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(54) Title: HARD SURFACE CLEANER COMPRISING ABRASIVE PARTICLES

(57) Abstract: The present invention relates to an aqueous cleaning composition comprising i) a polysaccharide polymer; ii) a further polysaccharide polymer different from i); iii) at least one abrasive particle having an mean particle size of 0.01 to 1000 µm; iv) at least one acidic compound; v) water; vi) optionally at least one surfactant; and vii) optionally at least one additive; wherein the composition has a pH of lower than 7. Use of the cleaning composition according to the invention for cleaning the bathroom, cleaning a toilet, or cleaning a sink and a specific method of producing the aqueous composition according to the present invention.



## Hard surface cleaner comprising abrasive particles

The present invention relates to acidic cleaning compositions, which comprise abrasive particles and which exhibit good cleaning characteristics and stability of the composition. In particular, the present invention provides acidic hard surface cleaning compositions, which are especially useful for lavatory cleaning. Moreover, a method of manufacturing the composition is contained in the present invention as well.

Acidic cleaners, especially cleaners that are employed in lavatory cleaning are known for decades. In order to ensure satisfactory cleaning it is necessary to ensure that the cleaner stays at the surface initially applied and can work there for a certain period. Especially for limescale removal, the cleaner should be able to work for a certain time. Therefore, the aqueous compositions in general comprise a thickener. This is especially important when the cleaners are employed in lavatory cleaning since, e.g., toilets, have inclined surfaces which impede the cleaner to stay at the place to be cleaned due to gravity.

For example WO 03/020863 A1 discloses an aqueous hard surface cleaning composition which comprises: an acidic constituent which comprises either citric acid alone or citric acid in combination with an acid selected from the group consisting of sorbic acid, acetic acid, boric acid, formic acid, maleic acid, adipic acid, lactic acid, malic acid, malonic acid, glycolic acid, and mixtures thereof; 0.001-10% by weight of at least one anionic surfactant; 0.001-5% by weight of a thickener selected from the group consisting of cellulose, alkyl celluloses, alkoxy celluloses, hydroxy alkyl celluloses, alkyl hydroxy alkyl celluloses, carboxy alkyl celluloses, carboxy alkyl hydroxy alkyl celluloses, xanthan gum, and mixtures thereof; 0-10% by weight of one or more optional constituents; and the balance to 100% by weight, water; wherein the aqueous hard surface cleaning composition exhibits a pH of 6.0 or less.

The above-mentioned reference teaches conventional cleaners. However, when cleaning compositions contain abrasive particles the composition has to ensure that storage stability over a long period of time is given as well. In particular that the abrasive particles are homogeneously distributed in the cleaner. Therefore, the teaching of conventional cleaners cannot be applied to cleaning compositions which comprise abrasive particles.

Cleaners comprising abrasive particles are for example described in WO 03/070872 which discloses an aqueous hard surface cleaning composition which comprises: an acidic constituent which comprises either citric acid alone or citric acid in combination with an acid selected from the group consisting of sorbic acid, acetic acid, boric acid, formic acid, maleic acid, adipic acid, lactic acid, malic acid, malonic acid, glycolic acid, and mixtures thereof; 0.001-10% by weight of at least one anionic surfactant ; 0.001-10% by weight of thickener selected from the group consisting of cellulose, alkyl

celluloses, alkoxy celluloses, hydroxy alkyl celluloses, alkyl hydroxy alkyl celluloses, carboxy alkyl celluloses, carboxy alkyl hydroxy alkyl celluloses, succinoglycan, xanthan gum, guar gum, locust bean gum, tragacanth gum or derivatives thereof, clays selected from kaolinite, dicktite, hectorite, bentonite, nacrite, halloysite, endillite, chrysotile, amesite, beidellite, nontronite, saponite, sauconite, illites ; glauconite, chlorite, vermiculite, attapulgite, sepiolit, allophane, and imogolite, and silicas selected from diatomite, precipitated silica and fumed silica, and mixtures thereof; 10-30% by weight of a scrubbing agent selected from quartzes, siliceous chalk, diatomaceous earth, colloidal silicon dioxide, alkali metasilicates, organic abrasive materials selected from polyolefins, polyethylenes, polypropylenes, polyesters, polystyrenes, acetonitrile-butadiene-styrene resins, melamines, polycarbonates, phenolic resins, epoxies and polyurethanes and mixtures thereof; 0-10% by weight of one or more optional constituents; and the balance to 100% by weight, water.

However, there is still a need for acidic cleaner compositions, in the following referred to as composition as well, which comprise abrasive particles and which are based on biodegradable thickeners. These compositions should have a good storage stability as well as good release properties for the acidic component and/or surfactant. Moreover, the thickener should be available for reasonable costs.

The object has been solved by the composition of the present invention as described in detail below.

In the present specification, the terms “a” and “an” and “at least one” are the same as the term “one or more” and can be employed interchangeably.

“One or more”, as used herein, relates to at least one and comprises 1, 2, 3, 4, 5, 6, 7, 8, 9 or more of the referenced species. Similarly, “at least one” means one or more, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9 or more. “At least one”, as used herein in relation to any component, refers to the number of chemically different molecules, i.e. to the number of different types of the referenced species, but not to the total number of molecules. For example, “at least one abrasive particle” means that at least one type of abrasive particles is used but that also two or more different particles of one type can be present. It does not mean that a single abrasive particle is present.

The term “essentially free” within the context of this invention is to be interpreted as the respective compound is contained in the composition in an amount of less than 1 wt.-%, 0.5 wt.-%, 0.1 wt.-%, 0.05 wt.-%, 0.001 wt.-%, 0.001 wt.-% based on the total weight of the composition, wherein the amounts are respectively more preferred in descending order. For example, 0.1 wt.-% is more preferred than 0.5 wt.-% and 0.01 wt.-% is more preferred than 0.1 wt.-%.

The particle size of the abrasive particles in the present invention is measured according to ISO 13320:2009.

If reference is made herein to a molecular weight of a polymer, this reference refers to the average number molecular weight  $M_n$ , if not explicitly stated otherwise. The number average molecular weight  $M_n$  of a polymer can, for example, be determined by gel permeation chromatography according to

DIN 55672-1:2007-08 with THF as the eluent. If not stated otherwise, all given molecular weights are those determined by GPC, calibrated with polystyrene standards. The weight average molecular weight  $M_w$  can also be determined by GPC, as described for  $M_n$ .

