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(71) Applicant: **HENKEL AG & CO. KGAA** [DE/DE]; Henkelstr. 67, 40589 Düsseldorf (DE).

(72) Inventors: **KANDZIA, Michael**; Kleinenbergerstraße 12, 42719 Solingen (DE). **WEIDE, Mirko**; Anton-Betz-Str. 50, 40223 Düsseldorf (DE).

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(54) Title: METHOD FOR CONTROLLING MALODORS WITH REGARD TO SANITARY APPLICATIONS, USING BACTERIAL SPORES CAPABLE OF INHIBITING OR PREVENTING THE PRODUCTION OF MALODOR

(57) Abstract: The present invention relates to a method for degrading malodors in the in the area of sanitary facilities by using bacterial spores of Bacillus.

Method for controlling malodors with regard to sanitary applications, using bacterial spores capable of inhibiting or preventing the production of malodor

The present invention generally relates to a method for degrading malodors in the in the area of sanitary ware.

Malodor is a growing problem, particularly in the kitchen, bathroom or toilet, because hard surfaces which are repeatedly exposed to the action of moisture are frequently colonized by microorganisms, resulting in the formation of biofilms. Biofilms consist of a mucilaginous layer (film) in which microorganisms (for example bacteria, algae, fungi, protozoa) are embedded. This may constitute a problem of not only a hygienic but also an esthetic and olfactive nature. Biocidal substances are frequently used as countermeasures. However, this is not always without its own problems due to the ecotoxicological properties of many of these substances and the associated restrictions on their use. Biofilms contribute to the formation of unpleasant smelling substances and are therefore a source of unwanted malodors, in particular in sanitary applications.

An important consumer requirement, therefore consists in the elimination or at least diminution of malodors (i.e. off-odors) or undesired odors. Off-odors derive from specific olfactorily active compounds that are also referred to as "malodorants." Malodorants are foul-smelling compounds having so-called kakosmophoric groups, e.g. amine derivatives and sulfur derivatives. The presence of such off-odors generally results in a negative effect on human comfort, and for that reason the consumer makes an effort to extinguish these odors. Often, however, the off-odors are not extinguished but merely masked. It is usual to use for this purpose products that contain volatile, usually pleasant-smelling substances, and that even in small quantities can mask foul odors.

These solutions, however, are not completely effective as they are short-term. There is a need in the art for new solutions for controlling the problem of malodor.

It is therefore the object of the present invention to provide the consumer with a further capability for bringing about an inhibition, degradation or prevention of malodors.

The present invention provides a method of inhibiting or preventing the production of malodor with regard to sanitary applications, comprising contacting hard surfaces of sanitary facilities with bacterial spores of at least one species of *Bacillus*, which is selected from the group consisting of

Bacillus amyloliquefaciens, Bacillus tequilensis, Bacillus subtilis, Bacillus atrophaeus, Bacillus vallismortis and/or Bacillus mojavensis.

The Bacillus species mentioned above or mixtures of those are commercially available as Freshen Herbal® and Drain Ease Open® from Novozymes A/S, Denmark, and UBFE Kultur® and WC Kultur® from Julius Hoesch GmbH & Co.KG, 52353 Düren-Hoven, Germany.

The contacting can occur before, during, or after a cleaning process. Preferably sanitary applications are contacted with the bacterial spores during a cleaning process.

Combinations of bacterial spores of such species and/or isolates may also be used, such as blends of two or more species and/or isolates, three or more species and/or isolates, etc. Preferred are combinations comprising spores of Bacillus subtilis and Bacillus mojavensis. Also preferred are combinations comprising spores of Bacillus subtilis and Bacillus atrophaeus and/or Bacillus vallismortis.

The present invention also provides the use of said bacterial spores for inhibiting malodor on hard surfaces of sanitary facilities, in particular in cleaning agents for sanitary installations.

The methods and compositions of the present invention may be used to treat an existing odor problem and/or as a preventative treatment to prevent a potential odor problem. The present invention may be used, for example, to inhibit malodor in bathrooms, toilets, bidets, and closets.

Malodor may be generated from a number of sources, mostly microbial and in particular bacterial sources (including compounds derived or produced therefrom). Different surfaces or surfaces in different environments cause different habitats for microorganisms in household and household appliances. Important factors of influence on the microorganism habitat are the types of surface, such as textile, hard surfaces of plastic or ceramic, and sponges, the amounts of humidity, the sources of nutrients and their availabilities, growth conditions, and environmental sources of microbial contamination. While in most household surfaces waterborne germs, mainly gram negative bacteria, play a role, sanitary environments additionally are prone to infestation by enterobacteria, such as Salmonella, Escherichia coli, Klebsiella, Shigella, Proteus, Enterobacter, Serratia, and Citrobacter. The current invention is capable to inhibit or prevent the production of malodor of such sources, so that preferred embodiments of the invention relate to inhibiting or preventing the production of malodor caused by enterobacteria and/or substances derived therefrom.

