(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 065 265 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.01.2001 Bulletin 2001/01

(51) Int. Cl.[7]: **C11D 3/48**, C11D 3/39, C11D 3/386

(21) Application number: **00113168.9**

(22) Date of filing: **30.06.2000**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **30.06.1999 JP 18510199**

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(54) Germicidal detergent composition

(57) The present invention provides a germicidal detergent composition comprising (a) an inorganic peroxide, (b) tetraacetylethylenediamine and (c) protease in a specific ratio.

EP 1 065 265 A1

Description

Technical Field

[0001] The present invention relates to a germicidal detergent composition. The term "germicidal" in the present invention may mean bactericidal, sporicidal, sterilizing, germ-eliminating, pasteurizing, disinfectant, microbicidal, germ-(, bacterium-, fungus-, bacillus-, microorganism or the like) lethal or the like. That is, the present invention can be applied to germs, bacteria, spores, funguses, microbes, microorganisms and so on.

Prior Art

[0002] Killing and sterilizing a microorganism such as a germ are a big subject in various fields including a medical cure and a food industry, and many proposals concerning them have been carried out already. For example, in JP-A 62-63504, a germicide composition containing a cationic surfactant, an inorganic peroxide and an activator for the inorganic peroxide is disclosed; in JP-A 3-131700, a detergent composition for a drainpipe having its germ-eliminating and/or germicidal effect and containing each of an inorganic peroxide, a nonionic surfactant and tetraacetylethylenediamine in a specific proportion is disclosed; and, in JP-A 8-502047, use of an aqueous solution containing an aliphatic peracid and the corresponding aliphatic acid in a specific molar ratio and containing hydrogen peroxide as a germicidal detergent is disclosed.

[0003] Especially, in the case of a medical instrument and a furnishing used in a hospital, a protective institution and so on, it is necessary to fully carry out the germicidal deterging treatment from the viewpoint of prevention of infection and the like in the hospital and so on. There have been known various germicides and disinfectants using benzalkonium chloride, chlorhexidine gluconate, an iodine compound, an alcohol, a hypochlorite, glutaraldehyde, peracetic acid, etc.

[0004] Examples of the germicidal deterging treatment using glutaraldehyde and/or peracetic acid include that, in case of a germicidal deterging of an endoscope, a sterilizing treatment is carried out by means of glutaraldehyde and/or peracetic acid after a primary disinfection using a germicide of a quaternary ammonium salt type, an alcohol, a superoxidized water, an amphoteric surfactant, etc. and/or a deterging step using an enzyme preparation, a neutral detergent, etc. and, if necessary, a disinfection in an autoclave and/or a dry sterilization by heat is carried out.

[0005] However, the above-mentioned treatment takes so long time, therefore there has been a demand for further reduction and simplification of the steps. At that time, it is necessary that a reliable germicidal effect is obtained. Although the compositions mentioned in JP-A 62-63504 and JP-A 3-131700 are relatively effective to common germs and molds, a satisfactory effect by them in a simple operation cannot be expected to viruses and bacterial spores having higher resistance against medicines. In addition, glutaraldehyde has a problem that it generates toxic gas of aldehyde to deteriorate the working environment and that it reacts with protein adhering to the medical instrument, etc. to generate a firmly adhesive matters making the deterging difficult. On the other hand, peracetic acid has a strong irritating smell and a strong oxidizing property, therefore it is feared that the peracetic acid erodes a container thereof, a treated matter thereby, etc. depending upon the material used therefor. An aqueous solution containing peracid and hydrogen peroxide as mentioned in JP-A 8-502047 has the same problem, too.

Disclosure of the Invention

[0006] An object of the present invention is to obtain a germicidal detergent composition by which a sure germicidal effect is obtained by a simple operation and which is excellent in safety and workability.

[0007] Then, the present invention provides a germicidal detergent composition comprising (a) an inorganic peroxide, (b) tetraacetylethylenediamine and (c) protease at the ratio of (a)/(b) by weight being from 10/1 to 1/2.

