

Title of Invention: METHOD AND APPARATUS FOR TREATING
COPPER-CONTAINING WASTEWATER

Field of Invention

[0001] The present invention relates to a method and an apparatus for treating copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide and to a method and an apparatus for treating the copper-containing wastewater which enable further reductions in concentrations of copper, fluorine, and phosphorus in the treated water and thereby reduce the amount of chemicals used in the treatment and the amount of sludge generated in the treatment.

Background of Invention

[0002] Copper-wiring substrates, which include copper wires having low wiring resistance, have been increasingly commonly used as a substrate in semiconductor devices. The step of forming copper wires on a silicon substrate requires wet etching. The etching liquid used in this step contains hydrogen peroxide used as an agent for etching copper. The etching liquid also contains a fluorine compound, a phosphate, an organic acid, a chelating agent, a nitrogen compound, and the like in order to, for example, control the etching rate. Examples of the fluorine compound include HF, NaF, AlF_3 , HF_4 , and NH_4F . Examples of the phosphate include

K_2HPO_4 , Na_2HPO_4 , $CaHPO_4$, $BaHPO_4$, $(NH_4)H_2PO_4$, and $(NH_4)_3PO_4$.

Examples of the organic acid include acetic acid, butanoic acid, citric acid, formic acid, gluconic acid, glycolic acid, malonic acid, and oxalic acid. Examples of the chelating agent include nitrilotriacetic acid, ethylenediaminetetraacetic acid, and diethylenetrinitrilepentaacetic acid. Examples of the nitrogen compound include heterocyclic aromatic compounds such as pyrrole, oxazole, imidazole, pyrazole, and triazole; and heterocyclic aliphatic compounds such as piperazine and methylpiperazine (see, Patent Literatures 1 to 4).

[0003] Thus, wastewater from copper-etching, which is discharged from the step of forming copper wires by wet etching, contains hydrogen peroxide, fluoride ions, phosphate ions, and an organic substance, which originate from the etching liquid. The wastewater from copper-etching also contains copper removed by etching, and a part of the copper forms a complex with the chelating agent contained in the etching liquid.

[0004] There have been proposed methods for treating wastewater from copper-etching containing hydrogen peroxide (see, Patent Literatures 5 and 6), in which acidic wastewater is neutralized in order to decompose hydrogen peroxide, a coagulant is added to the neutralized wastewater in order to form a precipitate containing copper by

coagulation, and the precipitate is separated and removed.

[0005] There have also been proposed methods for treating wastewater containing a heavy-metal complex (see, Patent Literatures 7 and 8), in which a magnesium compound is added to the wastewater and solid-liquid separation is conducted at a pH of 9 or more in order to remove heavy metals from the wastewater.

List of Literature

Patent Literature

[0006] Patent Literature 1: International Publication
W02013/077580

Patent Literature 2: Japanese Patent No. 4448322

Patent Literature 3: Japanese Patent No. 4843637

Patent Literature 4: Japanese Patent Publication 2004-
193620 A

Patent Literature 5: Japanese Patent Publication 2011-
20034 A

Patent Literature 6: Japanese Patent Publication 2012-
55825 A

Patent Literature 7: Japanese Patent Publication H1-
28635 B

Patent Literature 8: Japanese Patent Publication 2003-
293157 A

Summary of Invention

Problem to be solved

[0007] The technique disclosed in Patent Literature 5 enables the removal of hydrogen peroxide and copper that has not formed a complex. However, it is not possible to remove copper that has formed a complex because such copper does not precipitate. Therefore, it is not possible to meet the wastewater quality standard by the technique. In addition, although there have recently been an increasing number of cases where the wastewater from copper-etching contains fluoride ions and phosphate ions, it is not possible to remove these ions by the above technique. As a result, it is not possible to meet the wastewater quality standard by the technique as is the case for copper.

[0008] In the techniques disclosed in Patent Literatures 7 and 8, treating copper that has formed a complex until the concentration of copper is reduced to meet or be within the limit specified by the wastewater quality standard requires a large amount of magnesium compound used as a treatment chemical. This disadvantageously increases the treatment cost and the amount of sludge generated. Moreover, since a magnesium compound also reacts with fluoride ions and phosphoric acid, the amount of magnesium used is likely to increase when the wastewater contains fluoride ions and phosphate ions. This disadvantageously further increases the amount of magnesium hydroxide sludge, which has a high water content.

[0009] An object of the present invention is to address the above-described issues and to provide a method and an apparatus for treating copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide. The method and the apparatus for treating the copper-containing wastewater enable further reductions in the concentrations of copper, fluorine, and phosphorus in the treated water without excessively increasing the amount of chemicals used in the treatment and the amount of sludge generated in the treatment.