All percentages given herein in relation to the compositions or formulations relate to weight % relative to the total weight of the respective composition or formula, if not explicitly stated otherwise.

In particular, the present invention in particular refers to:

1. An aqueous cleaning composition, preferably a sanitary cleaning composition, more preferably a toilet cleaning composition comprising, preferably consisting of,
  - i) a polysaccharide polymer;
  - ii) a further polysaccharide polymer different from i);
  - iii) at least one abrasive particle having an mean particle size of 0.01 to 1000  $\mu\text{m}$ ;
  - iv) at least one acidic compound;
  - v) water;
  - vi) optionally at least one surfactant; and
  - vii) optionally at least one additive;wherein the composition has a pH of lower than 7, preferably from 6 to 1, more preferably from 5 to 1.5, most preferably from 3 to 2.5.
2. The cleaning composition according to item 1, wherein  
the polysaccharide polymer i) comprises a compound selected from carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan gum, xanthan gum, gellan gum, guar gum, locust bean gum, tragacanth gum.
3. The cleaning composition according to item 2, wherein  
i) is succinoglycan gum.
4. The cleaning composition according to any of items 1 to 3, wherein  
the polysaccharide polymer ii) comprises a compound selected from carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan gum, xanthan gum, gellan gum, guar gum, locust bean gum, tragacanth gum or combinations thereof.
5. The cleaning composition according to item 4, wherein  
ii) is xanthan gum.

6. The cleaning composition according to any of items 1 to 5, wherein
  - iii) has an mean particle size of 1 to 500  $\mu\text{m}$ , preferably 20 to 300  $\mu\text{m}$  more preferably 50 to 200  $\mu\text{m}$  measured according to ISO13320:2009.
7. The cleaning composition according to any of items 1 to 6, wherein
  - iii) has a bulk density of 1.01 to 1.1  $\text{g/cm}^3$ , preferably 1.02 to 1.05  $\text{g/cm}^3$ , measured according to ISO 903: 1976-09.
8. The cleaning composition according to any of items 1 to 7, wherein  
the at least on abrasive particle iii) comprises a compound selected from aluminum oxide, pumice, microcrystalline cellulose, silica, grinded kernels, like apricot kernel, grinded shells like, walnut shell or combinations thereof, preferably comprised aluminum oxide, microcrystalline cellulose or silica, more preferably comprises aluminum oxide, most preferably is aluminum oxide.
9. The cleaning composition according to any of items 1 to 8, wherein  
the at least on acidic component iv) comprises a compound selected from lactic acid, phosphoric acid, sulfamic acid, hydrochloric acid, citric acid, maleic acid, acetic acid, formic acid or combinations thereof, preferably a compound selected from lactic acid, formic acid, hydrochloric acid, citric acid, acetic acid or combinations thereof; most preferably iv) is formic acid.
10. The cleaning composition according to any of claims 1 to 9, wherein the at least one surfactant vi) comprises a non-ionic surfactant or an anionic surfactant, preferably a non-ionic surfactant, more preferably alkyl polyglucoside, ethoxylated alcohol or a combination thereof.
11. The cleaning composition according to any of items 1 to 10, wherein  
the at least on additive vii) comprises a compound selected from perfumes, colorants, bittering agents, alkaline compounds, defoamer, thickener, capsules, like dye capsules or dye microcapsules, pH buffers, antioxidants or combinations thereof.
12. The cleaning composition according to any of items 1 to 11, wherein the composition has a viscosity of 300 to 1200 mPas, preferably 500 to 900 mPas, more preferably 600 to 800 mPas measured according to DIN 51398:1983-07.
13. The cleaning composition according to any of items 1 to 11, wherein the composition contains
  - i) 0.02 to 1 wt.-%, preferably 0.05 to 0.5 wt.-%, more preferably 0.1 to 0.2 wt.-%;
  - ii) 0.05 to 1 wt.-%, preferably 0.1 to 0.7 wt.-%, more preferably 0.2 to 0.3 wt.-%;

- iii) 0.1 to 20 wt.-%, preferably 1 to 10 wt.-%, more preferably 3 to 6 wt.-%;
  - iv) 1 to 20 wt.-%, preferably 3 to 12 wt.-%, more preferably 4 to 9 wt.-%;
  - v) balance add to 100 wt.-%;
  - vi) 0.1 to 10 wt.-%, preferably 0.5 to 6 wt.-%, more preferably 1 to 3 wt.-%; and
  - vii) 0 to 10 wt.-%, preferably 0.001 to 7 wt.-%, more preferably 0.1 to 5 wt.-%;
- based on the total weight of the composition.

14. Use of the cleaning composition according to any of items 1 to 13 for cleaning the bathroom, cleaning a toilet, or cleaning a sink.
15. A method of manufacturing the cleaning composition according to any of items 1 to 13, comprising the steps:
  - a) mixing components i), ii), iv), v) and optionally vi), and vii) as defined in any of claims 1 to 5 in a vessel using a jetstream mixer, preferably a Ystral mixer, and preferably reducing the mixing speed after 1 minute;
  - b) adding component iii) as defined in any of claims 1 or 6 to 8 directly into the vessel and
  - c) stirring the resulting mixture for 5 to 15 minutes.

The compositions of the present invention have a pH of lower than 7, preferably 1 to 5, more preferably 1.5 to 3.5, most preferably 1.8 to 2.5.

In preferred embodiments, the cleaning composition is essentially free of copper based biocides.

The compositions of the present invention comprise at least two different polysaccharide polymers, which function as thickener.