[0008] The inorganic peroxide (a) is preferably sodium percarbonate.

[0009] Further, the germicidal detergent composition of the present invention may preferably comprise (d) a surfactant. The surfactant (d) is preferably at least one selected from the group consisting of a nonionic surfactant, an anionic surfactant, an amphoteric surfactant and a cationic surfactant.

[0010] Then, the germicidal detergent composition of the present invention may further comprises (e) a salt of an alkali metal with an inorganic acid and/or of an alkaline earth metal with an inorganic acid.

[0011] The germicidal detergent composition of the present invention is desirably an aqueous solution having pH 6 to 9.

[0012] The germicidal detergent composition of the present invention may preferably incorporate protease (c) in such an amount that the activity thereof is from 20 APU/L to 10 mAPU/L during a time for use.

[0013] The present invention provides also a method of killing a germ, which comprises bringing an aqueous solution of a germicidal detergent composition into contact with a microorganism in the range of pH 6 to 9. The method of the invention treats medical instruments, medical goods and other goods to wash and pasteurize. It is applied to a locus

where pasterization is intended.

[0014] Furthermore, the present invention provides use of the composition as shown above for germicidal deterging or for manufacturing an aqueous solution of a germicide.

Modes for Carrying Out the Invention

[0015] With regard to the inorganic peroxide (a) used in the present invention, sodium percarbonate, sodium perborate, etc. may be exemplified and sodium percarbonate is preferable. Then, the ratio of the component (a) to tetraacetylethylenediamine (b), i.e. (a)/(b), by weight is from 10/1 to 1/2, preferably from 3/1 to 1/1 and particularly preferably from 2/1 to 1/1 from the viewpoint of the germicidal effect.

[0016] With regard to the protease (c) used in the present invention, an alkaline protease is preferable. Particularly preferable one is an alkaline protease produced by Bacillus sp. KSM-K16, deposited as FERM BP-3376 according to Budapest Treaty dated on 19th April 1990 in Fermentation Research Institute as the international depositary authority, now reorganized to National Institute of Bioscience and Human-Technology Agency of Industrial Science and Technology, at 1-3, Higashi 1 chome Tsukuba-shi Ibaraki-ken 305-8566, Japan. For example, specified one is preferably an alkaline protease K-16 described in JP-A 4-349882, and KAP 11.1G [Kao Corp.] being commercially available may be used. It is preferable that protease (c) is incorporated in the composition in such an amount that the activity thereof is from 20 APU/L to 10 mAPU/L and particularly from 10 APU/L to 100 mAPU/L. The protease activity mentioned here was measured by the following method.

〈Method for measuring the protease activity〉

[0017] It is measured by an improved method of Anson-hemoglobin method (Anson, M. L., *J. Gen. Physiol.*, Vol. 22, p 79 (1938)). Thus, a reaction is carried out at the temperature of 25°C in pH 10.5 for 10 minutes in a solution which is prepared so as to make the final concentration of an urea-modified hemoglobin used as a reaction-substrate 14.7 mg/mL and, after that, trichloroacetic acid is added to the reaction solution to make its final concentration 31.25 mg/mL. The parts dissolved in trichloroacetic acid of the reaction solution are colored by folin-ciocalteu's phenol reagent. The degree colored by 1 mmol of tyrosine is calculated in terms of 1APU to make its calibration curve (or line), and then the activity per ten minutes of the reaction is determined by the calibration curve. Then, this is calculated in terms of one minute to measure the degree colored by the above-mentioned floin-ciocalteu's phenol reagent. That is, 1APU is the amount of protease which provides the same degree colored by the parts dissolved in trichloroacetic acid in one minute as those colored by 1mmol of tyrosine with the folin-ciocalteu's phenol reagent.

[0018] It is preferable that the germicidal detergent composition of the present invention comprises (d) at least one surfactant which is selected from the group consisting of a nonionic surfactant, an anionic surfactant, an amphoteric surfactant and a cationic surfactant.