Solution to Problem

[0010] The inventors of the present invention conducted extensive studies in order to address the above-described issues and, as a result, found that, in the treatment of copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide, it is possible to produce treated water having sufficiently reduced concentrations of copper, fluorine, and phosphorus with consistency by controlling the pH of the wastewater to 4 or more in order to decompose and remove hydrogen peroxide, adding a calcium compound and a magnesium compound to the resulting wastewater, subsequently

conducting a reaction at a pH of 9 to 13 in order to form insoluble matter, and removing the insoluble matter by solid-liquid separation. The inventors also found that it is possible to limit an increase in the amount of magnesium compound used and thereby reduce the formation of magnesium hydroxide sludge having a high water content by setting the amount of calcium compound added to be larger than the reaction equivalent of fluoride ions and phosphate ions and by performing the treatment in which the calcium compound and the magnesium compound are added to the wastewater, a reaction is subsequently conducted at a pH of 9 to 13 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation in two stages in which the addition of the magnesium compound and the removal of the resulting insoluble matter by solid-liquid separation are conducted after the addition of the calcium compound and the removal of the resulting insoluble matter by solid-liquid separation.

[0011] The present invention was made on the basis of the above-described findings. The summary of the present invention is as described below.

[0012] [1] A method for treating copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide, the

method comprising: a first step in which a pH of the wastewater is controlled to be 4 or more; and a second step in which a calcium compound and a magnesium compound are added to water treated in the first step, a reaction is conducted at a pH of 9 to 13 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation.

[0013] [2] The method for treating the copper-containing wastewater according to [1], wherein the second step includes: a first substep in which the calcium compound is added to the water treated in the first step, a reaction is conducted at a pH of 6 to 10 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation; and a second substep in which the magnesium compound is added to water treated in the first substep, a reaction is conducted at a pH of 9 to 13 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation.

[0014] [3] The method for treating the copper-containing wastewater according to [1] or [2], further comprising a pretreatment step in which an aluminium compound is added to the wastewater and a reaction is conducted at a pH of 1 to 4, the pretreatment step being conducted prior to the first step.

[0015] [4] The method for treating the copper-containing

wastewater according to any one of [1] to [3], wherein the amount of the calcium compound added in the second step is larger than the reaction equivalent of fluoride ions and phosphate ions included in the water treated in the first step by 20 to 2000 mg-Ca/L.

[0016] [5] The method for treating the copper-containing wastewater according to any one of [1] to [4], further comprising a nitrification-denitrification step in which water treated in the second step is subjected to nitrification and denitrification.

[0017] [6] An apparatus for treating copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide, the apparatus comprising: a first treatment unit that controls a pH of the wastewater to be 4 or more; and a second treatment unit that adds a calcium compound and a magnesium compound to water treated in the first treatment unit, conducts a reaction at a pH of 9 to 13 in order to form insoluble matter, and removes the insoluble matter by solid-liquid separation.

[0018] [7] The apparatus for treating the copper-containing wastewater according to [6], wherein the second treatment unit includes: a first subunit that adds the calcium compound to the water treated in the first treatment unit,

conducts a reaction at a pH of 6 to 10 in order to form insoluble matter, and removes the insoluble matter by solid-liquid separation; and a second subunit that adds the magnesium compound to water treated in the first subunit, conducts a reaction at a pH of 9 to 13 in order to form insoluble matter, and removes the insoluble matter by solid-liquid separation.

[0019] [8] The apparatus for treating the copper-containing wastewater according to [6] or [7], further comprising a pretreatment unit that adds an aluminium compound to the wastewater and conducts a reaction at a pH of 1 to 4, the pretreatment unit being disposed upstream of the first treatment unit.

[0020] [9] The apparatus for treating the copper-containing wastewater according to any one of [6] to [8], wherein the amount of the calcium compound added by the second treatment unit is larger than the reaction equivalent of fluoride ions and phosphate ions included in the water treated in the first treatment unit by 20 to 2000 mg-Ca/L.

[0021] [10] The apparatus for treating the copper-containing wastewater according to any one of [6] to [9], further comprising a nitrification-denitrification unit that subjects water treated in the second treatment unit to nitrification and denitrification.

Advantageous Effects of Invention

[0022] According to the present invention, in the treatment of copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide, such as wastewater from copper-etching, it is possible to produce high-quality treated water having sufficiently reduced concentrations of copper, fluorine, and phosphorus with consistency without excessively increasing the amount of chemicals used in the treatment and the amount of sludge generated in the treatment.

Brief Description of Drawings

[0023] [Fig. 1] Fig. 1 is a system diagram illustrating an example of an apparatus for treating copper-containing wastewater according to an embodiment of the present invention.

