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(54) [Title of Invention] STERILIZING CLEANER COMPOSITION FOR HARD SURFACES

(57) [Abstract]

[Problem] Provided is a sterilizing cleaner composition for hard surfaces that exhibits high sterilization effect against spore-forming bacteria and mold.

[Resolution Means] A sterilizing cleaner composition for hard surfaces, containing water and an organic peracid obtained by reacting (A) an ester of a polyhydric alcohol and an organic acid with (B1) hydrogen peroxide in a specific molar ratio in water at a pH of 8 to 12, and having a pH of 1 or more and less than 7 at 25°C.

[Selected Drawing] None

CLEAN CHEMISTRY EXH 1013
IPR2025-01458

[Scope of Patent Claims]

[Claim 1]

A sterilizing cleaner composition for hard surfaces, comprising water and an organic peracid obtained by reacting (A) an ester of a polyhydric alcohol and an organic acid having a hydrocarbon group that may have a hydroxyl group and (B1) hydrogen peroxide in water at a molar ratio of $(A)/(B1) = 1/10$ to $20/1$ and at a pH of 8 to 12, and which has a pH of 1 or more to 7 or less at 25°C.

[Claim 2]

The sterilizing cleaner composition for hard surfaces according to claim 1, wherein a hydrogen peroxide content is 0.5 wt% or less.

[Claim 3]

The sterilizing cleaner composition for hard surfaces according to claim 1 or 2, wherein the organic acid constituting (A) is a fatty acid having 1 to 8 carbon atoms.

[Claim 4]

The sterilizing cleaner composition for hard surfaces according to any one of claims 1 to 3, further comprising a surfactant.

[Claim 5]

The sterilizing cleaner composition for hard surfaces according to claim 4, wherein the surfactant is at least one type selected from the group consisting of anionic surfactants and nonionic surfactants.

[Claim 6]

A method for producing a sterilizing cleaner composition for hard surfaces, comprising steps for reacting (A) an ester of a polyhydric alcohol and an organic acid having a hydrocarbon group, which may have a hydroxyl group, and (B1) hydrogen peroxide in a molar ratio of $(A)/(B1) = 1/10$ to $20/1$ in water at a pH of 8 to 12, and then adjusting the pH of the reaction system to 1 or higher but less than 7.

[Detailed Description of Invention]

[Technical Field]

[0001]

The present invention relates to a sterilizing cleaner composition for hard surfaces that is suitable for sterilizing and cleaning hard surfaces such as plastics, metals, glass, and tiles.

[Background Art]

[0002]

There are many facilities where a hygienic environment is desired, such as food production plants, pharmaceutical production plants, hospitals, nursing homes, kitchens, bathrooms, and the like. In such cases, careful sterilization of floors, walls, and equipment used and the like is essential in order to maintain a hygienic environment.

[0003]

cleaners, sterilizing agents, and sterilizing cleaners for liquids or powders that contain surfactants, sterilizing agents, and the like are mainly used to sterilize and clean such hard surfaces. Furthermore, when a sterilization and cleaning process is incorporated into an industrial production process, steps such as supplying, mixing, and applying (painting, spraying, and the like) the active ingredient are often automated.

[0004]

As sterilizing cleaners used for sterilization cleaning of such hard surfaces, those containing a chlorine-based disinfectant are known. For example, patent document 1 discloses a sterilizing cleaner composition for hard surfaces that contains a hypochlorite, an amphoteric surfactant and/or a cationic surfactant, and a pH adjusting agent. Furthermore, patent document 2 discloses that hypochlorite can be used in an aqueous composition that contains a specific long-chain amine oxide mixture.

[Patent Document 1] JP 2001-342496 A

[Patent Document 2] JP H9-500680 A (Translation of PCT Application)

[Disclosure of Invention]

[Problem to Be Solved by Invention]

[0005]

However, conventional sterilizing cleaner compositions for hard surfaces have a low sterilizing effect on spores and molds formed by spore bacteria that are difficult to sterilize, and in order to obtain a sufficient sterilizing and cleaning effect, treatment at a high temperature for a long time is required. In food processing plants, hospitals, and the like, hard surfaces such as floors, walls, equipment, and utensils and the like are susceptible to microbial contamination, and thus sufficient sterilizing and cleaning of these hard surfaces is critical.

[0006]

Disinfectant compositions for hard surfaces that use an oxygen-based disinfectant is advantageous in that the effect on the environment is mild, but further improvement is desired in the sterilizing effect on microorganisms with strong chemical resistance such as bacterial spores. It is known that disinfectants containing peracetic acid are effective against spore-forming bacteria to a certain extent, but they have problems such as being difficult to use because of their odor and creating a poor working environment.

[0007]

An object of the present invention is to provide an oxygen-based sterilizing cleaner composition for hard surfaces which exhibits a high sterilization effect even against highly drug-resistant microorganisms such as spore-forming bacteria.

[Means for Solving Problem]

[0008]

The present invention relates to a sterilizing cleaner composition for hard surfaces, containing water and an organic peracid obtained by reacting (A) an ester of a polyhydric alcohol and an organic acid having a hydrocarbon group that may have a hydroxyl group (herein referred to as component (A)) and (B1) hydrogen peroxide (herein referred to as component (B1)) in water at a molar ratio of (A)/(B1) = 1/10 to 20/1 and at a pH of 8 to 12, and which has a pH of 1 or more to 7 or less at 25°C.

[0009]

The present invention also relates to a method for producing a sterilizing cleaner composition for hard surfaces, having steps for reacting (A) an ester of a polyhydric alcohol and an organic acid having a hydrocarbon group, which may have a hydroxyl group, and (B1) hydrogen peroxide in a molar ratio of (A)/(B1) = 1/10 to 20/1 in water at a pH of 8 to 12, and then adjusting the pH of the reaction system to 1 or higher but less than 7.

[Effect of Invention]

[0010]

According to the present invention, a sterilizing cleaner composition for hard surfaces is obtained which exhibits excellent detergency on hard surfaces and also exhibits excellent sterilizing power against spores and mold even when treated at a lower temperature and for a shorter period of time than in conventional operations. Furthermore, the composition of the present invention has no odor problem and has little impact on the working environment.