[0019] The nonionic surfactant includes a polyoxyethylene alkyl ether, a polyoxyethylene alkylene ether, a polyoxyethylene sorbitan fatty acid ester, an alkyl polyglycoside, a sucrose fatty acid ester and an alkyl polyglycerol ether. Among them, a polyoxyethylene (the average number of added ethylene oxide being 2 to 300) alkyl (the number of carbon atoms being 12 to 18) ether is preferable.

[0020] The anionic surfactant includes a higher fatty acid salt, a higher alcohol sulfate salt, a higher alcohol sulfonate, a sulfated fatty acid salt, a sulfonated fatty acid salt, a phosphate salt, a sulfate salt of a fatty acid ester, a sulfonate salt of a fatty acid ester, a sulfate salt of a higher alcohol ether, a sulfonate salt of a higher alcohol ether, an acetate substituted with a higher alcohol ether, a condensation product of a fatty acid with an amino acid, an alkylolated sulfate salt of a fatty acid amide, an alkylated sulfonate salt of a fatty acid amide, a sulfosuccinate salt, an alkylbenzene sulfonate, an alkylphenol sulfonate, an alkylnaphthalene sulfonate, an alkylbenzimidazole sulfonate, an amidoether carboxylic acid or a salt thereof, an ether carboxylic acid or a salt thereof, N-acyl-N-methyltaurine or a salt thereof, an amidoether sulfuric acid or a salt thereof, an N-acylglutamic acid or a salt thereof, an N-amidoethyl-N-hydroxyethylacetic acid or a salt thereof, an acyloxyethanesulfonic acid or a salt thereof, an N-acyl-β-alanine or a salt thereof, an N-acyl-N-carboxyethyltaurine or a salt thereof, an N-acyl-N-carboxyethylglycine or a salt thereof and an alkyl- or alkenyl- aminocarbonylmethylsulfuric acid or a salt thereof. Among them, a higher alcohol sulfate salt is preferable.

[0021] Then, the amphoteric surfactant includes an amine oxide such as an alkyldimethylamine oxide and a betaine such as an alkyldimethylaminofatty acid betaine and an alkylcarboxymethylhydroxyethylimidazolium betaine. A betaine is preferable.

[0022] The cationic surfactant includes an alkyl trimethyl ammonium salt such as lauryl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride and cetyl trimethyl ammonium chloride; a dialkyl dimethyl ammonium salt such as distearyl dimethyl ammonium chloride and a dialkyl(C_{12}-C_{18}) dimethyl ammonium chloride; an alkyl dimethyl benzyl ammonium salt such as an alkyl(C_{12}-C_{14}) dimethyl benzyl ammonium chloride; a substituted benzalkonium salt; a mono-cationic compound such as a benzethonium salt and, besides, a polycationic compound such as an N-alkyl-

N,N,N',N',N'-pentamethyl-propylene ammonium salt. Among them, an alkyl trimethyl ammonium salt, a dialkyl dimethyl ammonium salt, an alkyl dimethyl benzyl ammonium salt or a substituted benzalkonium salt is preferable. Lauryl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, cetyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, a dialkyl(C_{12}-C_{18}) dimethyl ammonium chloride or an alkyl(C_{12}-C_{14}) dimethyl benzyl ammonium chloride is particularly preferable.

[0023] It is preferable that the surfactant (d) is used in the amount as compared with tetraacetylethylenediamine (b) in terms of the ratio of (b)/(d) of from 20/1 to 2/1 by weight.

[0024] Further, it is preferable that the germicidal detergent composition of the present invention comprises (e) the salt of the alkali metal with the inorganic acid and/or of the alkali earth metal with the inorganic acid. The component (e) includes sodium sulfate, sodium nitrate, sodium chloride, sodium carbonate, sodium hydrogen carbonate, magnesium sulfate, magnesium nitrate, magnesium chloride and magnesium carbonate. Among them, sodium sulfate or magnesium sulfate is preferable. It is preferable that the component (e) is used in an amount as compared with the inorganic peroxide (a) in terms of the ratio by weight of (a)/(e) of from 1/1 to 4/1. Each of the salts of the alkali metal with the inorganic acid and of the alkali earth metal with the inorganic acid may be used solely. However, they are preferably combined and used from the viewpoint of drying the inorganic peroxide and improving the germicidal activity.

