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(54) Titre : COMPOSE CHIMIQUE ET METHODE CONNEXE  
(54) Title: CHEMICAL COMPOSITION AND METHOD

(57) **Abrégé/Abstract:**

The invention relates to a process for cleaning metals comprising a step of contacting a metal with an aqueous solution comprising hydrogen peroxide and at least one compound selected from the group consisting of complexing agents based on phosphonic acids, salts and degradation products thereof in an amount from about 10 to about 60 wt% based on the amount of hydrogen peroxide.



## ABSTRACT

The invention relates to a process for cleaning metals comprising a step of contacting a metal with an aqueous solution comprising hydrogen peroxide and at least one compound selected from the group consisting of complexing agents based on phosphonic acids, salts and degradation products thereof in an amount from about 10 to about 60 wt% based on the amount of hydrogen peroxide.

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## CHEMICAL COMPOSITION AND METHOD

Field of the invention

The present invention relates to a process for cleaning of metals.

Background of the invention

5 Solutions of hydrogen peroxide are widely used in various commercial applications, such as processes for bleaching, cleaning, disinfection, sterilization, oxidation, and etching of metals. In most applications diluted solutions are used, normally containing from about 0.1 to about 20 wt% of hydrogen peroxide. In many cases the hydrogen peroxide is present in a formulation together with other additives, such as  
10 surfactants, organic acids, inorganic acids, or the like. However, for practical and economic reasons it is desirable to produce and transport hydrogen peroxide as more concentrated solutions, generally containing from about 30 to about 80 wt% of hydrogen peroxide, which solutions can be diluted on site to a desired concentration.

Hydrogen peroxide is sensitive to impurities catalyzing its decomposition,  
15 particularly heavy metal ions, but also some organic substances. Therefore, small amounts of stabilizers are normally added to the hydrogen peroxide by the manufacturer to inhibit its decomposition. It has, however, been found that under certain conditions even hydrogen peroxide solutions containing stabilizers do not have satisfactory stability, particularly those prepared by dilution of more concentrated solutions.

20 Hydrogen peroxide may be included in various cleaning compositions. However, when such compositions are used for cleaning metals it has been found that the metal surfaces rapidly become tarnished again.

US Patents 3122417 and 4304762 disclose use of certain phosphonic acids for stabilizing hydrogen peroxide. It is not recommended to add too high levels of phosphonic  
25 acids as it increases the costs and tends to give reduced activity of the hydrogen peroxide. It is also strongly believed among those skilled in the art, that excessive amounts of commonly used stabilizers will actually de-stabilize hydrogen peroxide.

US Patent 4070442 teaches that in order to stabilize hydrogen peroxide in the presence of high concentrations of heavy metal ions it is necessary to add both an  
30 alkylidene di-phosphonic acid and an organic hydroxy compound.

US Patent 5885953 discloses a compositions suitable for cleaning, disinfection or bleaching comprising hydrogen peroxide.

US Patent 5810939 discloses a process for pickling of stainless steel using a solution comprising hydrogen peroxide.

Summary of the invention

It is an object of the invention to provide a hydrogen peroxide solution that can be used for the preparation of various formulations in which the hydrogen peroxide still has high stability.

5 It is another object of the invention to provide a hydrogen peroxide solution that can be used for the preparation of various formulations containing heavy metal ions or organic materials in high concentrations.

It is a further object of the invention to provide a process for cleaning metals.

Description of the invention

10 The invention concerns a process for cleaning metals comprising a step of contacting a metal with an aqueous cleaning solution comprising hydrogen peroxide and at least one compound selected from the group consisting of complexing agents based on phosphonic acids, salts and degradation products thereof in an amount from about 10 to about 60 wt%, preferably from about 20 to about 50 wt%, most preferably from about 35  
15 to about 45 wt% based on the amount of hydrogen peroxide.