The ability to prepare spores and vegetative cells is considered routine in the art. See Tzeng, Y. M., Y. K. Rao, et al. (2008). "Effect of cultivation conditions on spore production from *Bacillus amyloliquefaciens* B128 and its antagonism to *Botrytis elliptica*." *Journal of Applied Microbiology* 104(5): 1275-1282.

Compositions of the invention comprise bacterial spores as described herein. The bacterial spores should be present in effective amounts. The terms "effective amount", "effective concentration" or "effective dosage" are defined herein as the amount, concentration or dosage of odor-controlling bacterial spores that can inhibit the malodor caused by the odor causing organism or substances derived therefrom. The actual effective dosage in absolute numbers depends on factors including: the odor causing organisms(s) in question; whether the aim is prevention or reduction of malodor; other ingredients present in the composition, and also the hard surfaces in question.

In an embodiment an effective dosage of the bacterial spores of the strains as described herein would be introduced to a cleaning agent at a final concentration of 1×10^2 - 1×10^9 CFU/g of cleaning agent, with a preferred range of 1×10^3 - 1×10^6 CFU/g of cleaning agent.

Effective amounts can be determined by one skilled in the art using routine assays.

The bacterial spores of the invention can be used in combination with or as an ingredient of an agent for treating hard surfaces, such as cleaning agents in particular, including but not limited to aerosols, powders, solids, foams, creams, etc., for use, e.g., in cleaning sanitary installations.

An aspect of the present invention also includes cleaning compositions or compositions for use in cleaning processes which comprise bacterial spores described herein and a carrier. The composition may be in the form of a solid, semi-solid, gel, liquid, aerosol, emulsion, and/or powder. The bacterial spores are of at least one species of *Bacillus*, which is selected from the group consisting of *Bacillus amyloliquefaciens*, *Bacillus tequilensis*, *Bacillus subtilis*, *Bacillus atrophaeus*, *Bacillus vallismortis* and/or *Bacillus mojavensis*.

The compositions may in particular embodiments comprise blends of bacterial spores of two or more of such species and/or isolates, including at least two, at least three or more species and/or isolates of the bacterial spores described herein.

The compositions of the present invention may in an embodiment have a pH in the range of 5-10 and may further include water and/or one or more preservatives. For preservation of compositions comprising bacterial spores of *Bacillus amyloliquefaciens*, for example, the following preservatives can be useful: chloromethylisothiazolinone/methylisothiazolinone (CMIT/MIT) (Kathon or others);

MIT (Neolone or others); 1,2-benzisothiazolin-3-one (BIT) (if allowed in personal care); CMIT/MIT + EDTA; CMIT/MIT + Biodegradable Chelator; MIT + EDTA; MIT + Biodegradable Chelator; BIT + EDTA; BIT + Biodegradable Chelator; Bronopol; 2-Phenoxyethanol; 2-Phenoxyethanol + Biodegradable Chelator; Potassium sorbate (used at low pH); Sodium benzoate (used at low pH); Salt; Glycerol; Propylene Glycol; Essential Oils; Dichlorobenzyl alcohol; Triclosan; Parabens; and 1-Phenoxy-2-propanol and 2-Phenoxy-1-propanol. In an embodiment, the preservative is 2-Phenoxyethanol; 2-Phenoxyethanol + Biodegradable Chelator; Potassium Sorbate (used at low pH); Sodium Benzoate (used at low pH); Salt; Glycerol; Propylene Glycol; or one of more Essential Oils - e.g., white mustard seed, tea tree, rosewood, or some citrus oils. In another embodiment, the preservative is 2-Phenoxyethanol; 2-Phenoxyethanol + Biodegradable Chelator; or Glycerol. Accordingly, an embodiment of the present invention is directed to a composition comprising bacterial spores as described herein and a preservative selected from the group consisting of chloromethylisothiazolinone/ methylisothiazolinone (CMIT/MIT) (Kathon or others); MIT (Neolone or others); 1,2-benzisothiazolin-3-one (BIT) (if allowed in personal care); CMIT/MIT + EDTA; CMIT/MIT + Biodegradable Chelator; MIT + EDTA; MIT + Biodegradable Chelator; BIT + EDTA; BIT + Biodegradable Chelator; Bronopol; 2-Phenoxyethanol; 2-Phenoxyethanol + Biodegradable Chelator; Potassium sorbate (used at low pH); Sodium benzoate (used at low pH); Salt; Glycerol; Propylene Glycol; Essential Oils; Dichlorobenzyl alcohol; Triclosan; Parabens; and 1-Phenoxy-2-propanol and 2-Phenoxy-1-propanol. In an embodiment, the preservative is 2-Phenoxyethanol; 2-Phenoxyethanol + Biodegradable Chelator; Potassium Sorbate (used at low pH); Sodium Benzoate (used at low pH); Salt; Glycerol; Propylene Glycol; or one of more Essential Oils - e.g., white mustard seed, tea tree, rosewood, or some citrus oils, 2-Phenoxyethanol; 2-Phenoxyethanol + Biodegradable Chelator; or Glycerol, and wherein the composition is a liquid, solid or gel composition.