[0025] When the germicidal detergent composition of the present invention is in a solid form such as a powder, a granule or a tablet, it is used as an aqueous solution at a time for use. In the case, the concentration of the organic peracid is made into preferably 150 to 3200 ppm, more preferably 250 to 3200 ppm and particularly preferably 450 to 3200 ppm. Then, the pH of the aqueous solution is preferably 6 to 9 and particularly preferably 6.5 to 7.5. Adjustment of the pH of the aqueous solution can be achieved by an inorganic acid or an organic acid, and the inorganic acid or the organic acid may be previously added to the solid composition or the inorganic acid or the organic acid may be added to the aqueous solution. In case the acid is previously added to the solid composition as in the former case, the rate of dissolving the acid can be adjusted by coating the acid with a water-soluble substance such as a water-soluble inorganic salt. It is also possible to conduct the coating by means of the above-mentioned component (e).

[0026] The germicidal detergent composition of the present invention is suitable for germ-killing of instruments and furnishings used in medical institutions, etc. Then, it is particularly useful as a germicidal detergent composition for medical devices and instruments including a device or an instrument, for an operation, such as a surgical knife, a scissors and a surgical clamp; a device or an instrument, for a diagnosis, such as endoscope; and a device or an instrument, for a cure, such as an instrument for blood transfusion and a device for dialysis.

[0027] In accordance with the present invention, a germicidal detergent composition having a high germicidal effect and being excellent in safety and workability can be obatined.

Examples

〈Germicidal detergent composition〉

[0028] The germicidal detergent compositions as shown in Table 1 were prepared and used in the following Examples and Comparative Examples.

Table 1

Components of composition (% by weight)	Composition										
	A	B	C	D	E	F	a	b	c	d	e	f
Sodium percarbonate	50	35	35	35	35	35	100	0	50	50	50	50
Tetraacetyl ethylenediamine	50	35	35	35	35	35	0	0	0	0	0	0
Pentaacetylglucose	0	0	0	0	0	0	0	0	50	0	0	0
p-Nonanoyloxybenzene sulfonic acid	0	0	0	0	0	0	0	0	0	50	0	0
Sodium p-nonanoyloxybenzoate	0	0	0	0	0	0	0	0	0	0	50	0
Triacetin	0	0	0	0	0	0	0	0	0	0	0	50
Sodium sulfate	0	15	10	10	10	10	0	0	0	0	0	0
Magnesium sulfate	0	15	10	10	10	10	0	0	0	0	0	0
Sodium laurylsulfate *1	0	0	10	0	0	0	0	0	0	0	0	0
Polyoxyethylene lauryl ether *2	0	0	0	10	0	0	0	0	0	0	0	0
Laurylbetaine *3	0	0	0	0	10	0	0	0	0	0	0	0
Peracetic acid solution *4	0	0	0	0	0	0	0	100	0	0	0	0
Dialkyl (C_{12}-C_{18}) dimethylammonium chloride *5	0	0	0	0	0	10	0	0	0	0	0	0

(Note)

*1: Tradename of EMAL O [manufactured by Kao Corp.]

*2: Tradename of EMULGEN 109P [manufactured by Kao Corp.]

*3: Tradename of AMPHITOL 20BS [manufactured by Kao Corp.]

*4: Comprising 7% by weight of peracetic acid, 8% by weight of hydrogen peroxide, 34% by weight of acetic acid and the balance of water.

*5: Tradename of QUARTAMIN D2345P [manufactured by Kao Corp.]