[Fig. 2] Fig. 2 is a system diagram illustrating another example of an apparatus for treating copper-containing wastewater according to an embodiment of the present invention.

[Fig. 3] Fig. 3 is a system diagram illustrating another example of an apparatus for treating copper-containing wastewater according to an embodiment of the present invention.

Description of Embodiments

[0024] The embodiment of the present invention is described below in detail with reference to the attached drawings.

[0025] Figs. 1 to 3 are system diagrams illustrating examples of an apparatus for treating copper-containing wastewater according to an embodiment of the present invention. In Figs. 1 to 3, members having the same function are denoted by the same reference numeral.

[0026] <Raw Water>

One of the most common examples of the copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide (hereinafter, may be referred to as "raw water") which is to be treated in the present invention is a waste liquid from copper-etching generated in the production of semiconductors or printed circuit boards. However, the copper-containing wastewater that is to be treated in the present invention is not limited to a waste liquid from copper-etching and may be any copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide, such as wastewater from CMP or wastewater from copper-plating.

[0027] The typical qualities of a waste liquid from

copper-etching suitable as raw water are as follows.

<Qualities of Waste Liquid from Copper-etching Generated in
Production of Liquid Crystals>

pH: 1 to 3

TOC: 50 to 20,000 mg/L

Cu: 50 to 5,000 mg/L

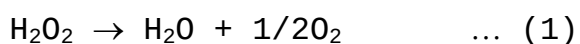
F: 5 to 2,000 mg/L

P: 10 to 5,000 mg/L

H₂O₂: 1,000 to 300,000 mg/L

[0028] <First Step>

In the first step according to the present invention, an alkaline agent is added to the raw water in order to control the pH of the raw water to be 4 or more and hydrogen peroxide contained in the raw water is thereby decomposed. The first step is conducted in the first reaction tank 1 illustrated in Figs. 1 and 2, which serves as a first treatment unit. The pH of the raw water introduced to the first reaction tank 1 is controlled to be 4 or more as a result of the addition of the alkaline agent such as sodium hydroxide (NaOH). This causes hydrogen peroxide contained in the raw water to decompose. Decomposition of hydrogen peroxide proceeds by the reaction of Equation (1) below.



[0029] Controlling the pH of the raw water to be 4 or more causes a part of copper contained in the wastewater to

precipitate and SS including copper to be formed. The copper included in the SS serves as a catalyst in the decomposition of hydrogen peroxide. Therefore, it is possible to decompose and remove hydrogen peroxide with efficiency by controlling only the pH of the raw water without using energies such as heat.

[0030] Examples of the alkaline agent added to the raw water in the first step include sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide (Ca(OH)₂). The above alkaline agents may be used alone or in combination of two or more. The reaction is conducted at a pH of 4 or more, is preferably conducted at a pH of 6 to 13, and is further preferably conducted at a pH of 8 to 11. The higher the pH of the raw water, the higher the rate of decomposition of hydrogen peroxide and the higher the efficiency of the treatment. However, the pH of the raw water in the reaction is preferably within the above range in order to reduce the amount of alkaline agent used and ensure the safety of the work environment.

Stirring may optionally be performed in order to prevent the deposition of SS generated as a result of controlling the pH of the raw water. Stirring can be performed by using a stirring machine (mechanical mixing) or aeration.

[0031] Normally, the amount of time during which the

reaction is conducted in the first step is preferably about 0.25 to 10 hours. Accordingly, it is preferable to design the first reaction tank 1 such that the HRT (retention time in the tank) of the first reaction tank 1 falls within the above range.

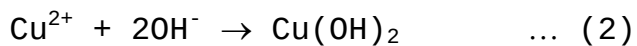
[0032] In the case where calcium hydroxide is used as an alkaline agent in the first step, the reactions of Equations (8) and (10) below, which are to occur in the second step, may occur depending on the pH condition. Furthermore, in the case where aeration is performed, precipitation of calcium carbonate proceeds partially. Although the occurrence of the reactions of Equations (8) and (10) below in the first step does not particularly pose problems, a large amount of SS may result in, for example, a significant degree of deposition of the SS. Moreover, scale may adhere to an aeration tube. Therefore, in the first step, it is preferable to use an alkaline agent other than a calcium compound.

[0033] <Second Step>

In the second step, a calcium compound and a magnesium compound are added to water treated in the first step, from which hydrogen peroxide contained in the raw water has been decomposed and removed in the first step. A reaction is subsequently conducted at a pH of 9 to 13 in order to form insoluble matter, which is subsequently removed by solid-

liquid separation. Thus, treated water having reduced concentrations of copper, fluorine, and phosphorus is produced.

