

A method for comprehensive treatment of waste copper containing solution and regeneration of metallic copper or copper compounds thereof

TECHNICAL FIELD

[1] The present invention relates to methods for comprehensive treatment of waste copper containing solution and regeneration of metallic copper or copper compounds from waste copper containing solution of the print circuit board (PCB) industries.

BACKGROUND OF INVENTION

[2] Both acidic and alkaline etching processes are widely used during the production of PCBs and a large amount of waste corrosion solution is therefore generated. One can take the statistics data for China as an example, which is the world's largest manufacturing site of PCBs, by the end of year 2014, the annual production of PCB is over 5.3 million tons therein however a large quantity of approximately 100,000 tons of waste copper containing solution is also generated annually. The copper contained solution comprises of complex components which incline to cause the pollution of environment. For example, the major components in the waste copper contained solution from acid etching process are generally CuCl_2 and HCl , where the copper content can be up to 130g / L, rendering the said waste copper contained solution a dangerous waste.

[3] Various processes in the PCB production generate waste copper contained solution, whose physicochemical properties and copper contents thereof are differed. The waste copper containing solutions can be divided into the following four categories according to the main type of anions contained in the solution: waste acidic etching solution (WESA) from major acidic based etching processes

(excluding the microetching processes), waste alkaline etching solution (WESK) from various alkaline based etching processes, waste copper deposition solution (WCDS) from both the electrolessplating for through hole processes and the electroplating for pattern electroplating processes, and waste microetching solution (WMES) from the microetching processes. However, many PCB manufacturers would discharge all the waste solutions into a single setting pond to reserve a so called terminal waste solution collected from all processes and intend to treat the waste solutions with a uniform approach, which not only bring a certain degree of difficulty to the treatment but also reduce the efficiency of resource recycling.

[4] The common treatment approaches in a traditional copper waste treatment plants for the terminal waste solution are neutralization and electrolysis. The neutralization method is to remove the copper ions in an alkaline condition through coagulation and/or flocculation and/or sedimentation and/or some other similar processes so as to meet the wastewater discharge standards; however, it normally generates a lot of sludge. The electrolysis method is to remove the copper ions by forming metallic copper; however, the residual electrolysis water normally requires a further treatment processing before discharging. Moreover, both the neutralization and electrolysis methods only minimize the toxic copper ion pollution but not maximize the value of the copper ions such as recycling for use, wasting a lot of resources and energy.

DISCLOSURE

[5] The purpose of the present invention is to provide methods for regeneration of metallic copper or copper compounds from waste copper containing solution and simple, comprehensive but low-cost treatment methods for waste copper containing solution of the print circuit board (PCB) industries.

[6] As a first aspect of this invention, a method for regeneration of copper compounds from waste copper containing solution is disclosed to achieve the

purpose of this invention, characterized in that the said method comprises the following steps in a sequence of:

(1) collect waste copper containing solution according to four categories of waste alkaline etching solution A, waste acid etching solution B, waste copper deposition
5 solution C and waste microetching solution D from a PCB production line;

(2) distill the waste alkaline etching solution A and the acid etching solution B separately to recover alkali or acidic distillate and cool their residue to crystallize blister copper compounds E1 and E2;

(3) distill the copper deposition solution C and waste microetching solution D
10 separately to remove water fraction and cool their residue to crystallize blister copper compounds E3 and E4;

(4) mix the blister copper compounds E1-E4 into blister copper compound mixture E, prepare an aqueous solution from the said mixture E, recover copper compounds after purification of the said aqueous solution, and recycle its residue F into any one
15 of the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D for further treatment.

[7] As a second aspect of this invention, a method for regeneration of metallic copper from waste copper containing solution is disclosed to achieve the purpose of
20 this invention, characterized in that the said method comprises the following steps in a sequence of:

(1) collect waste copper containing solution according to four categories of waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D from a PCB production line;

25 (2) distill the waste alkaline etching solution A and the acid etching solution B

separately to recover alkali or acidic distillate and cool their residue to crystallize blister copper compounds E1 and E2;

(3) distill the copper deposition solution C and waste microetching solution D separately to remove water fraction and cool their residue to crystallize blister copper compounds E3 and E4;

(4) mix the blister copper compounds E1-E4 into blister copper compound mixture E, prepare an aqueous solution from the said mixture E, recover metallic copper by electrolysis after purification of the said aqueous solution, and recycle its residue G into any one of the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D for further treatment.

[8] Preferably, purities of the said blister copper compounds E1-E4 are not less than 65% when the copper concentrations in the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D are not less than 30g / L. More preferably, purities of the said blister copper compounds E1-E4 are not less than 75% when the copper concentration in the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D are not less than 50g / L. More preferably, purities of the said blister copper compounds E1-E4 are not less than 85% when the copper concentration in the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D are not less than 70g / L. More preferably, purities of the said blister copper compounds E1-E4 are not less than 95% when the copper concentration in the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D are not less than 90g / L.

