present invention, preferably have an average particle size from 50 to 2500 μm , preferably from 80 to 2200 μm , most preferably from 100 to 2000 μm . The particle size can be determined by sieving and / or laser diffraction

[0055] The thickness of the coating layer preferably is at least 10 nm, more preferably at least 100 nm, even more preferred at least 1 μm and most preferred at least 10 μm , whereas the coating preferably is at most 1 mm, more preferably at most 800 μm , even more preferred at most 500 μm and most preferred at most 200 μm .

[0056] Coated manganese-amino acid compound particles according to the present invention preferably have an average particle size from 50 to 5000 μm , preferably from 200 to 3000 μm .

[0057] The cleaning compositions according to the present invention comprise a co-granulated and/or coated man-

ganese-amino acid compound, wherein the manganese in the manganese-amino acid compound is bound to, associated with or complexed with at least one single amino acid or at least one amino acid residue being part of a protein.

[0058] The cleaning compositions according to the present invention preferably may comprise a co-granulated and or coated manganese-amino acid compound selected from a manganese-single amino acid compound and a manganese-protein compound, as specified herein.

[0059] In case of cleaning compositions comprising manganese-single amino acid compounds, manganese glycinate is a preferred manganese-single amino acid compound. Furthermore, in case of cleaning compositions that comprise manganese-single amino acid compounds the manganese-single amino acid compounds are preferably uncoated and/or non-co-granulated manganese-single amino acid compounds.

[0060] The present invention also relates to the use of manganese glycinate as silver corrosion protection in cleaning compositions, preferably automated dishwashing cleaning compositions.

[0061] The cleaning composition of the present invention may further comprise at least any of the following further ingredients

BUILDERS

[0062] One common ingredient of cleaning compositions, in particular ADD compositions are builders. Thus, to include at least one builder is preferred for the composition of the present invention.

[0063] The term "builder" as used herein includes sequestering (e.g., phosphates, aminopolycarboxylates and citrates) and precipitating builders (e.g., carbonates) but excludes materials that function primarily as alkalis such as caustic soda, caustic potash and alkaline silicates such as sodium metasilicate and amorphous silicates having an SiO_2 to Na_2O ratio of greater than 1. The compositions of the invention may however comprise alkali metal silicates in order to provide protection against corrosion of metals and against attack on dishware, including china and glassware, and for pH control, although the compositions are preferably free of metasilicates. Metasilicates give rise to high pH compositions which can be aggressive, producing corrosion and attacking the dishware/tableware. Preferably, the composition has a pH in the wash liquor of from about 7 to 13, preferably 8 to about 11, and more preferably from about 8.5 to about 10.8.

[0064] Builders suitable for use in detergent and cleaning compositions herein include builder which forms water-soluble hardness ion complexes (sequestering builder) such as citrates, aminopolycarboxylates and polyphosphates e.g. sodium tripolyphosphate and sodium tripolyphosphate hexahydrate, potassium tripolyphosphate and mixed sodium and potassium tripolyphosphate salts and builder which forms hardness precipitates (precipitating builder) such as carbonates e.g. sodium carbonate. The builder component(s) is/are typically present at a level of from about 30 to about 80 percent, preferably from about 40 to about 70 percent by weight of composition (as the sum of the builder components). It can also be suitable that the ratio of sequestering builder to precipitating builder is from about 10:1 to about 1:1, preferably from about 8:1 to 2:1.

[0065] Alkali metal phosphate detergent builder salts suitable for phosphate-containing compositions according to the present invention include the polyphosphates, such as alkali metal pyrophosphate, alkali metal tripolyphosphate, alkali metal metaphosphate, and the like, for example, sodium or potassium tripolyphosphate (hydrated or anhydrous), tetrasodium or tetrapotassium pyrophosphate, sodium or potassium hexa-metaphosphate, trisodium or tripotassium orthophosphate and the like. Sodium tripolyphosphate is more preferred. The alkali metal nonphosphate detergent builder salts include sodium or potassium carbonate, sodium or potassium citrate, sodium or potassium nitrilotriacetate, and the like, wherein sodium carbonate is preferred.

[0066] The preferred compositions herein comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders. The pH-adjusting components are selected so that when the ADCC is dissolved in water at a concentration of 1,000 - 5,000 ppm, the pH remains in the range of above about 8, preferably from about 9 to about 12, particularly preferred from pH 10 to 11. The preferred non-phosphate pH-adjusting component(s) of the invention (partially also representing builder components) is/are selected from the group consisting of:

- (i) sodium carbonate or sesquicarbonate;
- (ii) sodium silicate, preferably hydrous sodium silicate having $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of from about 1:1 to about 2:1, and mixtures thereof with limited quantities of sodium metasilicate;
- (iii) sodium citrate;
- (iv) citric acid;
- (v) sodium bicarbonate;
- (vi) sodium borate, preferably borax;
- (vii) sodium hydroxide; and
- (viii) mixtures of (i)-(vii).

[0067] Preferred embodiments contain low levels of silicate (i.e. from about 0.5% to about 5% SiO₂) or no silicate.

[0068] The amount of the pH adjusting component(s) or builder in the preferred non-phosphate containing ADCs is preferably from about 1% to about 50%, by weight of the composition. In a preferred embodiment, the pH-adjusting component is present in the ADCC in an amount from about 5% to about 40%, preferably from about 10% to about 30%, by weight.

[0069] For compositions herein having a pH between about 7 and about 12 of the initial wash solution, particularly preferred non-phosphate ADC embodiments comprise, by weight of ADC, from about 5% to about 40%, preferably from about 10% to about 30%, most preferably from about 15% to about 20%, of sodium citrate with from about 5% to about 35%, preferably from about 7% to 30%, most preferably from about 8% to about 25% sodium carbonate. Phosphate containing compositions according to the invention preferably comprise by weight of ADC, from about 5 to about 60%, preferably from about 10% to about 50%, most preferably from about 15% to about 45% of a phosphate builder with from about 5% to about 35%, preferably from about 7% to 30%, most preferably from about 8% to about 25% sodium carbonate.

[0070] The pH-adjusting system can be complemented (i.e. for improved sequestration in hard water) by other optional detergency builder salts selected from non-phosphate detergency builders known in the art, which include the various water-soluble, alkali metal, ammonium or substituted ammonium borates, hydroxysulfonates, polyacetates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of such materials. Alternate water-soluble, non-phosphorus organic builders can be used for their sequestering properties. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid; nitrilotriacetic acid, tartrate monosuccinic acid, tartrate disuccinic acid, oxydisuccinic acid, carboxymethylxysuccinic acid, mellitic acid, and sodium benzene polycarboxylate salts.

[0071] When present, sodium and potassium, especially sodium, silicates are preferred. A particularly preferred alkali metal silicate is a granular hydrous sodium silicate having a SiO₂:Na₂O ratio of about 2.0 or about 2.4 available from PQ Corporation, named Britesil H20 and Britesil H24. Most preferred is a granular hydrous sodium silicate having a SiO₂:Na₂O ratio of 2.0. While typical forms, i.e., powder and granular, of hydrous silicate particles are suitable, preferred silicate particles have a mean particle size between about 300 and about 900 μm with less than 40% smaller than 150 microns and less than 5% larger than 1700 μm. Particularly preferred is a silicate particle with a mean particle size between about 400 and about 700 μm with less than 20% smaller than 150 microns and less than 1% larger than 1700 μm.