Examples 1 to 6 and Comparative Examples 1 to 2

[0029] The compositions as shown in Table 1 were diluted stepwise by a sterilized water into 0.5 to 0.01 % by weight to make preparations. Protease [KAP11.1G, manufactured by Kao Corp.] was added into each of the preparations to make it 1APU/L and then Staphylococcus aureus (IFO 12732, being shown in LIST OF CULTURE, MICROORGANISMS 10^{TH} EDITION 1996 published by INSTITUTE FOR FERMENTATION, OSAKA at 17-85, Juso-honmachi 2-chome, Yodogawa-ku, Osaka 532, Japan) was added in the concentration of 1.0×10^7 cells/mL thereto. Incidentally, all of Examples were adjusted to pH 7.0 with citric acid. The resultant solution was allowed to stand at 25°C for 30 minutes, 100μL from this solution were taken, 0.9 mL of a 1% aqueous solution of sodium thiosulfate was added to inactivate the preparation, and 5μL of the resultant mixture were inoculated on an incubating medium (200μL of an SCDLP medium) and incubated at 35°C. Then, the minimum lethal concentration (MLC) was determined. The concentration of the produced organic peracid in each of the preparations was 15 to 800 ppm and then the concentration of the produced organic peracid in the preparation showing the MLC is shown in Table 2. Here, a method for quantitating the concentration of the organic peracid is as follows (and that is the same in the succeeding Examples as well).

〈Method for quantitating the concentration of the organic peracid〉

(α) A method for quantitating the hydrogen peroxide

[0030] About 2 g of the diluted preparation are precisely weighed in a conical beaker having its capacity of 200mL, the solution is cooled by adding 10 mL of 20% sulfuric acid and 2 or 3 pieces of ice thereto, and then 1 or 2 drops of a saturated aqueous solution of manganese sulfate as catalyst are added. Further, a titration is carried out using an N/2 solution of potassium permanganate. When the solution colors in pale pink for 1 to 10 seconds, the titration is made into finish. The concentration of hydrogen peroxide is calculated by the following Formula (1-1).

$$\text{Hydrogen peroxide (\%)} = \frac{0.85 \times T_1 \times F_1}{W_1} \qquad (1\text{-}1)$$

T_1: Amount (mL) required for the titration of potassium permanganate
F_1: Factor of potassium permanganate
W_1: Weight (g) of the preparation

(β) Method for quantitating the organic peracid

[0031] About 1 g of the diluted preparation is precisely weighed in an Erlenmeyer flask having its capacity of 300mL and having its connective stopper therewith. Then, 10 mL of 20% sulfuric acid, 20 mL of pure water and 2 mL of a saturated aqueous solution of potassium iodide are added thereto and the flask is tightly closed and gently shaken. This is allowed to quietly stand in a cool and dark place for 5 minutes and then titrated with an N/5 solution of sodium thiosulfate. When the solution colors in light yellow, a few drops of a 2% solution of starch were added thereto and the titration is continued. When violet color of the solution disappears, the titration is made into finish. The concentration of the organic peracid is calculated as the concentration of peracetic acid by the following Formula (1-2).

$$\text{Peracetic acid (\%)} = 76 \times \left(\frac{T_2 \times F_2}{100 \times W_2} - \frac{H}{34}\right) \quad (1\text{-}2)$$

T_2: Amount (mL) required for the titration of sodium thiosulfate
F_2: Factor of sodium thiosulfate
W_2: Weight (g) of the preparation
H: The concentration (%) of hydrogen peroxide calculated from Formula (1-1)

Table 2

		Composition No.	pH of the preparation	MLC	Concentration of the organic peracid in the preparation showing the MLC
Examples	1	A	7.0	110ppm	25ppm
	2	B	7.0	100ppm	16ppm
	3	C	7.0	100ppm	15ppm
	4	D	7.0	100ppm	15ppm
	5	E	7.0	100ppm	15ppm
	6	F	7.0	100ppm	15ppm
Comparative Examples	1	a	11.0	5.0 % by weight	—
	2	b	4.0	400ppm	28ppm

* The concentration of the organic peracid in the preparation was determined in terms of the concentration of the peracetic acid (that is the same in the succeeding cases as well).

