DISINFECTING COMPOSITION BASED ON H_2O_2, ACIDS AND METAL IONS

Field of the invention

The present invention concerns, as a novel industrial product, an aqueous composition, in particular in gel form, based on H_2O_2, acids and Ag^{II}, Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions. The invention also relates to a preparation process, in particular when said ions are Ag^{2+}, and to the use of this composition in the field of disinfection, hygiene and/or decontamination, on the one hand, and in the field of surface treatment (in particular cleaning, stripping and/or passivation), on the other hand.

Prior art

The closest prior art consists of patent document WO-A-96/18301. Before the publication of this document, aqueous disinfecting compositions, some containing hydrogen peroxide and a carboxylic acid/carboxylic peracid mixture of the type RCO_2H/RCO_3H (in which R is essentially CH_3 or CH_3CH_2) (see in particular to this end EP-A-0 370 850, EP-A-0 193 416, EP-B-0 087 343, FR-A-2 321 301 and FR-A-2 321 302), and others containing hydrogen peroxide and Ag^{+} ions (see in particular to this end US-A-3 035 698 and GB-A-2 189 394), had already been proposed in the past, said aqueous disinfecting compositions being stabilized in each case with a strong acid (essentially H_3PO_4).

These prior aqueous disinfecting compositions, namely (i) those of the type H_2O_2 + RCO_2H/RCO_3H + H_3PO_4 and (ii) those of the type H_2O_2 + Ag^{+} + H_3PO_4, are insufficient as regards their absence of efficacy on several strains of bacteria and molds, and in particular on the strains of ***Penicillium verrucosum***.

A more recent and markedly more effective technique (in particular with regard to said strains of ***Penicillium verrucosum*** which were resistant to the two abovementioned types of aqueous disinfecting compositions) was described in the abovementioned WO-A-96/18301, which is incorporated herein by way of reference. According to WO-A-96/18301, the recommended technique uses an aqueous disinfecting, hygiene and decontaminating composition, which comprises, in water:

(A) H_2O_2,

(B) an RCO_2H/RCO_3H mixture (in which R is CH_3 or CH_3CH_2),

(C) a silver component as a source of Ag^+ ions, and

(D) a stabilizer (mainly H_3PO_4),

Table IX of WO-A-96/18301 demonstrating the synergy of the aqueous composition containing the components A+B+C+D, compared with the aqueous compositions containing the components A+B+D and A+C+D.

It is found that the aqueous solution of A+B+C+D according to WO-A-96/18301 does not act quickly enough with regard to inhibiting or, better still, destroying microorganisms, such as bacteria, molds, viruses and microscopic algae, in particular by making their wall brittle, especially by degrading their biofilm, by perforating their wall or by preventing them from penetrating into the cells of the body or by protecting said cells against their toxins.

Moreover, the procedures described in GB-A-2 189 394 as regards the preparation of the concentrated aqueous silver solution (i.e. component C above) in the presence of H_3PO_4, on the one hand, and that of the resulting stabilized concentrated aqueous solution of silver and of hydrogen peroxide (i.e. the aqueous solution containing A+C+D), on the other hand, do not lead to the production of Ag^{2+} ions or to that of Ag^{3+} ions.

Specifically, GB-A-2 189 394, which recommends a process comprising:

- mixing a strong mineral acid (pH <1.6) with a silver component (a silver salt or a silver complex), at a temperature of 50-60°C, the strong mineral acid/silver component molar ratio being greater than or equal to 1/1;
- cooling the resulting mixture to a temperature of 25-30°C and adding a stabilizing organic acid optionally with gelatin; and
- incorporating H_2O_2 into the resulting mixture,

cites (see page 1, lines 46-50) silver (I) compounds which give Ag^+ ions in strong acid medium, these compounds are silver (I) salts and a silver (I) complex salt, namely $AgNaCl_2$, on the one hand, and silver (II) and (III) compounds which are soluble only in basic medium, these compounds are silver (II) and (III) oxides which, in strong acid medium, mainly give metallic silver *in fine*, on the other hand.

More specifically, the silver (I), (II) and (III) oxides give rise, in acid medium, to the following reactions, in which s denotes a solid product:

(1) $Ag_2O(s) + 2H^+ + 2e \rightarrow 2Ag(s) + H_2O$

(2) $2AgO(s) + 2H^+ + 2e \rightarrow Ag_2O(s) + H_2O$

(3) $Ag_2O_3(s) + 2H^+ + 2e \rightarrow 2AgO(s) + H_2O$

Since the direct placing in contact (i.e. without a strong acid stabilizer) of H_2O_2 and of a silver component is liable to cause an explosion, a process different from that recommended by GB-A-2 189 394 should be used to obtain the Ag^{2+} ions that are useful according to the present invention.

For the same reasons, the procedures described in WO-A-96/18301 do not allow the oxidation in acid medium of silver (I) to silver (II) according to the reaction: $Ag^+ \rightarrow Ag^{2+} + e$.

It is known that, according to US-A-5 017 295 and US-A-5 078 902, Ag^{2+} ions have been presented as being more active as bactericidal agents than Ag^{+} ions. Now, it is found that the procedures given in these two documents do not promote the production of Ag^{2+} or Ag^{2+} + Ag^{3+} ions since, with regard to reaction (2) above, the silver (II) oxide gives in acid medium a precipitate of silver (I) oxide. Thus, the reactions outlined in Example 1 of US-A-5 017 295 and in Examples 1 and 2 of US-A-5 078 902, namely:

$$3AgO + 2H_3PO_4 \rightarrow Ag_3(PO_4)_2 + 3H_2O,$$

$$AgO + 2HNO_3 \rightarrow Ag(NO_3)_2 + H_2O, \text{ and}$$

$$AgO + 2HCl \rightarrow AgCl_2 + H_2O,$$

cannot take place. Furthermore, by reproducing the other method for obtaining Ag^{2+} ions indicated in Example 2 of US-A-5 078 902, which comprises the dissolution of AgO in alkaline medium, followed by the addition of an oxidizing source [i.e. oxone (Na_2O_2)] which can give hydrogen peroxide [this addition is carried out in alkaline medium (i.e. under conditions in which H_2O_2 intervenes as the reducing agent)], the resulting concentration of Ag^{2+} ions is very low, such that the redox potential of the aqueous solution containing Ag^{+} and Ag^{2+} is always less than 650 mV (at 298 K). Thus, according to US-A-5 017 295 and US-A-5 078 902, the beneficial effects as stated for the Ag^{2+} ions cannot be manifested.

Finally, US-A-3 702 298 proposes the use of Ag^{3+} ions as a germicidal means. However, the mixture Ag^{+} + Ag^{2+} + Ag^{3+} effectively obtained has a redox potential ranging from 0.15 mV to 0.4 mV, which is markedly lower than that desired according to the present invention which is greater than 1 000 mV.

It is also known that molybdenum intervenes in human beings and warm-blooded animals as a coenzyme for the detoxifying enzymes located in the liver, such as xanthine oxidase, aldehyde oxidase and sulfite oxidase.

Mo is essential for converting purine bases into uric acid, and it promotes the intestinal absorption of iron and the retention of fluorine in the body.

It is also known from US-A-4 995 987 that molybdate and tungstate ions have been proposed, as agents for inhibiting the growth of sulfate-reducing bacteria, in combination with antimicrobial agents. Document US-A-4 995 987 neither describes nor suggests the subject of the present invention.

In the field of treating metal surfaces, in particular to strip and/or passivate them, it is known that the conventional oxidizing means, such as chromic acid, chromates and nitric acid, are considered as being products that are harmful to the environment.