A composition of the invention may be in solid or liquid form. The composition may be a concentrate to be diluted, rehydrated and/or dissolved in a solvent, including water, before use. The composition may also be a ready-to-use (in-use) composition. The composition may furthermore be an active cleaning base ingredient to be incorporated into other cleaning compositions (cleaning agents).

Preferred embodiments of the present invention encompass cleaning agents comprising bacterial spores described herein.

Cleaning agents of the invention can furthermore contain other usual constituents of cleaning agents, in particular builders, surfactants, polymers, enzymes, disintegration adjuvants, scents, and perfume carriers.

For the purposes of the present invention, hard surfaces in particular comprise surfaces of stone or ceramic materials, rigid plastics materials, glass or metal. Hard surfaces may be, for example, walls, flooring or sanitary articles. In particular, the use, methods, and compositions of the invention relate to sanitary ware with ceramic surfaces, and very particularly to toilet bowls.

Embodiments of the present invention encompass any presentations of the agents according to the invention which are established in the prior art and/or are convenient. These include for example solid, pulverulent, liquid, gel-form or pasty agents, optionally also comprising two or more phases, compressed or uncompressed; they furthermore include extrudates, granules, tablets or pouches, packaged both in large containers and in portions.

An agent according to the invention is preferably a toilet cleaner, a bathroom cleaner or a multipurpose cleaner. When used as a toilet cleaner, the agent according to the invention preferably has a pH value of 1 to 5, in particular of 1 to 3; when used as a bathroom cleaner it preferably has a pH value of 1 to 6, in particular of 3 to 5; and when used as a multipurpose cleaner it preferably has a pH value of 8 to 12, in particular of 9 to 11.

Methods suitable for treating a surface are any conventional methods with which the agent may be applied onto the surface. For the particularly preferred case in which the agent is liquid at room temperature, the surface is preferably treated by the agent being transferred onto the surface with the assistance of an absorbent fabric or by the agent being sprayed onto the surface. However, treatment may, for example, also proceed by immersing the surface in the agent.

For the purposes of the invention, dirt or soiling should in particular be taken to mean fecal soiling and/or biofilms.

The further components present in the agents according to the invention should be selected in accordance with their nature and the quantity used such that no undesired interactions occur with the polymers to be used according to the invention.

Anionic surfactants which are preferably suitable are C8-C18 alkylbenzene sulfonates, in particular with around 12 C atoms in the alkyl moiety, C8-C20 alkane sulfonates, C8-C18 monoalkyl sulfates, C8-C18 alkyl polyglycol ether sulfates with 2 to 6 ethylene oxide units (EO) in the ether moiety and sulfosuccinic acid mono- and di-C8-C18-alkyl esters. It is furthermore also possible to use C8-C18 α -olefin sulfonates, sulfonated C8-C18 fatty acids, in particular dodecylbenzenesulfonate, C8-C22 carboxylic acid amide ether sulfates, C8-C18 alkyl polyglycol ether carboxylates, C8-C18 N-acyl taurides, C8-C18-N-sarcosinates and C8-C18 alkyl isethionates or mixtures thereof. The anionic surfactants are preferably used as sodium salts, but may also be present as other alkali or alkaline

earth metal salts, for example magnesium salts, and in the form of ammonium or mono-, di-, tri- or tetraalkylammonium salts, in the case of sulfonates, also in the form of their corresponding acid, for example dodecylbenzenesulfonic acid. Examples of such surfactants are sodium cocoalkyl sulfate, sodium sec.-alkanesulfonate with approx. 15 C atoms and sodium dioctylsulfosuccinate. Sodium fatty alkyl sulfates and fatty alkyl+2EO ether sulfates with 12 to 14 C atoms have proved particularly suitable.