[Best Mode for Carrying Out Invention]

[0011]

<Component (A)>

An ester between a polyhydric alcohol and an organic acid having a hydrocarbon group, which may have a hydroxyl group, of a component (A) reacts with hydrogen peroxide to produce an organic peracid.

[0012]

The polyhydric alcohol constituting the component (A) preferably has 2 to 12 carbon atoms, and examples of such polyhydric alcohols include glycerins such as glycerin, diglycerin, and triglycerin, sugars such as glucose, sucrose, fructose, sorbitol, pentaerythritol, alkyl polyglycosides, and alkyl furanosides.

[0013]

Furthermore, examples of organic acids constituting the component (A) include aliphatic monocarboxylic acids such as acetic acid, propionic acid, butyric acid, valeric acid, caproic acid,

and octanoic acid, aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, maleic acid, and fumaric acid, and hydroxycarboxylic acids having a hydroxyl group such as citric acid, tartaric acid, and malic acid, but are preferably saturated or unsaturated aliphatic mono- or dicarboxylic acids having 1 to 8 carbon atoms, more preferably saturated or unsaturated aliphatic monocarboxylic acids having 1 to 8 carbon atoms, even more preferably fatty acids having 1 to 8 carbon atoms, and particularly preferably fatty acids having 2 to 8 carbon atoms. The degree of esterification of component (A) is not limited.

[0014]

Specifically, the component (A) is preferably an ester of glycerin and an aliphatic monocarboxylic acid having 1 to 8 carbon atoms, and among these, triacetin is preferable.

[0015]

The sterilizing cleaner composition for hard surfaces of the present invention contains water and an organic peracid obtained by reacting component (A) and component (B1) in water in a molar ratio of (A)/(B1) = 1/10 to 20/1 and at a pH of 8 to 12, and has a pH of 1 or more and less than 7 at 25°C. That is, as described above, the sterilizing cleaner composition for hard surfaces of the present invention is prepared by reacting component (A) and component (B1) in water in a specific molar ratio at a pH of 8 to 12, and then adjusting the pH to 1 or more and less than 7, preferably 1 to 6, and more preferably 1 to 5.

[0016]

The sterilizing cleaner composition for hard surfaces of the present invention may contain, in addition to the components (A) and (B1), surfactants, inorganic or organic salts, chelating agents, fragrances, pigments, dyes, and the like.

[0017]

The surfactant used to further improve the detergency includes one or more surfactants selected from amphoteric surfactants, cationic surfactants, anionic surfactants, and nonionic surfactants, preferably one or more surfactants selected from anionic surfactants and nonionic surfactants. The surfactants can be used alone or in combination of two or more types.

[0018]

Examples of amphoteric surfactants include amine oxides such as alkyl dimethyl amine oxide, betaines such as alkyl dimethyl amino fatty acid betaines, alkyl carboxymethyl hydroxyethyl imidazolium betaines, and the like. Among these, alkyl dimethylamine oxides having an alkyl group with 8 to 18 carbon atoms are preferable. Furthermore, examples of cationic surfactants include primary amine salts, secondary amine salts, tertiary amine salts, and quaternary ammonium salts, but quaternary ammonium salts are particularly preferable among these. Examples of quaternary ammonium salts include compounds in which at least one of the four substituents is an alkyl or alkenyl group having a total of 8 to 28 carbon atoms, and the remainder are groups selected from a benzyl group, alkyl groups having 1 to 5 carbon atoms, and hydroxyalkyl groups having 1 to 5 carbon atoms. The alkyl or alkenyl group having a total of 8 to 28 carbon atoms may be substituted with an alkoxyl group, an alkenyloxy group, an alkanoylamino group, an alkenoylamino group, an alkanoyloxy group or an alkenoyloxy group within this carbon number range. The amount of the amphoteric surfactant and/or cationic surfactant blended in the composition is preferably 1 ppm to 5 wt%, more preferably 5 ppm to 1 wt%, and even more preferably 10 ppm to 0.5 wt%.

[0019]

In addition, it is preferable to add an anionic surfactant and a nonionic surfactant in order to improve the penetration into dirt and the foaming property. Examples of anionic surfactants include higher fatty acids, higher alcohol sulfate ester salts, higher alcohol sulfonates, sulfated fatty acid salts, sulfonated fatty acid salts, phosphate ester salts, sulfate ester salts of fatty acid esters, sulfonic acid ester salts of fatty acid esters, sulfate ester salts of higher alcohol ethers, acetates substitute with higher alcohol ethers, condensates of fatty acids and amino acids, alkylol sulfate salts of fatty acid amides, alkylated sulfonates of fatty acid amides, sulfosuccinate salts, alkylbenzene sulfonates, alkylphenol sulfonates, alkyl naphthalene sulfonates, alkylbenzimidazole sulfonates, amide ether carboxylic acids or salts thereof, ether carboxylic acids or salts thereof, N-acyl-N-methyl taurines or salts thereof, amide ether sulfuric acids or salts thereof, N-acyl glutamic acids or salts thereof,

N-amidoethyl-N-hydroxyethyl acetic acids or salts thereof, acyloxyethanesulfonic acids or salts thereof, N-acyl- β -alanines or salts thereof, N-acyl-N-carboxyethyl taurines or salts thereof, N-acyl-N-carboxyethyl glycines or salts thereof, alkyl or alkenyl aminocarbonyl methyl sulfates, and the like. The amount of the anionic surfactant to be blended in the composition is preferably 1 ppm to 5 wt%, more preferably 10 ppm to 0.5 wt%, and even more preferably 50 ppm to 0.5 wt%.

[0020]

Examples of nonionic surfactants include monohydric alcohol derivative nonionic surfactants such as polyoxyethylene (hereinafter referred to as POE) alkyl ether, POE alkyl phenyl ether, polyoxypropylene-POE (block or random) alkyl ether, POE aryl phenyl ether, POE styrenated phenyl ether, and POE tribenzyl phenyl ether; and polyhydric alcohol derivative nonionic surfactants such as (poly)glycerin fatty acid esters, sucrose fatty acid esters, sorbitan fatty acid esters, alkyl polyglycosides, and the like. The amount of the nonionic surfactant in the composition is preferably 1 ppm to 5 wt%, more preferably 10 ppm to 1 wt%, and even more preferably 100 ppm to 0.5 wt%.