US-A-4 537 778 moreover discloses an aqueous mouthwash or oral rinse composition which comprises 0.5-5% by weight of H_2O_2, 3-15% by weight of ethanol, 0.5-2% by weight of a nonionic and water-soluble surfactant of the polyoxyethylenated polyoxypropylene glycol type, 0.3-2% by weight of a nonionic and water-soluble surfactant of the type such as a C_{10}-C_{18} fatty acid monoester with polyoxyethylenated sorbitol, a sweetener and a fragrance. This composition may be produced in the form of a paste or a gel by means of a thickener or a gelling agent, respectively. The gelling agent proposed is a gum (xanthan gum or guar gum), a carboxylic interpolymer described in US-A-2 798 053 or a polyol of the PLURONIC® type comprising 70% to 20% of hydrophobic groups and 30% to 80% of hydrophilic groups, the preferred gelling agent being PLURONIC® 127 (see column 4, lines 28-29, column 5, lines 34 and 49, and column 6, lines 5-6). Now, it is found that such a gelling agent, which is of the organic polymer type, is degraded more or less quickly (within the space of a few minutes to a few days) by oxidizing compositions of

high redox potential (in particular a redox potential of greater than or equal to 800 mV).

Finally, DE-A-2 659 462 discloses a pharmaceutical composition containing a specific silica gel, namely a silicic acid hydrogel which is usually used in the pharmaceutical field but has never been used under highly oxidizing conditions.

Finally, the prior art neither describes nor suggests the effective use of ions containing a metal with a degree of oxidation close to (in the particular case of Ag^{II}) or equal to (in the case of Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III}) its maximum value, in a disinfecting composition or a composition for treating surfaces.

Aim of the invention

It is desired, on the one hand, to overcome the abovementioned drawbacks of the prior art, and, on the other hand, to provide a novel technical solution which is effective and unexpected when compared with the teaching of the prior art.

According to a first aspect of the invention, it is proposed to provide a novel technical solution to the problem of disinfection and/or of treating surfaces, which is more effective as regards the speed of action than the technical solution recommended by WO-A-96/18301.

According to a second aspect, it is proposed to provide a novel technical solution which has long-lasting action in order to obtain a persistence of the activity over a longer period of time, in particular when the surface to be treated is inclined or vertical.

Subject of the invention

The novel technical solution according to the invention for achieving the aforementioned aim is based on the use of specific metal ions, namely Ag^{II}, Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions.

Thus, an aqueous oxidizing composition (I) is recommended, which is useful in particular in the field of disinfection, hygiene and decontamination, on the one hand, and in the field of treating a metal surface (in particular for cleaning, stripping and/or passivating it) or a nonmetal surface (in particular a plastic or ceramic surface, especially for cleaning and/or stripping it), on the other hand, said composition, which contains, in water, hydrogen peroxide, an RCO_2H/RCO_3H mixture (in which R is a C_1-C_6 aliphatic residue containing a linear or branched, saturated or unsaturated hydrocarbon chain) and a stabilizer which is a strong acid and, where appropriate, Ag^{+} ions, being characterized in that it contains ions of at least one metal M which are Ag^{II}, Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions, the source L, which gives Ag^{II} ions or Ag^{II} + Ag^{III} ions, being such that, starting with 100 g of silver (i.e. 157 g of $AgNO_3$) and 1 liter of demineralized water, the concentration of Ag^{+} + Ag^{2+} or Ag^{+} + Ag^{2+} + Ag^{3+} ions in the resulting solution gives a redox potential of greater than 1 000 mV.

More specifically, the composition (I) according to the invention is characterized in that it contains, in water:

(A) H_2O_2;

(B) an RCO_2H/RCO_3H mixture (in which R is a C_1-C_6 aliphatic residue containing a linear or branched, saturated or unsaturated hydrocarbon-based chain;

(C) metal ions from a source L and chosen from the set consisting of:

(1) ions of a metal M which are Ag^{II}, Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions,

(2) combinations of Ag^{+} ions and of ions of said metal M, and

(3) mixtures thereof;

the source L, which gives Ag^{II} ions or Ag^{II} + Ag^{III} ions, being such that, starting with 100 g of silver (i.e. 157 g of $AgNO_3$) and 1 liter of demineralized water, the concentration of Ag^{+} + Ag^{2+} or Ag^{+} + Ag^{2+} + Ag^{3+} ions in the resulting solution gives a redox potential of greater than 1 000 mV; and

(D) a stabilizer which is an acid.

This composition may be prepared according to a method which is known per se. The process which is recommended herein comprises the steps consisting in:

(a) using an aqueous solution of a source L giving metal ions chosen from the set consisting of

(1) ions of a metal M which are Ag^{II}, Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions,

(2) combinations of Ag^{+} ions and of ions of said metal M, and

(3) mixtures thereof;

the source L, which gives Ag^{II} ions or Ag^{II} + Ag^{III} ions, being such that, starting with 100 g of silver (i.e. 157 g of $AgNO_3$) and 1 liter of demineralized water, the concentration of Ag^{+} + Ag^{2+} or Ag^{+} + Ag^{2+} + Ag^{3+} ions in the resulting solution gives a redox potential of greater than 1 000 mV;

(b) introducing the stabilizer into said solution:

(c) introducing said resulting solution thus obtained into aqueous hydrogen peroxide solution or introducing the aqueous hydrogen peroxide solution into said resulting solution;

(d) introducing into the resulting solution thus obtained an acidic substance which is RCO_3H, RCO_2H

or a mixture thereof RCO_3H + RCO_2H in which R is defined as indicated above;

(e) leaving the resulting solution thus obtained to stand until the equilibrium H_2O_2 + RCO_2H ⇔ H_2O + RCO_3H is established; and

(f) making up to 100% by weight with water.

The process for preparing a composition according to the invention which contains Ag^{2+} ions and, where appropriate, Ag^{3+} ions is characterized in that it comprises the steps consisting in:

(1°) preparing an aqueous solution of a silver component, which acts as a source of Ag^+ ions;

(2°) oxidizing at least some of the Ag^+ ions to Ag^{2+} ions using persulfate, preferably with sodium persulfate $Na_2S_2O_8$ or ammonium persulfate $(NH_4)_2S_2O_8$, so as to obtain a redox potential of greater than or equal to 1 000 mV, starting with 1 liter of demineralized water and 157 g of $AgNO_3$, and filtering to remove any insoluble material which may be present;

(3°) introducing the stabilizer into the resulting solution thus obtained;

(4°) introducing said resulting solution thus obtained into aqueous hydrogen peroxide solution or introducing the aqueous hydrogen peroxide solution into said resulting solution;

(5°) introducing into the resulting solution thus obtained an acidic substance which is RCO_3H, RCO_2H or a mixture thereof RCO_3H + RCO_2H in which R is defined as indicated above;

(6°) leaving the resulting solution thus obtained to stand until the equilibrium H_2O_2 + RCO_2H ⇔ H_2O + RCO_3H is established; and

(7°) making up to 100% by weight with water.

When carrying out this process, Ag^{3+} ions are liable to be obtained at least in trace amount.

According to the invention, a gelled composition (II) is also recommended, which is characterized in that it comprises:

- the aqueous composition (I) mentioned above, and
- a gelling agent.

In practice, the gelled composition (II) will comprise 50% to 99.7% by weight of said aqueous composition (I) and 50% to 0.3% by weight of gelling agent. More specifically, the preferred gelling agent will be a pyrogenic colloidal silica or a compound of the polyacrylic type such as CARBOPOL® ETD 2623 from the company Goodrich, which is a copolymer of a C_{10}-C_{30} alkyl acrylate, or CARBOPOL® 672 also from the company Goodrich, which is a polyacrylic homopolymer.

The process for preparing the gelled composition (II) consists (i) in placing said composition (I) in contact with the gelling agent, (ii) in stirring the resulting mixture for 3 to 20 minutes, and (iii) in leaving the resulting mixture to stand in order for it to set to a gel.