Nonionic surfactants which may primarily be mentioned are C8-C18 alcohol polyglycol ethers, i.e. ethoxylated and/or propoxylated alcohols with 8 to 18 C atoms in the alkyl moiety and 2 to 15 ethylene oxide (EO) and/or propylene oxide (PO) units, C8-C18 carboxylic acid polyglycol esters with 2 to 15 EU, for example tallow fatty acid+6 EO esters, ethoxylated fatty acid amides with 12 to 18 C atoms in the fatty acid moiety and 2 to 8 EO, long-chain amine oxides with 14 to 20 C atoms and long-chain alkyl polyglycosides with 8 to 14 C atoms in the alkyl moiety and 1 to 3 glycoside units. Examples of such surfactants are oleyl-cetyl alcohol with 5 EO, nonylphenol with 10 EO, lauric acid diethanolamide, cocoalkyl dimethylamine oxide and cocoalkyl polyglucoside with on average 1.4 glucose units. C8-18 fatty alcohol polyglycol ethers with in particular 2 to 8 EO, for example C12 fatty alcohol+7-EO ether, and C8-10 alkyl polyglucosides with 1 to 2 glycoside units are particularly preferably used.

In a preferred embodiment of the invention, the nonionic surfactant is selected from the group comprising polyalkylene oxides, in particular alkoxyated primary alcohols, the polyalkylene oxides possibly also being end group-terminated, alkoxyated fatty acid alkyl esters, amine oxides and alkyl polyglycosides and mixtures thereof.

Suitable amphoteric surfactants are for example betaines of the formula $(R^{iii})(R^{iv})(R^v)N^+CH_2COO^-$, in which R^{iii} means an alkyl residue with 8 to 25, preferably 10 to 21 carbon atoms optionally interrupted by heteroatoms or groups of heteroatoms and R^{iv} and R^v mean identical or different alkyl residues with 1 to 3 carbon atoms, in particular C10-C18 alkyl dimethyl carboxymethyl betaine and C11-C17 alkyl amidopropyl dimethyl carboxymethyl betaine.

Suitable cationic surfactants are inter alia the quaternary ammonium compounds of the formula $(R^{vi})(R^{vii})(R^{viii})(R^{ix})N^+X^-$, in which R^{vi} to R^{ix} denote four identical or different, in particular two long-chain and two short-chain, alkyl residues and X^- denotes an anion, in particular a halide ion, for example didecyldimethylammonium chloride, alkylbenzylididecylammonium chloride and mixtures thereof.

In a preferred embodiment, however, the only surfactant components the agent contains are one or more anionic surfactants, preferably C8-C18 alkyl sulfates and/or C8-C18 alkyl ether sulfates,

and/or one or more nonionic surfactants, preferably C8-18 fatty alcohol polyglycol ethers with 2 to 8 EO and/or C8-10 alkyl polyglucosides with 1 to 2 glycoside units.

In a particularly preferred embodiment of the invention, the agents according to the invention contain at least one nonionic surfactant, which is/are in particular selected from ethoxylated and/or propoxylated alcohols with 8 to 18 C atoms in the alkyl moiety and 2 to 15 ethylene oxide (EO) and/or propylene oxide (PO) units and alkyl polyglycosides with 8 to 14 C atoms in the alkyl moiety and 1 to 3 glycoside units.

The agents according to the invention preferably contain surfactants in quantities of 0.01 to 20 wt. %, in particular of 0.05 to 10 wt. %, preferably of 0.1 to 5 wt. % and particularly preferably of 0.2 to 1 wt. %, in each case relative to the total weight of the agent.

The agents according to the invention contain water and/or at least one nonaqueous solvent. Nonaqueous solvents which may preferably be considered are those solvents which are water-miscible in any desired ratio. The nonaqueous solvents include, for example, mono- or polyhydric alcohols, alkanolamines, glycol ethers and mixtures thereof. 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 nonaqueous solvent.

Nonaqueous solvents may be present in the agents according to the invention in quantities of 0.01 to 99.9 wt. %, in particular of 0.1 to 50 wt. %, and particularly preferably of 2 to 20 wt. %, in each case relative to the total weight of the agent.

Water is present in the agents according to the invention in quantities of 1 to 98 wt. %, in particular of 50 to 95 wt. %, and particularly preferably of 80 to 93 wt. %, in each case relative to the total weight of the agent.