[0034] Normally, it is possible to convert copper ions that have not formed a complex into insoluble matter by the reaction of Equation (2) below by controlling only the pH of the raw water.



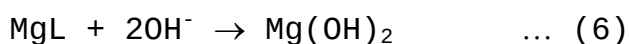
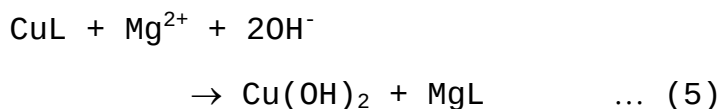
However, when the raw water contains a chelating agent, copper ions " Cu^{2+} " and the chelating agent "L" form a stable complex as in Equation (3) below, which retards the reaction of Equation (2) above.



Similarly, magnesium " Mg^{2+} " forms a complex with the chelating agent "L" as in Equation (4) below.

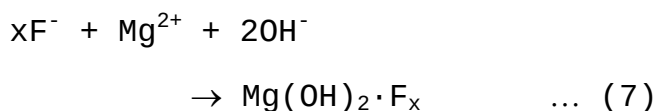


Therefore, making the raw water alkaline in the presence of magnesium allows the reactions of Equations (5) and (6) to proceed. This converts the copper ions that have formed a complex into insoluble matter.



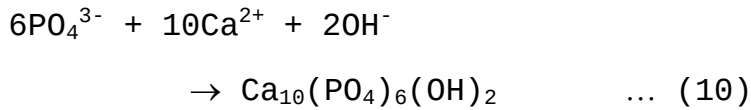
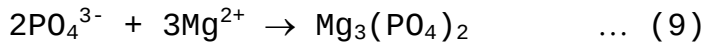
[0035] Fluoride ions can be made to be insoluble by the reactions of Equations (7) and (8) below. The reaction of

Equation (7) below is a reaction in which fluoride ions are removed by coprecipitation when magnesium hydroxide is precipitated. Removing a high concentration of fluoride ions by this reaction requires a large amount of magnesium compound and is not effective. Accordingly, in the present invention, the most part of fluoride ions are precipitated in the form of calcium fluoride by the reaction of Equation (8) below, and the remaining small amount of fluoride ions are removed by Equation (7) below. This limits an increase in the amount of magnesium compound used. Limiting an increase in the amount of magnesium compound used, in turn, limits an increase in the amount of magnesium hydroxide sludge generated.



[0036] Phosphate ions can be made to be insoluble by the reactions of Equations (9) and (10) below. In the present invention, the most part of phosphate ions are precipitated in the form of hydroxyapatite by the reaction of Equation (10) below, and the remaining small amount of phosphate ions are removed by Equation (9) below. This limits an increase in the amount of magnesium compound used. Limiting an increase in the amount of magnesium compound used, in turn, limits an increase in the amount of magnesium hydroxide

sludge generated.



[0037] Examples of the magnesium compound include magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and magnesium chloride (MgCl_2). The above magnesium compounds may be used alone or in combination of two or more. Examples of the calcium compound include calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium carbonate (CaCO_3), and calcium chloride (CaCl_2). The above calcium compounds may be used alone or in combination of two or more. The amount of calcium compound is preferably larger than the reaction equivalent of fluoride ions and phosphate ions contained in the water treated in the first step (in the case where a calcium compound is not used as an alkaline agent in the first step, this reaction equivalent is equal to the reaction equivalent of fluoride ions and phosphate ions contained in the raw water) by 20 to 2000 mg-Ca/L. In other words, the amount of calcium compound is preferably larger than the total of the reaction equivalents in Equations (8) and (10) above by 20 to 2000 mg-Ca/L and particularly preferably 50 to 500 mg-Ca/L in terms of calcium concentration. If the amount of excess calcium compound is less than the above lower limit, an increase in the amount of magnesium compound used may fail to be limited

to a sufficient degree by the addition of the calcium compound. If the amount of excess calcium compound is more than the above upper limit, the advantageous effect may stop increasing and only the amount of calcium compound used may disadvantageously increase.

[0038] The amount of magnesium compound may be set such that the amounts of the copper, fluorine, and phosphorus contained in the raw water are reduced to a sufficient degree by the reactions of Equations (5), (6), (7), and (9) above and, normally, is preferably about 5 to 100 times (mol/mol) the amount of complex-type copper.

[0039] The pH at which a reaction is conducted in the second step is 9 to 13 and is preferably 10 to 12. Thus, an alkaline agent is added to the water treated in the first step as needed in order to control the pH of the water. In the case where the magnesium compound and the calcium compound are alkaline, they may serve also as alkaline agents.