[0021]

In addition to being used as pH adjusters, salts are mainly used for the purpose of stabilizing disinfectants, and specific examples include: organic salts such as metal salts of carboxylates, such as succinic acid, malonic acid, citric acid, gluconic acid, and glutaric acid; metal salts of phosphate compounds, such as tripolyphosphate, hexametaphosphoric acid, and phosphoric acid; inorganic salts such as sulfates, such as sodium sulfate and potassium sulfate; and the like. These may be used alone or in combination of two or more types.

[0022]

The chelating agent includes ethylenediaminetetraacetic acid, nitrilotriacetic acid, tripolyphosphoric acid, polyhydroxyacrylic acid, organic phosphonic acid, and the like, or salts thereof.

[0023]

In addition, the amount of water in the sterilizing cleaner composition for hard surfaces of the present invention is preferably 50 wt% or more but less than 100 wt%, more preferably 60 wt% or more but less than 100 wt%, and particularly preferably 70 wt% or more but less than 100 wt%. Furthermore, the sterilizing cleaner composition for hard surfaces of the present invention is an aqueous solution containing an organic peracid, and the concentration of the organic peracid in the composition is preferably 10 to 20,000 ppm, more preferably 10 to 10,000 ppm. In addition, in terms of sterilizing effect, it is preferable that the hydrogen peroxide content of the sterilizing cleaner composition for hard surfaces of the present invention is 0.5 wt% or less, more preferably 0.3 wt% or less, and even more preferably 0.2 wt% or less. This hydrogen peroxide content is preferably achieved immediately after preparation of the composition, and even more so at the time of use.

[0024]

In the present invention, from the perspective of stability, the weight ratio of the organic peracid to the surfactant is preferably 0.01 to 20, more preferably 0.1 to 10, and particularly preferably 0.5 to 5.

[0025]

The sterilizing cleaner composition for hard surfaces of the present invention has a high sterilizing effect and thus can be used to sterilize a variety of objects containing various microorganisms. Examples of bacteria include *Escherichia coli*, *Salmonella*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and the like that cause food poisoning and hospital-acquired infections, fungi such as *Aspergillus niger* and *Candida albicans*, and furthermore bacterial spores such as *Bacillus subtilis* and fungal spores such as *Aspergillus niger* that are highly resistant to disinfectants. Among these, bacterial spores are durable dormant cells that are produced in environments that are not suitable for bacterial growth, and have a multi-layered exoskeleton on the outside of the bacterial body. Such bacterial spores are highly resistant to chemicals and heat and are difficult to completely destroy using conventional sterilization methods. However, the

sterilizing cleaner composition for hard surfaces of the present invention exhibits sufficient sterilization effect even against such bacterial spores.

[0026]

Thus, the sterilizing cleaner composition for hard surfaces of the present invention has a broad disinfecting spectrum and is highly effective not only against bacteria but also against fungi and spores, and is therefore useful for sterilizing and cleaning various hard surfaces.

[0027]

The sterilizing cleaner composition for hard surfaces of the present invention can be prepared from a composition for producing sterilizing cleaner as described below.

[0028]

(1) A composition for producing sterilizing cleaner, containing (A) an ester of a polyhydric alcohol and an organic acid having a hydrocarbon group which may have a hydroxyl group, and (B1) hydrogen peroxide, and having a water content of 1 to 25% by weight (hereinafter referred to as the first composition for producing sterilizing cleaner).

[0029]

(2) A composition for composition for producing sterilizing cleaner, containing (A) an ester of a polyhydric alcohol and an organic acid having a hydrocarbon group which may have a hydroxyl group, and (B1) hydrogen peroxide or (B2) an inorganic peroxide which releases hydrogen peroxide in water, with the molar ratio of (B1) produced from (A) and (B1) or (A) and (B2) being $(A)/(B1) = 1/10$ to $20/1$, said composition for producing a sterilizing cleaner being used as an aqueous solution prepared by adjusting the pH to 8 to 12 and then adjusting the pH to 1 or more but less than 7 (hereinafter referred to as the second composition for producing sterilizing cleaner).

[0030]

(3) A composition for producing sterilizing cleaner obtained by mixing (A) an ester of a polyhydric alcohol and an organic acid having a hydrocarbon group which may have a hydroxyl group, and (B1) hydrogen peroxide or (B2) an inorganic peroxide that releases hydrogen peroxide in water, in a molar ratio of $(A)/(B1) = 1/10$ to $20/1$ of (B1) produced from (A) and (B1) or (A)

and (B2), said composition for producing sterilizing cleaner being used as an aqueous solution prepared by adjusting the pH to 8 to 12 and then adjusting the pH to 1 or more and less than 7 (hereinafter referred to as the third composition for producing sterilizing cleaner).

[0031]

Hereinafter, the inorganic peroxide that releases hydrogen peroxide in water (B2) will be referred to as component (B2), and the components (B1) and (B2) will be collectively described as component (B).

[0032]

In addition, the number of moles of hydrogen peroxide produced from component (B2) of component (B) is a value determined by multiplying the hydrogen peroxide concentration (wt%) in component (B2) determined by permanganate titration by the amount (g) of component (B2) in the composition, and dividing the result by 34, which is the molecular weight of hydrogen peroxide.

[0033]

<Component (B)>

In the component (B), the inorganic peroxide that releases hydrogen peroxide in the water of the component (B2) is preferably hydrogen peroxide when the composition for producing sterilizing cleaner is liquid, preferably percarbonate, perborate, and the like when the composition is granular, powdery, or the like, and particularly sodium percarbonate, sodium perborate, and the like when the composition is solid.

[0034]

<First Composition for Producing Sterilizing Cleaner>

The first composition for producing sterilizing cleaner of the present invention contains component (A) and component (B1), and in order to suppress reaction between component (A) and component (B1) during storage and maintain the stability of the composition, the moisture content of the composition is 1 to 25 wt%, preferably 5 to 20 wt%, and particularly preferably 5 to 15 wt%.