In a further preferred embodiment, the agent according to the invention contains a thickener. Any viscosity regulators used in the prior art in washing and cleaning agents may in principle be considered for this purpose, such as for example organic natural thickeners (agar-agar, carrageenan, tragacanth, gum arabic, guar gum, gellan gum, xanthan gum, alginates, pectins, polyoses, guar flour, locust bean flour, starch, dextrans, gelatin, casein), modified organic natural substances (carboxymethylcellulose and other cellulose ethers, hydroxyethylcellulose and

hydroxypropylcellulose and the like, seed flour ethers as well as further derivatives of polysaccharides and heteropolysaccharides), 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). In a preferred embodiment, the agent according to the invention contains xanthan gum and succinoglycan gum.

If the agent according to the invention contains a thickener, the latter is generally present in quantities of 0.01 to 30 wt. %, in particular of 0.2 to 15 wt. %.

Depending on the intended application, the viscosity of the agents according to the invention may be adjusted within a wide range. Accordingly, low viscosity, virtually watery formulations may be preferred for multipurpose and bathroom cleaners, while higher viscosity, thickened formulations may be preferred for other applications, for example cleaning agents. In general, the viscosity of the agents according to the invention is in the range from 1 to 3,000 mPa·s, preferably from 200 to 1,500 mPa·s and particularly preferably from 400 to 900 mPa·s (Brookfield Rotovisco LV-DV II plus viscometer, spindle 31, 20° C., 20 rpm).

In a preferred embodiment, the agent according to the invention has a pH value of less than 9, in particular a pH value of 0 to 6, preferably of 1 to 5 and particularly preferably of 2 to 4.

In a further, particularly preferred embodiment the agent according to the invention contains at least one acid. Suitable acids are in particular organic acids such as formic acid, acetic acid, citric acid, glycolic acid, lactic acid, succinic acid, adipic acid, malic acid, tartaric acid and gluconic acid or also amidosulfonic acid. It may, however, be preferred for acetic acid not to be used as the acid. The inorganic acids hydrochloric acid, sulfuric acid, phosphoric acid and nitric acid or mixtures thereof may, however, additionally be used. 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. %, in each case relative to the total weight of the agent.

The agents according to the invention may furthermore contain other conventional components of agents, in particular cleaning agents, for treating hard surfaces, provided that these do not interact in undesired manner with the substances used according to the invention.

Other such components which may for example be considered are further acids, salts, film formers, antimicrobial active ingredients, builders, corrosion inhibitors, complexing agents, sequestering agents, electrolytes, foam inhibitors, disintegration auxiliaries, soil-release active ingredients or soil-

repellents, UV absorbers, alkalis, preservatives, bleaching agents, bleach activators, bleach catalysts, enzymes, enzyme stabilizers, abrasives, polymers together with fragrances and dyes. Overall, the agents should preferably contain no more than 30 wt. %, preferably 0.01 to 30 wt. %, in particular 0.2 to 15 wt. % of further ingredients.

The agents according to the invention may contain 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. %.

Agents according to the invention may furthermore contain 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. %. 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. It is furthermore also possible to use antimicrobially active essential oils which simultaneously fragrance the cleaning agent.

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

Suitable corrosion inhibitors are 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.

Complexing agents, which are also known as sequestrants, 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, Citric Acid, 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.

Agents according to the invention may furthermore contain alkalis. 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 up to 9 C atoms per molecule, preferably ethanolamines, in particular monoethanolamine.

Agents according to the invention may likewise contain preservatives. The substances stated in relation to the antimicrobial active ingredients may essentially be used for this purpose.

According to the invention, the agents may furthermore contain 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, but may be used in alkaline cleaning agents. Under certain circumstances, a bleach activator may be present in addition to the bleaching agent.

The agent according to the invention may also contain enzymes, preferably proteases, lipases, amylases, hydrolases and/or cellulases. They may be added to the agent 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 polymeric film formers, and stable in storage thanks to the coating.

Agents 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 agent according to the invention may finally contain 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 toilet ceramics, even in the event of an extended period of action. Selection of a suitable scent is likewise limited only by possible interactions with the other components of the cleaning agent.

A cleaning product for hard surfaces according to the invention may also contain one or more propellants (INCI Propellants), conventionally in a quantity of 1 to 80 wt. %, preferably of 1.5 to 30 wt. %, in particular of 2 to 10 wt. %, particularly preferably of 2.5 to 8 wt. %, extremely preferably of 3 to 6 wt. %.