The complexing agent may be based on various phosphonic acids, salts and degradation products thereof. Examples of such phosphonic acids include 1-hydroxyethylidene-1,1-diphosphonic acid, 1-aminoethane-1,1-diphosphonic acid, aminotri  
20 methylene diamine tetra (methylenephosphonic acid), ethylene diamine tetra (methylenephosphonic acid), hexa-  
methylene diamine tetra (methylenephosphonic acid), diethylenetriamine penta (methylenephosphonic acid) and diethylenetriamine hexa (methylenephosphonic acid). 1-hydroxyethylidene-1,1-diphosphonic acid is particularly preferred.

The term degradation products as used herein refer to compounds formed by reactions between phosphonic acids or salts thereof with hydrogen peroxide and/or other  
25 components in the solution. Salts usually include alkali metal salts, e.g. of sodium or potassium, but also other metal salts are possible.

The cleaning solution preferably comprises hydrogen peroxide in an amount from about 0.1 to about 50 wt%, most preferably from about 0.5 to about 20 wt%, particularly most preferably from about 1 to about 10 wt%

30 The cleaning solution preferably comprise at least one mineral acid, most preferably sulfuric acid. The amount of mineral acid is preferably from about 0.1 to about 50 wt%, most preferably from about 0.5 to about 20 wt%, particularly most preferably from about 1 to about 10 wt%. However, also alkaline cleaning solutions can be used, preferably comprising alkali metal hydroxide.

35 The cleaning solution may also comprise further components such as surfactants, corrosion inhibitors and impurities, such as soil from the surface of the article so cleaned.

Examples of surfactants that can be used include non-ionic, amphoteric, an-ionic and cat-ionic surfactants. Non-ionic surfactants are preferred and may, for example, include one or more of ethoxylated and/or propoxylated fatty acids, alcohols, amines or amides, preferably comprising from 1 to 12 most preferably from 4 to 8 mols ethylene oxide and/or propylene oxide per mol acid, alcohol, amine or amide. Preferably the acid, alcohol or amide comprises from 7 to 15, most preferably from 9 to 11 carbon atoms. Useful non-ionic surfactants can be high foaming such as an ethoxylated alcohol containing 11 carbon atoms and 8 ethylene oxides, or low foaming such as a narrow range ethoxylated alcohol containing 9 carbon atoms and 6 ethylene oxides. Further surfactants may include alkyl polyglucosides and other carbohydrate derivatives.

The temperature and contact time during the cleaning may vary within wide ranges. The temperature may, for example, be from about 0 to about 100°C, preferably from about 20 to about 80°C. The contact time between the metal and the cleaning solution may, for example, be from about 5 seconds up to about 10 hours or more, preferably from about 10 seconds to about 2 hours.

The process of the invention has been found advantageous for cleaning several kinds of metals, such as aluminium, copper and steel, for example carbon steel. It has surprisingly been found that the metal surface become passivated and protected against further oxidation. Furthermore, it has been found the consumption of hydrogen peroxide during the course of cleaning is low, so the concentration thereof remains at a satisfactory level even after a long time of contact with the metal surface.

It should be noted that the term cleaning as used herein is not the same as pickling, or etching where substantial amounts of metal is dissolved. Thus, in the cleaning process of the invention only small amounts of metal is dissolved.

The cleaning solution may be prepared by diluting a more concentrated hydrogen peroxide solution and adding any other optional component, such as a mineral acid. The concentrated hydrogen peroxide solution may, for example, be an aqueous solution consisting essentially of:

- (a) hydrogen peroxide, preferably in an amount from about 20 to about 70 wt%, most preferably from about 25 to about 55 wt%, based on the entire solution;
- (b) at least one compound selected from the group consisting of complexing agents based on phosphonic acids, salts and degradation products thereof in an amount from about 10 to about 60 wt%, preferably from about 20 to about 50 wt%, most preferably from about 35 to about 45 wt%, based on the amount of hydrogen peroxide;
- (c) water; and,

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(d) components other than (a) through (c) in an amount from 0 up to about 10 wt%, preferably from 0 up to about 5 wt%, most preferably from 0 up to about 2 wt%, particularly most preferably from 0 up to about 1 wt%, based on the amount of hydrogen peroxide.