[0040] In the present invention, the second step, in which a calcium compound and a magnesium compound are added to the water treated in the first step, a reaction is conducted at a pH of 9 to 13 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation, may be conducted in one stage or two stages. In the case where the second step is conducted in two stages, a first substep

and a second substep are conducted. In the first substep, the calcium compound is added to the water treated in the first step, a reaction is conducted at a pH of 6 to 10 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation. In the second substep, the magnesium compound is added to water treated in the first substep (water produced by solid-liquid separation), a reaction is conducted at a pH of 9 to 13 and is preferably conducted at a pH of 10 to 12 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation.

[0041] In the case where the above two-stage treatment is performed, in the first substep, the calcium compound is added to the water treated in the first step, a reaction is conducted at a pH of 6 to 10 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation in order to produce treated water having reduced concentrations of copper, fluorine, and phosphorus.

In the first substep, copper ions, fluoride ions, and phosphate ions are made to be insoluble by the reactions of Equations (2), (8), and (10) above, respectively, in order to roughly remove copper, fluorine, and phosphorus. Performing the above two-stage treatment further reduces the amount of magnesium compound used in the second substep.

[0042] The amount of calcium compound used in the first

substep in the case where the two-stage treatment is performed is, as described above, preferably larger than the reaction equivalent of fluoride ions and phosphate ions contained in the water treated in the first step (in the case where a calcium compound is not used as an alkaline agent in the first step, this reaction equivalent is equal to the reaction equivalent of fluoride ions and phosphate ions contained in the raw water) by 20 to 2000 mg-Ca/L and particularly preferably 50 to 500 mg-Ca/L in terms of calcium concentration. While the pH at which the reaction is conducted in the first substep is 6 to 10, the pH is preferably 6 to 7 in the case where priority is given to the removal of fluoride ions and to 8 to 10 in the case where priority is given to the removal of copper ions and phosphate ions. Therefore, in the first substep, an acid such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) may optionally be used in order to control the pH.

[0043] In the first substep, a coagulant aid such as ferric chloride, polysteel, polyaluminium chloride (PAC), or aluminium sulfate may optionally be used. In the case where priority is given to the removal of fluorine, it is preferable to use an aluminium compound such as polyaluminium chloride or aluminium sulfate at a concentration of about 20 to 500 mg/L and conduct a reaction at a pH of 6 to 7.

[0044] Fig. 1 illustrates a treatment apparatus that conducts the second step in one stage. In a second reaction tank 2, a calcium compound such as CaCl_2 , a magnesium compound such as MgCl_2 , and, optionally, an alkaline agent such as NaOH are added to the water treated in a first reaction tank 1, and a treatment is performed at a pH of 9 to 13 and preferably at a pH of 10 to 12 in order to form insoluble matter. The resulting reaction liquid containing the insoluble matter is fed to a coagulation tank 3, in which a polymer coagulant is added to the reaction liquid in order to perform coagulation. The coagulated water is subjected to solid-liquid separation in a sedimentation tank 4, and the separated water is extracted as treated water.

[0045] In the above one-stage treatment, normally, the reaction is preferably conducted for about 5 to 60 minutes. Accordingly, it is preferable to design the second reaction tank 2 such that the HRT (retention time in the tank) of the second reaction tank 2 falls within the above range.

The polymer coagulant used in the coagulation tank 3 may be anionic, nonionic, or cationic and is preferably an anionic polymer coagulant. The amount of the polymer coagulant used is preferably about 1 to 30 mg/L.

The conditions under which a treatment is performed in the sedimentation tank 4 are not limited; the LV at which the water is passed through the sedimentation tank 4 is

preferably about 1 to 5 m/h.

[0046] Fig. 2 illustrates a treatment apparatus that conducts the second step in two stages. In a 2-1 second reaction tank 2A, an acid such as H_2SO_4 , a calcium compound such as CaCl_2 , and a coagulant aid such as PAC are added to the water treated in a first reaction tank 1, and the water is subsequently treated at a pH of 6 to 10, preferably at a pH of 6 to 7 or a pH of 8 to 10 in order to form insoluble matter. The resulting reaction liquid containing the insoluble matter is fed to a first coagulation tank 3A, in which a polymer coagulant is added to the reaction liquid in order to perform coagulation. The resulting coagulated water is subjected to solid-liquid separation in a first sedimentation tank 4A. In a 2-2 second reaction tank 2B, a magnesium compound such as MgCl_2 and, optionally, an alkaline agent such as NaOH are added to the water treated in the first sedimentation tank 4A (separated water), and the water is treated at a pH of 9 to 13 and preferably at a pH of 10 to 12 in order to form insoluble matter. The resulting reaction liquid containing the insoluble matter is fed to a second coagulation tank 3B, in which a polymer coagulant is added to the reaction liquid in order to perform coagulation. The coagulated water is subjected to solid-liquid separation in a second sedimentation tank 4B. The resulting separated water is extracted as treated water.