Detailed description of the invention

In the text hereinbelow, except where otherwise mentioned, the respective amounts of the ingredients of the aqueous decontaminating composition according to the invention are expressed as percentages by weight, and the dilutions of said composition are expressed according to the ratio of the initial volume to the volume of the resulting dilute composition.

- Hydrogen peroxide

In general, the aqueous composition (I) according to the invention contains an H_2O_2 content which is less than or equal to 60% by weight relative to the weight of said composition. Thus, the composition (I)

according to the invention may contain 0.1% to 60% by weight of H_2O_2 and may be diluted at the time of use (when the H_2O_2 concentration is greater than or equal to 4% by weight in particular.

In practice, since hydrogen peroxide raises transportation difficulties, when an aqueous hydrogen peroxide solution with an H_2O_2 content of greater than 8% by weight is used, especially with regard to the French and EC regulations, it would be advisable to provide an aqueous composition (I) containing not more than 8% by weight and better still not more than 7.9% by weight of H_2O_2.

Consequently, the aqueous composition (I) according to the invention will advantageously comprise an H_2O_2 content of about 7.5-7.9% by weight and will be diluted, at the time of use, with water in particular to a final H_2O_2 concentration of less than or equal to 4% by weight.

- RCO_2H/RCO_3H mixture

With regard to the equilibrium reaction (4):

(4) $H_2O_2 + RCO_2H \Leftrightarrow H_2O + RCO_3H$

the respective amounts of RCO_3H and RCO_2H in the mixture RCO_3H/RCO_2H are not critical. It suffices to have in contact in H_2O either H_2O_2 and RCO_3H or H_2O_2 and RCO_2H in order to obtain a ternary mixture $H_2O_2 + RCO_3H + RCO_2H$ provided that H_2O_2 is in excess relative to the RCO_2H/RCO_3H pair. Thus it suffices, as it were, to incorporate:

(i) RCO_2H in the presence of H_2O_2, or

(ii) RCO_3H (which in concentrated form generally contains H_2O_2 and RCO_2H according to documents FR-A-2 321 301 and FR-A-2 321 302 mentioned above),

in H_2O, in order to obtain at equilibrium the combination $H_2O_2 + RCO_3H + RCO_2H$.

As mentioned above, the group R of the acid/peracid pair represents a C_1-C_6 aliphatic residue containing a linear or branched, saturated or unsaturated hydrocarbon chain. Advantageously, use will be made of a group R containing a saturated linear hydrocarbon chain such as CH_3; CH_3CH_2 or $CH_3(CH_2)_4$ or alternatively of a group R containing an unsaturated linear hydrocarbon chain such as, in particular, CH_3-CH=CH, CH_3-CH=CH-CH_2 or CH_3-CH=CH-CH=CH.

The preferred groups R are (in order of increasing preference): CH_3-CH=CH-CH=CH, CH_3CH_2 or CH_3. In general, the pair

CH_3CO_2H/CH_3CO_3H (i.e. R = methyl)

is preferred to the pair

$CH_3CH_2CO_2H/CH_3CH_2CO_3H$ (i.e. R = ethyl)

since the first pair is more active than the second pair as a disinfecting/decontaminating means in the aqueous composition according to the invention.

Advantageously, in the aqueous composition (I) according to the invention, the weight ratio B/A of the mixture RCO_2H/RCO_3H to the hydrogen peroxide will be between 0.15/1 and 0.85/1. Preferably, this weight ratio will be between 0.5/1 and 0.7/1.

- The source L

The source L serves to provide the ions that are useful according to the invention, namely the ions containing the metal M (i.e. Ag^{II}, Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions), the combination Ag^{+}/ions of the metal M, or mixtures thereof.

When V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions are desired, use will be made of a source L which is a salt in which said metal M is in its maximum oxidation state. As a variant, a source L which may be used is an

oxide of said metal M (in this case an oxide of V^V, Nb^V, Ta^V, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III}) if said oxide is soluble in acids.

When Ag^{2+} ions are desired, the oxidation of Ag^+ (advantageously obtained from $AgNO_3$ or from colloidal silver) to Ag^{2+} should be carried out.

The procedures recommended for the reaction $Ag^+ \rightarrow Ag^{2+} + e$ are given later. Since this reaction is generally incomplete, it mainly gives a mixture of Ag^+/Ag^{2+} ions [and, where appropriate, a mixture of $Ag^+/Ag^{2+}/Ag^{3+}$ ions in which the Ag^{3+} ions are at least in trace amount].

When Ag^+ ions are desired in combination with V^V, Nb^V, Ta^V, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions, the ions obtained from the corresponding two sources are mixed together.

Finally, when an ionic mixture $Ag^+/Ag^{2+}/V^V$, Nb^V, Ta^V, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions is desired, the Ag^+/Ag^{2+} ions obtained from their source by oxidation as indicated above are mixed with the ions from the abovementioned source of V^V, Nb^V, Ta^V, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions.

The preferred ions according to the invention comprise the V^V, Mo^{VI}, W^{VI} and Tl^{III} ions, on the one hand, and the ion mixtures Ag^+/Ag^{2+}, Ag^+/Mo^{VI}, Ag^+/W^{VI}, Ag^+/Tl^{III} and $Ag^+/Ag^{2+}/Mo^{VI}$, on the other hand, the most advantageous ions being Ag^+/Ag^{2+}, Ag^+/Mo^{VI}, $Ag^+/Ag^{2+}/Mo^{VI}$ and above all the Mo^{VI} ions.

It has been found, unexpectedly, during the use of the aqueous composition (I) according to the invention, that molybdenum has a twofold advantage over silver (in the form Ag^+ or Ag^+/Ag^{2+}):

- as regards microorganisms, it is more active than silver, and
- during the cold sterilization of instruments (in particular dental or surgical instruments), it does not give the unattractive gray or black deposits of silver.

The main source of V^{V} ions is a VO_2^+ (or, where appropriate, VO_3^-) salt, that of Nb^{V} ions is an NbO^{3+} salt, that of Mo^{VI} ions is an MoO_3^{2+} or MoO_4^{2-} salt, that of Co^{III} ions is a Co^{3+} salt, that of W^{VI} ions is a WO_4^{2-} salt, that of Ta^{V} ions is a Ta^{5+} salt, that of In^{III} ions is an In^{3+} salt, and that of Tl^{III} ions is a Tl^{3+} salt.

The ions of the component C according to the invention act on microorganisms by making their wall brittle or by degrading it, on the one hand, and they also act as oxidizing means, in particular according to the following reactions, on the other hand.

(5) $VO_2^+ + 2H^+ + e \rightarrow VO^{2+} + H_2O$ or, where appropriate,

(5a) $VO_3^- + 4H^+ + e \rightarrow VO^{2+} + 2H_2O$

(6) $Nb^{V} + 2e \rightarrow Nb^{III}$ or

(6a) $NbO^{3+} + 2H^+ + 2e \rightarrow Nb^{3+} + H_2O$

(7) $MoO_2^{2+} + 2H^+ + e \rightarrow MoO^{3+} + H_2O$ or

(7a) $MoO_4^{2-} + 4H^+ + e \rightarrow MoO_2^+ + 2H_2O$

(8) $Co^{3+} + e \rightarrow Co^{2+}$ (in acidic medium)

(9) $In^{3+} + 2e \rightarrow In^+$

(10) $Tl^{3+} + 2e \rightarrow Tl^+$.

In practice, it is recommended as regards efficacy for the source L to be able to give, starting with an amount corresponding to 100 g of metal M and 1 liter of demineralized water, a resulting solution containing Ag^{II}, Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} and/or Tl^{III} ions with a redox potential of greater than 1 V.