[0035]

The first composition for producing sterilizing cleaner of the present invention is a single-liquid liquid composition containing components for obtaining an organic peracid. The amount of component (A) in the composition for producing sterilizing cleaner is preferably 20 to 90 wt%, further 30 to 90 wt%, and even more preferably 40 to 80 wt%, and the amount of component (B1) is preferably 1 to 30 wt%, more so 5 to 25 wt%, and even more preferably 10 to 25 wt%. The molar ratio of the component (A) to the component (B1), (A)/(B1), is preferably 1/10 to 20/1, more preferably 1/10 to 10/1, and even more preferably 1/5 to 10/1. Furthermore, the molar ratio of the component (B1) per ester group of the component (A) is preferably mole increased by a factor of 2 or less, and particularly preferably mole increased by a factor of 0.3 to 2, from the viewpoints of efficiently generating an organic peracid and reducing unreacted hydrogen peroxide.

[0036]

In addition, the first composition for producing sterilizing cleaner may contain a chelating agent, a pH adjuster, a solvent, and the like as necessary. Chelating agents are useful for suppressing catalytic decomposition caused by the inclusion of trace amounts of metal ions such as Fe and Cr. The pH (20°C) of the original solution of the first composition for producing sterilizing cleaner is preferably 0.5 to 6, more preferably 1 to 5, and particularly preferably 1 to 4, from the standpoint of storage stability. A compound having both a function as a pH adjuster and a function as a chelating agent is preferred, and specifically, phosphoric acid, polymerized phosphoric acid, organic phosphonic acid, aminocarboxylic acid, hydroxycarboxylic acid, or a salt thereof is preferable. Of these, an organic phosphonic acid or a salt thereof is preferable. As the solvent, a polyhydric alcohol solvent is preferable, and a glycol solvent such as propylene glycol is even more preferable.

[0037]

<Second Composition for Producing sterilizing cleaner>

The second composition for producing sterilizing cleaner of the present invention contains component (A) and component (B), and it is preferable that the ratio of the two is in a range in which component (B1) and component (A) react efficiently, and taking into consideration the

efficiency of organic peracid generation, bactericidal effect, formulation stability, and the like, the molar ratio of component (A) to component (B1) is $(A)/(B1) = 1/10$ to $20/1$, preferably $1/10$ to $10/1$, and more preferably $1/5$ to $10/1$. From the viewpoints of efficiently generating an organic peracid and reducing unreacted hydrogen peroxide, the molar ratio of component (B1) per ester group of component (A) is preferably 2 times as many moles or less, particularly preferably 0.3 to 2 times as many moles. When component (B2) is used, it is also preferable to compound such in an amount that generates component (B1) in the above range.

[0038]

Preferably, in addition to satisfying the molar ratio, the composition for producing the second sterilizing cleaner of the present invention contains 0.1 to 90 wt% component (A), more so 0.5 to 70 wt%, particularly 1 to 50 wt% component (B), and 0.1 to 50 wt% component (B1), preferably 0.1 to 30 wt%, and even more preferably 0.1 to 20 wt%.

[0039]

When using the second composition for producing sterilizing cleaner of the present invention, the aqueous solution that is the sterilizing cleaner composition is prepared by setting the pH to 8 to 12, preferably to 9 to 11 (first step), and then setting the pH to 1 or more and less than 7, preferably to 1 to 6, and more preferably to 1 to 5 (second step). In the first step, an alkaline pH adjusting agent is preferably used, and in the second step, an acidic pH adjusting agent is preferably used. This pH may be at the time of use, but preferably satisfies the above pH at 25°C. Note that the first composition for producing sterilizing cleaner of the present invention described above may also be used in the same manner.

[0040]

Examples of alkaline pH adjusting agents include alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, calcium hydroxide, and barium hydroxide, alkaline earth metal hydroxides such as sodium silicate, alkali metal silicate such as potassium silicate, alkaline alkali metal salts such as trisodium phosphate, and alkali metal carbonates such as sodium carbonate and potassium carbonate, but from the perspective of alkalinity and water solubility, alkali metal

hydroxides such as sodium hydroxide and potassium hydroxide, alkali metal salts such as trisodium phosphate and tripotassium phosphate, and alkali metal carbonate salts such as sodium carbonate and potassium carbonate and the like are preferable. Furthermore, examples of acidic pH adjusting agents include inorganic acids such as hydrochloric acid, sulfuric acid, and phosphoric acid and organic acids such as formic acid, acetic acid, citric acid, succinic acid, and gluconic acid, but from the perspective of acidity and water solubility, liquid inorganic acids such as sulfuric acid and phosphoric acid and highly water-soluble organic acids such as citric acid and acetic acid are preferable. These may be used alone or in combination of two or more types. Furthermore, these pH adjusting agents may remain present in the second composition for producing sterilizing cleaner of the present invention. Note that these pH adjusting agents may also be present in the first composition for producing sterilizing cleaner of the present invention described above.

[0041]

The second composition for producing sterilizing cleaner of the present invention may also contain, in addition to component (A) and component (B), surfactants, inorganic or organic salts, chelating agents, perfumes, pigments, dyes, and the like. Note that these components may also be present in the first composition for producing sterilizing cleaner of the present invention described above.

[0042]

The second composition for producing sterilizing cleaner of the present invention may take a variety of forms, but when in a liquid state, one with high fluidity is preferred, and in addition to an aqueous solution, a slurry, gel, paste, or the like with fluidity may also be used. Furthermore, in the case of a solid, examples of shapes include granules, powders, granules, pellets, and the like.

[0043]

The second composition for producing sterilizing cleaner of the present invention may package all of the blended components together, but from a perspective of stability, a multi-part form where component (A) and component (B) are packaged separately is preferable. For example, a three-part composition for producing sterilizing cleaner may be made from a package (1) of a

composition containing component (A), a package (2) of a composition containing component (B), and a package (3) of a composition containing a pH adjusting agent (an acidic pH adjusting agent such as citric acid) for finally setting the pH to 1 or more and less than 7. In this case, it is preferable that an alkali agent is added to the package (2) and the mixture of the package (1) and the package (2) is adjusted so as to have a pH of 8 to 12. Furthermore, component (A) and component (B) may also be co-located in one package, particularly for a powder composition, and a two-part composition for producing sterilizing cleaner may be made from, for example, a package (I) of a composition containing component (A), component (B), and an alkali agent for adjusting the pH to 8 to 12, and a package (II) of a composition containing a pH adjusting agent (an acidic pH adjusting agent such as citric acid) for finally making the pH to be 1 or more and less than 7.