[0072] Alternate silicate-containing materials which can be used in the pH-adjusting component or as builders include zeolites, such as zeolites A and P, including recently described assertedly "maximum aluminium" variants; or, more preferably, layer silicates such as SKS-6, a wide variety of such silicates are available from Hoechst Corp. or from PQ Corp. When used in the instant compositions for pH-adjusting, aluminium anticorrosion or surfactant-absorbing effects, the levels of any limited water-solubility silicates should not be such as to result in deposition on dishware.

SURFACTANTS

[0073] Further common ingredients of cleaning compositions are surfactants, in particular nonionic, anionic, cationic or amphoteric surfactants. The cleaning compositions according to the present invention preferably may comprise one or more surfactants.

[0074] Preferred surfactants can be nonionic surfactants, gemini surfactants, amphoteric surfactants, anionic surfactants, zwitterionic surfactants, cationic surfactants or a combination thereof.

[0075] It is preferred that the composition of the present invention comprises at least a nonionic surfactant. Nonionic surfactants are commonly known and comprise e.g. fatty alcohol glycol ether (alkoxylated fatty alcohols), like fatty alcohol ethoxylates and fatty alcohol propoxylates, alkylglucosides, alkylpolyglucosides and phenoethoxylates, like octyl- or nonyl phenoethoxylates.

[0076] Preferred nonionic surfactants are alkoxylated fatty alcohols, alkoxylated fatty acids or combinations thereof. The relative hydrophilic alkoxy-chain comprises or essentially consists of ethylene oxide, propylene oxide or butylene oxide or combinations thereof. The length of this chain can vary between averagely 1 and averagely 200 ethylene oxide-, propylene oxide- or butylene oxide-groups or combinations thereof, including 4, 6, 8, 10, 13, 15, 20, 25, 30, 40, 50, 80, 100 and the ranges between the particularly mentioned.

[0077] The relative hydrophobic hydrocarbon-chain from the fatty alcohol or fatty acid can be saturated, mono-unsaturated or poly-unsaturated and linear or branched. The length of this hydrocarbon-chain varies between 4 and 30 carbon molecules, including 6, 8, 10, 11, 12, 14, 16, 18, 20, 22, 24, 26 or 28.

[0078] Preferred surfactants of this type may be represented by the formula R¹O (CH₂CH₂O)_x (CH(CH₃)CH₂O)_y H, wherein R¹ is a linear or branched, saturated or unsaturated hydrocarbon residue having 4 to 30 C atoms, preferably 6 to 26, even more preferred 10 to 24 C atoms, x preferably is an integer of from 8 to 200, preferably from 20 or from 25 to 200, y preferably is an integer of at most 100 and x+y is below 200. In a preferred embodiment in at least one of the "carry over" surfactants x is at least 26, preferably at least 30, and even more preferred at least or more than 40, however,

below 200. R¹ preferably is a linear, saturated hydrocarbon residue.

[0079] Particularly preferred are alcohol ethoxylates that can be prepared by ethoxylation of a fatty chain alcohol. The preferred alcohol ethoxylates have a hydrocarbon-chain that ranges from 4 up to 26 carbon molecules, including 4, 6, 8, 10, 12, 14, 16, 18, 20, 22 and between averagely 1 and averagely 200 ethylene oxide-groups, including averagely 4, 6, 8, 10, 13, 15, 20, 25, 30, 40, 50, 80, 100 ethylene oxide-groups.

[0080] Also preferred are fatty acid ethoxylates that can be prepared by a reaction of fatty acid with ethylene oxide or a polyglycol with the general formula RCOO-(CH₂CH₂O)_nH. When a polyglycol is used a mixture of mono- and di-esters (RCOO-(CH₂CH₂O)_n-OCOR) is produced. The preferred fatty acid has a hydrocarbon-chain R that varies from 4 up to 26 carbon molecules, including 4, 6, 8, 10, 12, 14, 16, 18, 20, 22. The number of ethylene oxide-groups in the fatty acid ethoxylate is between averagely 1 and averagely 200 ethylene oxide-groups, including averagely 4, 6, 8, 10, 13, 15, 20, 25, 30, 40, 50, 80, 100 ethylene oxide-groups.

[0081] Less preferred are alkyl phenol ethoxylates that can be prepared by ethoxylation of the appropriate alkyl phenol because this nonionic surfactant has undesired environmental/ecological properties.

[0082] Preferred are amine ethoxylates that can be prepared by addition of ethylene oxide to primary or secondary fatty amines. With primary amines both hydrogen atoms on the amine group react with ethylene oxide. This surfactants has a cationic character when there are a few ethylene oxide units and the pH is low. Under alkaline conditions the surfactants is water soluble when the alkyl chain is not long.

[0083] Preferred are ethylene oxide-propylene oxide co-polymers which may be prepared with a starting material that reacts with ethylene oxide (EO) or propylene oxide (PO) or a mixture of EO and PO (resulting in block copolymers). The starting materials that can be used are (difunctional) poly(oxypropylene glycol) or (difunctional) poly(oxyethylene glycol) or glycerol (for trifunctional products) or ethylene diamine (for tetrafunctional products).

[0084] Further preferred are sucrose esters that may be produced by esterification of sucrose with fatty acids or fatty glycerides. Alkyl polyglucosides (APG) may be produced by a reaction of a fatty alcohol with a glucose. Preferred APGs can have averagely one to averagely four glucose units and has a hydrocarbon-chain that varies from 4 up to 26 carbon molecules, including 4, 6, 8, 10, 12, 14, 16, 18, 20, 22.

[0085] Nonionic surfactants can be "end-capped" by a methyl or a ethyl group at the end of the alkoxy-chain. This effects the properties of the surfactant, e.g. it decreases the foaming behaviour. It is also known that nonionic surfactants can be "end-capped" with a fatty alcohol or a fatty acid where the hydrocarbon-chain varies from 4 up to 26 carbon molecules, including 4, 6, 8, 10, 11, 12, 14, 16, 18, 20, 22. The structure of the surfactants than is "hydrocarbon chain - alkoxy chain - hydrocarbon chain".

[0086] The cleaning composition, in particular the ADD compositions of the present invention can preferably comprise low foaming nonionic surfactants (LFNIs). LFNI can be present in amounts from 0 to about 30% by weight, preferably from about 0.01 to 20% by weight, more preferred from about 0.25% to about 10% by weight and most preferred from about 1 to 6 % by weight. LFNIs are most typically used in ADDs on account of the improved water-sheeting action (especially from glass) which they confer to the ADD product. They also encompass non-silicone, nonphosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

[0087] Preferred LFNIs include nonionic alkoxyated surfactants, especially ethoxylates derived from primary alcohols, and blends thereof with more sophisticated surfactants, such as the polyoxypropylene/polyoxyethylene/polyoxypropylene reverse block polymers. The PO/EO/PO polymer-type surfactants are well-known to have foam suppressing or defoaming action, especially in relation to common food soil ingredients such as egg.