5 Components other than (a) through (c) may include low concentrations of various additives and degradation products thereof, as well as impurities, particularly those originating from the hydrogen peroxide production process. Examples of additives usually added at the production or shortly after include phosphoric acid, pyrophosphates, phosphonic acids and their salts, butane diols, phenol sulfonates, alkali metal stannate and  
10 alkali metal nitrate. Examples of impurities include metal ions (particularly heavy metal ions) and organic residues, e.g. originating from the working solution of the anthraquinone process.

The pH of the concentrated solution is suitably below 7, preferably from about 0 to about 6, most preferably from about 0.5 to about 5.

15 As only a few components in the concentrated hydrogen peroxide solution are present in significant amounts, the solution can be used for the preparation of a great variety of formulations with different additives. Such formulations may, for example, be those suitable for cleaning, disinfection, sterilization, bleaching, odor control, cleaning and passivating metals (e.g. copper or iron), or as a micronutrient and/or other soil treatment  
20 compositions. The formulations may comprise various additives and impurities, such as mineral acids (e.g. sulfuric acid, phosphoric acid, nitric acid or hydrochloric acid), organic acids (e.g. glycolic acid, oxalic acid, acetic acid, or phosphonoacetic acid), surfactants, detergent builders, alkali metal silicate, alkali metal hydroxides, dyes and metal ions. A formulation comprising a solution as described combined with sulfuric acid has been found  
25 particularly useful for metal cleaning as it does not destroy the metal.

The invention will be further described in connection with the following examples, which, however, are not intended to limit the scope thereof. Unless otherwise stated, all parts and percentages refer to parts and percent by weight.

Example 1: Two metal cleaning solutions were made from different concentrated  
30 aqueous solutions of hydrogen peroxide. Cleaning solution A was made from "Grade I", a conventional 50 wt% H<sub>2</sub>O<sub>2</sub> solution containing about 175 mg/L phosphonic acid based complexing agents and about 500 mg/L sodium nitrate; Cleaning solution B was made from Grade II, an aqueous hydrogen peroxide solution containing 31.5 wt% H<sub>2</sub>O<sub>2</sub>, 15.65 wt% 1-hydroxyethylidene-1,1-diphosphonic acid, less than 175 mg/L of other phosphonic  
35 acid based complexing agents and less than 500 mg/L sodium nitrate. The concentrated solutions were diluted with water and supplied with sulfuric acid to obtain a cleaning solution comprising 5 wt% hydrogen peroxide and 5 wt% sulfuric acid. Sample of copper wire were

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immersed in the two cleaning solutions for 120 minutes at 30°C. The hydrogen peroxide concentrations were monitored and the results are shown in the table below:

Elapsed Time (min.)	Cleaning solution A H <sub>2</sub> O <sub>2</sub> Concentration (gm/l)	Cleaning solution B H <sub>2</sub> O <sub>2</sub> Concentration (gm/l)
0	50.03	50.26
5	49.75	50.02
15	49.08	45.91
30	46.33	44.52
60	44.76	43.87
120	40.17	42.39

The copper wire samples were removed and rinsed. The samples from the cleaning solution A tarnished within 15 seconds, while the samples from cleaning solution B remained bright even after six weeks.

Example 2: Example 1 was repeated with the exception that the temperature was 50°C. The results are shown in the table below:

Elapsed Time (min.)	Cleaning solution A H <sub>2</sub> O <sub>2</sub> Concentration (gm/l)	Cleaning solution B H <sub>2</sub> O <sub>2</sub> Concentration (gm/l)
0	50.12	49.25
5	48.22	42.99
10	47.66	38.75
15	46.55	37.92
30	38.52	28.99
60	0.74	24.59
90	0.55	22.28
120	0.61	20.28

It appears that between 30 and 60 minutes the cleaning solution A loses virtually all of its hydrogen peroxide content, while at the same time solution B turns towards a zero slope and no significant amounts of hydrogen peroxide is consumed any longer.