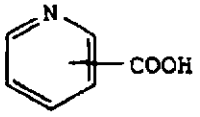
Advantageously, the weight ratio of the source L of ions to the hydrogen peroxide will be between 0.0005/1

and 0.015/1. In practice, this weight ratio will be even more advantageously between 0.0008/1 and 0.005/1 and better still about 0.001/1.

- The stabilizer

The stabilizer, which protects H_2O_2 and the ions from the source L and which avoids any risk of explosion, in particular using concentrated solutions of (i) H_2O_2 and (ii) Ag^+ and/or Ag^{2+}, is chosen from the combination consisting of mineral acids such as H_3PO_4 and H_2SO_4 (nitric acid and hydrochloric acid being strongly advised against, in particular on account of their harmful effects on metal surfaces and/or the environment), on the one hand, and organic acids such as pyridinecarboxylic acids, on the other hand. The preferred stabilizer according to the invention is H_3PO_4 or (especially when the source L provides Mo^{VI} ions) a pyridinecarboxylic acid.

Pyridinecarboxylic acids are substances of formula:



namely, 2-pyridinecarboxylic acid (picolinic acid), 3-pyridinecarboxylic acid (nicotinic acid) and 4-pyridinecarboxylic acid (isonicotinic acid).

When the source L of ions gives Ag^+ or Ag^+/Ag^{2+} ions, it is advantageous to add, where appropriate, a small amount of gelatin to the acidic stabilizer of the component D.

Advantageously, the weight ratio of the stabilizer to the hydrogen peroxide will be between 0.0005/1 and 0.025/1. In practice, this weight ratio will be even

more advantageously between 0.0008/1 and 0.005/1 and better still about 0.001/1.

- The other additives

At least one of the following components may also be incorporated into the aqueous composition (I) according to the invention:

(E) wetting agent;

(F) anticorrosion agent; and

(G) fragrance.

The wetting agent which is included herein is (i) an amphiphilic, amphoteric, anionic or nonionic surfactant compound, such as polyols that are suitable in particular for contact with foodstuffs and, where appropriate, suitable for oral administration with drinking water at the dose considered for use, or (ii) a mixture of such compounds. The product sold under the name Tegol® 2000 is suitable for this purpose as an amphoteric wetting agent.

In the aqueous composition (I) according to the invention, the weight ratio of the wetting agent to the hydrogen peroxide will advantageously be between 0.00005/1 and 0.01/1. In practice, this weight ratio will be even more advantageously about 0.005/1.

It is recommended to incorporate into the aqueous composition (I) according to the invention an anticorrosion agent which, at the dose used, is suitable for contact with foodstuffs and/or oral administration with drinking water. As anticorrosion agents which may be used for this purpose, mention may be made in particular of aminophosphonic acids as described in the abovementioned FR-A-2 321 302, the sodium, potassium, ammonium and alkanolamine salts thereof, and mixtures thereof. Hydroxyethanedi-phosphonic acid, dimethylaminomethanediphosphonic acid

and ethylenediaminotetrakis(methylenephosphonic acid), the Na, K, NH_4^+ or alkanolamine salts thereof, and mixtures thereof, are particularly suitable for the aqueous composition (I) according to the invention. 1,2,3-Benzotriazole is also suitable as an anticorrosion agent.

In practice, the anticorrosion agent will be present in the aqueous composition (I) at low concentration. If it is used, said anticorrosion agent will be included especially in an amount such that the weight ratio of said anticorrosion agent to the hydrogen peroxide is between 0.00005/1 and 0.03/1 and preferably between 0.001/1 and 0.005/1.

As indicated in WO-A-96/18301, it is prudent to limit the corrosion of metal surfaces (mainly made of iron or copper) in very prolonged contact with the aqueous composition (I) of the invention to a value of less than 200 μm/year.

As the corrosion of metal surfaces is mainly reflected by a phenomenon known as "pitting", it is appropriate to avoid the formation of said pitting in which the microorganisms which it is desired to irradicate would live and grow.

The fragrance component in point (G) will be included in the aqueous decontaminating composition in an amount of less than or equal to that of the anticorrosion agent in point (F).

The water which is included in the decontaminating composition according to the invention is advantageously a purified water, namely distilled water, demineralized water or, better still, deionized water. Preferably, the deionized water used herein will be a water with a resistivity of greater than 10^5 Ω/cm and better still greater than or equal to 10^6 Ω/cm.

The water used for any diluting of said decontaminating composition according to the invention will advantageously be purified water as indicated above.

The pH of the aqueous composition according to the invention is (before dilution and then use) generally between 1.2 and 5 and better still between 1.5 and 4. It is adjusted by means of the preferred component D: H_3PO_4 or pyridinecarboxylic acid.

- The aqueous composition (I)

Preferably, the aqueous composition (I) according to the invention, with regard to the foregoing text, contains, in water:

(A) not more than 8% by weight of H_2O_2;

(B) a mixture RCO_2H/RCO_3H (in which R is CH_3 or CH_3CH_2), in a weight ratio of said mixture RCO_2H/RCO_3H to hydrogen peroxide of from 0.15/1 to 0.85/1 and preferably from 0.5/1 to 0.7/1;

(C) a source L providing metal ions chosen from the combination consisting of:

(1) ions of a metal M which are Ag^{II}, Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions,

(2) combinations of Ag^{+} ions and of ions of said metal M, and

(3) mixtures thereof,

the source L, which gives Ag^{II} ions or Ag^{II} + Ag^{III} ions, being such that, starting with 100 g of silver (i.e. 157 g of $AgNO_3$) and 1 liter of demineralized water, the concentration of Ag^{+} + Ag^{2+} or Ag^{+} + Ag^{2+} + Ag^{3+} ions in the resulting solution gives a redox potential of greater than 1 000 mV;

according to a weight ratio of said source L to hydrogen peroxide of from 0.0005/1 to 0.015/1 and preferably from 0.0008/1 to 0.005/1; and,

(D) a stabilizer, in a weight ratio of said stabilizer to hydrogen peroxide of from 0.0005/1 to 0.015/1 and preferably from 0.0008/1 to 0.005/1.

Even more practically, a standard composition (i.e. a stock composition) which is intended to be diluted at the time of use is recommended. This standard composition contains:

(A) 7.5-7.9% by weight of H_2O_2;

(B) 4.5% to 4.8% by weight of a mixture CH_3CO_3H + CH_3CO_2H;

(C) 0.005% to 0.01% by weight of the source L;

(D) 0.0005% to 0.01% by weight of H_3PO_4 or of pyridinecarboxylic acid;

(E) where appropriate, 0.0075% to 0.04% by weight of surfactant;

(F) where appropriate, 0.003% to 0.04% by weight of anticorrosion agent;

(G) where appropriate, a fragrance; and

water (distilled, demineralized or deionized) to make up to 100% by weight.

It may be advantageous, in particular in the context of the cleaning, stripping and/or passivation treatment of a metal surface or in the context of the cleaning and/or stripping treatment of a nonmetal surface, for the weight ratio C/D to be less than 1/1.

Moreover, when the component C is a mixture of Ag^+ ions and of M ions, it suffices, according to the invention, for the metal ions of M to be in trace amount in order for the beneficial effects to be manifested.

- Preparation of the composition (I)

The process for preparing the aqueous composition (I) according to the invention, which is given above and comprises steps (a)-(f), is carried out directly when the source L contains no Ag^{2+} (or Ag^{2+}/Ag^{3+}) ions. In

this case, said composition may be produced according to the teaching of GB-A-2 189 394 (in order to obtain a high concentration of H_2O_2), on the one hand, and then by diluting (for an H_2O_2 concentration of less than or equal to 8% by weight and better still less than or equal to 7.9% by weight) with distilled, demineralized or deionized water for the purpose of transportation, on the other hand. As a variant, said composition may be produced directly in the form of a standard composition.