The present invention also provides a product containing a cleaning product for hard surfaces according to the invention and a spray dispenser. The product may here be both a single chamber and a multichamber container, in particular a two-chamber container. The spray dispenser is here preferably a manually actuated spray dispenser, in particular selected from the group encompassing aerosol spray dispensers (pressurized gas container; also inter alia known as a spray can), self-pressurizing spray dispensers, pump spray dispensers and trigger spray dispensers, in particular pump spray dispensers and trigger spray dispensers with a container made from transparent polyethylene or polyethylene terephthalate. Trigger spray dispensers and pump atomizers have the advantage over pressurized gas containers that no propellant need be used. Suitable attachments, nozzles etc. ("nozzle-valves") on the spray dispenser through which particles can pass mean that an optionally present enzyme may in this embodiment optionally also be added to the agent in a form immobilized on particles and accordingly be dispensed as a cleaning foam.

The agent according to the invention is preferably a cleaning agent, in particular a cleaning agent for ceramics, particularly preferably for ceramic sanitary ware.

The agent according to the invention may be produced in a manner conventional in the art by suitably mixing the components present in the agent with one another.

The present invention accordingly also provides a method for producing an agent according to the invention, in which the individual components are mixed with one another.

The present invention also provides a method for treating a hard surface, in which the surface is brought into contact with an agent according to the invention, as described in the preceding text.

This method may be carried out as an independent treatment method for the surface, for example in order to provide it with malodor-reducing properties or one or more of the other properties brought about by the agents according to the invention in accordance with the teaching of the present invention. The surface is here brought into contact with an agent according to the invention.

The method according to the invention is preferably carried out in such a manner that the agent is distributed over the surface and advantageously then either rinsed off after a period of action of 1 second to 20 minutes, preferably of 1 to 10 minutes, or alternatively left to dry.

In a preferred embodiment of the method, contacting proceeds at a temperature of 5 to 50° C., in particular of 15 to 35° C.

In a particularly preferred embodiment, the method according to the invention is a cleaning method which serves for surface cleaning.

In particular, the method according to the invention serves for treating a surface of ceramics, glass, stainless steel or plastics material.

Another embodiment of the invention relates to the use of an agent according to the invention for protecting a hard surface from soiling and/or for easier detachment of renewed soiling from the surface, the soiling in particular involving fecal soiling and/or biofilms and/or protein deposits.

In a preferred embodiment of the invention, agents according to the invention serve for the improved removal of fecal soiling and/or biofilms from the surfaces of flush toilets and/or for reducing renewed soiling of such surfaces with fecal soiling and/or biofilms. To this end, the agent is advantageously distributed over the surface and either rinsed off after a period of action of preferably 1 to 10 minutes or alternatively left to dry. Once the surface has been treated in this manner, fecal soiling is easier to remove, often without the assistance of mechanical aids, such as for instance a toilet brush. Any dried on cleaning agent residues may additionally be rinsed away more easily.

Another embodiment of the invention relates to the use of an agent according to the invention for providing a water-repellent finish on a hard surface and/or for shortening the drying time of a hard surface after exposure to water.

For cleaning reasons, it is on the one hand more favorable for surfaces to comprise hydrophilic properties, since such surfaces can readily be wetted with conventional water-based cleaning

fluids, so facilitating washing processes. On the other hand, it is also desired for the surfaces, once they have been cleaned with water or with water-based cleaning agents, to be free of the film of water again as quickly as possible, i.e. for the water to drain away as quickly and completely as possible, so that no film of water remains on the surface. Otherwise, when the film of water dries out, residual soiling may remain on the surface, such as for example lime deposit, which looks unattractive and may promote renewed soiling, for example also due to proteins and microorganisms. For this reason, it is highly advantageous that treating a surface with the agents according to the invention renders this surface hydrophilic. This facilitates wetting and detachment of dirt and simultaneously ensures that the surface is readily "dewetted" of a film of water, so avoiding water drops being formed and residual soiling being left behind. This property is particularly beneficial where surfaces are particularly exposed to lime and dirt and biofilm deposits, such as typically toilet bowls, washbasins, bathtubs and shower cubicles. Another advantage of this property is that water drains away faster from treated surfaces and these consequently dry more quickly. In a cleaning process, rinsing with clean water is generally required after treating the surface with cleaning product. It is desirable for the surfaces to dry quickly after this rinsing, for example because a quickly drying surface enhances the consumer's impression of cleanliness.

The present invention also provides the use of an agent according to the invention for providing a bacteriostatic finish on a hard surface.