[9] The inventor surprisingly found that the purities of the recovered copper

compounds and/or metallic copper strongly affected by the mixture ratio between the blister copper compounds E1-E4. Optimized range of the mixture ratio in mass of E1:E2:E3:E4 into blister E can be of 1: 1: 1: 1-1: 1: 2: 4. Preferably, the mixture ratio in mass of E1:E2:E3:E4 into blister E can be of 1: 1: 1: 2. More preferably, the mixture ratio in mass of E1:E2:E3:E4 into blister E can be of 1: 1: 2: 3. More preferably, the mixture ratio in mass of E1:E2:E3:E4 into blister E can be of 1: 1: 2: 4.

[10] Further, at least one of the waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D contains copper nitrate, acidic copper chloride or alkali copper chloride.

[11] The recovered acidic distillate is nitric acid or hydrochloric acid, the recovered alkali distillate is ammonia. Both the recovered acidic and alkali distillates are used in the said copper compound recovery process.

[12] Furthermore, the said recovered copper compound from the blister copper compound mixture E is at least one from the group consisting of copper sulfate, copper nitrate, alkali copper carbonate, copper oxide and cuprous oxide;

[13] The distillation can be atmospheric distillation or vacuum distillation. Preferred conditions for distillation under reduced pressure are, a negative pressure not higher than 0.09MPa, a temperature not lower than 90 °C, a density of the liquid in the autoclave not less than 1.0g / cm³ before stirring for discharge. More preferably, the liquid density in the autoclave should be not less than 1.1g / cm³ before stirring for discharge.

[14] The said recovery process of copper compound from the blister copper compound mixture E includes at least one selected from the group consisting of recovery of copper sulfate or copper nitrate, recovery of alkali copper carbonate, recovery of copper oxide and recovery of cuprous oxide.

[15]The recovery process of copper sulfate or copper nitrate is characterized in that, after the said blister copper compound E is dissolved in an aqueous solution, a sulfuric acid or nitric acid is added into the said solution to supersaturate SO_4^{2-} or NO_3^- , and then the said solution is distilled to crystallize CuSO_4 or $\text{Cu}(\text{NO}_3)_2$.

5 [16]The recovery process of alkali copper carbonate is characterized in that, after the said blister copper compound E is dissolved in an aqueous solution, at least one from the group comprising sodium carbonate, ammonium carbonate, ammonium bicarbonate is added into the said solution, and the alkali copper carbonate is then recovered by stirring under a condition of a pH value of 7-10 and a reaction
10 temperature of 70- 85°C.

[17]The recovery process of copper oxide is characterized in that, after the said blister copper compound E is dissolved in an aqueous solution, a caustic soda is added into the said solution, and the copper oxide is then recovered by stirring for 1-4 hours under a condition of a pH value larger than 12 and a reaction temperature
15 of 70- 85°C.

[18]The recovery process of cuprous oxide is characterized in that, at least one agent selected from the group consisting of glucose, hydrazine hydrate, sodium hypophosphite is dissolved in an aqueous solution, a pH value larger than 12 is then controlled when an amount of 0.75-1 times of the theoretical reductant amount of
20 the said blister copper compound mixture E is added into the said solution, and the cuprous oxide is then recovered by stirring for 1-4 hours under room temperature.

[19]Furthermore, the process for recovering metallic copper by electrolytic process is characterized in that, after the said blister copper compound E is dissolved in an aqueous solution, a pH value of 1-3 is then controlled in the said solution, a current
25 density of 0.5-3A /dm² is selected to pump into an electrolytic cell to recover a metallic copper foil. Preferably, the recovery efficiency of copper with such electrolytic process can recover more than 95% of copper from the blister copper

compound mixture. More preferably, the recovery efficiency of copper with such electrolytic process can recover more than 99% of copper from the blister copper compound mixture. The said electrolytic cell for recovering metallic copper used in the process of this invention can be any form of copper electrolysis cells.

5 [20]Furthermore, the deployment of the pH value in the said solution may be inorganic acids, organic acids or mixtures thereof, which can be hydrochloric acid alone or hydrochloric acid together with at least one selected from the group comprising sulfuric acid, nitric acid, phosphoric acid, hypochlorous acid, carbonate and organic acids.

10 [21]Furthermore, the deployment of the pH value in the said solution may be an alkali or alkaline substance, which can be sodium hydroxide, potassium hydroxide or their mixture or their mixture with a certain weak alkali solution.

[22]The present invention separately collects waste copper containing solutions with four different categories, prepares blister copper compounds from the
15 categorized solution, and mixes the blister copper compounds in an optimized mass ratio for recovering a copper compound or metallic copper end-products. Such disclosure not only simplifies the copper recycling process without complicated equipment, but also reduces secondary pollution by eliminating sludge dewatering or sludge melting. The recycled copper compound or metallic copper and the
20 recovered acid, alkali can be reused in the recovery treatment processes, which enables a person skilled in the art to achieve the result of recycling all the resources in the waste copper containing solution with a minimized energy consumption.

[23]The following content with specific preferred embodiments of the present invention will be described in further detail, it cannot be identified that the
25 embodiment of the present invention is limited to these specific instructions. For ordinary person skilled in the art, without departing from the inventive concept of the premise, one can also make a number of simple deductions or replacement to

carry out the invention which should be considered as belonging to the scope of the present invention.