[0044]

In the second composition for producing sterilizing cleaner of the present invention, an aqueous solution that is a sterilizing cleaner composition containing organic peroxy acid is prepared by adjusting the pH value through the first step and second step above during use. The organic peroxy acid concentration in the aqueous solution is preferably 10 to 20,000 ppm (weight ratio, same as below) and more so 10 to 10,000 ppm. Furthermore, it is preferred that the hydrogen peroxide content in the aqueous solution be 0.5 wt% or less, more preferably 0.3 wt% or less, and particularly preferably 0.2 wt% or less, from the perspective of the sterilizing effect. These findings are similar to the first composition for producing sterilizing cleaner of the present invention described above.

[0045]

<Third Composition for Producing Sterilizing Cleaner>

The third composition for producing sterilizing cleaner of the present invention is obtained by blending component (A) and component (B) of the present invention, and similar to the second composition for producing sterilizing cleaner, the molar ratio of component (A) and component (B1) derived from component (B) is $(A)/(B1) = 1/10$ to $20/1$, and after the pH is 8 to 12, it is used as an aqueous solution prepared with a pH of 1 or more but less than 7. The specific compounds

of component (A) and component (B) and the preferred molar ratio of component (A)/(B1) are also similar to those of the second composition for producing sterilizing cleaner. Furthermore, the third composition for producing sterilizing cleaner may also contain the aforementioned surfactant, inorganic or organic salts, chelating agents, perfumes, pigments, dyes, and the like, and the packaging form may be the same.

[0046]

<Sterilizing Cleaner Kit>

A sterilizing cleaner kit suitable for obtaining the sterilizing cleaner composition for hard surfaces of the present invention is configured to contain the composition for producing sterilizing cleaner of the present invention, a reaction initiator (hereinafter referred to as component (C)) that initiates the reaction of component (A) and component (B1) brought about by the composition, and a pH adjusting agent (hereinafter referred to as component (D)). Furthermore, the sterilizing cleaner kit may also be configured to include component (A), component (B), component (C), and component (D).

[0047]

The sterilizing cleaner kit for obtaining the sterilizing cleaner composition for hard surfaces of the present invention may be a single-part form in which all of the formulated components are packaged together in consideration of the simplicity during organic peroxy acid production, but may be a multi-part form in which component (A), component (B), component (C), and component (D) are individually packaged in consideration of the stability during storage. A preferred form of the sterilizing cleaner kit is a multi-part form, such as a two-part form or a three-part form that includes a package in which a composition containing two or more components from among components (A) through (D) is packaged, in consideration of both convenience during organic peroxy acid production and storage stability of the composition for production.

[0048]

The component (A) and the component (B1) react under alkaline conditions (water temperature 5 to 50 is suitable) in water to generate an organic peroxy acid, and therefore, a component that

gives such a pH may be used as the component (C). Specifically, examples include alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, calcium hydroxide, and barium hydroxide, alkaline earth metal hydroxides, alkali metal silicate salts such as sodium silicate and potassium silicate, alkali metal phosphate salts that exhibit alkalinity, such as trisodium phosphate, and alkali metal carbonate salts such as sodium carbonate and potassium carbonate, which were given as examples of alkaline pH adjusting agents; however, from the perspective of alkalinity or water solubility, alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, alkali metal phosphate salts such as trisodium phosphate and tripotassium carbonate and alkali metal carbonate salts such as sodium carbonate and potassium carbonate are preferable.

[0049]

On the other hand, it is preferable that the sterilizing cleaner containing organic peroxy acid use components that bring the pH that was in the alkaline region due to component (D) and component (C) into the acidic region, because it peroxy acids are preferable in terms of sterilizing effect. Specifically, examples include inorganic acids such as hydrochloric acid, sulfuric acid, and phosphoric acid and organic acids such as formic acid, acetic acid, citric acid, succinic acid, and gluconic acid, which were given as examples of acidic pH adjusting agents, but liquid inorganic acids such as sulfuric acid and phosphoric acid and highly water soluble organic acids such as citric acid and acetic acid are preferable from the perspective of acidity and water solubility.

[0050]

Specific forms of the sterilizing cleaner kit include:

(I) a form of three parts or more, including a package (X1) of a composition for producing sterilizing cleaner containing component (A) and component (B), a package (X2) of a composition containing component (C), and a package (X3) of a composition containing component (D),

(II) a form of three parts or more, including a package (Y1) of a composition containing component (A), a package (Y2) of a composition containing component (B) and component (C), and a package (X3) of a composition containing component (D), and

(III) a form of two parts or more, including a package (Z1) of a composition containing component (A), component (B), and component (C) and a package (Z2) of a composition containing component (D).

[0051]

In the form of (I), the form of the composition for producing sterilizing cleaner is not limited to a powder, a solid, a liquid, or the like, but from the perspective of simplicity, liquid is more preferable. In order to suppress reaction between component (A) and component (B) during storage and maintain stability when the composition is in a liquid form, the water content in the liquid composition is preferably 1 to 25 wt%, more preferably 5 to 20 wt%, and even more preferably 5 to 15 wt%. Furthermore, as necessary, a chelating agent or a solvent may be added to the liquid composition. Chelating agents are useful for suppressing catalytic decomposition caused by the inclusion of trace amounts of metal ions such as Fe and Cr. Furthermore, the stock solution pH (20°C) of the liquid composition is preferably 0.5 to 6, more preferably 1 to 5, and even more preferably 1 to 4, in as this contributes to storage stability. As described above, it is preferable to use a component that acts both as a pH adjusting agent and as a chelating agent, and specifically, phosphoric acid, polymerized phosphoric acid, organic phosphonic acid, aminocarboxylic acid, hydroxycarboxylic acid, or a salt thereof is preferable. Of these, an organic phosphonic acid or a salt thereof is preferable. As the solvent, a polyhydric alcohol solvent is preferable, and a glycol solvent such as propylene glycol is even more preferable.

[0052]

Furthermore, when the composition for producing sterilizing cleaner in the form of (I) is a powder in solid form, sodium percarbonate, sodium perborate, or the like is preferably used as component (B). Similarly, from the perspective of storage stability, in the form of (II) and the form of (III) as well, the composition containing component (B) is also preferably in a solid form or powder in which sodium percarbonate, sodium perborate, or the like is used as component (B).