Example 3: Samples of carbon steel and aluminum were treated at 50°C with cleaning solutions as described in Example 1. After several weeks the samples treated with solution A were highly oxidized, while the samples treated with solution B remained substantially bright.

Example 4: Samples of aluminum were treated at 50°C for 25 minutes using two cleaning solutions. These two metal cleaning solutions were made from different concentrated aqueous solutions of hydrogen peroxide. Cleaning solution C was made from "Grade I" as described in Example 1 and Cleaning solution D was made from "Grade II", also as described in Example 1. The concentrated solutions were diluted with water and supplied with a nonionic/cationic surfactant blend (Berol<sup>®</sup> 226SA, supplied by Akzo Nobel) to obtain a cleaning solution of 5 wt% hydrogen peroxide and 5 wt% surfactant blend. Both solutions were adjusted to a pH of 10.0 to 10.5 with sodium hydroxide. Once at temperature it was noted that solution C was virtually opaque with bubbles, presumably from the

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decomposition of the hydrogen peroxide. Solution D showed no such activity. There was some bubbling at the metal surface indicating active cleaning, but the bulk of the solution remained clear. The aluminum sample treated in solution C was stained by a black smut, as well as an iridescent film, presumed to be surfactant breakdown products. The sample  
5 treated in solution D showed no such imperfections. This sample also had no trace of the ink applied for initial sample identification, whereas the sample treated in solution C still had visible traces remaining.

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CLAIMS

1. A process for cleaning metals comprising a step of contacting a metal with an aqueous solution comprising hydrogen peroxide and at least one compound selected from the group consisting of complexing agents based on phosphonic acids, salts and degradation products thereof in an amount from about 10 to about 60 wt% based on the amount of hydrogen peroxide.

2. A process as claimed in claim 1, wherein the aqueous solution comprises at least one compound selected from the group consisting of complexing agents based on phosphonic acids, salts and degradation products thereof in an amount from about 20 to about 50 wt% based on the amount of hydrogen peroxide.

3. A process as claimed in claim 2, wherein the aqueous solution comprises at least one compound selected from the group consisting of complexing agents based on phosphonic acids, salts and degradation products thereof in an amount from about 35 to about 45 wt% based on the amount of hydrogen peroxide.

4. A process as claimed in anyone of the claims 1-3, wherein the complexing agent is based on at least one compound selected from the group consisting of 1-hydroxyethylidene-1,1-diphosphonic acid, 1-aminoethane-1,1-diphosphonic acid, aminotri(methylenephosphonic acid), ethylene diamine tetra (methylenephosphonic acid), hexamethylene diamine tetra (methylenephosphonic acid), diethylenetriamine penta (methylenephosphonic acid), diethylenetriamine hexa (methylenephosphonic acid), salts and degradation products thereof.

5. A process as claimed in claim 4, wherein the complexing agent is based on at least one compound selected from the group consisting of 1-hydroxyethylidene-1,1-diphosphonic, salts and degradation products thereof.

6. A process as claimed in anyone of the claims 1-5, wherein the solution comprises hydrogen peroxide in an amount from about 0.5 to about 20 wt%.

7. A process as claimed in anyone of the claims 1-6, wherein the solution comprises at least one mineral acid.

8. A process as claimed in claim 7, wherein the solution comprises sulfuric acid.

9. A process as claimed in claim 8, wherein the solution comprises sulfuric acid in an amount from about 0.5 to about 20 wt%.

10. A process as claimed in anyone of the claims 1-9, wherein the solution comprises at least one surfactant.

11. A process as claimed in claim 10, wherein the solution comprises at least one non-ionic surfactant.

12. A process as claimed in anyone of the claims 1-11, wherein the metal is selected from the group consisting of aluminium, copper and steel.