[0047] In the above two-stage treatment, normally, the amount of time during which the reaction is conducted in the first substep is preferably about 5 to 60 minutes. Accordingly, it is preferable to design the 2-1 second reaction tank 2A such that the HRT (retention time in the tank) of the 2-1 second reaction tank 2A falls within the above range.

The polymer coagulant used in the first coagulation tank 3A may be anionic, nonionic, or cationic and is preferably an anionic polymer coagulant. The amount of the polymer coagulant used is preferably about 1 to 10 mg/L.

The conditions under which the treatment is performed in the first sedimentation tank 4A are not limited; the LV at which the water is passed through the first sedimentation tank 4A is preferably about 1 to 5 m/h.

[0048] Normally, the amount of time during which the reaction is conducted in the second substep is preferably about 5 to 60 minutes. Accordingly, it is preferable to design the 2-2 second reaction tank 2B such that the HRT (retention time in the tank) of the 2-2 second reaction tank 2B falls within the above range.

The polymer coagulant used in the second coagulation tank 3B may be anionic, nonionic, or cationic and is preferably an anionic polymer coagulant. The amount of the polymer coagulant used is preferably about 1 to 30 mg/L.

The conditions under which the treatment is performed in the second sedimentation tank 4B are not limited; the LV at which the water is passed through the second sedimentation tank 4B is preferably about 1 to 5 m/h.

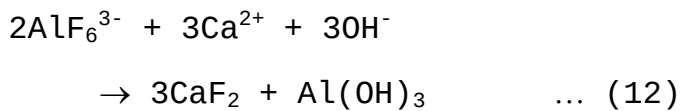
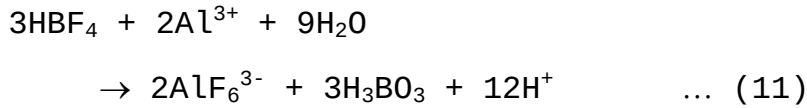
[0049] Through the above second step, the concentrations of Cu, F, and P in the treated water are reduced to about 0.1 to 1 mg-Cu/L, about 0.5 to 8 mg-F/L, and about 0.1 to 1 mg-P/L, respectively.

[0050] <Pretreatment Step>

In the present invention, a pretreatment step in which an aluminium compound is added to the raw water and a reaction is subsequently conducted at a pH of 1 to 4 may optionally be conducted prior to the first step, in which the pH of the raw water is controlled in order to decompose and remove hydrogen peroxide. Conducting the pretreatment step is advantageous in the case where the raw water contains borofluoride. Adding an aluminium compound to the raw water and subsequently conducting a reaction at a pH of 1 to 4 causes borofluoride contained in the raw water to decompose. Fluorine that originates from borofluoride can be removed in the second step.

[0051] In the above pretreatment step, borofluoride contained in the raw water is decomposed by the reaction of Equation (11) below. The resulting aluminium fluoride is made to be insoluble by the reaction of Equation (12) below

in the second step.



[0052] Examples of the aluminium compound used in the pretreatment step include aluminium chloride, polyaluminium chloride (PAC), and aluminium sulfate. The above aluminium compounds may be used alone or in combination of two or more.

The amount of aluminium compound used may be equal to or larger than the reaction equivalent of borofluoride contained in the raw water and is preferably, for example, $\text{Al/F} = 1$ to 20 mol/mol relative to the amount of fluorine contained in the raw water.

In the case where the raw water is a waste liquid from copper-etching, it is not necessary to control the pH of the raw water since the copper etching waste liquid commonly has a pH of about 1 to 4. However, when the pH of the raw water is more than 4, an acid such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) is preferably added to the raw water as needed in order to control the pH of the raw water to be about 1 to 4 and particularly preferably about 1.5 to 2.5.

The amount of time during which the reaction is conducted in the pretreatment step is preferably about 0.5 to 5 hours.

[0053] Fig. 3 illustrates a treatment apparatus based on that illustrated in Fig. 2 which further includes a pretreatment tank 5 used for conducting the above pretreatment step. Specifically, the treatment apparatus includes a pretreatment tank 5 disposed upstream of the first reaction tank 1. The pretreatment tank 5 adds an aluminium compound such as PAC and, optionally, an acid such as H_2SO_4 to the raw water and subsequently causes a reaction. The treatment apparatus has the same structure as that illustrated in Fig. 2, except that the first reaction tank 1 is fed with the water treated in the pretreatment tank 5.

[0054] The pretreatment tank 5 may also be disposed upstream of the first reaction tank 1 in the treatment apparatus illustrated in Fig. 1.

[0055] <Other Treatment Steps>

In the present invention, steps other than the above-described treatment steps may be conducted between the above-described treatment steps or prior to or subsequent to the above-described treatment steps.