Suitable polysaccharide polymers can be derived from plant, animal and microbial sources. Exemplary polysaccharides include but are not limited to maltodextrins, starches, cellulose, gums (e.g., gum arabic, succinoglycan, and tragacanth), alginates, agar-agar, pectin, carrageenan and gellan. Suitable starches include those derived from maize, potato, tapioca, wheat, rice, pea, sago, oat, barley, rye, and amaranth, including conventional hybrids or genetically engineered materials. Additional example polysaccharides include hemicellulose or plant cell wall polysaccharides such as D-xylans. Furthermore, polyoses, guar flour, locust bean flour, and dextrins, modified organic natural substances (carboxymethylcellulose and other cellulose ethers, hydroxyethylcellulose and hydroxypropylcellulose and the like, seed flour ethers) are suitable. Further exemplary polysaccharides and heteropolysaccharides include, in particular polysaccharide gums, for example gum arabic, agar, alginates, carrageenans and the salts thereof, guar, guaran, tragacanth, gellan, ramsan, dextran or xanthan and the derivatives thereof, for example propoxylated guar, and mixtures

thereof. Other polysaccharide thickeners, such as starches or cellulose derivatives, may as well be used, for example starches of the most varied origin and starch derivatives, for example hydroxyethyl starch, starch phosphate esters or starch acetates, or carboxymethylcellulose or the sodium salt thereof, methyl-, ethyl-, hydroxyethyl-, hydroxypropyl-, hydroxypropylmethyl- or hydroxyethylmethylcellulose or cellulose acetate. One particularly preferred polysaccharide thickener is the microbial anionic heteropolysaccharide xanthan gum, which is produced by *Xanthomonas campestris* and some other species under aerobic conditions, with a molecular weight of  $2 \cdot 10^6$  to  $15 \cdot 10^6$  and is obtainable for example from Kelco under the trade names Keltrol® and Kelzan® or also from Rhodia under the trade name Rhodopol®. A further preferred polysaccharide thickener according to the present invention is succinoglycan gum which is commercially available under the tradename Rheozan® from Rhodia.

Further non polysaccharide thickeners can be optionally present. Suitable thickeners include casein, gelatin, completely synthetic organic thickeners (polyacrylic and polymethacrylic compounds, vinyl polymers, polycarboxylic acids, polyethers, polyimines, polyamides) and inorganic thickeners (polysilicic acids, clay minerals such as montmorillonites, zeolites, silicas). The polyacrylic and polymethacrylic compounds include, for example, the high molecular weight homopolymers, crosslinked with a polyalkenyl polyether, in particular an allyl ether of sucrose, pentaerythritol or propylene, of acrylic acid (INCI name according to International Dictionary of Cosmetic Ingredients of The Cosmetic, Toiletry, and Fragrance Association (CTFA): Carbomer), which are also known as carboxyvinyl polymers. Such polyacrylic acids are obtainable inter alia from 3V Sigma under the trade name Polygel®, for example Polygel® DA, and from B.F. Goodrich under the trade name Carbopol®, for example Carbopol® 940 (molecular weight approx. 4,000,000), Carbopol® 941 (molecular weight approx. 1,250,000) or Carbopol® 934 (molecular weight approx. 3,000,000). They furthermore include the following acrylic acid copolymers: (i) copolymers of two or more monomers from the group of acrylic acid, methacrylic acid and the simple esters thereof, preferably formed with C1-4 alkanols (INCI Acrylates Copolymer), which include for instance the copolymers of methacrylic acid, butyl acrylate and methyl methacrylate (CAS name according to Chemical Abstracts Service: 25035-69-2) or of butyl acrylate and methyl methacrylate (CAS 25852-37-3) and which are obtainable for example from Rohm & Haas under the trade names Aculyn® and Acusol® and from Degussa (Goldschmidt) under the trade name Tego® Polymer, for example the anionic non-associative polymers Aculyn® 22, Aculyn® 28, Aculyn® 33 (crosslinked), Acusol® 810, Acusol® 823 and Acusol® 830 (CAS 25852-37-3); (ii) crosslinked high molecular weight acrylic acid copolymers, which include for instance the copolymers, crosslinked with an allyl ether of sucrose or of pentaerythritol, of C10-30 alkyl acrylates with one or more monomers from the group of acrylic acid, methacrylic acid and the simple esters thereof, preferably formed with C1-4 alkanols (INCI Acrylates/C10-30 Alkyl Acrylate Crosspolymer) and which are obtainable for example from B.F. Goodrich under the trade name Carbopol®, for example hydrophobized Carbopol® ETD 2623 and

Carbopol® 1382 (INCI Acrylates/C10-30 Alkyl Acrylate Crosspolymer) and Carbopol® Aqua 30 (formerly Carbopol® EX 473).

Phyllosilicates may furthermore be used as thickeners. These include for example the magnesium or sodium/magnesium phyllosilicates obtainable under the trade name Laponite® from Solvay Alkali, in particular Laponite® RD or also Laponite® RDS, and the magnesium silicates from Sud-Chemie, especially Optigel® SH.

In a preferred embodiment of the present invention, the composition comprises succinoglycan gum and xanthan gum. When using these two specific thickeners stable compositions can be obtained having good cleaning properties due to a good balance of stickiness to the bowl while being able to sufficiently release the acid and /or surfactant. Without wishing to be bound by theory the lower viscosity of xanthan gum and its lower pseudoplastic behavior compared to succinoglycan gum ensure the sufficient release of the acid and / or surfactant while the higher viscosity of the succinoglycan gum ensures that the composition remains on the ceramic for a sufficient period of time.

The composition according to the present invention requires at least one abrasive particle having an mean particle size of 0.01 to 1000 µm. Suitable abrasive particles can be selected from kaolinite, dicktite, hectorite, bentonite, nacrite, halloysite, endillite, chrysotile, amesite, beidellite, nontronite, saponite, sauconite, illites ; glauconite, chlorite, vermiculite, attapulgite, sepiolit, allophane, and imogolite, aluminum oxide, pumice, microcrystalline cellulose, grinded kernel, like apricot kernel, grinded shells like, walnut shell, and silicas selected from diatomite, precipitated silica and fumed silica, quartzes, siliceous chalk, diatomaceous earth, colloidal silicon dioxide, alkali metasilicates, organic abrasive materials selected from polyolefins, polyethylenes, polypropylenes, polyesters, polystyrenes, acetonitrile- butadiene-styrene resins, melamines, polycarbonates, phenolic resins, epoxies and polyurethanes and mixtures thereof.

In preferred embodiments the at least one abrasive particle has an mean particle size of 1 to 500 µm, preferably 20 to 300 µm more preferably 50 to 200 µm measured according to ISO13320:2009. When having a mean particle size of 50 to 200 µm the compositions show a good cleaning performance while being visible for the human eye in the composition.

The compositions of the present inventions comprise at least one acidic compound. Exemplary compounds are in particular organic acids such as formic acid, acetic acid, citric acid, glycolic acid, lactic acid, succinic acid, adipic acid, malic acid, hydrochloric acid, maleic acid, tartaric acid and gluconic acid, amidosulfonic acid or combinations thereof. The inorganic acids hydrochloric acid, sulfuric acid, sulfamic acid, phosphoric acid and nitric acid or mixtures thereof may be used alternatively or additionally. Particularly preferred acids are those selected from the group comprising amidosulfonic acid, citric acid, lactic acid and formic acid. They are preferably used in quantities of

0.01 to 30 wt. %, particularly preferably of 0.2 to 15 wt. %, based on the total weight of the composition.