[0088] The invention encompasses preferred embodiments wherein LFNI is present, and wherein this component is solid at about 35°C, more preferably solid at about 25°C. For ease of manufacture, a preferred LFNI has a melting point between about 25°C and about 60°C, more preferably between about 27°C and 45°C.

[0089] In a preferred embodiment, the LFNI is an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol containing from about 8 to about 20 carbon atoms with from about 6 to about 80 moles of ethylene oxide per mole of alcohol on an average basis.

[0090] A particularly preferred LFNI is derived from a straight chain fatty alcohol containing from about 16 to about 20 carbon atoms (C₁₆-C₂₀ alcohol), preferably a C₁₈ alcohol, condensed with an average of from about 6 to about 15 moles, preferably from about 7 to about 12 moles, and most preferably from about 7 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

[0091] The LFNI can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred LFNI surfactants can be prepared by the processes described in U.S. Patent 4,223,163.

[0092] ADDs described herein wherein the LFNI is present can make use of ethoxylated monohydroxy alcohol or alkyl phenol and additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound; the ethoxylated monohydroxy alcohol or alkyl phenol fraction of the LFNI comprising from about 20% to about 80%, preferably from about 30% to about 70%, of the total LFNI.

[0093] Suitable block polyoxyethylene-polyoxypropylene polymeric compounds may include those based on ethylene

glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initiator compounds with a single reactive hydrogen atom, such as C₁₂₋₁₈ aliphatic alcohols, do not generally provide satisfactory suds control in the instant ADDs. Certain of the block polymer surfactant compounds designated PLURONIC® and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention.

[0094] A particularly preferred LFNI contains from about 40% to about 70% of a polyoxypropylene/polyoxyethylene/polyoxypropylene block polymer blend comprising about 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and polyoxypropylene containing 17 moles of ethylene oxide and 44 moles of propylene oxide; and about 25%, by weight of the blend, of a block copolymer of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane and containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylolpropane.

[0095] Suitable for use as LFNI in the ADD compositions are those LFNI having relatively low cloud points and high hydrophilic-lipophilic balance (HLB). Cloud points of 1% solutions in water are typically below about 32°C and preferably lower, e.g., 0°C, for optimum control of sudsing throughout a full range of water temperatures.

[0096] LFNIs which may also be used include a C₁₈ alcohol polyethoxylate, having a degree of ethoxylation of about 8, commercially available as SLF18 from Olin Corp., and any biodegradable LFNI having the melting point properties discussed hereinabove.

[0097] Compositions of the present invention can optionally comprise limited quantities (up to about 2%) of nitrogen-containing nonionic surfactants, such as alkyl dimethyl amine oxides or fatty glucosamides; when present, such surfactants normally require suds suppression e.g., by silicone suds suppressors.

[0098] Another preferred type of surfactants is a 'carry-over' surfactant which is a non-ionic surfactant commonly used in ADD. A 'carry-over' surfactant has the property that an amount of the surfactant remains in the dishwasher after the cleaning or rinsing cycles to give a performance during the final rinsing cycle and eventually the drying phase of the whole washing cycle of the dishwasher. This type of surfactant is e. g. described in EP 1 524 313 A in more detail.

[0099] A further type of particularly preferred surfactants are anionic surfactants. Preferably such surfactants can be used having a melting point of at least 30°C.

[0100] Preferred anionic surfactants comprise or consist of a hydrophobic chain and an anionic hydrophilic group. The hydrophilic group can be a carboxylate, C_nH_{2n+1}COO⁻X, a sulphate, C_nH_{2n+1}OSO₃⁻X, a sulphonate, C_nH_{2n+1}SO₃⁻X, phosphate, C_nH_{2n+1}OPO(OH)O⁻X, a sulphosuccinate, an isethionate, a taurate or an other anionic hydrophilic group.

[0101] Particularly preferred anionic surfactants are sulphates and sulphonates. Sulphate surfactants can be produced by a reaction of an alcohol with sulphuric acid, chlorosulphonic or sulphur dioxide and are esters of sulphuric acid. The surfactant properties can optionally be modified by, for example, introducing ethylene oxide units in the chain so it becomes an alcohol ether sulphate.

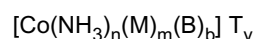
[0102] Suitable examples of preferred surfactants are alkyl benzene sulfonates, alkanesulfonates, fatty alcohol sulfates or similar suitable anionic surfactants. Common types of sulphonate surfactants are alkyl aryl sulphonates (e.g. sodium alkyl benzene sulphonate, naphthalene sulphonate, alkyl naphthalene sulphonate), paraffin sulphonates, linear alkyl benzene sulphonates (LABS), alpha-olefin sulphonates, sulphosuccinates (as mono- or di-esters or a mixture thereof). Alpha-olefin sulphonates can be prepared by reacting linear alpha-olefin with sulphur trioxide, yielding in a mixture of alkene sulphonates, 3- and 4-hydroxyalkane sulphonates, di-sulphonates and other species. The properties of sulphonate surfactants can optionally be modified by introducing ethylene oxide units in the chain.

[0103] Preferred alkyl phosphates and alkyl ether phosphates can be made by treating fatty alcohols or alcohol ethoxylates with a phosphorylating agent which yields in a mixture of mono- and di-esters of phosphoric acid.

[0104] Preferably, the (combined) amount of surfactant present in the cleaning composition according to the invention ranges from 0.5 to 40 wt.-%, preferably from 1 to 20 wt.-%, more preferably from 2 to 8 wt.-% based on the total weight of the composition.

BLEACHING SYSTEM

[0105] Additionally to the manganese-amino acid compound the compositions may comprise an additional bleaching system which is a source of hydrogen peroxide, preferably perborate and/or percarbonate, and may also comprise a bleach catalyst, e.g. a cobalt-containing bleach catalyst or a manganese-containing bleach catalyst. Preferred cobalt-containing bleach catalysts have the formula:



wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand coordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more counteranions present in a number y, where y is an integer to obtain a chargebalanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged

anion); and wherein further said catalyst has a base hydrolysis rate constant of less than $0.23 \text{ M}^{-1} \text{ s}^{-1}$ (250°C). Also, in another mode, the compositions comprise a bleach catalyst selected from the group consisting of manganese bleach catalysts as described more fully hereinafter.

[0106] Additional bleach-improving materials can be present such as bleach activator materials, including tetaaacetylenehydrazine ("TAED") or similar and cationic bleach activators, e.g., 6-trimethylammoniocaproyl caprolactam, tosylate salt.

[0107] Further usual transition metal bleach catalysts can be contained in the composition. Transition metal bleach catalysts can range from supported or unsupported transition metal salts, including but not limited to those of iron, manganese, copper, cobalt and ruthenium; see for example U.S. Patent 3,398,096 simple water-soluble salts of iron and manganese such as the divalent, trivalent, tetravalent and quadrivalent salts; to more sophisticated catalysts such as those of the following references:

One group of usually used catalysts are those comprising manganese. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and EP-A 549 271, EP-A 549 272, EP-A 544 440, and EP-A 544 490. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

[0108] Iron or Manganese salts of aminocarboxylic acids in general are used; these include iron and manganese aminocarboxylate salts disclosed for bleaching in the photographic color-processing arts. A particularly useful transition metal salt is derived from ethylenediaminedisuccinate, and any complex of this ligand with iron or manganese can be used.