[0053]

The amounts of components (A) through (D) in each of these forms may be selected within respective suitable ranges based on the method used for the first through third compositions for producing sterilizing cleaner of the present invention described above. Furthermore, components other than the components (A) through (D) may be added to any package containing the components (A) through (D), or added to another package.

[0054]

The composition for producing sterilizing cleaner and the sterilizing cleaner kit may be applied to a method for producing a sterilizing cleaner composition for hard surfaces, which has a step wherein an ester (A) of a polyhydric alcohol with an organic acid having a hydrocarbon group which may have a hydroxyl group and hydrogen peroxide (B1) are reacted with each other in water at a molar ratio of (A)/(B1) = 1/10 to 20/1 at a pH of 8 to 12, and then the reaction system is set at a pH of 1 or more but less than 7.

[0055]

The sterilizing cleaner composition for hard surfaces of the present invention is also suitable for systems that use automatic spray devices and spray guns. Furthermore, foam cleaning and sterilization using the addition of a foam increasing agent is also possible.

[Examples]

[0056]

Example 1

Below, % indicates wt%.

[0057]

<Preparation of Sterilizing Cleaner Composition (I)>

(A) 50 g of triacetin (made by Cognis Japan, active ingredient 100%) and (B) 25 g of hydrogen peroxide (made by Ube Chemira, active ingredient 60%) were mixed with 850 g of ion exchanged water, 75 g of an alkaline aqueous solution containing 27% sodium hydroxide and 1.3% of organic phosphonic acid (product name: Dequest 2010, made by Solucia) was poured in, and this was then mixed and stirred for 5 minutes. Afterward, 75 g of a mixed acid solution containing 30% sulfuric

acid and 6% phosphoric acid was immediately added to prepare the sterilizing cleaner composition (I) containing the organic peroxy acid. The pH (25°C) of the composition (I) was about 2, and the hydrogen peroxide content was about 1500 ppm.

[0058]

<Preparation of Sterilizing Cleaner Composition (II)>

(A) 50 g of D-glucose-O-pentaacetate (reagent: made by Tokyo Chemical Industry Co., Ltd., active ingredient 100%) and 25 g of (B) 25 g of hydrogen peroxide (product of Ube Chemira Co., Ltd., active ingredient 60%) were mixed with 850 g of ion exchange water, and 75 g of an alkaline aqueous solution containing 27% sodium hydroxide and 1.3% of organic phosphonic acid (product name: Dequest 2010, product of Solucia Co., Ltd.) was poured in this solution, then mixed and stirred for 5 minutes. Afterward, 75 g of a mixed acid solution containing 30% sulfuric acid and 6% phosphoric acid was immediately added to prepare the sterilizing cleaner composition (II) containing the organic peroxy acid. The pH (25°C) of the composition (II) was about 2, and the hydrogen peroxide content was about 1500 ppm.

[0059]

<Measurement of Organic Peroxy Acid Concentration>

About 1 g of the sterilizing cleaner composition (I) or (II) prepared in a 100 mL beaker was weighed precisely, and approximately 50 mL of ion exchanged water and approximately 1 mL of a hydrogen peroxide decomposer (product name: Asksuper G, Mitsubishi Gas Chemical Co., Ltd.) were poured and stirred well to decompose only hydrogen peroxide in the composition. Afterward, 5 mL of 20% sulfuric acid and 5 mL of a 10% potassium iodide aqueous solution were poured, stirred, titrated using a 0.1 mol/L sodium thiosulfate aqueous solution, and an organic peroxy acid concentration (as peracetic acid concentration) was found using the following formula.

$$\text{Organic peroxy acid (peracetic acid) concentration (\%)} = T \times 38/W/100$$

T: Amount require for titration of 0.1 mol/L sodium thiosulfate aqueous solution (mL)

W: Collected amount of the sterilizing cleaner composition (g)

[0060]

<Evaluation>

Evaluation tests of detergency and sterilizing power were performed by the following methods using a test aqueous solution where a composition obtained using the sterilizing cleaner compositions (I) and (II) and the components shown in Tables 1 and 2 were diluted with water so as to achieve the organic peroxy acid concentration in Tables 1 and 2. The results are shown in Tables 1 and 2. Note that, when there were no sterilizing solution components as a comparative control product of the sterilizing cleaner composition, a formulation that uses hydrogen peroxide, which is a typical oxygen based sterilizing solution, and sodium hypochlorite, which is a chlorine based sterilizing solution, was prepared, and the same evaluation test was performed.

[0061]

(1) Detergency Evaluation Test

After detergency model stains of oil stains and protein stains were prepared, each detergency was evaluated by a modified Leanut test method in accordance with JIS K-33629.2 Synthetic Dishwashing Cleaner Detergency Evaluation Methods.

[0062]

(1-1) Oil Stain Detergency Evaluation

20 g of oil and fat, 0.25 g of monoolein, and 0.1 g of oil red mixed with beef tallow and soybean oil at a 1:1 volume ratio, were dissolved in 60 mL of chloroform to prepare an oil stain solution. Sets of six clean slide glasses were each measured up to a mass of 1 mg. Glass slides were immersed about 55 mm in a $25\pm 1^{\circ}\text{C}$ oil stain solution one by one for about 2 seconds, and then removed after oil stain had adhered thereto. A mass of oil stain adhering to the lower part of the slide glass was sucked out by using a clean cloth such as gauze or filter paper, the adhesion of the oil stain was made uniform, this was air-dried as $25\pm 1^{\circ}\text{C}$, and the mass was measured. Model dirty glass pieces were used for the test within 1 hour or more and 2 hours of air-drying time. In this case, the amount of oil stain adhered to the model dirty glass pieces per 6 sheets was made to be 0.140 ± 0.010 g.

[0063]

The 6 groups of model dirty glass pieces were washed for 5 minutes at $25\pm 2^{\circ}\text{C}$ using a modified Leanut washer and then rinsed with ion exchange water at $25\pm 2^{\circ}\text{C}$ for 30 seconds. The rinsed glass pieces were dried overnight. The evaluation of the detergency was calculated from the weight before and after washing the model dirty glass pieces. That is, the weight difference between before and after cleaning was found, and the cleaning rate (%) was calculated according to the following formula.

Cleaning rate (%) = $((\text{Weight before cleaning} - \text{Weight after cleaning}) / \text{Amount of stain adhered}) \times 100$

The cleaning rates of each of the six glass pieces were found, and the average value of the four cleaning rates excluding the maximum value and the minimum value was the cleaning rate of the composition.