The compositions of the present invention optionally comprise at least one surfactant. Suitable exemplary surfactants are disclosed in the following:

#### Anionic Surfactants

Suitable anionic surfactants for use in the composition may include, but are not limited to, aliphatic sulfates such as fatty alcohol sulfates, fatty alcohol ether sulfates, dialkyl ether sulfates, monoglyceride sulfates, and aliphatic sulfonates such as alkane sulfonates, ether sulfonates, n-alkyl ether sulfonates, ester sulfonates and lignin sulfonates. Fatty acid cyanamides, sulfosuccinates, particularly the C8 to C18 alkyl mono and diesters of succinic acid, sulfosuccinamates, sulfosuccinamides, fatty acid isethionates, acylaminoalkane sulfonates (fatty acid taurides), fatty acid sarcosinates, ether carboxylic acids and alkyl (ether) phosphates as well as alpha-sulfofatty acid salts, acylglutamates, monoglyceride disulfates and alkyl ethers of glycerin disulfate can be used as well in the present invention.

The anionic surfactants preferably comprise fatty alcohol sulfates and/or fatty alcohol ether sulfates, in particular the fatty alcohol sulfates, in a more preferred embodiment of the present invention. Fatty alcohol sulfates are products from sulfating reactions on corresponding alcohols, whereas fatty alcohol ether sulfates are products of sulfating reactions on alkoxyated alcohols. In the present invention, alkoxyated alcohols are generally understood by the person skilled in the art to be the reaction products of alkylene oxide, preferably ethylene oxide, with alcohols, preferably with longer chain alcohols having at least six carbon atoms. As a rule, n moles of ethylene oxide react with one mole of alcohol to form, depending on the reaction conditions, a complex mixture of addition products with different degrees of ethoxylation. Another embodiment of the alkoxylation consists in the use of mixtures of the alkylene oxides, preferably a mixture of ethylene oxide and propylene oxide. Preferred fatty alcohol ether sulfates are the sulfates of low-ethoxyated fatty alcohols with 1 to 4 ethylene oxide units (EO), in particular 1 to 2 EO, for example 1.3 EO.

Exemplary useful anionic surfactants which may be used in the composition of the invention can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric acid reaction products having in their molecular structure an alkyl or alkaryl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals (included in the term alkyl is the alkyl portion of higher acyl radicals). Suitable examples of the anionic surfactants which can be employed in the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C8 to C18 carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); paraffin sulfonate surfactants having

the general formula  $\text{RSO}_3\text{M}$ , wherein R is a primary or secondary alkyl group containing from about 8 to about 22 carbon atoms (preferably 10 to 18 carbon atoms) and M is an alkali metal, e.g., sodium, lithium or potassium; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from about 8 to about 12 carbon atoms; the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil and sodium or potassium /3-acetoxy- or /3-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

In a preferred embodiment the anionic surfactants comprise one or more linear alkyl benzene sulfonate surfactant wherein the alkyl portion contains 8 to 16 carbon atoms, and most preferably about 11 to 13 carbon atoms. A further preferred class of anionic surfactants are alpha olefin sulfonates, as well as salts thereof, e.g., alkali metal salts. Preferred are C9 to C22 alpha olefin sulfonates, particularly C12 to C18 as well as blends of two or more thereof. According to particularly preferred embodiments of the invention, the solid block compositions necessarily include an alpha olefin sulfonate anionic surfactant. Toluene and isopropylene benzene sulfonates are particularly preferred.

#### Nonionic Surfactants

Nearly any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a hydrogen group attached to the nitrogen can be condensed with an alkylene oxide, especially ethylene oxide or with the polyhydration product thereof, a polyalkylene glycol, especially polyethylene glycol, to obtain a water soluble or water dispersible nonionic surfactant compound

In preferred embodiments of the present invention nonionic surfactants comprise alkoxylates such as polyglycol ethers, fatty alcohol polyglycol ethers, alkylphenol polyglycol ethers, end-capped polyglycol ethers, mixed ethers and hydroxy mixed ethers, and fatty acid polyglycol esters or mixtures thereof. Ethylene oxide/propylene oxide block polymers, fatty acid alkanolamides and fatty acid polyglycol ethers may be comprised as well. Another important class of nonionic surfactants that may be comprised are the polyol surfactants and in particular the glycol surfactants, such as alkyl polyglycosides and fatty acid glucamides. The alkyl polyglycosides are particularly preferred, in particular the alkyl polyglucosides as well as the fatty alcohol alkoxylates (fatty alcohol polyglycol ethers).

Preferred alcohol ethoxylates include the condensation products of aliphatic alcohols with 1 to 60 moles, preferably 5 to 30, more preferably 6 to 25, of an alkylene oxide, especially ethylene oxide or propylene oxide or mixtures thereof. Most preferred is ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms, preferably 8 to 16, more preferably 8 to 12. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of alcohol and the condensation product of about 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from about 10 to 14 carbon atoms). Other examples are those C6 to C22 straight-chain alcohols having 3 to 6 moles of ethylene oxide. Commercially available products include Alfonic® 810-4.5, comprising C8 to C10 straight-chain alcohols having 4.85 moles EO (in the following EO is used as abbreviation for ethoxylation units = degree of ethoxylation); Alfonic® 810-2, comprising C8 to C10 straight-chain alcohols having 2.1 moles EO; and Alfonic® 610-3.5, having 3.1 moles EO. Other examples of alcohol ethoxylates are C10 oxo-alcohol ethoxylates available from BASF under the Lutensol® ON tradenamelike Lutensol® ON 30; Lutensol® ON 50; Lutensol® ON 60; Lutensol® ON 65; Lutensol® ON 66; Lutensol® ON 70; Lutensol® ON 80; and Lutensol® ON 110. Other examples of ethoxylated alcohols include the Neodol® 91 series non-ionic surfactants available from Shell Chemical Company which are described as C9 to C11 ethoxylated alcohols, like Neodol® 91-2.5, Neodol® 91-6, and Neodol® 91-8. Neodol® 91-2.5 have been described as having about 2.5 EO; Neodol® 91-6 has been described as having about 6 EO; and Neodol® 91-8 has been described as having about 8 EO. Further examples of ethoxylated alcohols include the Rhodasurf® DA series non-ionic surfactants available from Rhodia which are described to be branched isodecyl alcohol ethoxylates, like Rhodasurf® DA-530 having 4 moles EO; Rhodasurf® DA-630 having 6 moles EO; and Rhodasurf® DA-639 is a 90% solution of DA-630. Further examples of ethoxylated alcohols include those from Tomah Products (Milton, WI) under the Tomadol®. A further class of useful nonionic surfactants include primary and secondary linear and branched alcohol ethoxylates, such as those based on C6 to C18 alcohols which further include an average of from 2 to 80 moles of ethoxylation per mol of alcohol. These examples include the Genapol® UD like Genapol® UD 030 with 3 EO; Genapol® UD 050 with 5 EO; Genapol® UD 070 with 7 EO; Genapol® UD 080 with 8 EO; Genapol® UD 088 with 8 EO; and Genapol® UD 110 with 11 EO. Exemplary useful nonionic surfactants include the condensation products of a secondary aliphatic alcohols containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide, like commercially available under the trade name of Tergitol®. Examples include Tergitol 15-S-12 having 9 EO, or Tergitol 15-S-9 which having 12 EO.