[0109] The bleach catalysts useful in machine dishwashing compositions and concentrated powder detergent compositions may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084.

[0110] See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(IV) (1,4,7-trimethyl-1,4,7-triazacyclononane)- $(\text{OCH}_3)_3(\text{PF}_6)$.

[0111] Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (II), (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

[0112] U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand.

[0113] Other examples include Mn gluconate, $\text{Mn}(\text{CF}_3\text{SO}_3)_2$, $\text{Co}(\text{NH}_3)_5\text{Cl}$, and the binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $(\text{N}_4\text{Mn(III)}(\mu\text{-O})_2\text{Mn(IV)N}_4)^+$ and $[\text{Bipy}_2\text{Mn(III)}(\mu\text{-O})_2\text{Mn(IV)bipy}_2](\text{ClO}_4)_3$.

[0114] The bleach catalysts may also be prepared by combining a water-soluble ligand with a water-soluble transition metal salt such as one of manganese in aqueous media and concentrating the resulting mixture by evaporation. Any convenient water-soluble salt of the transition metal can be used herein provided that the metal is one known to react with hydrogen peroxide. The (II), (III), (IV) and/or (V) oxidation states may be used.

[0115] Other bleach catalysts are described, for example, in EP-A 408 131 (cobalt complex catalysts), EP-A 384 503, and EP-A 306 089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and EP-A 224 952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), DE 2,054,019 (cobalt chelant catalyst) CA 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

[0116] Bleach Catalysts, when used in the present invention, are preferably segregated from the hydrogen peroxide source, or from quarternary substituted bleach activators (OSBA's), quarternary substituted peracids (QSP's) or diacyl peroxides. A convenient approach, which can have the additional advantage of conferring a protective effect upon enzymes as used herein, is to process the enzymes with a coating of transition metal bleach catalyst, optionally with a waxy nonionic surfactant.

[0117] In addition, the bleach system will generally contain a hydrogen peroxide source, as further defined hereinafter, whenever the bleach improving material or materials selected from the group consisting of:

- i) organic peroxides, especially diacyl peroxides;
- ii) quaternary substituted bleach activators;
- iii) quaternary substituted peracids;
- iv) transition-metal bleach catalysts;
- v) peroxidase enzymes; and

vi) mixtures thereof

do not themselves contain a source of bleaching oxygen. That is, when the bleach improving material (b) comprises only component (ii), (iv) or (ii) +(iv), then a hydrogen peroxide source must be added to complete a minimum bleach system. On the other hand, when the bleach improving material is selected from components (i), (iii), (v), and mixtures thereof, it is not essential to add a hydrogen peroxide source.

[0118] In preferred embodiments of the invention, a hydrogen peroxide source is provided regardless of whether the bleach improving material provides bleaching oxygen. The hydrogen peroxide source is typically hydrogen peroxide itself, or a compound which delivers hydrogen peroxide on dissolution, such as is the case with sodium perborate monohydrate, sodium perborate tetrahydrate, sodium percarbonate, or mixtures thereof. Coated forms of these solid hydrogen peroxide sources can be used.

[0119] Preferred hydrogen peroxide sources include sodium perborate, commercially available, e.g., in the form of mono- or tetra-hydrate; urea peroxyhydrate, sodium percarbonate, and sodium peroxide. Particularly preferred are sodium perborate, sodium perborate monohydrate and sodium percarbonate. Percarbonate is especially preferred because of environmental issues associated with boron. Many geographies are forcing legislation to eliminate elements such as boron from formulations.

[0120] Highly preferred percarbonate can be in uncoated or coated form. The average particle size of uncoated percarbonate ranges from about 400 to about 1200 microns, most preferably from about 400 to about 600 microns. If coated percarbonate is used, the preferred coating materials include carbonate, sulphate, silicate, borosilicate, and mixtures thereof.

[0121] The mole ratio of hydrogen peroxide to bleach-improving material in the present invention preferably ranges from about 10:1 to about 1:1. Highly preferred ratios range from about 10:1 to about 3:1.

ENZYMES

[0122] The cleaning compositions described herein preferably comprise further a protease and/or amylase enzyme. Whereas conventional amylases such as TERMAMYL or Stainzyme (Novozym) may be used with excellent results. Preferred ADD compositions can use oxidative stability-enhanced amylases. Such an amylase is available from Novo Nordisk (described more fully in WO 94/02597, published February 3, 1994) and from Genencor International (described more fully in WO 94/18314, published August 18, 1994). Oxidative stability is enhanced by substitution of the methionine residue located in position 197 of *B. licheniformis* or the homologous position variation of a similar parent amylase.

[0123] Any suitable protease may be added. Protease enzymes are usually present in preferred embodiments of the invention at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. More preferred is serine proteolytic enzyme of bacterial origin. Purified or non purified forms of enzyme may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants. Particularly preferred by way of proteolytic enzyme is bacterial serine proteolytic enzyme obtained from *Bacillus*, *Bacillus subtilis* and/or *Bacillus licheniformis*. Suitable commercial proteolytic enzymes include Alcalase TM, Esperase TM, Durazym TM, Savinase TM, Maxatase TM, Maxacal TM, and Maxapem TM 15 (protein engineered Maxacal); Purafect TM and subtilisin BPN and BPN' are also commercially available. Preferred proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in EP-A 251 446 and which is called herein "Protease B", and in EP-A 199 404, Venegas, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A". More preferred is what is called herein "Protease C", which is a triple variant of an alkaline serine protease from *Bacillus* in which tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in WO 91/06637. Genetically modified variants, particularly of Protease C, are also included herein. Some preferred proteolytic enzymes are selected from the group consisting of Savinase TM, Esperase TM, Maxacal TM, Purafect TM, BPN', Protease A and Protease B, and mixtures thereof. Bacterial serine protease enzymes obtained from *Bacillus subtilis* and/or *Bacillus licheniformis* are preferred. An especially preferred protease herein referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76 in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +107 and +123 in *Bacillus amyloliquefaciens* subtilisin as described in the U.S. patent applications of A. Baeck, C.K. Ghosh, P.P. Greycar, R.R. Bott and L.J. Wilson, entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/136,797, and "Bleaching Compositions Comprising Protease Enzymes" having U.S. Serial No. 08/136,626.

[0124] Additional enzymes can be included in the formulations herein for a wide variety of substrate cleaning purposes, including removal of colored or triglyceride-based stains. Such enzymes include but are not limited to mannanase(s), carboxyhydrase(s), lipase(s), cellulase(s), pectinase(s) and peroxidase(s), as well as mixtures thereof. Other types of

enzymes of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin, may be added to further supplement the cleaning, stain-removing or anti-spotting action.