One particular advantage of the invention is that colonization by and the growth of microorganisms is suppressed on surfaces treated therewith, without biocides being required for this purpose. In this manner, a surface finish is obtained on which bacterial multiplication is prevented or substantially delayed. This is a distinct advantage relative to the prior art, in particular in the light of the fact that the use of biocides is regarded increasingly more critically with regard to environmental and consumer protection.

Another embodiment of the invention accordingly relates to the use of bacterial spores according to the invention for providing a bacteriostatic finish on a hard surface.

Bathroom cleaners which are particularly preferred according to the invention comprise:

- (a) 0.5 to 12 wt. %, preferably 1 to 10 wt. % and in particular 2 to 8 wt. % of an organic acid and/or of a salt of organic acids preferably selected from formic acid, citric acid, lactic acid and mixtures thereof and salts of these organic acids;
- (b) 0.1 to 5 wt. %, preferably 0.2 to 4 wt. % and in particular 0.5 to 3 wt. % of surfactant(s), preferably nonionic and/or anionic surfactant(s), particularly preferably nonionic surfactant(s), in particular alkyl polyglycoside(s);
- (c) 0.1 to 5 wt. %, preferably 0.2 to 4 wt. % and in particular 0.5 to 3 wt. % of thickeners; and

(d) 0.01 to 5 wt. %, preferably 0.02 to 4 wt. % and in particular 0.05 to 3 wt. % of at least two polymers selected from the group consisting of a multi-armed polyalkoxylate, in particular silyl polyalkoxylate, a polyesteramide and a copolymer prepared from a quaternary ammonium acrylamide and acrylic acid;

wherein the cleaners have a pH value of 1 to 6, preferably of 3 to 5.

Toilet cleaners which are particularly preferred according to the invention comprise:

(a) 0.5 to 12 wt. %, preferably 1 to 10 wt.% and in particular 2 to 8 wt. % of an organic acid and/or of a salt of organic acids preferably selected from formic acid, citric acid, lactic acid and mixtures thereof and salts of these organic acids;

(b) 0.1 to 5 wt. %, preferably 0.2 to 4 wt. % and in particular 0.5 to 3 wt. % of surfactant(s), preferably nonionic and/or anionic surfactant(s), particularly preferably nonionic surfactant(s), in particular alkyl polyglycoside(s);

(c) 0.1 to 5 wt. %, preferably 0.2 to 4 wt. % and in particular 0.5 to 3 wt. % of thickeners; and

(d) 0.01 to 5 wt. %, preferably 0.02 to 4 wt. % and in particular 0.05 to 3 wt. % of at least two polymers selected from the group consisting of a multi-armed polyalkoxylate, in particular silyl polyalkoxylate, a polyesteramide and a copolymer prepared from a quaternary ammonium acrylamide and acrylic acid;

wherein the cleaners have a pH value of 1 to 5, preferably of 1 to 3.

Multipurpose cleaners which are particularly preferred according to the invention comprise:

(a) 0.05 to 5 wt. %, preferably 0.1 to 2 wt. % and in particular 0.2 to 1 wt. % of an organic acid and/or of a salt of organic acids, preferably selected from formic acid, citric acid, lactic acid and mixtures thereof and salts of these organic acids;

(b) 0.1 to 8 wt. %, preferably 0.2 to 6 wt. % and in particular 0.5 to 5 wt. % surfactant(s), preferably nonionic and/or anionic surfactant(s), particularly preferably sulfate(s), sulfonate(s), fatty alcohol ethoxylate(s), alkyl polyglycoside(s) or mixtures thereof;

(c) 0.1 to 8 wt. %, preferably 0.5 to 6 wt. % and in particular 1 to 5 wt. % of fatty acid(s), in particular of C12-18 fatty acid(s), and/or of a salt thereof; 0.1 to 6 wt. %, preferably 0.2 to 5 wt. % and in particular 0.5 to 4 wt. % of an organic solvent, in particular ethanol; and

(d) 0.01 to 5 wt. %, preferably 0.02 to 4 wt. % and in particular 0.05 to 3 wt. % of at least two polymers selected from the group consisting of a multi-armed polyalkoxylate, in particular silyl polyalkoxylate, a polyesteramide and a copolymer prepared from a quaternary ammonium acrylamide and acrylic acid;

wherein the cleaners have a pH value of 8 to 12, preferably of 9 to 11.

EXAMPLES

Odor Mitigation in toilets by bacterial spores

Biofilms were grown in DURAN flasks (500 ml) using bacteria from toilets. Biofilms were activated by wetting and contacted for 60 minutes with cleaning agents and spores to be tested. Test preparations and controls (water only, cleaning agent only) were incubated for up to 3 days (72 hours) at room temperature.