[0064]

(1-2) Protein Stain Detergency Evaluation

20 g of skim milk powder was diluted and dissolved in 60°C ion exchange water to make a total of 100 g, which was then used as a protein stain solution. Clean glass slides were each immersed about 55 mm in the protein stain solution at $25\pm 1^{\circ}\text{C}$ for about 2 seconds, and after adhering the protein stain, these were removed. The collection of protein stains adhering to the lower part of the slide glass was sucked out by using a clean cloth such as gauze or filter paper, the adhesion of the protein stain was made uniform, and this was air-dried at $25\pm 1^{\circ}\text{C}$. This was repeated once again, and after the stain on one side had been completely removed, air drying was performed, and denaturation was performed for one hour at 110°C to make a test piece. This test piece was used for tests within 12 hours to 24 hours. The test piece was washed for 5 minutes at $25\pm 2^{\circ}\text{C}$ using a modified Leanut washer and then rinsed with ion-exchange water at $25\pm 2^{\circ}\text{C}$ for 30 seconds. After rinsing, the sample was dried at 70°C for 30 minutes, colored with an erythrosine 1 wt% solution, the colored area (S_1) was measured by a photographic determination, and the cleaning rate (%) was calculated from the protein stain adhered area (S_0) in the initial period (before cleaning) by the following formula.

$$\text{Cleaning rate (\%)} = ((S_0 - S_1) / S_0) \times 100$$

The cleaning rates of each of the six glass pieces were found, and the average value of the four cleaning rates excluding the maximum value and the minimum value was the cleaning rate of the composition.

[0065]

(1-3) Oil Stain Detergency Evaluation Using Foam

20 g of oil and fat, 0.25 g of monoolein, and 0.1 g of oil red mixed with beef tallow and soybean oil at a 1:1 volume ratio, were dissolved in 60 mL of chloroform to prepare an oil stain solution. Each set of six clean slide glasses (76 mm × 26 mm × 1 mm) was measured at a mass up to 1 mg. Glass slides were immersed about 55 mm in a 25±1°C oil stain solution one by one for about 2 seconds, and then removed after oil stain had adhered thereto. A mass of oil stain adhering to the lower part of the slide glass was sucked out by using a clean cloth such as gauze or filter paper, the adhesion of the oil stain was made uniform, this was air-dried as 25±1°C, and the mass was measured. Model dirty glass pieces were used for the test within 1 hour or more and 2 hours of air-drying time. At this time, the sticking amount of oil stain per 6 sheets of model dirty glass pieces was set to 0.140±0.010 g.

[0066]

300 mL (25°C) of a test aqueous solution was placed in a 300 mL beaker, a silicone hose with an air tone attached to the tip was immersed in the test solution, air was sent by an air pump (flow rate was 1.5 liters/minute), and bubbles were produced. Model dirty glass pieces were brought into contact with overflowing foam for five minutes one by one and rinsed with ion exchange water for 25±2°C 30 seconds. The rinsed glass pieces were dried overnight. The evaluation of the detergency was calculated from the weight before and after washing the model dirty glass pieces. That is, the weight difference between before and after cleaning was found, and the cleaning rate (%) was calculated according to the following formula.

$$\text{Cleaning rate (\%)} = ((\text{Weight before cleaning} - \text{Weight after cleaning}) / \text{Amount of stain adhered}) \times 100$$

The cleaning rates of each of the six glass pieces were found, and the average value of the four cleaning rates excluding the maximum value and the minimum value was the cleaning rate of the composition.

[0067]

(2) Sterilizing Capacity Evaluation Test

After culturing *Bacillus subtilis* (ATCC6633), which is a spore-forming bacterium, in an SCD agar medium (made by Nihon Pharmaceutical Co., Ltd.) at about 30°C for approximately one week, the colonies formed on the agar medium were scraped, suspended in 1 mL of sterile water, and then the formation of bacterial spores (hereinafter referred to as spore) was confirmed by a microscope. After heat treatment at 65°C for 30 minutes, after performing two centrifuge washings, the bacterial concentration was adjusted to about 10^8 cell/mL using an appropriate amount of sterilized water. After preparing 1.0 mL of this spore fungus solution in the same manner as the detergency evaluation test described above in (1) and uniformly inoculating in one model dirty glass piece, air drying was performed to obtain glass pieces for a sterilization test.

[0068]

The glass piece for the sterilizing test was contacted for 5 minutes by bubbles in the test aqueous solution produced in a similar manner as item (1-3) of the detergency evaluation test (1) described above, and was quickly rinsed with sterilized water. Before the surface of the glass piece dried, a predetermined area (20 mm × 20 mm) of the glass piece was wiped off with a sterile cotton swab, and the cotton swab was immersed in 1 mL of sterile water (3.3% sodium thiosulfate added) and the adherend was suspended. 100 µL of the suspension was inoculated into a sterilized test tube containing 2.0mL of an SCD medium for post culture (made by Nippon Pharmaceutical Co., Ltd.). This was cultured for 48 hours at 35°C, growth of bacteria was observed with the naked eye, "○" was defined as a case where there was no growth of bacteria, and "×" was defined as a case where there was growth of bacteria.

[0069]

[Table 1]

	Present invention							
	1	2	3	4	5	6	7	8
Sterilizing cleaner composition (I)	2000ppm				1000ppm	1000ppm	1500ppm	3000ppm
Sterilizing cleaner composition (II)		1500ppm	1500ppm	1000ppm				
Hydrogen peroxide								
Sodium hypochlorite								
Sodium polyoxyethylene lauryl ether sulfate ⁽¹⁾	500ppm		1000ppm			500ppm		
Lauryldimethylamine oxide ⁽²⁾				200ppm				
Benzalkonium chloride ⁽³⁾					100ppm			
Alkyl polyglycosides ⁽⁴⁾		1000ppm		500ppm	1000ppm	300ppm		
Polyoxyethylene lauryl ether ⁽⁵⁾							1000ppm	
(1-1) Oil stain cleaning rate (%)	59	62	60	56	63	61	58	41
(1-2) Protein stain cleaning rate (%)	60	60	59	58	61	60	59	40
(1-3) Oil stain cleaning rate (%)	56	58	58	57	58	57	58	41
Sterilization power	○	○	○	○	○	○	○	○
Test solution								
Evaluation								