5 [0125] When present, lipases comprise from about 0.001 to about 0.01% of the instant compositions and are optionally combined with from about 1% to about 5% of a surfactant having limesoap-dispersing properties, such as an alkylidimethylamine N-oxide or a sulfobetaine. Suitable lipases for use herein include those of bacterial, animal and fungal origin, including those from chemically or genetically modified mutants. Suitable bacterial lipase include those produced by *Pseudomonas*, such as *Pseudomonas stutzeri* ATCC 19.154 as disclosed in GB 1,372,034. Suitable lipases include those which provide a positive immunological cross-reaction with the antibody of the lipase produced from the micro-organism *Pseudomonas fluorescens* IAM 1057. This lipase and a method for its production have been described in JP 53-20487, Laid-Open Feb. 24, 1978. This lipase is available under the tradename Lipase P Amano, hereinafter "Amano-P". For additional lipase disclosures, see also U.S. 4,707,291, EP-B 0218272, EP-A 339,681, EP-A 385,401, and PCT/DK 88/00177.

10 [0126] When incorporating lipases into the instant compositions, their stability and effectiveness may in certain instances be enhanced by combining them with small amounts (e.g., less than 0.5% of the composition) of oily but non-hydrolyzing materials.

15 [0127] Peroxidase enzymes are also useful in the present invention. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in WO 89/099813.

20 [0128] Mannanase types usable in the present invention are those described in EP-A 1 007 617 in section "the mannanase enzyme" or any other type of protein comprising a mannanase activity.

[0129] All the mentioned enzymes individually can be included in amounts that 0.0001 wt% to 0.2 wt% of the according active protein is provided in one gram of the ADCC.

25 [0130] The enzyme-containing compositions, especially liquid compositions, herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergent enzyme. Such stabilizing systems can comprise for example calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, and mixtures thereof.

30 [0131] The stabilizing system of the ADCCs herein may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during dishwashing is usually large; accordingly, enzyme stability in-use can be problematic.

35 [0132] Suitable chlorine scavenger anions are widely known and readily available, and are illustrated by salts containing ammonium cations or sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by several of the ingredients separately listed under better recognized functions, (e.g., other components of the invention such as sodium perborate), there is no requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any scavenger which is majorly incompatible with other ingredients, if used. For example, formulation chemists generally recognize that combinations of reducing agents such as thiosulfate with strong oxidizers such as percarbonate are not wisely made unless the reducing agent is protected from the oxidizing agent in the solid-form ADC composition. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in U.S. Patent 4,652,392.

55 CORROSION INHIBITORS

[0133] The present compositions further may contain one or more commonly known corrosion inhibitors, also called corrosion protection agents or anti-tarnish aids, besides the herein disclosed manganese-amino acid compound. Such materials are preferred components of machine dishwashing compositions especially in European countries where the

use of electroplated nickel silver and sterling silver is still comparatively common in domestic flatware, or when aluminium protection is a concern and the composition is low in silicate. In particular, cleaning compositions according to the present invention may, in addition to the manganese-amino acid compound, preferably comprise a second corrosion inhibitor.

[0134] When present, such protecting materials are preferably incorporated at low levels, e.g., from about 0.01 % to about 5% of the ADCC. Suitable corrosion inhibitors include paraffin oil, typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from about 20 to about 50; preferred paraffin oil is selected from predominantly branched C 25-45 species with a ratio of cyclic to noncyclic hydrocarbons of about 32:68. A paraffin oil meeting those characteristics is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

[0135] Other corrosion protection compounds include benzotriazole, tolyltriazole and comparable compounds; mercaptans or thiols including thionaphthol and thioanthranol; and finely divided aluminium fatty acid salts, such as aluminium tristearate.

[0136] The formulator will recognize that such materials will generally be used judiciously and in limited quantities so as to avoid any tendency to produce spots or films on glassware or to compromise the bleaching action of the compositions. For this reason, mercaptan anti-tarnishes which are quite strongly bleach-reactive and common fatty carboxylic acids which precipitate with calcium in particular are preferably avoided.

OPTIONAL INGREDIENTS

[0137] The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates. Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitritotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriamine-pentaacetates, and ethanoldiglycines, iminodisuccinate, polyaspartic acid, methylglycindiacyeticacid alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

[0138] Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediamine-tetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

[0139] Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

[0140] A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233 or carboxymethylinuline.

[0141] If utilized, these chelating agents or transition-metal selective sequestrants will generally comprise from about 0.01% to about 10%, more preferably from about 0.05% to about 1% by weight of the ADCCs of the invention.

[0142] The compositions of the invention may additionally contain (a) dispersant polymer(s) independent from the use of said polymers for co-granulating and/or coating the manganese compound. If a coated manganese compound is used (a) further dispersant polymer(s) may be added. When present, a (further) dispersant polymer in the instant ADCCs is typically in the range from 0 to about 25%, preferably from about 0.2% to about 20%, more preferably from about 0.5% to about 12% by weight of the ADCC composition. Besides their use for co-granulating and/or coating of the manganese compound, dispersant polymers as described hereinabove are additionally useful for improved filming performance of the present ADCCs, especially in higher pH embodiments, such as those in which wash pH exceeds about 9.0. Particularly preferred are polymers which inhibit the deposition of calcium carbonate or magnesium silicate on dishware. Suitable dispersant polymers are such as described above for co-granulating and/or coating of the manganese compound.

[0143] The ADCCs of the invention can optionally contain an alkyl phosphate ester suds suppressor, a silicone suds suppressor, or combinations thereof. Levels in general are from 0% to about 10%, preferably, from about 0.001% to about 5%. Typical levels tend to be low, e.g., from about 0.01% to about 3% when a silicone suds suppressor is used. Preferred non-phosphate compositions omit the phosphate ester component entirely.

[0144] Silicone suds suppressor technology and other defoaming agents useful herein are extensively documented in "Defoaming, Theory and Industrial Applications", Ed., P.R. Garrett, Marcel Dekker, N.Y., 1973, ISBN 0-8247-8770-6. See especially the chapters entitled "Foam control in Detergent Products" (Ferch et al) and "Surfactant Antifoams" (Blease et al). See also U.S. Patents 3,933,672 and 4,136,045. Highly preferred silicone suds suppressors are the compounded types known for use in laundry detergents such as heavy-duty granules, although types hitherto used only in heavy-duty liquid detergents may also be incorporated in the instant compositions. For example, polydimethylsiloxanes having trimethylsilyl or alternate endblocking units may be used as the silicone. These may be compounded with silica

and/or with surface-active nonsilicon components, as illustrated by a suds suppressor comprising 12% silicone/ silica, 18% stearyl alcohol and 70% starch in granular form. A suitable commercial source of the silicone active compounds is Dow Corning Corp.

5 [0145] Levels of the suds suppressor depend to some extent on the sudsing tendency of the composition, for example, an ADCC for use at 2000 ppm comprising 2% octadecyldimethylamine oxide may not require the presence of a suds suppressor. Indeed, it is an advantage of the present invention to select cleaning-effective amine oxides which are inherently much lower in foam-forming tendencies than the typical coco amine oxides. In contrast, formulations in which amine oxide is combined with a high-foaming anionic cosurfactant, e.g., alkyl ethoxy sulfate, benefit greatly from the presence of suds suppressor.