For example, in the case where the raw water contains a nitrogen compound, a step in which the water treated in the second step is further subjected to nitrification and denitrification may be conducted. Conducting such a nitrification-denitrification step enables the nitrogen compound remaining in the water treated in the second step

to be decomposed and removed and thereby further increases the quality of the treated water.

A solid-liquid separation unit used in the present invention is not limited to a sedimentation tank and may be a membrane separation device, a flotation-separation tank, or the like.

EXAMPLES

[0056] The present invention is described more specifically with reference to Invention examples and Comparative examples below.

[0057] [Examples 1 and 2]

Wastewater from copper-etching having the qualities described in Table 1 was used as raw water and treated with the apparatus illustrated in Fig. 1. The polymer coagulant used was an anionic polymer coagulant "KURIFLOCK PA331" produced by Kurita Water Industries Ltd.

Table 2 summarizes the conditions under which a treatment was performed in each tank. Table 4 summarizes the qualities of the treated water and the amount of sludge generated per liter of the raw water.

[0058] Note that the amount of CaCl_2 corresponding to the total of the reaction equivalents of fluoride ions and phosphate ions contained in the raw water was 78 mg-Ca/L. Thus, 400 mg-Ca/L of CaCl_2 added was larger than the reaction equivalent by 322 mg-Ca/L.

[0059] [Table 1]

Item	Unit	Value
pH	—	3.5
TOC	mg/L	90
Cu	mg/L	100
F	mg/L	15
P	mg/L	30
H ₂ O ₂	mg/L	5000

[0060] [Comparative Examples 1 and 2]

In Comparative Examples 1 and 2, the raw water was treated as in Examples 1 and 2, respectively, except that CaCl₂ was not added to the second reaction tank.

Table 2 summarizes the conditions under which a treatment was performed in each tank. Table 4 summarizes the qualities of the treated water and the amount of sludge generated per liter of the raw water.

[0061] [Comparative Example 3]

The raw water was treated as in Comparative Examples 1 and 2 such that the Cu concentration of the treated water reached 1 mg/L or less by using only MgCl₂, but not CaCl₂.

Table 2 summarizes the conditions under which a treatment was performed in each tank. Table 4 summarizes the qualities of the treated water and the amount of sludge generated per liter of the raw water.

[0062] [Table 2]

Item※		Unit	Example 1	Example 2	Comparative example 1	Comparative example 2	Comparative example 3
First reaction tank	HRT	min	120	120	120	120	120
	pH	—	10	10	10	10	10
Second reaction tank	HRT	min	20	20	20	20	20
	pH	—	11.5	11.5	11.5	11.5	11.5
	MgCl ₂	mg—Mg/L	200	500	200	500	1000
	CaCl ₂	mg—Ca/L	400	400	0	0	0
Coagulation tank	HRT	min	5	5	5	5	5
	Polymer coagulant	mg/L	3	3	3	3	3
Sedimentation tank	LV	m/h	3	3	3	3	3

※"MgCl₂", "CaCl₂", and "Polymer coagulant" refer to the amounts of MgCl₂, CaCl₂, and polymer coagulant that were added to the tank, respectively.

[0063] [Examples 3 and 4]

Wastewater from copper-etching having the qualities described in Table 1 was used as raw water and treated with the apparatus illustrated in Fig. 2. The polymer coagulant used was an anionic polymer coagulant "KURIFLOCK PA331" produced by Kurita Water Industries Ltd.

Table 3 summarizes the conditions under which a treatment was performed in each tank. Table 4 summarizes the qualities of the treated water and the amount of sludge generated per liter of the raw water.

[0064] [Table 3]

Item※		Unit	Example 3	Example 4
First reaction tank	HRT	min	120	120
	pH	—	10	10
2-1 second reaction tank	HRT	min	20	20
	pH	—	9. 0	9. 0
	CaCl ₂	mg—Ca/L	400	400
	PAC	mg—Al/L	5	5
First coagulation tank	HRT	min	5	5
	Polymer coagulant	mg/L	1	1
First sedimentation tank	LV	m/h	3	3
2-2 second reaction tank	HRT	min	20	20
	pH	—	11. 5	11. 5
	MgCl ₂	mg—Mg/L	50	200
Second coagulation tank	HRT	min	5	5
	Polymer coagulant	mg/L	3	3
Second sedimentation tank	LV	m/h	3	3

※“MgCl₂”, “CaCl₂”, “PAC”, and “Polymer coagulant” refer to the amounts of MgCl₂, CaCl₂, PAC, and polymer coagulant that were added to the tank, respectively.