When the source L gives Ag^{2+} (or Ag^{2+}/Ag^{3+}) ions, step (a) is then replaced with steps (1°) and (2°) to make use of a source of Ag^{+} ions, which are oxidized to Ag^{2+} ions. This oxidation is carried out (i) using a persulfate, preferably sodium persulfate or ammonium persulfate, as oxidizing agent, and (ii) in the absence of white light to avoid the UV-mediated reduction of the silver ions to metallic silver which precipitates *in situ*. The oxidation $Ag^{+} \rightarrow Ag^{2+} + e$ will advantageously be performed in darkness (i.e. in opaque reactors) or in red light.

The filtration included at the end of step (2°) has the purpose of removing any insoluble material which may be present in the reaction medium. The presence of an insoluble material is mainly manifested when the persulfate used is ammonium persulfate. Advantageously, this filtration is carried out using a filter membrane having pores with a diameter of about 3 μm.

In step (3°) - i.e. step (b) of the general process - the silver ions obtained (generally a mixture of Ag^{+}, Ag^{2+} and, where appropriate, Ag^{3+}) are preferably stabilized using H_3PO_4 (as an aqueous solution at 70-85% by weight) or using a pyridinecarboxylic acid.

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Even more advantageously, a small amount of gelatin will be added before, during or after the addition of H_3PO_4 or of a pyridinecarboxylic acid.

As indicated above, if it contains Ag^{2+} or Ag^{2+} + Ag^{3+} ions, the aqueous composition according to the invention may be produced either in the form of a standard solution or in the form of a solution with a high H_2O_2 content before dilution for transportation.

One of the preferred modes (mode A) for carrying out the process for preparing the composition (I) according to the invention, when the source L gives V^V, Nb^V, Ta^V, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions, comprises the following steps (for the production of a standard composition containing 7.5-7.9% by weight of H_2O_2) consisting in:

(a) preparing a solution of a V^V, Nb^V, Ta^V, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} salt (advantageously in acidic medium) in a portion of the total amount of water required to prepare said aqueous disinfecting composition;

(b) introducing into the resulting solution thus obtained an aqueous phosphoric acid solution containing 70% to 85% by weight of H_3PO_4 or an aqueous pyridinecarboxylic acid solution;

(c) introducing the resulting solution thus obtained into an aqueous hydrogen peroxide solution containing 50% to 60% by weight of H_2O_2, with stirring, at a temperature of between 0°C and 25°C (preferably at a temperature of between 4°C and 15°C), and with a rate of introduction of the solution obtained in step (b) of between 3 and 6 l/h;

(d) introducing into the resulting solution thus obtained the acidic substance CH_3CO_2H, with stirring, at a temperature of between 0°C and 25°C (preferably at a temperature of between 4°C and

15°C) and with a rate of introduction of the acidic substance CH_3CO_2H of between 3 and 6 l/h;

(e) leaving the resulting solution thus obtained to stand for 48 hours (preferably in darkness), at a temperature of between 0°C and 25°C (preferably at a temperature of between 4°C and 15°C), in order for the equilibrium

$$H_2O_2 + CH_3CO_2H \Leftrightarrow CH_3CO_3H + H_2O$$

to be established, and

(f) adding the remaining water to make up to 100% by weight.

In step (d) of the preparation of this composition, the acid CH_3CO_2H may be introduced in the form of an aqueous solution.

Another preferred mode (mode B) for carrying out the process for preparing the composition (I) according to the invention, when the source L provides Ag^{2+} ions (with, where appropriate, Ag^{3+} ions) comprises the following steps (for the production of a standard composition containing 7.5-7.9% by weight of H_2O_2) consisting in:

(1°) dissolving $AgNO_3$ in demineralized water with a resistivity of 10^6 Ω/cm (in a proportion of 157 g of silver nitrate - i.e. 100 g of silver - to 1 liter of demineralized water), the redox potential of the solution thus obtained being about 600 mV;

(2°) oxidizing at least a portion of the Ag^+ ions of the above solution to Ag^{2+} or to Ag^{2+} + Ag^{3+} by addition of sodium persulfate or ammonium persulfate, so as to obtain a redox potential of greater than or equal to 1 000 mV (in particular a redox potential of greater than or equal to 1 600 mV); filtering (on a membrane with pores 3 μm in diameter);

(3°) stabilizing the resulting solution thus obtained using an aqueous phosphoric acid solution

containing 70% to 85% by weight of H_3PO_4 [in a proportion of from 10 to 100 ml of aqueous H_3PO_4 solution at 70% to 85% by weight per 1 liter of demineralized water used in step (1°)] or using an aqueous pyridinecarboxylic acid solution [after stirring for 24 hours at room temperature, the solution of silver ions thus stabilized having a redox potential of greater than or equal to 1 000 mV];

(4°) introducing the resulting solution thus obtained into an aqueous hydrogen peroxide solution containing 50% to 60% by weight of H_2O_2, with stirring, at a temperature of between 0°C and 25°C (preferably at a temperature of between 4°C and 15°C), and with a rate of introduction of the solution obtained in step (3°) of between 3 and 6 l/h;

(5°) introducing into the resulting solution thus obtained the acidic substance CH_3CO_2H, with stirring, at a temperature of between 0°C and 25°C (preferably at a temperature of between 4°C and 15°C), and with a rate of introduction of the acidic substance CH_3CO_2H of between 3 and 6 l/h;

(6°) leaving the resulting solution thus obtained to stand for 48 hours, in darkness (or in red light) at a temperature of between 0°C and 25°C (preferably at a temperature of between 4°C and 15°C), in order for the equilibrium

$$H_2O_2 + CH_3CO_2H \Leftrightarrow CH_3CO_3H + H_2O$$

to be established, and

(7°) adding water to make up to 100% by weight.

In step (5°) of the preparation of this standard composition, the acid CH_3CO_2H may be introduced in the form of an aqueous solution.

- The gelled composition (II)

The gelled composition (II) in accordance with the invention is obtained using the aqueous composition (I) and a specific gelling agent, which is a mineral substance or an organic substance. When this gelling agent is a mineral substance, it is advantageously pyrogenic colloidal silica which is, in dry form, in the form of particles with an area per unit mass of from 80 to 400 m^2/g and a mean particle size of from 7 to 20 nm. Among the silicas which are suitable for this purpose, mention may be made in particular of those sold by the company Cabot under the name CAB-O-SIL®, and in particular the products CAB-O-SIL® LM-150, CAB-O-SIL® M-5, CAB-O-SIL® EH-5 and CAB-O-SIL® M-7D, which are hydrophilic.

In order to produce a gelled composition (100 parts by weight) containing pyrogenic silica, the process is performed as follows:

- placing composition (I) (50 to 99 parts by weight) and the pyrogenic colloidal silica (50 to 1 parts by weight) in contact,
- stirring for 3-10 minutes with an angular speed of the stirrer of from 1 500 to 2 000 rpm, and then
- leaving to stand at room temperature.

When the gelling agent is an organic substance, it is advantageously a polyacrylic material as indicated above. In this case, the gelled composition (100 parts by weight) which contains said polyacrylic material will be prepared as follows:

- placing the composition (I) (90 to 99.7 parts by weight) and the organic gelling material (10 to 0.3 parts by weight) in contact,
- stirring for 10-20 minutes with an angular speed of the stirrer of from 1 000 to 2 000 rpm, and then
- leaving to stand at room temperature.

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The gelled composition (II) containing a polyacrylic organic gelling material can be used only at a pH of greater than or equal to 3.5; in practice, it will be used at a pH of from 3.5 to 7 and preferably at pH 5. Moreover, it is suitable for the preparation of transparent gels that are valued by the public in dermatology and in cosmetology.