10 [0146] Phosphate esters have also been asserted to provide some protection of silver and silver-plated utensil surfaces; however, the instant compositions can have excellent silvercare without a phosphate ester component.

[0147] If it is desired nonetheless to use a phosphate ester, suitable compounds are disclosed in U.S. Patent 3,314,891. Preferred alkyl phosphate esters contain from 16-20 carbon atoms. Highly preferred alkyl phosphate esters are mono-stearyl acid phosphate or monooleyl acid phosphate, or salts thereof, particularly alkali metal salts, or mixtures thereof.

15 FILLERS/FURTHER OPTIONAL INGREDIENTS

[0148] Depending on whether a greater or lesser degree of compactness is required, filler materials can also be present in the instant ADCCs. These include sucrose, sucrose esters, sodium sulfate, potassium sulfate, etc., in amounts up to about 70%, preferably from 0% to about 40% of the ADCC. Preferred filler is sodium sulfate, especially in good grades having at most low levels of trace impurities.

20 [0149] Sodium sulfate used herein preferably has a purity sufficient to ensure it is non-reactive with bleach; it may also be treated with low levels of sequestrants, such as phosphonates or EDDS in magnesium-salt form. Note that preferences, in terms of purity sufficient to avoid decomposing bleach, applies also to pH-adjusting component ingredients, specifically including any silicates used herein.

25 [0150] Hydrotrope materials such as sodium benzene sulfonate, sodium toluene sulfonate, sodium cumene sulfonate, etc., can be present in minor amounts.

[0151] The composition further can comprise lime soap dispersants and 'carry-over' surfactants as described in EP1 520 908 A1.

30 [0152] Bleach-stable perfumes (stable as to odour); and bleach-stable dyes such as those disclosed in U.S. Patent 4,714,562 can also be added to the present compositions in appropriate amounts. Other common detergent ingredients consistent with the intention of the present invention are not excluded.

35 [0153] In a preferred embodiment of the invention the cleaning composition is an ADCC for use in a dishwashing machine, and is preferably in the form of a tablet, granulate, powder, pearls, liquid, solution, gel, melt or a products appearance with a combination of two or more of these physical forms. Preferably, at least a part of the cleaning composition is in solid form, i.e. a tablet, granulate, powder, pearls or similar.

[0154] Preferably, a tableted cleaning composition the composition additionally contains a bleaching agent whereby the manganese compound and the bleaching agent are provided in separate layers of the tablet.

40 [0155] More preferably, if the cleaning composition is in form of granulates, wherein the manganese-amino acid compound and a bleaching agent are mixed within a cleaning composition, the manganese compound and the bleaching agent have no direct contact.

45 [0156] The cleaning composition preferably is a phosphate-containing or a non-phosphate containing cleaning composition, preferably an automatic dishwasher detergent composition (ADD), also called automatic dishwasher cleaning composition (ADCC). The cleaning composition preferably is a dishwashing cleaning composition, comprising further at least one of the ingredients such dishwashing compositions usually contain, selected from but not limited to the following ingredients: builders(s), surfactant(s), in particular nonionic surfactants, a bleaching system, comprising preferably a peroxide or a peroxide generating component and optionally a bleach activator, optionally any phosphonate and preferably enzymes for supporting the cleaning performance. Preferably the composition comprises at least a builder and at least one surfactant.

50 [0157] Since ADCC can contain water-sensitive ingredients or ingredients which can co-react when brought together in an aqueous environment, it is desirable to keep the free moisture content of the ADCCs at a minimum, e.g., 7% or less, preferably 4% or less of the ADCC; and to provide packaging which is substantially impermeable to water. Coating measures have been described to illustrate a way to protect the ingredients from each other and from air and moisture. Plastic bottles, including refillable or recyclable types, as well as conventional barrier cartons or boxes are another helpful means of assuring maximum shelf-storage stability. As noted, when ingredients are not highly compatible, it may further be desirable to coat at least one such ingredient with a low-foaming non-ionic surfactant for protection. There are numerous waxy materials which can readily be used to form suitable coated particles of any such otherwise incompatible components; however, the formulator prefers those materials which do not have a marked tendency to deposit or form

films on dishes including those of plastic construction.

METHODS FOR CLEANING

5 **[0158]** The present invention also encompasses a method for cleaning soiled tableware comprising contacting said tableware with an aqueous medium having an initial pH in a wash solution of above about 8, more preferably from about 8.5 to about 12, most preferably from about 9 to about 11, and comprising at least about 500 ppm of a cleaning composition comprising the co-granulated and/or coated or un-coated manganese-amino acid complex or composition or a coated manganese proteinate as hereinbefore defined. The cleaning composition may also comprise a mixture of coated or
10 uncoated manganese-amino acid compound with a coated manganese proteinate.

[0159] Some preferred granular or tableted ADCCs of the invention are as follows:

An ADCC comprising at least one builder and a manganese-amino acid compound, complex or composition and/or a co-granulated and/or coated manganese compound as hereinbefore defined, preferably a bleach system comprising a source of hydrogen peroxide selected from sodium perborate and sodium percarbonate and/or preferably a non-ionic surfactant.
15

An ADCC comprising at least one builder and a manganese-amino acid compound, complex or composition and/or a co-granulated and/or coated manganese compound as hereinbefore defined, preferably a bleach system comprising a source of hydrogen peroxide selected from sodium perborate and sodium percarbonate and optionally but preferably supplemented by a bleach activator selected from TAED and NOBS.
20

[0160] In both of said preferred embodiments the builder system can either comprise at least one phosphate builder as mentioned above or can be represented by a phosphate-free builder system.
25

[0161] In a preferred embodiment of the invention the ADCC comprises the manganese compound in an amount of from 0.005 to 5 wt-%, preferably in an amount of 0.01 to 4 wt-%, particularly preferred in an amount of from 0.05 to 2 wt-%, based on the total amount of the composition. The manganese compound can be selected from a co-granulated and/or coated or uncoated manganese-amino acid compound, a co-granulated and/or coated manganese proteinate or a mixture of these compounds. Further any of the other manganese compounds suitable in ADCCs as known in the art can be used when they are coated as described hereinabove as co-granulated and/or coated manganese compounds according to this invention.
30

[0162] It may be further preferred to provide a combination of a commonly used silver protecting agent, like e.g. benzotriazole, with the manganese-amino acid compound of the present invention. Said combination gives particular satisfying protecting results. In this case the commonly used silver protecting agent, e.g. benzotriazole, as well can be added to the ADCC in an amount of from 0.005 to 5 wt-%, preferably in an amount of 0.01 to 4 wt-%, particularly preferred in an amount of from 0.05 to 2 wt-%, based on the total amount of the composition. It is particularly preferred to provide a manganese glycinate, that may be co-granulated and/or coated or uncoated, and a benzotriazole; or a co-granulated and/or coated manganese proteinate and a benzotriazole, in a ratio of from 3:1 to 1:3, preferably 2:1 to 1:2 more preferred 1.5:1 to 1:1.5 and particularly preferred in a ratio of 1:1.
35