Most preferred fatty alcohol alkoxyates are unbranched or branched, saturated or unsaturated C8 to C22 alcohols alkoxyated with ethylene oxide (EO) and/or propylene oxide (PO) with a degree of alkoxylation 2 to 30, preferably ethoxylated C12 to 22 fatty alcohols with a degree of ethoxylation of

10 to 30, preferably 12 to 28, particularly 20 to 28, particularly preferably 25, for example C16 to 18 fatty alcohol ethoxylates containing 25 EO.

Alkyl polyglycosides which are as well suitable for the composition of the present invention are surfactants that can be obtained by the reaction of sugars and alcohols using appropriate methods of preparative organic chemistry, whereby according to the method of preparation, one obtains a mixture of monoalkylated, oligomeric or polymeric sugars. They are for example commercially available under the trade name Pluronics® (ex. BASF). The compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion of the molecule is of the order of 950 to 4,000 and preferably 200 to 2,500. The addition of polyoxyethylene radicals of the hydrophobic portion tends to increase the solubility of the molecule as a whole so as to make the surfactant water-soluble. Preferably, these surfactants are in liquid form at 25°C and particularly satisfactory surfactants are available as those marketed as Pluronics® L62 and Pluronics® L64. Preferred alkyl polyglycosides are the alkyl polyglucosides, wherein the alcohol is particularly preferably a long-chain fatty alcohol or a mixture of long-chain fatty alcohols with branched or unbranched C8 to C18 alkyl chains and the degree of oligomerization (DP) of the sugar is between 1 and 10, advantageously 1 to 6, particularly 1.1 to 3, most preferably 1.1 to 1.7, for example C8 to 10 alkyl-1.5-glucoside (DP of 1.5). Their preparation is known to the skilled person. Exemplary methods can be found in K. Hill, W. von Rybinski, G. Stoll "Alkyl Polyglycosides, Technology, Properties and Applications", VCH, 1996.

Fatty alcohol ethoxylates are preferably employed in amounts of 0.1 to 10 wt.-%, particularly preferably 0.5 to 8 wt.-%, and particularly preferably from 1 to 5 wt.-%. Additional nonionic surfactants, such as fatty acid monoalkanolamides and/or alkyl polyglycosides, may be included in amounts of 0.1 to 10 wt.-%, preferably 0.5 to 6 wt.-%, more preferably 1 to 4 wt.-% based on the total weight of the composition.

In a preferred embodiment the nonionic surfactants can comprise polyalkylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with an alkylene oxide, especially an ethylene oxide, the ethylene oxide being present in an amount equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerized propylene, diisobutylene and the like. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol and diisooctyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol.

The nonionic surfactants can alternatively be selected from alkoxylated alkanolamides, preferably C8 to C24 alkyl di(C2 to C3 alkanol amides), as described in WO 2007148054 A1.

Alternatively, the nonionic surfactants preferably comprise nonionic amine oxide surfactants. Exemplary amine oxides include: A) Alkyl di (lower alkyl) amine oxides in which the alkyl group has about 10 to 20, and preferably 12 to 16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. The lower alkyl groups include between 1 and 7 carbon atoms.

Examples include lauryl dimethyl amine oxide, myristyl dimethyl amine oxide, and those in which the alkyl group is a mixture of different amine oxide, dimethyl cocoamine oxide, dimethyl (hydrogenated tallow) amine oxide, and myristyl/palmityl dimethyl amine oxide; B) Alkyl di (hydroxy lower alkyl) amine oxides in which the alkyl group has about 10 to 20, and preferably 12 to 16 carbon atoms, and can be straight or branched chain, saturated or unsaturated.

Besides the previously cited surfactant types, the composition according to the invention can comprise cationic surfactants and/or amphoteric surfactants.

The compositions of the present invention can optionally comprise at least one additive. Suitable additives are disclosed in the following. Suitable additional thickener are disclosed above.

The compositions according to the present invention may additionally comprise nonaqueous solvents, preferably water-soluble organic solvents. These include, for example, lower alcohols and/or ether alcohols, lower alcohols being taken for the purposes of the present invention to mean straight-chain or branched C1-6 alcohols. The alcohols used are in particular ethanol, isopropanol and n-propanol. Ether alcohols which may be considered are adequately water-soluble compounds with up to 10 C atoms per molecule. Examples of such ether alcohols are ethylene glycol monobutyl ether, propylene glycol monobutyl ether, diethylene glycol monobutyl ether, propylene glycol mono-tert.-butyl ether and propylene glycol monoethyl ether, among which ethylene glycol monobutyl ether and propylene glycol monobutyl ether are in turn preferred. In a preferred embodiment, however, ethanol is used as the solvent. Solvents may be present in the cleaning agent in quantities of 0.01 to 30 wt. %, preferably of 0.2 to 15 wt. %, based on the total amount of the composition.

In preferred embodiments the composition comprises at least one bittering agent. Bittering agents are known in the field of cleaning products like laundry detergents or hard surface cleaning compositions. For example suitable bittering agents are disclosed in WO2014/026855 A1 and WO2014/026856 A1. The addition of bittering agent to the composition leads to a further increase of child safety of the product.