On the other hand, the gelled composition (II) containing pyrogenic silica will advantageously be used at a pH of from 1.5 to 4.

The gel obtained has thixotropic properties: it becomes fluid under a stress such as stirring, friction or shear and sets to a solid quickly (in less than 5 minutes) when the stirring, friction or shear stops.

Moreover, this gel is stable in acidic or weakly alkaline medium; it is also stable up to the degradation temperature of its constituents.

Depending on the water content, said gel may be prepared in a wide range of viscosities.

On account of its thixotropic properties, the gelled composition (II) according to the invention is particularly suitable for decontaminating aged oils and greases (which are the nutrient media of several microorganisms liable to be pathogenic) *in situ* in industrial plants and devices.

- The uses

The uses of the aqueous oxidizing composition (I) according to the invention comprise (i) those envisaged in the abovementioned publication WO-A-96/18301 (see page 20, line 11 to page 22, line 15) in particular as regards the disinfection of water to make it fit for drinking, the hygiene of industrial premises and

swimming pools, the cold sterilization of surgical and dental instruments, the protection of plants and crops against bacteria, molds, viruses and parasites, the protection of fish, crustaceans and shellfish against pathogenic algae such as ***Euglena***, and the decontamination of mining sites, and (ii) the novel uses which relate to the cleaning, stripping and/or passivation of metal surfaces (in particular surfaces made of steel or aluminum) or nonmetal surfaces (in particular plastic or ceramic surfaces, the plastic surfaces comprising herein those of floor-covering or wall panels which are exposed and which are generally made of PVC, polyacrylate, polycarbonate or the like).

Advantageously, the composition (I) intended for disinfection and hygiene will be obtained by diluting a standard composition so as to have an H_2O_2 concentration of from 1% to 2% by weight.

Also advantageously, the composition (I) intended for decontaminating mining sites will have an H_2O_2 content of from 4% to 7.9% by weight and will be diluted at the time of use to a final working concentration of less than or equal to 1/100 (i.e. a final H_2O_2 content of less than or equal to 0.04% by weight).

In the field of treating surfaces, the composition (I) will advantageously have an H_2O_2 content of between 1% and 7.9% by weight and will comprise a weight ratio C/D of less than 1/1 and greater than 1/2.

The gelled composition (II) according to the invention offers the advantage of providing, in the region of the article or surface to be treated, a source of H_2O_2 and of ions originating from L which is stabilized and which ensures long-lasting action.

The gelled composition (II) is particularly useful with regard to surfaces that are not horizontal, i.e.

vertical, curved or inclined surfaces. It is most particularly suitable for protecting constructions against microorganisms liable to grow in the cavities of the outer walls of buildings exposed to dust and to bird droppings, on the one hand, and for stripping and passivating metal reactors or tanks, on the other hand.

The gelled composition II is thus recommended according to the invention for use, on the one hand, as a germicidal product for preparing a medicinal product intended for therapeutic use with regard to oral conditions, in particular of the periodontium, caused by bacteria and/or fungi, and, on the other hand, as a cosmetic product, in particular in the form of a toothpaste, for oral hygiene.

In the dental field, it has been found that the gelled composition (II) serves as a hemostatic agent, dispenses with the administration of antibacterial and/or antifungal agents, inhibits catalase and ensures the passivation of the metal surfaces of bridges (said passivation preventing the deposition of bacteria and fungi over a long period of time), and also the temporary protection of plastic or ceramic surfaces against said bacteria and fungi (their deposition thus being prevented). This gelled composition is suitable for preparing toothpastes containing 1% to 2% by weight of hydrogen peroxide.

Other advantages and characteristics of the invention will emerge more clearly on reading the embodiments and comparative tests which follow. Needless to say, this set of data is not limiting in any way, but is given for illustrative purposes. For convenience, where the component (C) is concerned, the source of ions L, its proportion by weight and the ions it gives are indicated below in Ex. 1-Ex. 6.

Example 1

A standard composition is prepared according to mode B given above, containing:

H_2O_2	7.8%	by weight
CH_3CO_2H + CH_3CO_3H mixture	4.8%	by weight
$AgNO_3$ (source of Ag^+/Ag^{2+})	0.008%	by weight
H_3PO_4 or pyridinecarboxylic acid	0.008%	by weight
Surfactant (anionic wetting agent)	0.04%	by weight
H_2O (demineralized) to make up to	100%	by weight

Example 2

A standard composition is prepared according to mode A given above, containing:

H_2O_2	7.8%	by weight
CH_3CO_2H + CH_3CO_3H mixture	4.8%	by weight
Na_2MoO_4 (source of MoO_4^{2-})	0.008%	by weight
Pyridinecarboxylic acid	0.008%	by weight
Surfactant (anionic wetting agent)	0.04%	by weight
H_2O (demineralized) to make up to	100%	by weight

When the source of ions L gives Mo^{VI} ions, it is important not to use H_3PO_4 as stabilizer. It should be avoided to place H_3PO_4 in contact with MoO_4^{2-}, as this would give a complex of the phosphonomolybdate type which is insoluble.

Example 3

A standard composition is prepared according to mode A given above, containing:

H_2O_2	7.8%	by weight
CH_3CO_2H + CH_3CO_3H mixture	4.8%	by weight
NH_4VO_3 (source of VO_3^-, VO_2^+ or V^{5+})	0.008%	by weight

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H_3PO_4 or pyridinecarboxylic acid	0.008%	by weight
Surfactant (anionic wetting agent)	0.04%	by weight
H_2O (demineralized) to make up to	100%	by weight

Example 4

A standard composition is prepared according to mode A given above, containing:

H_2O_2	7.8%	by weight
CH_3CO_2H + CH_3CO_3H mixture	4.8%	by weight
Na_2WO_4 (source of WO_4^{2-})	0.008%	by weight
H_3PO_4 or pyridinecarboxylic acid	0.008%	by weight
Surfactant (anionic wetting agent)	0.04%	by weight
H_2O (demineralized) to make up to	100%	by weight

Example 5

The standard composition of Example 5 is prepared from a 1/1 mixture by weight of the compositions of Examples 1 and 2. This standard composition contains:

H_2O_2	7.8%	by weight
CH_3CO_2H + CH_3CO_3H mixture	4.8%	by weight
$AgNO_3$ (source of Ag^+/Ag^{2+})	0.004%	by weight
Na_2MoO_4 (source of MoO_4^{2-})	0.004%	by weight
Pyridinecarboxylic acid	0.008%	by weight
Surfactant (anionic wetting agent)	0.04%	by weight
H_2O (demineralized) to make up to	100%	by weight

Comparative example CP1

The composition of Example 1 of prior art document WO-A-96/18301 is used as comparative product. Its formulation is as follows:

H_2O_2	8%	by weight
CH_3CO_2H + CH_3CO_3H mixture	4.8%	by weight
$AgNO_3$ (source of Ag^+)	0.008%	by weight
H_3PO_4	0.008%	by weight
Surfactant (anionic wetting agent)	0.04%	by weight
H_2O (demineralized) to make up to	100%	by weight

Example 6

Starting with a 1/1 mixture by weight of the compositions of Ex. 2 and CP1, a standard composition

is obtained (after replacing the phosphoric acid in CP1 with a pyridinecarboxylic acid), having the formulation:

H_2O_2	7.9%	by weight
CH_3CO_2H + CH_3CO_3H mixture	4.8%	by weight
$AgNO_3$ (source of Ag^+)	0.004%	by weight
Na_2MoO_4 (source of MoO_4^{2-})	0.004%	by weight
Pyridinecarboxylic acid	0.008%	by weight
Surfactant (anionic wetting agent)	0.04%	by weight
H_2O (demineralized) to make up to	100%	by weight

Comparative tests I

The germicidal activity of Ex.1-Ex. 6 and CP1 was determined with respect to three bacterial strains (1-3) and one strain of mold (4) which are pathogenic to man (1-2) or phytopathogenic (3-4), especially for tomatoes grown in the open air, namely:

(1) ***Staphylococcus aureus***

(2) ***Pseudomonas aerugina,***

(3) ***Pseudomonas syringea,*** and

(4) ***Alternaria solani.***

If $[S]_0$ is the concentration of a strain S at time 0 and $[S]_T$ is the concentration of the same strain at the time T (T = 1 hour for bacteria and T = 2 hours for molds), the germicidal activity is measured by the difference:

$$\Delta = \log[S]_0 - \log[S]_T$$

a product being active when it reduces the number of live strains such that $\Delta \geq 4$ for bacteria and $\Delta \geq 3$ for molds.