[0163] The ADCC of the present invention preferably is provided in powder, granular or tablet form. If the ADCC is provided as a tablet it is preferred that the bleaching agent and the manganese compound are separated, e.g. they are contained in different layers or regions of the tablet. In case of granulated ADCC the ingredients of the bleaching agent and the manganese compound preferably are not in direct contact, particularly they are not cogranulated. Particularly preferred is that these ingredients are contained in different granules.
40

[0164] A further advantage of the use of the manganese compounds in cleaning compositions according to the invention is that the manganese (-amino acid compound) is stabilized by the amino acid(s) or the amino acid residues within the protein.
45

[0165] The improved silver corrosion protection and silver cleaning properties of the inventive cleaning compositions containing (co-granulated and/or coated) low valent manganese glycinate or co-granulated and/or coated manganese-proteinates can be seen from the following example 1.
50

[0166] The improved removal of tea stains of the inventive cleaning composition containing cogranulated and/or coated manganese-amino acid compounds can be seen in the following example 2.
55

EXAMPLES

Example 1

5 Test 1: Silver Protection

[0167] To compare the performance for silver protection of cleaning compositions of the prior art and compositions according to the invention silver spoons were washed ten times in a dishwashing machine with cleaning compositions comprising a silver protecting system as shown below, wherein (A) to (E) are phosphate comprising ADCCs, or (F) to (K) are non-phosphate ADCCs. (A) and (G) are dishwashing cleaning compositions without "silver protection", (B) to (F) and (H) to (L) comprise silver protecting ingredients. Compositions (C), (D), (E), (F), (I), (J), (K) and (L) are according to the invention. In standard ADCCs comprising phosphate, bleach system, builder and surfactant the "silver protection system" was added as shown below

15 Phosphate comprising ADCCs used in test 1: amounts are given in % by weight

[0168]

	Ingredient	Comp. A	Comp. B	Comp. C	Comp. D	Comp. E	Comp. F
20	Benzotriazole	-	0.21	-	0.11	-	0.11
	Manganese glycinate (not co-granulated)	-	-	0.21	0.1	-	-
	Manganese glycinate (1)	-	-	-	-	0.21	-
	Manganese-proteininate (1)	-	-	-	-	-	0.1
25	(1): cogranulated or coated with Accusol 588 (Rohm & Haas) 1:1						

Non-phosphate comprising ADCCs used in test 1: amounts are given in % by weight

[0169]

	Ingredient	Comp. G	Comp. H	Comp. I	Comp. J	Comp. K	Comp. L
30	Benzotriazole	-	0.2	-	0.1	-	0.1
	Manganese glycinate (not co-granulated)	-	-	0.2	0.1	-	-
	Manganese glycinate (1)	-	-	-	-	0.2	-
35	Manganese-proteininate (1)	-	-	-	-	-	0.1
	(1): coated with Acusol 588 (Rohm & Haas) 1:1						

[0170] A normal cleaning program at the dishwashing machine was selected (Miele turbothermic plus, program "universal", or Bosch SKT5002, program "normal"; 55°C, water hardness 21°GH). Each time 15 g of a standard soil mixture (2,5 % tomato ketchup, 2,5 % mustard, 2,4 % gravy powder, 0,5 % potato starch, 0,1 % benzoic acid, 6 % egg yolk, 5 % milk, 10 % margarine and 71 % water) was added in the cleaning cycle. The discoloration of the spoons is estimated visually and scaled according to Fresenius Institute scale.

[0171] 5 = no discoloration (like new spoon); 4 = minor discoloration; 3 = slight discoloration; 2 = strong discoloration; 1 = very strong discoloration.

[0172] The results of the tests were as follows:

	Cleaning composition	Discoloration score
50	A	2
	B	3
	C	4-5
	D	5
	E	4-5
55	F	4
	G	2
	H	3

EP 3 075 832 A1

(continued)

Cleaning composition	Discoloration score
I	4-5
J	5
K	4-5
L	4

Example 2:

[0173] The following ADCCs have been tested on cleaning performance on tea-soiling in an IKW-based cleaning test. The basic cleaning compositions used in this test represent phosphate-free ADCCs (Comp. M to Comp. R and Comp. U to Comp. W) or phosphate comprising ADCCs (Comp. S and Comp. T). The silver protecting system is specified in the table below. Amounts are given in % by weight:. Further dishwashing ingredients except silver protection ad 100

Composition	M	N	O	P	Q	R
Sodium disilicate	-	-	-	-	3	3
Coated Mn-proteinat (1)	-	0,05	0,10	0,20	-	0,2
Perfume	pos.	pos.	pos.	pos.	-	-
Dye	pos.	pos.	pos.	pos.	-	-

(1) manganese-proteinat (SICIT) co-granulated with Acusol 588 (Rohm& Haas)

Composition	S	T
Coated Mn-proteinat (1)	-	0,4

(1) manganese-proteinat (SICIT) co-granulated with Acusol 588 (Rohm& Haas)

Composition	U	V	W
Manganese-proteinat (2)	-	-	0.2
Coated Mn-proteinat (1)	-	0.4	-

(1) manganese-proteinat (SICIT) co-granulated with Acusol 588 (Rohm& Haas)
 (2) manganese-proteinat (SICIT)

[0174] With ADCCs 'M' to 'W' IKW-based cleaning tests were performed with 4 different types of soil (tea, milk, egg-yolk, starch-mix) in a Miele G651 SC plus -3 domestic dishwasher at the '50°C normal' program which reaches a maximum temperature in the cleaning phase of about 55°C. The scores on removal of the tea soil are on a scale from 1 to 10, where 10 is completely clean. The IKW-cleaning test including details of the test method is published in SOFW-Journal 3/2006 page 55-70.

[0175] Compositions 'M', 'N', 'O' and 'P' are dosed as 11.0 gram tablets, washed at a water hardness of 6°dH, and have a score on tea-soil of respectively 2.4, 3.5, 5.3 and 6.3 .

[0176] Compositions 'Q' and 'R' are dosed as 14.0 gram powder, washed at a water hardness of 2°dH, and have a score on tea-soil of respectively 4.6 and 5.8 .

[0177] Compositions 'S' and 'T' are dosed as 20.0 gram powder, washed at a water hardness of 21°dH, and have a score on tea-soil of respectively 3.6 and 7.3 .

[0178] Compositions 'U', 'V' and 'W' are dosed as 14.1 gram tablets, washed at a water hardness of 6°dH, and have a score on tea-soil of respectively 4.1, 8.0 and 6.8 .

[0179] These test results show that addition of co-granulated manganese-proteinat to the ADCC results in an improvement of the removal of tea stains. These test results also shows that the obtained improvement with the co-granulated manganese-proteinat is higher than the improvement that is obtained with the non-co-granulated manganese-proteinat.

[0180] Example 3:

[0181] The below listed ADCCs have been tested on the discoloration of the composition. The layer which contains

EP 3 075 832 A1

manganese-amino acid compound (or co-granulated manganese-amino acid compound) has the tendency to show black/gray discoloration.