[0032] From the result of Table 2, it is recognized that the preparations of Examples 1 to 6 are more excellent in the germicidal effect than those of Comparative Examples 1 to 2.

Examples 7 to 12 and Comparative Examples 3 to 4

[0033] The following tests were carried out by using the composition of Table 1. The result is shown in Table 3.

〈Spores for the test〉

[0034] *Bacillus cereus* (IFO 13494, being available in same way as IFO 12732 mentioned above) was heated by a conventional manner and the obtained spores were used for the test.

〈Test method〉

[0035] The compsitions as shown in Table 1 were diluted stepwise by a sterilized water into 5 to 0.1 % by weigtht to make preparations. Protease [KAP11.1G, manufactured by Kao Corp.] was added into each of the preparations to make it 1APU/L and then the above-mentioned spores were added in concentration of the 1.0×10^7 cells/mL thereto. Incidentally, all of Examples were adjusted to pH 7.0 with citric acid. The resultant solution was allowed to stand at 25°C for 30 minutes, 100μL from this solution were taken, 0.9 mL of a 1% aqueous solution of sodium thiosulfate was added to inactivate the preparation, and 5μL of the resultant mixture were inoculated on an incubating medium (200μL of an SCDLP medium) and incubated at 35°C. Then, the minimum lethal concentration (MLC) was determined. The concentration of the produced organic peracid in each of the preparations was 150 to 10000 ppm and then the concentration of the produced organic peracid in each of the preparations showing the MLC is shown in Table 3.

Table 3

		Composition No.	pH of the preparation	MLC (% by weight)	Concentration of the organic peracid in the prepration showing the MLC
Examples	7	A	7.0	0.20	450ppm
	8	B	7.0	0.15	250ppm
	9	C	7.0	0.15	240ppm
	10	D	7.0	0.15	240ppm
	11	E	7.0	0.15	240ppm
	12	F	7.0	0.15	240ppm
Comparative Examples	3	a	11.0	In-effective	—
	4	b	4.0	3.5	2500ppm

[0036] From the result of Table 3, it is recognized that the preparations of Examples 7 to 12 are more excellent in the sporicidal effect than those of Comparative Examples 3 to 4.

Examples 13 to 24 and Comparative Examples 5 to 8

[0037] The following tests were carried out using the compositions of Table 1. The result is shown in Tables 4 and 5.

〈Viruses for use〉

[0038]

① Poliovirus: poliovirus type 3, vaccinal strain (Sabin strain)

② Herpes simplex virus: HF strain
Here, FL cells were used for measuring the growth of the virus and the infection value with the virus.

〈Test method〉

[0039]

① Each of the compositions as shown in Table 1 was diluted with a sterilized water to the concentration as shown in Tables 4 and 5 to prepare the preparations for the poliovirus and for the herpes simplex virus.
② Each of the preparations was mixed with protease [KAP11.1G, manufactured by Kao Corp.] to make it 1 APU/L. Incidentally, all of Examples were adjusted to pH 7.0 with citric acid. The concentration of the produced organic peracid in each of the preparations was 160 to 3200 ppm for Examples 13 to 24 and 210 to 3500 ppm for Comparative Examples 6 and 8. No organic peracid was produced in Comparative Examples 5 and 7.
③ 50μL of the protease-containing preparation were mixed with 50μL of a virus solution.
④ The resultant mixture was allowed to stand at 25°C for 30 minutes and then 50μL of a 2% aqueous solution of sodium thiosulfate were added thereto.
⑤ The resultant solution as a mixed system of the above-mentioned 3 components was diluted stepwise at the interval of 10-fold to measure the infection value with virus. Incidentally, 50μL of a 2% aqueous solution of sodium thiosulfate were added to 50μL of the preparation containing no protease, the resultant mixture was allowed to stand for 30 minutes and then 50μL of a virus solution was added thereto to prepare a virus control.