The results obtained for Δ given in Table I below show that CP1 at a dilution of 1/5 is effective with respect to bacteria but is virtually lacking in activity on the strain of ***Alternaria solani.*** These results also show that, at the same dilution of 1/5, Ex. 1-Ex. 6 are (i)

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effective on bacteria and molds, and (ii) more active than CP1.

Example 7

10 g of CAB-O-SIL® M-5 pyrogenic silica are added with vigorous stirring (2 000 rpm) to one liter of the aqueous composition of Ex. 1 over 6 minutes. The mixture is left to stand and a gel with a viscosity of 10^6 Pa.s is obtained.

Comparative tests II

The action of the aqueous composition CP1 was compared with the gel of Ex. 7. The two products were applied for 4 hours to a roof made of anodized aluminum alloy with a westerly aspect and coated with mosses and lichens. The treatment with CP1 was found to be ineffective on account of the insufficient contact time due to the evaporation of the solution. On the other hand, all of the mosses and lichens were removed by a simple rinsing with running water after the 4 hours of the experiment.

Example 8

100 g of CAB-O-SIL® M-5 pyrogenic silica and 500 ml of aqueous phosphoric acid solution containing 75% by weight of H_3PO_4 are added with vigorous stirring (2 000 rpm) to one liter of the aqueous composition of Ex. 1, over 6 minutes. The mixture is left to stand and a gel with a viscosity of 10^7 Pa.s is obtained.

The gel thus obtained is highly thixotropic.

Tests III

The gel of Ex. 8, applied to an industrial kitchen extractor hood made of 316L stainless steel

depassivated after a fire which released chlorine-rich vapors, and left in contact for 3 hours, allowed the 316L stainless steel to be completely decontaminated and to regain its passivity potential.

Example 9

The aqueous composition of Ex. 1 is diluted with demineralized water so as to obtain an H_2O_2 content of 1% to 2% by weight. The resulting solution is then gelled according to the process of Example 7 above.

Tests IV

The gel of Ex. 9 was applied once a day for 5 days to the teeth and the mucosa of the periodontium in the region of the teeth, to patients suffering from dental plaque and/or oral mycosis, and who had bad breath. Biopsies of the mucosa of the periodontium showed a total reduction *in situ* in the bacteria and fungi responsible for the dental plaque and the mycoses, respectively. The treated patients no longer had bad breath.

Example 10

The aqueous composition of Ex. 1 is diluted with demineralized water so as to obtain an H_2O_2 content of 4% by weight. The resulting solution is then gelled according to the process of Example 8 above.

Tests V

The gel of Ex. 10 was applied to stainless steel tanks used for manufacturing champagne. Statistically, it is known that the contents of one tank in every five or six is lost due to (i) the growth of inappropriate microorganisms and/or (ii) the degradation of the inner wall. By treating the inner wall of the tanks for

5 hours with the gel of Ex. 10 followed by rinsing with water, once before the grape harvesting and once after emptying the tanks following fermentation, all the tanks are kept active while avoiding the conventional loss mentioned above.

Tests VI

Each of the compositions of Ex. 1, Ex. 2, Ex. 5 and CP1 is diluted extemporaneously (i.e. at the time of use) so as to obtain a dilution of 1/5. 50 ml of each of the solutions thus diluted are placed in batches of transparent glass containers and, at time T = 0, a dental prosthesis, which (a) comprises metal, plastic and/or ceramic surfaces, (b) is infested with bacteria and/or molds, and (c) is soiled with traces of tissues (coagulated blood, mucosa, flesh) and adhesive, is immersed in these solutions. The open containers are left to stand. The prostheses in the batches of containers are observed at times T = 1 hour, T = 2 hours, T = 15 days and T = 90 days.

It is found that, at T = 1 hour, the prostheses immersed in the dilute compositions of Ex. 1, Ex. 2 and Ex. 5 are clean and essentially free of bacteria and molds; at T = 2 hours, the prostheses immersed in the dilute compositions of Ex. 1, Ex. 2 and Ex. 5 are clean and essentially free of bacteria and molds, and the prostheses immersed in the dilute composition of CP1 are clean, free of bacteria, but are still contaminated with molds (population $\geq 10^4$ microorganisms/ml; at T = 15 days, all the prostheses are clean and free of bacteria, those immersed in the dilute composition of CP1 having a mold population of greater than 10^4 microorganisms/ml, whereas those treated with the dilutions of Ex. 1, Ex. 2 and Ex. 5 are free of molds; at T = 90 days, only the prostheses treated with the dilutions of Ex. 1, Ex. 2 and Ex. 5 are clean and free

of bacteria and molds, those treated with the dilution of CP1 are again contaminated with bacteria and molds.

In brief, after treatment for one hour with Ex. 1, Ex. 2 and Ex. 5, each prosthesis is considered as "being entirely new and reusable". It is moreover found that, unlike CP1, Ex. 1, Ex. 2 and Ex. 5 prevent the bacteria and molds from attaching to a surface.

Table I

Germicidal activity

$$\Delta = \log[S]_0 - \log[S]_T$$

Product	Strains			
	(a)	(b)	(c)	(d)
CP1	4.56	5.38	3.97	1.61
Ex. 1	6.27	6.14	5.23	4.42
Ex. 2	6.25	6.17	5.25	4.44
Ex. 3	5.0	5.19	4.67	4.45
Ex. 4	6.27	5.17	5.30	4.43
Ex. 5	6.25	5.67	5.27	4.42
Ex. 6	5.37	5.70	5.27	4.42

Notes:
(a) ***Staphylococcus aureus***
(b) ***Pseudomonas aerugina***
(c) ***Pseudomonas syringae***
(d) ***Alternaria solani***

Example 11

A dermatological or cosmetic composition is prepared using the following formulation:

H_2O_2	1 part by weight
CH_3CO_2H + CH_3CO_3H mixture	0.5 part by weight
CH_3-CH=CH-CH=CH-CO_2H	0.1 part by weight
Pyridinecarboxylic acid	0.004 part by weight

Na_2MoO_4 (source of MoO_4^{2-})	0.004 part by weight
Surfactant (nonionic wetting agent)	0.02 part by weight
H_2O (demineralized) to make up to	95.5 parts by weight

The ingredients are introduced into a portion of the demineralized water required, in the following order: (i) H_2O_2, (ii) CH_3CO_2H/CH_3CO_3H + CH_3-CH=CH-CH=CH-CO_2H + pyridinecarboxylic acid, (iii) Na_2MoO_4, and then (iv) demineralized water up to a total weight of 95.5 parts by weight.