Persons trained in olfaction smelled the biofilms when fresh, after 1 day, after 2 days and after 3 days and rated the intensity of the malodor on a scale of 0 to 3 (0 being no odor, 1 = weak odor, 2 = moderate odor, and 3 = strong odor).

The results after 1 day are presented in Tables 1 and 2:

Table 1: Malodor score

Control (without spores, water only)	Control (without spores, cleaning agent only, dilution 10g/l)	With spores isolated from Freshen Herbal®, dosage 1x10 ⁶ CFU/g	With spores isolated from Freshen Herbal®, dosage 1x10 ⁶ CFU/g in cleaning agent, dilution 10g/l
1.3	1.0	0.3	0.6

Table 2: Malodor score

Control (without spores, water only)	Control (without spores, cleaning agent only, dilution 10g/l)	With spores isolated from Drain Ease Open®, dosage 1x10 ⁶ CFU/g	With spores isolated from Drain Ease Open®, dosage 1x10 ⁶ CFU/g in cleaning agent, dilution 10g/l
1.3	1.0	0.1	0.4

The results show the significantly improved performance of the inventive use of bacterial spores for the elimination of malodors.

While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention, it being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims and their legal equivalents.

Claims

1. Method of inhibiting or preventing the production of malodor with regard to sanitary applications, comprising contacting hard surfaces of sanitary facilities with bacterial spores of at least one species of *Bacillus*, which is selected from the group consisting of *Bacillus amyloliquefaciens*, *Bacillus tequilensis*, *Bacillus subtilis*, *Bacillus atrophaeus*, *Bacillus vallismortis* and/or *Bacillus mojavensis*.
2. Method according to claim 1, wherein the method comprises contacting hard surfaces of sanitary facilities with combinations of bacterial spores of one or more of the strains of claim 1, in particular blends of two or more strains, three or more strains, four or more strains or five or more strains.
3. The method according to claim 1 or 2, wherein the malodor is caused by enterobacteria and/or substances derived therefrom.
4. Composition for inhibiting or preventing the production of malodor for sanitary applications, comprising bacterial spores of at least one species of *Bacillus*, which is selected from the group consisting of *Bacillus amyloliquefaciens*, *Bacillus tequilensis*, *Bacillus subtilis*, *Bacillus atrophaeus*, *Bacillus vallismortis* and/or *Bacillus mojavensis*.
5. Composition according to claim 4 for use as a cleaning composition for hard surfaces, in particular surfaces of sanitary facilities, which further comprises a carrier.
6. Use of bacterial spores of at least one species of *Bacillus*, which is selected from the group consisting of *Bacillus amyloliquefaciens*, *Bacillus tequilensis*, *Bacillus subtilis*, *Bacillus atrophaeus*, *Bacillus vallismortis* and/or *Bacillus mojavensis*, for inhibiting malodor on hard surfaces of sanitary facilities.
7. Use of bacterial spores of at least one species of *Bacillus*, which is selected from the group consisting of *Bacillus amyloliquefaciens*, *Bacillus tequilensis*, *Bacillus subtilis*, *Bacillus atrophaeus*, *Bacillus vallismortis* and/or *Bacillus mojavensis*, in cleaning agents for sanitary installations for inhibiting malodor.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/055631

A. CLASSIFICATION OF SUBJECT MATTER
INV. C12R1/07 C12R1/125 C11D3/00 C11D3/38
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)
C12R C11D C12N
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		
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X	EP 2 759 590 A1 (POLLET SA [BE]) 30 July 2014 (2014-07-30) claims 1,2,15 page 5, paragraphs 0030,0037 page 3, paragraph 0008 page 2, paragraph 0002 page 12, paragraph 0063	1-7
X	WO 00/63338 A1 (SPARTAN CHEMICAL COMPANY INC [US]) 26 October 2000 (2000-10-26) page 1, paragraph 3; claim 1 page 2, last paragraph - page 3, paragraph 1 page 9, last paragraph - page 10, paragraph 1 page 11, paragraph 2	1-7
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Further documents are listed in the continuation of Box C. 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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 24 May 2017	Date of mailing of the international search report 01/06/2017
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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 Gault, Nathalie
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	<p>DATABASE WPI Week 201363 Thomson Scientific, London, GB; AN 2013-P03028 XP002761779, -& CN 103 031 253 A (SHANGHAI ECO-WELL BIOSCIENCE CO LTD) 10 April 2013 (2013-04-10) abstract page 4, paragraph 0003</p> <p style="text-align: center;">-----</p>	1-7

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Information on patent family members

International application No

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