Examples of suitable glycosides are flavonoids such as quercetin or naringin, iridoid glycosides such as aucubin, and in particular secoiridoid glycosides such as amarogentin, dihydrofoliamentin, gentiopicroside, gentiopicrin, swertiamarin, sweroside, gentioflavosid, centaurosids, metafolin, harpagoside, and centapicine, saillcin, or condurangin.

Isoprenoids are compounds which are formally derived from isoprene. Examples are in particular terpenes and terpenoids. Examples of suitable isoprenoids include sesquiterpene lactones such as absinthin, artabsin, cnicin, lactucin, lactucopicrin, or salonitenolid, monoterpene ketones (thujones) such as alpha -thujone or beta -thujone, tetranortriterpenes (limonoids) such as deoxylimonene, deoxylimonenic acid, limonene, ichangin, isobacunonic acid, obacunone, obacunonic acid, nomilin, or nomilinic acid, and terpenes such as marrubin, premarrubin, carnosol, carnosolic acid, or quassin.

Alkaloids refer to naturally occurring, chemically heterogeneous, usually alkaline, nitrogen-containing organic compounds of the secondary metabolism which act on the animal or human organism. Examples of suitable alkaloids include quinine hydrochloride, quinine hydrogen sulfate, quinine dihydrochloride, quinine sulfate, columbin, and caffeine.

Examples of suitable amino acids include threonine, methionine, phenylalanine, tryptophan, arginine, histidine, valine, and asparagic acid.

Particularly preferred bittering agents having a bitterness value between 1,000 and 200,000 are quinine sulfate (bitterness value=10,000), naringin (bitterness value=10,000), saccharose octaacetate (bitterness value=100,000), quinine hydrochloride, and mixtures thereof.

The bitterness value is the reciprocal value of the dilution of an agent in a solvent or an extraction which barely tastes bitter.

The method to determine the bitterness value is disclosed in „Europäischen Arzneibuch (5. Ausgabe Grundwerk, Stuttgart 2005, Band 1 Allgemeiner Teil Monografiegruppen, 2.8.15 Bitterwert S. 278). In the measurement the comparative value is an aqueous solution of quinine hydrochloride whose bitterness value is determined at 200,000. This means that 1g of quinine hydrochloride turns 200 liter water bitter. The individual differences in taste in the organoleptic assessment of the bitterness are in this method balanced through a correction value.

The compositions according to the present invention can further comprise a defoamer. Defoamer are known in the field of cleaning compositions. Suitable compounds are for example disclosed in P. R. Garrett *“The Science of Defoaming”*, Taylor and Francis Group LLC, **2014**, Boca Raton, *Chapter 8* having the title “Antifoams for Detergent Products”. Especially polysiloxane compounds are preferred.

The compositions according to the present invention may furthermore comprise film formers which may assist in improving wetting of surfaces. Any film-forming polymers used in the prior art in laundry detergents and cleaning agents may in principle be considered for this purpose. Preferably, however, the film former is selected from the group comprising polyethylene glycol, polyethylene glycol derivatives and mixtures thereof, preferably with a molecular weight of between 200 and 20,000,000, particularly preferably of between 5,000 and 200,000. The film former is advantageously used in

quantities of 0.01 to 30 wt. %, in particular of 0.2 to 15 wt. %, based on the total weight of the composition.

Compositions according to the present invention may furthermore comprise one or more antimicrobial active ingredients, preferably in a quantity of 0.01 to 1 wt. %, in particular of 0.05 to 0.5 wt. %, particularly preferably of 0.1 to 0.3 wt. %, based on the total weight of the composition. Suitable antimicrobial active ingredients are for example those from the groups of alcohols, aldehydes, antimicrobial acids or the salts thereof, carboxylic acid esters, acid amides, phenols, phenol derivatives, diphenyls, diphenyl alkanes, urea derivatives, oxygen or nitrogen acetals and formals, benzamidines, isothiazoles and the derivatives thereof such as isothiazolines and isothiazolinones, phthalimide derivatives, pyridine derivatives, antimicrobial surface-active compounds, guanidines, antimicrobial amphoteric compounds, quinolines, 1,2-dibromo-2,4-dicyanobutane, iodo-2-propynyl butylcarbamate, iodine, iodophores and peroxides. Preferred antimicrobial active ingredients are preferably selected from the group comprising ethanol, n-propanol, i-propanol, 1,3-butanediol, phenoxyethanol, 1,2-propylene glycol, glycerol, undecenoic acid, citric acid, lactic acid, benzoic acid, salicylic acid, thymol, 2-benzyl-4-chlorophenol, 2,2'-methylene-bis(6-bromo-4-chlorophenol), 2,4,4'-trichloro-2'-hydroxydiphenyl ether, N-(4-chlorophenyl)-N-(3,4-dichlorophenyl)-urea, N,N'-(1,10-decanediyl-di-1-pyridinyl-4-ylidene)-bis-(1-octanamine) dihydro-chloride, N,N'-bis(4-chlorophenyl)-3,12-diimino-2,4,11,13-tetraazatetradecane diimide amide, antimicrobial quaternary surface-active compounds, guanidines. Preferred antimicrobially active surface-active quaternary compounds contain an ammonium, sulfonium, phosphonium, iodonium or arsonium group. It is furthermore also possible to use antimicrobially active essential oils which simultaneously fragrance the cleaning agent. Particularly preferred antimicrobial active ingredients are, however, selected from the group comprising salicylic acid, quaternary surfactants, in particular benzalkonium chloride, peroxide compounds, in particular hydrogen peroxide, alkali metal hypochlorite and mixtures thereof.

The compositions according to the present invention may optionally comprise water-soluble and/or water-insoluble builders. Water-soluble builders are preferred as they generally have a lesser tendency to leave insoluble residues behind on hard surfaces. Conventional builders which may be present in the composition of the invention are low molecular weight polycarboxylic acids and the salts thereof, homopolymeric and copolymeric polycarboxylic acids and the salts thereof, carbonates, phosphates and silicates. Water-insoluble builders include zeolites, which can be used, together with mixtures of the above-stated builder substances.

The compositions according to the present invention optionally comprise corrosion inhibitors for example the following substances listed by their INCI names: cyclohexylamine, diammonium phosphate, dilithium oxalate, dimethylamino methylpropanol, dipotassium oxalate, dipotassium phosphate, disodium phosphate, disodium pyrophosphate, disodium tetrapropenyl succinate, hexoxyethyl diethylammonium, phosphate, nitromethane, potassium silicate, sodium aluminate, sodium hexametaphosphate, sodium metasilicate, sodium molybdate, sodium nitrite, sodium

oxalate, sodium silicate, stearamidopropyl dimethicone, tetrapotassium pyrophosphate, tetrasodium pyrophosphate, triisopropanolamine.