Example 12

A gelled composition containing a polyacrylic organic material as gelling agent is prepared using the following formulation:

H_2O_2	1% by weight
CH_3CO_2H + CH_3CO_3H mixture	0.5% by weight
CH_3-CH=CH-CH=CH-CO_2H	0.1% by weight
Pyridinecarboxylic acid	0.004% by weight
Na_2MoO_4 (source of MoO_4^{2-})	0.004% by weight
NaOH (up to pH 5)	
Surfactant (nonionic wetting agent)	1% by weight
CARBOPOL® ETD 2623	0.5% by weight
H_2O (demineralized) to make up to	100% by weight

This composition is prepared by stirring (at 800-1 000 rpm) CARBOPOL® 2623 in a portion of the demineralized water required, maintaining this stirring for 15 minutes, heating to 45°C until completely dissolved, adding, in the following order, (i) H_2O_2, (ii) CH_3CO_2H/CH_3CO_3H, CH_3-CH=CH-CH=CH-CO_2H and then pyridinecarboxylic acid, and (iii) Na_2MoO_4 followed by surfactant, stirring for 15 minutes (at 1 000 rpm), adjusting the pH to 5 with NaOH, and (iv) demineralized water up to 100% by weight. The Brookfield viscosity at

20 rpm of this gelled composition is 15 Pa.s (i.e. 15 000 cP).

CLAIMS

1. An aqueous oxidizing composition (I) which is useful in particular in the field of disinfection, hygiene and decontamination, on the one hand, and in the field of treating surfaces (in particular for cleaning, stripping and/or passivating), on the other hand, said composition, which contains, in water, hydrogen peroxide, an RCO_2H/RCO_3H mixture (in which R is a C_1-C_6 aliphatic residue containing a linear or branched, saturated or unsaturated hydrocarbon chain) and a stabilizer which is an acid and, where appropriate, Ag^+ ions, being characterized in that it contains ions of at least one metal M which are Ag^{II}, Ag^{III}, V^V, Nb^V, Ta^V, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions, the source L, which gives Ag^{II} ions or Ag^{II} + Ag^{III} ions, being such that, starting with 100 g of silver (i.e. 157 g of $AgNO_3$) and 1 liter of demineralized water, the concentration of Ag^+ + Ag^{2+} or Ag^+ + Ag^{2+} + Ag^{3+} ions in the resulting solution gives a redox potential of greater than 1 000 mV.

2. The composition as claimed in claim 1, characterized in that it contains, in water:
   (A) H_2O_2;
   (B) an RCO_2H/RCO_3H mixture (in which R is a C_1-C_6 aliphatic residue containing a linear or branched, saturated or unsaturated hydrocarbon chain);
   (C) metal ions from a source L and chosen from the set consisting of:
      (1) ions of a metal M which are Ag^{II}, Ag^{III}, V^V, Nb^V, Ta^V, Mo^{VI}, W^{VI}, Co^{III}, In^{III} or Tl^{III} ions,
      (2) combinations of Ag^+ ions and of ions of said metal M, and
      (3) mixtures thereof;

the source L, which gives Ag^{II} ions or Ag^{II} + Ag^{III} ions, being such that, starting with 100 g of silver (i.e. 157 g of $AgNO_3$) and 1 liter of demineralized water, the concentration of Ag^{+} + Ag^{2+} or Ag^{+} + Ag^{2+} + Ag^{3+} ions in the resulting solution gives a redox potential of greater than 1 000 mV; and

(D) a stabilizer which is an acid.

3. The composition as claimed in claim 2, characterized in that said metal ions are Mo^{VI} ions, a mixture of Ag^{+}/Ag^{2+} ions, a mixture of Mo^{VI}/Ag^{+} ions or a mixture of $Mo^{VI}/Ag^{+}/Ag^{2+}$ ions.

4. A process for preparing an aqueous composition as claimed in claim 1 or 2, said process being characterized in that it comprises the steps consisting in

(a) using an aqueous solution of a source L giving metal ions chosen from the set consisting of

(1) ions of a metal M which are Ag^{II}, Ag^{III}, V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, In^{III} or Tl^{III} ions,

(2) combinations of Ag^{+} ions and of ions of said metal M, and

(3) mixtures thereof;

the source L, which gives Ag^{II} ions or Ag^{II} + Ag^{III} ions, being such that, starting with 100 g of silver (i.e. 157 g of $AgNO_3$) and 1 liter of demineralized water, the concentration of Ag^{+} + Ag^{2+} or Ag^{+} + Ag^{2+} + Ag^{3+} ions in the resulting solution gives a redox potential of greater than 1 000 mV;

(b) introducing the stabilizer into said solution:

(c) introducing said resulting solution thus obtained into aqueous hydrogen peroxide solution or introducing the aqueous hydrogen

peroxide solution into said resulting solution;

(d) introducing into the resulting solution thus obtained an acidic substance which is RCO_3H, RCO_2H or a mixture thereof RCO_3H + RCO_2H in which R is defined as indicated above;

(e) leaving the resulting solution thus obtained to stand until the equilibrium H_2O_2 + RCO_2H ⇔ H_2O + RCO_3H is established; and

(f) making up to 100% by weight with water.

5. The process as claimed in claim 4, for preparing a composition which contains Ag^{2+} ions, said process being characterized in that it comprises the steps consisting in

(1°) preparing an aqueous solution of a silver component, which acts as a source of Ag^+ ions;

(2°) oxidizing at least some of the Ag^+ ions to Ag^{2+} or Ag^{2+} + Ag^{3+} ions using persulfate, so as to obtain a redox potential of greater than or equal to 1 000 mV, starting with 1 liter of demineralized water and 157 g of $AgNO_3$, and filtering to remove any insoluble material which may be present;

(3°) introducing the stabilizer into the resulting solution thus obtained;

(4°) introducing said resulting solution thus obtained into aqueous hydrogen peroxide solution or introducing the aqueous hydrogen peroxide solution into said resulting solution;

(5°) introducing into the resulting solution thus obtained an acidic substance which is RCO_3H, RCO_2H or a mixture thereof RCO_3H + RCO_2H in which R is defined as indicated above;

(6°) leaving the resulting solution thus obtained to stand until the equilibrium H_2O_2 + RCO_2H ⇔ H_2O + RCO_3H is established; and

(7°) making up to 100% by weight with water.

6. The composition as claimed in claim 1 or 2, characterized in that it is in the form of a gelled composition (II) which comprises the aqueous composition as claimed in claim 1 or 2 and a mineral or organic gelling agent.

7. The composition as claimed in claim 6, characterized in that it comprises:

(α) 50% to 99% by weight of the aqueous composition (I) as claimed in claim 1 or 2, and

(β) 50% to 1% by weight of pyrogenic colloidal silica with an area per unit mass of from 80 to 400 m^2/g and a mean particle size of from 7 to 20 nm, as gelling agent.

8. The composition as claimed in claim 6, characterized in that it comprises:

(α) 90% to 99.7% by weight of the aqueous composition (I) as claimed in claim 1 or 2, and

(β) 10% to 0.3% by weight of a polyacrylic organic material as gelling agent.

9. The use of the gelled composition as claimed in any one of claims 6 to 8, characterized in that said gelled composition is used as a germicidal product for preparing a medicinal product intended for use with regard to oral conditions, in particular those of the periodontium, caused by bacteria and/or fungi.

10. The use of the gelled composition as claimed in any one of claims 6 to 8, characterized in that said gelled composition is used to prepare a cosmetic product for oral hygiene.

11. The use of the gelled composition as claimed in any one of claims 6 to 8, characterized in that said gelled composition (i) is used for cleaning, stripping and/or passivating a metal surface, or (ii) for cleaning and/or stripping a nonmetal surface.

12. A process for preparing the gelled composition (II) as claimed in claim 6, said process being characterized in that it consists (i) in placing said composition (I) in contact with a gelling agent, (ii) in stirring the resulting mixture for 3 to 20 minutes, and (iii) in leaving the resulting mixture to stand in order for it to set to a gel.