Table 4

		Composition No.	Poliovirus				
			Concentration of the preparation (% by weight)	pH of the preparation	Concentration of the organic peracid in the preparation (ppm)	Infection value with the virus ($log_{10}TCID_{50}$/ml)	Virus control
Examples	13	A	1.4	7.0	3200	2.0	7.5
			0.2	7.0	460	6.5	7.5
	14	B	2.0	7.0	3200	Less than 1.5	7.5
			0.2	7.0	320	5.0	7.5
	15	C	2.0	7.0	3200	Less than 1.5	7.5
			0.2	7.0	320	5.0	7.5
	16	D	2.0	7.0	3200	Less than 1.5	7.5
			0.2	7.0	320	5.0	7.5
	17	E	2.0	7.0	3200	Less than 1.5	7.5
			0.2	7.0	320	5.0	7.5
	18	F	2.0	7.0	3200	Less than 1.5	7.5
			0.2	7.0	320	5.0	7.5
Comparative Examples	5	a	2.0	11.0	—	7.5	7.5
			0.2	11.0	—	7.5	7.5
	6	b	5.0	4.0	3500	2.0	7.5
			0.5	4.0	350	6.75	7.5

Table 5

		Composition No.	Herpes simplex virus				
			Concentration of the preparation (% by weight)	pH of the preparation	Concentration of the organic peracid in the preparation (ppm)	Infection value with virus ($log_{10}TCID_{50}$/ml)	Virus control
Examples	19	A	0.7	7.0	1600	Less than 1.9	6.7
			0.1	7.0	230	2.5	6.7
	20	B	1.0	7.0	1600	Less than 1.9	6.7
			0.1	7.0	160	Less than 1.9	6.7
	21	C	1.0	7.0	1600	Less than 1.9	6.7
			0.1	7.0	160	Less than 1.9	6.7
	22	D	1.0	7.0	1600	Less than 1.9	6.7
			0.1	7.0	160	Less than 1.9	6.7
	23	E	1.0	7.0	1600	Less than 1.9	6.7
			0.1	7.0	160	Less than 1.9	6.7
	24	F	1.0	7.0	1600	Less than 1.9	6.7
			0.1	7.0	160	Less than 1.9	6.7
Comparative Examples	7	a	1.0	11.0	—	6.5	6.7
			0.1	11.0	—	6.7	6.7
	8	b	2.5	4.0	1750	Less than 1.9	6.7
			0.3	4.0	210	Less than 1.9	6.7

[0040] From the result of Tables 4 and 5, it is recognized that the preparations of Examples 13 to 24 are more excellent in the inhibitory property from both infections with poliovirus and with herpes simplex virus than those of Comparative Examples 5 to 8.

Examples 25 to 30 and Comparative Examples 9 to 22

〈Preparation of the test pieces〉

[0041] A dirt model by protein (a 30% aqueous solution of a skim milk) is applied on a piece of SUS 304 cut into the size of 2 cm × 3 cm, and modified by heating at 110°C for 2 hours. Then, 100μL of spores (1.0×10^7 spores/mL) of *Bacillus cereus* (IFO 13494) are applied thereon to obtain a test piece.

〈System for the test〉

① System 1 for the test (a system to which no protease was added)

[0042] Using the preparations which were prepared by diluting the compositions of Table 1 directly to the concen-

trations shown in Table 6, the following tests were carried out. All of Comparative Examples were adjusted to pH 7.0 with citric acid except those using the compositions a and b. Then, the concentration of the produced organic peracid in each of the preparations was 240 to 2500 ppm for Comparative Examples 10 to 16. For Comparative Example 9, no organic peracid was produced.

② System 2 for the test (a system to which protease was added)

[0043] The composition of Table 1 was mixed with protease [KAP11.1G, manufactured by Kao Corp.] to make it 1 APU/L, the resultant mixture was diluted to the concentration as shown in Table 6. Using the resultant preparation, the following tests were carried out. All of Examples and Comparative Examples were adjusted to pH 7.0 with citric acid except those using the compositions a and b. Then, the concentration of the produced organic peracid in each of the preparations was 240 to 450 ppm for Examples 25 to 30 and 2500 to 3000 ppm for Comparative Examples 18 to 19. For Comparative Examples 17 and 20 to 22, no organic peracid was produced.