The compositions according to the present invention can further optionally comprise complexing agents, which are also known as sequestrants. Complexing agents are ingredients which are capable of complexing and inactivating metal ions in order to prevent their disadvantageous effects on the stability or appearance, for example cloudiness, of the agents. On the one hand, it is important to complex the calcium and magnesium ions of water hardness which are incompatible with numerous ingredients. On the other hand, complexation of heavy metal ions such as iron or copper delays oxidative decomposition of the finished agents. Complexing agents additionally support the cleaning action. The following complexing agents, listed by their INCI names, are for example suitable: aminotrimethylene, phosphonic acid, beta-alanine diacetic acid, calcium disodium EDTA, cyclodextrin, cyclohexanediamine tetraacetic acid, diammonium citrate, diammonium EDTA, diethylenetriamine pentamethylene phosphonic acid, dipotassium EDTA, disodium azacycloheptane diphosphonate, disodium EDTA, disodium pyrophosphate, EDTA, etidronic acid, galactaric acid, gluconic acid, glucuronic acid, HEDTA, hydroxypropyl cyclodextrin, methyl cyclodextrin, pentapotassium triphosphate, pentasodium aminotrimethylene phosphonate, pentasodium ethylenediamine tetramethylene phosphonate, pentasodium pentetate, pentasodium triphosphate, pentetic acid, phytic acid, potassium citrate, potassium EDTMP, potassium gluconate, potassium polyphosphate, potassium trisphosphonomethylamine oxide, ribonic acid, sodium chitosan methylene phosphonate, sodium citrate, sodium diethylenetriamine pentamethylene phosphonate, sodium dihydroxyethylglycinate, sodium EDTMP, sodium gluceptate, sodium gluconate, sodium glycereth-1 polyphosphate, sodium hexametaphosphate, sodium metaphosphate, sodium metasilicate, sodium phytate, sodium polydimethylglycinophenolsulfonate, sodium trimetaphosphate, TEA-EDTA, TEA-polyphosphate, tetrahydroxyethyl ethylenediamine, tetrahydroxypropyl ethylenediamine, tetrapotassium etidronate, tetrapotassium pyrophosphate, tetrasodium EDTA, tetrasodium etidronate, tetrasodium pyrophosphate, tripotassium EDTA, trisodium dicarboxymethyl alaninate, trisodium EDTA, trisodium HEDTA, trisodium NTA and trisodium phosphate.

The compositions according to the present invention can optionally further comprise pH buffers, preferably alkaline materials. The bases used in agents according to the invention are preferably those from the group of alkali metal and alkaline earth metal hydroxides and carbonates, in particular sodium carbonate or sodium hydroxide. It is, however, also possible additionally to use ammonia and/or alkanolamines with 1 to 9 C atoms per molecule, preferably ethanolamines, in particular monoethanolamine.

The compositions according to the present invention can optionally further comprise bleaching agents. Suitable bleaching agents comprise peroxides, peracids and/or perborates; hydrogen peroxide is particularly preferred. Sodium hypochlorite, on the other hand, is less suitable in cleaning

agents with an acidic formulation due to the release of toxic chlorine gas vapors, can be used in alkaline cleaning agents. Under certain circumstances, a bleaching activator may be present in addition to the bleaching agent.

The compositions according to the present invention can also contain enzymes, preferably proteases, lipases, amylases, hydrolases and/or cellulases. They may be added to the composition in any form established in the prior art. In the case of agents in liquid or gel form, this in particular includes solutions of the enzymes, advantageously as concentrated as possible, with a low water content and/or combined with stabilizers. Alternatively, the enzymes may be encapsulated, for example by spray drying or extruding the enzyme solution together with a preferably natural polymer or in the form of capsules, for example those in which the enzymes are enclosed as a solidified gel or in those of the core-shell type, in which an enzyme-containing core is coated with a protective layer which is impermeable to water, air and/or chemicals. Further active ingredients, for example stabilizers, emulsifiers, pigments, bleaching agents or dyes may additionally be applied in superimposed layers. Such capsules are applied in accordance with per se known methods, for example by agitated or rolling granulation or in fluidized bed processes. Advantageously, such granules are low-dusting, for example due to the application of a polymeric film former, and stable in storage thanks to the coating.

Compositions according to the present invention containing enzymes may furthermore contain enzyme stabilizers in order to protect an enzyme present in an agent according to the invention from damage, such as for example inactivation, denaturation or disintegration, for instance due to physical influences, oxidation or proteolytic cleavage. Depending in each case on the enzyme used, suitable enzyme stabilizers are in particular: benzamidine hydrochloride, borax, boric acids, boronic acids or the salts or esters thereof, above all derivatives with aromatic groups, for instance substituted phenylboronic acids or the salts or esters thereof; peptide aldehydes (oligopeptides with a reduced C terminus), aminoalcohols such as mono-, di-, triethanol- and -propanolamine and mixtures thereof, aliphatic carboxylic acids up to C12, such as succinic acid, other dicarboxylic acids or salts of the stated acids; end group-terminated fatty acid amide alkoxylates; lower aliphatic alcohols and especially polyols, for example glycerol, ethylene glycol, propylene glycol or sorbitol; and reducing agents and antioxidants such as sodium sulfite and reducing sugars. Further suitable stabilizers are known from the prior art. Combinations of stabilizers are preferably used, for example the combination of polyols, boric acid and/or borax, the combination of boric acid or borate, reducing salts and succinic acid or other dicarboxylic acids or the combination of boric acid or borate with polyols or polyamino compounds and with reducing salts.

The composition according to the invention may optionally comprise one or more fragrances and/or one or more dyes as further ingredients. Dyes which may be used are both water-soluble and oil-soluble dyes, it being necessary on the one hand to ensure compatibility with further constituents, for example bleaching agents, and, on the other hand, that the dye used should not have a

substantive action towards the surfaces, in particular towards WC ceramics, even in the event of an extended period of action. Selection of a suitable fragrance is likewise limited only by possible interactions with the other components of the cleaning agent.

Compositions according to the invention, are preferably in the form of cleaning agents used in treating hard surfaces, in particular on ceramic sanitary ware. On the one hand, they may be used for providing a dirt-repellent finish on hard surfaces and for reducing resoiling of these surfaces, and, on the other hand, they permit more rapid and thorough cleaning of soiled surfaces.