[0182] The level of discoloration was evaluated visually according to the following scale;

- 5
- 1 - Original color of the composition
 - 2 - Slight discoloration of the composition
 - 3 - Medium discoloration of the composition
 - 4 - Strong discoloration of the composition
 - 5 - Extreme discoloration of the composition
- 10

[0183] In this example standard ADCCs were used in form of a 3-phase tablet (Test 3, Test 3-1 and Test 3-2) or a 2-phase tablet (Test 4 and Test 4-1), both tablet embodiments comprising bleach system, builder and surfactant. Composition 3A contains phosphate, while composition 3B is phosphate-free. In the test series 3, phase 1 of the tablet contained different amounts of manganese-amino acid compounds. In particular, composition 3A-1 had a phase 1 that contained no manganese-amino acid compound, composition 3A-2 had a phase 1 that contained 0.5 parts of manganese-amino acid compound, composition 3A-3 had a phase 1 that contained 1.0 parts of co-granulated manganese-amino acid compound. In test series 4, composition 3B-1 had a phase 2 that contained no manganese-amino acid compound, composition 3B-2 had a phase 2 that contained 0.55 parts of non-co-granulated manganese-amino acid compound, composition 3B-3 had a phase 2 that contained 1.1 parts of co-granulated manganese-amino acid compound.

15

20

Test 3:

[0184] Three different tablets were pressed in this test. As stated above, composition 3A-1 had a phase 1 that contained no manganese-amino acid compound, composition 3A-2 had a phase 1 that contained 0.5 parts of manganese-amino acid compound, composition 3A-3 had a phase 1 that contained 1.0 parts of co-granulated manganese-amino acid compound. In order to get a three layer detergent tablet the powder from phase 1 to 3 was compressed by using a tableting press. First 7.5 gram of phase 1 was compressed, on top of this 7.5 gram of phase 2 was compressed, on top of this 5.0 gram of phase 3 was compressed with such a force that the result was a three layer detergent tablet.

25

Test 3-1:

[0185] The tablets from composition 3A-1, 3A-2 and 3A-3 were stored unwrapped at 30°C and 65% relative humidity. Immediately after tableting and after 1, 2 and 7 days of storage the level of discoloration was visually estimated. The achieved scores are listed in the table below;

30

35

Composition	3A-1	3A-2	3A-3
Immediately after tableting	1	1	1
After 1 day	1	3	1
After 2 days	1	4	1
After 7 days	1	4	2

40

The tableted composition with co-granulated manganese-amino acid compound shows less discoloration in comparison with the composition containing (non-co-granulated) manganese-amino acid compound.

45

Test 3-2:

[0186] The tablets of composition 3A-2 and 3A-3 were wrapped in polypropylene foil and stored at 37°C. Immediately after tableting and after 2 weeks of storage the level of discoloration was visually estimated. The obtained scores are listed in the table below;

50

Composition	3A-2	3A-3
Immediately after tableting	1	1
After 2 weeks	5	2

55

[0187] The tableted composition with co-granulated manganese-amino acid compound shows less discoloration in comparison with the composition containing (non-co-granulated) manganese-amino acid compound.

Test 4:

[0188] Three different tablets were pressed in this test. As stated above, composition 3B-1 had a phase 2 that contained no manganese- amino acid compound, composition 3B-2 had a phase 2 that contained 0.55 parts of non-co-granulated manganese- amino acid compound, composition 3B-3 had a phase 2 that contained 1.1 parts of co-granulated manganese-amino acid compound.

[0189] In order to get a two layer detergent tablet the powder from phase 1 and 2 were compressed by using a tableting press. First 9.0 gram of phase 1 was compressed, on top of this 5.0 gram of phase 2 was compressed with such a force that the result was a two layer detergent tablet.

Test 4-1:

[0190] The tablets from compositions 3B-1, 3B-2 and 3B-3 were stored unwrapped at 30°C and 65% relative humidity. Immediately after tableting and after 1, 2 and 7 days of storage the level of discoloration was visually estimated. The achieved scores are listed in the table below;

Composition	3B-1	3B-2	3B-3
Immediately after tableting	1	1	1
After 1 day	1	3	2
After 2 days	2	4	3
After 7 days	2	5	4

[0191] The tabletted composition with co-granulated manganese- amino acid compound shows less discoloration in comparison with the composition containing (non-co-granulated) manganese- amino acid compound.

Claims

1. A manganese-amino acid compound co-granulated and/or coated with at least one polymer, wherein the manganese in the manganese-amino acid compound is bound to, associated with or complexed with at least one single amino acid or at least one amino acid residue being part of a protein.

2. A cleaning composition comprising a co-granulated and/or coated manganese-amino acid compound according to claim 1.

3. The manganese-amino acid compound or cleaning composition according to claim 1 or 2, wherein the manganese-amino acid compound is selected from a manganese-single amino acid compound and/or a manganese-protein compound, wherein the manganese-single amino acid compound comprises a manganese bound to, associated with or complexed with at least one single amino acid; and wherein the manganese-protein compound comprises a manganese bound to, associated with or complexed with at least one single amino acid residue that is part of a peptide or protein.

4. A cleaning composition comprising an uncoated manganese-single amino acid compound as defined in claim 3.

5. The compound or cleaning composition according to any of claims 1 to 4, wherein the at least one of the single amino acids is selected from glycine, alanine, valine, leucine, isoleucine, serine, threonine, lysine, arginine, histidine, aspartate, glutamate, asparagine or glutamine, and preferably is glycine.

6. The compound or cleaning composition according to any of claims 1 to 3 or 5, wherein at least one of the polymer(s) is selected from a co-polymer comprising at least one sulfonic, sulphate or sulfonate group comprising monomer.

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8. The compound or cleaning composition according to any of claims 1 to 3, 5 or 6, wherein at least one of the polymer(s) comprises or is consisting of the following monomers:

(i) unsaturated carboxylic acid

(ii) monomers containing sulfonic acid group

optionally further ionic or nonionic monomers

5 **9.** The cleaning composition according to any of claims 2 to 8, comprising further a second corrosion inhibitor, preferably benzotriazole.

10 **10.** The cleaning composition according to claim 9, comprising a manganese-amino acid compound and a second corrosion inhibitor in a ratio of 3:1 to 1:3, preferably of 2:1 to 1:2, more preferred of 1.5:1 to 1:1.5 and most preferred of 1:1.

11. The cleaning composition according to any of claims 2 to 10, which is an automatic dishwashing cleaning composition at least partially in the form of a tablet, a granulate or a powder.

15 **12.** The automatic dishwashing cleaning composition according to claim 11, wherein the tableted machine dishwashing cleaning composition additionally contains a bleaching agent wherein the manganese-compound and the bleaching agent are provided in separate layers of the tablet or a granulated composition additionally contains a bleaching agent wherein the manganese-compound and the bleaching agent have no direct contact.

20 **13.** Use of the compound or the cleaning composition of any of claims 1 to 12 or manganese-glycinate for cleaning and/or protecting silver against silver corrosion.

25 **13.** Method for preparing a co-granulated or coated manganese-amino acid compound as defined in any of claims 1 to 8 by contacting a liquid composition comprising at least one polymer with the manganese compound in powder or granulate form.

14. Method for cleaning dishware in a dishwashing machine using a compound or an automatic dishwashing composition according to any of claims 1 to 12.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 16 1672

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