〈Test method〉

① Germicidal evaluation

[0044] A test piece was dipped for 30 minutes in 10 mL of each of the preparations and then the surface of each of the test pieces was washed with 2 mL of a 1% aqueous solution of sodium thiosulfate. In case there were residual protein components, they were physically peeled off and dispersed in 2 mL of a 1% aqueous solution of sodium thiosulfate. 5 μL from this solution were taken and inoculated on an incubating medium (200μL of an SCDLP medium) whereupon the germicidal effect was evaluated.

② Detergent evaluation

[0045] A test piece was dipped for 30 minutes in 10 mL of each of the preparations and then the residual protein components were dyed with erythricin B. The evaluation was carried out according to the following criteria.

◯: Completely washed (not dyed)
△: Incompletely washed (dyed areas were noted)
X: Rarely washed (almost whole areas were dyed)

Table 6

		Composition	Concentration of the preparation (% by weight)	pH of the preparation	Protease	Concentration of the organic peracid in the preparation (ppm)	Germicidal evaluation	Detergent evaluation
Examples	25	A	0.20	7.0	Present	450	Completely sterilized	○
	26	B	0.15	7.0	Present	250	Completely sterilized	○
	27	C	0.15	7.0	Present	240	Completely sterilized	○
	28	D	0.15	7.0	Present	240	Completely sterilized	○
	29	E	0.15	7.0	Present	240	Completely sterilized	○
	30	F	0.15	7.0	Present	240	Completely sterilized	○
Comparative Examples	9	a	5.0	11.0	Absent	—	No germicidal effect	×
	10	b	3.5	4.0	Absent	2500	Incompletely sterilized	×
	11	A	0.20	7.0	Absent	450	Incompletely sterilized	×
	12	B	0.15	7.0	Absent	250	Incompletely sterilized	×
	13	C	0.15	7.0	Absent	240	Incompletely sterilized	×
	14	D	0.15	7.0	Absent	240	Incompletely sterilized	×
	15	E	0.15	7.0	Absent	240	Incompletely sterilized	×
	16	F	0.15	7.0	Absent	240	Incompletely sterilized	×
	17	a	5.0	11.0	Present	—	No germicidal effect	△
	18	b	3.5	4.0	Present	2500	Incompletely sterilized	×
	19	c	5.0	7.0	Present	3000	No germicidal effect	○
	20	d	5.0	7.0	Present	—	No germicidal effect	○
	21	e	5.0	7.0	Present	—	No germicidal effect	○
	22	f	5.0	7.0	Present	—	No germicidal effect	○

Claims

1. A germicidal detergent composition comprising (a)an inorganic peroxide, (b) tetraacetylethylenediamine and (c) protease at the ratio of (a)/(b) by weight being from 10/1 to 1/2.

2. The composition as claimed in Claim 1, wherein the inorganic peroxide (a) is sodium percarbonate.

3. The composition as claimed in Claim 1, which further comprises (d) a surfactant.

4. The composition as claimed in Claim 3, wherein the surfactant (d) is at least one selected from the group consisting of a nonionic surfactant, an anionic surfactant, an amphoteric surfactant and a cationic surfactant.

5. The composition as claimed in Claim 1, which further comprises (e) a salt of an alkaline metal with an inorganic acid and/or of an alkaline earth metal with an inorganic acid.

6. The composition as claimed in Claim 1, which is an aqueous solution having pH 6 to 9.

7. The composition as claimed in Claim 1, which incorporates protease (c) in such an amount that the activity thereof is from 20 APU/L to 10 mAPU/L during a time for use.

8. Use of a composition as defined in Claim 1 for germicidal deterging.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 11 3168

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Place of search	Date of completion of the search	Examiner
THE HAGUE	28 September 2000	Neys, P

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X : particularly relevant if taken alone
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