#### Examples

Abrasive particle 1: Aluminum oxide mean particle size 300  $\mu\text{m}$

Abrasive particle 2: grinded apricot kernel mean particle size 30  $\mu\text{m}$

Components	Ex. 1	Ex. 2	Comp Ex 3
Succinoglycan gum	0.15	0.15	-
Xanthan Gum	0.15	0.15	0.30
Nonionic surfactant	1.16	1.16	1.16
Formic acid	6.4	6.4	6.4
NaOH	0.35	0.35	0.35
Abrasive particle 1	-	1.0	1.0
Abrasive particle 2	1.0	-	-
Perfume	0.2	0.2	0.2
Defoamer	0.006	0.006	0.006
Bittering agent	0.001	0.001	0.001
Water	Add to 100	Add to 100	Add to 100
<b>pH</b>	<b>2.20</b>	<b>2.20</b>	<b>2.20</b>
<b>Storage stability</b>	<b>++</b>	<b>++</b>	<b>-</b>

Storage stability was evaluated as follows the compositions were stored for 12 weeks at 0°, 25 °C and 40°C. Furthermore, for 3 days at -20 °C and for 4 weeks at 50°C. The stability was visually evaluated.

Stability excellent ++; Stability good +, stability OK o ; stability poor -, stability not given --

## Claims

1. An aqueous cleaning composition comprising
  - i) a polysaccharide polymer;
  - ii) a further polysaccharide polymer different from i);
  - iii) at least one abrasive particle having an mean particle size of 0.01 to 1000  $\mu\text{m}$ ;
  - iv) at least one acidic compound;
  - v) water;
  - vi) optionally at least one surfactant; and
  - vii) optionally at least one additive;wherein the composition has a pH of lower than 7.
2. The cleaning composition according to claim 1, wherein  
the polysaccharide polymer i) comprises a compound selected from carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan gum, xanthan gum, gellan gum, guar gum, locust bean gum, tragacanth gum.
3. The cleaning composition according to claim 2, wherein  
i) is succinoglycan gum.
4. The cleaning composition according to any of claims 1 to 3, wherein  
the polysaccharide polymer ii) comprises a compound selected from carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan gum, xanthan gum, gellan gum, guar gum, locust bean gum, tragacanth gum or combinations thereof.
5. The cleaning composition according to claim 4, wherein  
ii) is xanthan gum.
6. The cleaning composition according to any of claims 1 to 5, wherein  
iii) has an mean particle size of 1 to 500  $\mu\text{m}$  measured according to ISO13320:2009.
7. The cleaning composition according to any of claims 1 to 6, wherein  
iii) has a bulk density of 1.01 to 1.1 g/cm measured according to ISO 903: 1976-09.

8. The cleaning composition according to any of claims 1 to 7, wherein  
the at least on abrasive particle iii) comprises a compound selected from aluminum oxide, pumice, microcrystalline cellulose, silica, grinded kernels, like apricot kernel, grinded shells like, walnut shell or combinations thereof.
9. The cleaning composition according to any of claims 1 to 8, wherein  
the at least on acidic component iv) comprises a compound selected from lactic acid, phosphoric acid, sulfamic acid, hydrochloric acid, citric acid, maleic acid, acetic acid, formic acid or combinations thereof.
10. The cleaning composition according to any of claims 1 to 9, wherein the at least one surfactant vi) comprises a non-ionic surfactant or an anionic surfactant.
11. The cleaning composition according to any of claims 1 to 10, wherein  
the at least on additive vii) comprises a compound selected from perfumes, colorants, bittering agents, alkaline compounds, defoamer, thickener different from i) and ii), capsules, like dye capsules or dye microcapsules, pH buffers, antioxidants or combinations thereof.
12. The cleaning composition according to any of claims 1 to 11, wherein the composition has a viscosity of 300 to 1200 mPas measured according to DIN 51398:1983-07.
13. The cleaning composition according to any of claims 1 to 11, wherein the composition contains
  - i) 0.02 to 1 wt.-%, preferably 0.05 to 0.5 wt.-%, more preferably 0.1 to 0.2 wt.-%;
  - ii) 0.05 to 1 wt.-%, preferably 0.1 to 0.7 wt.-%, more preferably 0.2 to 0.3 wt.-%;
  - iii) 0.1 to 20 wt.-%, preferably 1 to 10 wt.-%, more preferably 3 to 6 wt.-%;
  - iv) 1 to 20 wt.-%, preferably 3 to 12 wt.-%, more preferably 4 to 9 wt.-%;
  - v) balance add to 100 wt.-%;
  - vi) 0.1 to 10 wt.-%, preferably 0.5 to 6 wt.-%, more preferably 1 to 3 wt.-%; and
  - vii) 0 to 10 wt.-%, preferably 0.001 to 7 wt.-%, more preferably 0.1 to 5 wt.-%;based on the total weight of the composition.
14. Use of the cleaning composition according to any of claims 1 to 13 for cleaning the bathroom, cleaning a toilet, or cleaning a sink.
15. A method of manufacturing the cleaning composition according to any of claims 1 to 13, comprising the steps:

- a) mixing components i), ii), iv), v) and optionally vi), and vii) as defined in any of claims 1 to 5 in a vessel using a jetstream mixer;
- b) adding component iii) as defined in any of claims 1 or 6 to 8 directly into the vessel and
- c) stirring the resulting mixture for 5 to 15 minutes.

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/079554

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C11D3/04 C11D17/00	C11D3/14 C11D3/20 C11D3/22 C11D11/00
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 808 380 A1 (PROCTER & GAMBLE [US]) 3 December 2014 (2014-12-03) paragraphs [0008], [0013] paragraphs [0125], [0126]; example 21 paragraph [0128]; example 4 -----	1,2,4-7, 9-14
X	EP 2 821 472 A1 (PROCTER & GAMBLE [US]) 7 January 2015 (2015-01-07) paragraphs [0177], [0178]; examples 29, 30 paragraph [0198]; examples 21, 22 -----	1,2,4-7, 9-12
X	WO 2011/039524 A1 (RECKITT BENCKISER LLC [US]; RECKITT BENCKISER UK LTD [UK]) 7 April 2011 (2011-04-07) examples C7, C8; table 2 ----- -/-	1,2,4-14
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :  "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search  23 January 2018		Date of mailing of the international search report  31/01/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer  Bertran Nadal, Josep

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/079554

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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