[0070]

[Table 2]

	Comparison product							
	1	2	3	4	5	6	7	8
Sterilizing cleaner composition (I)								
Sterilizing cleaner composition (II)								
Hydrogen peroxide					1.0%	1.0%		
Sodium hypochlorite							400ppm	200ppm
Sodium polyoxyethylene lauryl ether sulfate ⁽¹⁾	500ppm		1000ppm			500ppm		
Lauryl dimethylamine oxide ⁽²⁾				200ppm				200ppm
Benzalkonium chloride ⁽³⁾					100ppm			
Alkyl polyglycosides ⁽⁴⁾		1000ppm		500ppm	1000ppm	300ppm		500ppm
Polyoxyethylene lauryl ether ⁽⁵⁾							1000ppm	
(1-1) Oil stain cleaning rate (%)	56	58	55	54	64	60	59	44
(1-2) Protein stain cleaning rate (%)	56	51	50	55	60	60	64	53
(1-3) Oil stain cleaning rate (%)	51	55	57	52	58	52	57	45
Sterilization power	×	×	×	×	×	×	×	×
Test solution								
Evaluation								

[0071]

The hydrogen peroxide concentration in the table indicates the hydrogen peroxide effective content concentration, and the sodium hypochlorite concentration indicates the effective chlorine concentration. Furthermore, the surfactant is as follows.

(1): The active ingredient concentration was determined to be the numerical value in Table 1 using Emal 20C (made by Kao Corp., active ingredient 25%).

(2): The active ingredient concentration was determined to be the numerical value in Table 1 using Anhitor 20N (made by Kao Corp., active ingredient 35%).

(3): The active ingredient concentration was determined to be the numerical value in Table 1 using Sanizor C (made by Kao Corp., active ingredient 50%).

(4): The active ingredient concentration was determined to be the numerical value in Table 1 using Midol 12 (made by Kao Corp., active ingredient 40%).

(5): The active ingredient concentration was determined to be the numerical value in Table 1 using Emulgen 106 (made by Kao Corp., active ingredient 100%).

[Procedural Amendment]

[Date Submitted] August 4, 2005 (Heisei 17)

[Procedural Amendment 1]

[Document to Be Amended] Specification

[Name of Item to Be Amended] 0064

[Amendment Method] Change

[Content of Amendment]

[0064]

(1-2) Protein Stain Detergency Evaluation

20 g of skim milk powder was diluted and dissolved in 60°C ion exchange water to make a total of 100 g, which was then used as a protein stain solution. A clean slide glass was immersed in a protein stain solution at $25 \pm 1^\circ\text{C}$ for about 2 seconds at approximately 55mm each, and after adhering the protein stain, this was removed. The collection of protein stains adhering to the lower

part of the slide glass is sucked out by using a clean cloth such as gauze or filter paper, the adhesion of the protein stain was made uniform, and this was air-dried at $25\pm 1^{\circ}\text{C}$. This was repeated once again, and after the stain on one side had been completely removed, air drying was performed, and denaturation was performed for one hour at 110°C to make a test piece. This test piece was used for tests within 12 hours to 24 hours. The test piece was washed for 5 minutes at $25\pm 2^{\circ}\text{C}$ using a modified Leanut washer and then rinsed with ion-exchange water at $25\pm 2^{\circ}\text{C}$ for 30 seconds. After rinsing, the sample was dried at 70°C for 30 minutes, colored with an erythrosine 1 wt% solution, the colored area (S_1) was measured by a photographic determination, and the cleaning rate (%) was calculated from the protein stain adhered area (S_0) in the initial period (before cleaning) by the following formula.

$$\text{Cleaning rate (\%)} = ((S_0 - S_1) / S_0) \times 100$$

The cleaning rates of each of the six glass pieces were found, and the average value of the four cleaning rates excluding the maximum value and the minimum value was the cleaning rate of the composition.

[Procedural Amendment 2]

[Document to Be Amended] Specification

[Name of Item to be Amended] 0065

[Amendment Method] Change

[Content of Amendment]

[0065]

(1-3) Oil Stain Detergency Evaluation Using Foam

20 g of oil and fat, 0.25 g of monoolein, and 0.1 g of oil red mixed with beef tallow and soybean oil at a 1:1 volume ratio, were dissolved in 60 mL of chloroform to prepare an oil stain solution. Each set of six clean slide glasses (76 mm × 26 mm × 1 mm) was measured at a mass up to 1 mg. Glass slides were immersed about 55 mm in a $25\pm 1^{\circ}\text{C}$ oil stain solution one by one for about 2 seconds, and then removed after oil stain had adhered thereto. A mass of oil stain adhering to the lower part of the slide glass was sucked out by using a clean cloth such as gauze or filter paper, the

adhesion of the oil stain was made uniform, this was air-dried as $25\pm 1^{\circ}\text{C}$, and the mass was measured. Model dirty glass pieces were used for the test within 1 hour or more and 2 hours of air-drying time. In this case, the amount of oil stain adhered to the model dirty glass pieces per 6 sheets was made to be 0.140 ± 0.010 g.

[Procedural Amendment 3]

[Document to Be Amended] Specification

[Name of Item to Be Amended] 0066

[Amendment Method] Change

[Content of Amendment]

[0066]

300 mL (25°C) of a test aqueous solution was placed in a 300 mL beaker, a silicone hose with an air tone attached to the tip was immersed in the test solution, air was sent by an air pump (flow rate was 1.5 liters/minute), and bubbles were produced. Model dirty glass pieces were brought into contact with overflowing foam for five minutes one by one and rinsed with ion exchange water at $25\pm 2^{\circ}\text{C}$ for 30 seconds. The rinsed glass pieces were dried overnight. The evaluation of the detergency was calculated from the weight before and after washing the model dirty glass pieces. That is, the weight difference between before and after cleaning was found, and the cleaning rate (%) was calculated according to the following formula.

Cleaning rate (%) = $((\text{Weight before cleaning} - \text{Weight after cleaning}) / \text{Amount of stain adhered}) \times 100$

The cleaning rates of each of the six glass pieces were found, and the average value of the four cleaning rates excluding the maximum value and the minimum value was the cleaning rate of the composition.

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