[0065] [Table 4]

Item		Unit	Example 1	Example 2	Example 3	Example 4	Comparative example 1	Comparative example 2	Comparative example 3
Qualities of treated water	Cu	mg/L	0.4	0.2	0.7	0.2	7.5	1.3	0.9
	F	mg/L	2.5	1.5	5.0	2.5	6.0	1.5	1.0
	P	mg/L	1.0	0.5	0.5	0.5	4.2	1.0	0.8
	H ₂ O ₂	mg/L	<1	<1	<1	<1	<1	<1	<1
Amount of sludge generated		mg-wet/L	3700	8700	1700	3700	3900	8500	16500

[0066] As is clear from Table 4, the method according to the present invention enabled the concentrations of copper, fluorine, and phosphorus in the treated water to be reduced to a lower level and achieved consistent water quality without excessively increasing the amount of magnesium compound used and the amount of sludge generated as a result of the addition of the magnesium compound even when the wastewater from copper-etching, which contained copper ions capable of forming a complex with an organic substance, further contained fluoride ions and phosphate ions.

Reference Signs List

- [0067] 1 FIRST REACTION TANK
2 SECOND REACTION TANK
2A 2-1 SECOND REACTION TANK
2B 2-2 SECOND REACTION TANK
3 COAGULATION TANK
3A FIRST COAGULATION TANK
3B SECOND COAGULATION TANK

4 SEDIMENTATION TANK

4A FIRST SEDIMENTATION TANK

4B SECOND SEDIMENTATION TANK

5 PRETREATMENT TANK

CLAIMS

[Claim 1]

A pH of copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide is controlled to be 4 or more; a calcium compound and a magnesium compound are added to water treated in the first step; a reaction is conducted at a pH of 9 to 13 in order to form insoluble matter; and the insoluble matter is removed by solid-liquid separation.

[Claim 2]

The method for treating the copper-containing wastewater according to Claim 1, wherein the second step includes:

a first substep in which the calcium compound is added to the water treated in the first step, a reaction is conducted at a pH of 6 to 10 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation; and

a second substep in which the magnesium compound is added to water treated in the first substep, a reaction is conducted at a pH of 9 to 13 in order to form insoluble matter, and the insoluble matter is removed by solid-liquid separation.

[Claim 3]

The method for treating the copper-containing wastewater according to Claim 1 or 2, further comprising a pretreatment step in which an aluminium compound is added to the wastewater and a reaction is conducted at a pH of 1 to 4, the pretreatment step being conducted prior to the first step.

[Claim 4]

The method for treating the copper-containing wastewater according to any one of Claims 1 to 3, wherein the amount of the calcium compound added in the second step is larger than the reaction equivalent of fluoride ions and phosphate ions included in the water treated in the first step by 20 to 2000 mg-Ca/L.

[Claim 5]

The method for treating the copper-containing wastewater according to any one of Claims 1 to 4, further comprising a nitrification-denitrification step in which water treated in the second step is subjected to nitrification and denitrification.

[Claim 6]

An apparatus for treating copper-containing wastewater containing an organic substance, copper ions capable of forming a complex with the organic substance, fluoride ions, phosphate ions, and hydrogen peroxide, the apparatus comprising:

a first treatment unit that controls a pH of the wastewater to be 4 or more; and

a second treatment unit that adds a calcium compound and a magnesium compound to water treated in the first treatment unit, conducts a reaction at a pH of 9 to 13 in order to form insoluble matter, and removes the insoluble matter by solid-liquid separation.

[Claim 7]

The apparatus for treating the copper-containing wastewater according to Claim 6, wherein the second treatment unit includes:

a first subunit that adds the calcium compound to the water treated in the first treatment unit, conducts a reaction at a pH of 6 to 10 in order to form insoluble matter, and removes the insoluble matter by solid-liquid separation; and

a second subunit that adds the magnesium compound to water treated in the first subunit, conducts a reaction at a pH of 9 to 13 in order to form insoluble matter, and removes the insoluble matter by solid-liquid separation.

[Claim 8]

The apparatus for treating the copper-containing wastewater according to Claim 6 or 7, further comprising a pretreatment unit that adds an aluminium compound to the wastewater and conducts a reaction at a pH of 1 to 4, the

pretreatment unit being disposed upstream of the first treatment unit.

[Claim 9]

The apparatus for treating the copper-containing wastewater according to any one of Claims 6 to 8, wherein the amount of the calcium compound added by the second treatment unit is larger than the reaction equivalent of fluoride ions and phosphate ions included in the water treated in the first treatment unit by 20 to 2000 mg-Ca/L.

[Claim 10]

The apparatus for treating the copper-containing wastewater according to any one of Claims 6 to 9, further comprising a nitrification-denitrification unit that subjects water treated in the second treatment unit to nitrification and denitrification.