DESCRIPTION OF FIGURE

[24] Figure 1 is a schematic process flow diagram of the methods disclosed in the present invention.

EMBODIMENTS

Embodiment 1

[25] Take 500L waste alkaline copper etching solution A from a PCB production line, distill the solution under a reduced pressure of 0.09MPa and a temperature of 90°C, discharge and stir the liquid for 1 hour when the liquid density within the reactor reaches 1.5 g / cm³, centrifuge the solids after the liquid is completely crystallized and thus obtain the blister copper compound E1 and the distillate is ammonia.

[26] Take 500L waste acidic copper etching solution B from the same PCB production line, distill the solution under a reduced pressure of 0.09MPa and a temperature of 90°C, discharge and stir the liquid for 1 hour when the liquid density within the reactor reaches 1.5 g / cm³, centrifuge the solids after the liquid is completely crystallized and thus obtain the blister copper compound E2 and the distillate is nitric acid or hydrochloric acid.

[27] Take 500L waste copper deposition solution C from the same PCB production line, distill the solution under a reduced pressure of 0.09MPa and a temperature of 90°C, discharge and stir the liquid for 1 hour when the liquid density within the reactor reaches 1.5 g / cm³, centrifuge the solids after the liquid is completely crystallized and thus obtain the blister copper compound E3 and the distillate is water.

[28]Take 500L waste microetching solution D from the same PCB production line, distill the solution under a reduced pressure of 0.09MPa and a temperature of 90°C, discharge and stir the liquid for 1 hour when the liquid density within the reactor reaches 1.5 g / cm³, centrifuge the solids after the liquid is completely crystallized
5 and thus obtain the blister copper compound E4 and the distillate is water.

[29]Mix the blister copper compounds E1-E4 in a mass ratio of 1: 1: 2: 4 mixed salt mixture blister E to form a blister copper compound mixture E and dissolve it with water to form an aqueous solution. A sulfuric acid with a concentration of 80% is added into the said solution at a ratio of 1:5 by volume, and the solution is then
10 distilled under a reduced pressure 0.09MPa and a temperature of 90°C. Discharge and stir the liquid for 1 hour when the liquid density reaches 1.1g / cm³ until the liquid is completely crystallized. After centrifugation, the obtained crystallization substance is copper sulfate, whose purity is higher than 98%. Meanwhile the residue after centrifugation is recycled to the waste acidic etching solution for
15 recovering a blister copper compound for next round treatment.

Embodiment 2

[30]In the embodiment 1, the blister copper compounds E1-E4 are mixed by mass at a ratio of 1: 1: 2: 4 to form the blister copper compound mixture E and dissolve it with water to form an aqueous solution. A nitric acid with a concentration of 60% is
20 added into the said solution at a ratio of 1:5 by volume, and the solution is then distilled under a reduced pressure 0.09MPa and a temperature of 90°C. Discharge and stir the liquid for 1 hour when the liquid density reaches 1.8g / cm³ until the liquid is completely crystallized. After centrifugation, the obtained crystallization substance is copper nitrate, whose purity is higher than 98%. Meanwhile the residue
25 after centrifugation is recycled to the waste acidic etching solution for recovering a blister copper compound for next round treatment.

Embodiment 3

[31]In the embodiment 1, the blister copper compounds E1-E4 are mixed by mass at a ratio of 1: 1: 2: 4 to form the blister copper compound mixture E and dissolve it with water to form an aqueous solution. Take the said solution 500L, add sodium carbonate, ammonium bicarbonate with a ratio of n (sodium carbonate): n

5 (ammonium bicarbonate): n (copper ions) = 1: 1: 1.2-1.5 within the autoclave, control the pH value to be 7-10, the reaction temperature to be 70- 85°C, stir the solution for 2-3h and filter the depositions to obtain the alkali copper carbonate, whose purity is more than 55% (as counted by copper). The filtrate is recycled to the waste alkali etching solution for recovering a blister copper compound for next
10 round treatment.

Embodiment 4

[32]In the embodiment 1, the blister copper compounds E1-E4 are mixed by mass at a ratio of 1: 1: 1: 2 to form the blister copper compound mixture E and dissolve it with water to form an aqueous solution. Take the said solution 500L, a caustic soda
15 is added to adjust the pH value to be greater than 12 and the temperature is controlled to be at 70-85°C. After stirring for 1-3h, copper oxide can be filtered out as the final product, whose purity is greater than 99% (as counted by copper). The filtrate is recycled to the waste alkali etching solution for recovering a blister copper compound for next round treatment.

20 Embodiment 5

[33]In the embodiment 1, the blister copper compounds E1-E4 are mixed by mass at a ratio of 1: 1: 1: 3 to form the blister copper compound mixture E and dissolve it with water to form an aqueous solution. Take the said solution 500L, a caustic soda is added to adjust the pH value to be greater than 12 and glucose is added after the
25 complete dissolution of caustic soda. A 1.2 times of the amount of glucose of the copper content in said blister copper compound aqueous solution is introduced. The reaction condition is controlled at a temperature of 70-85°C. The solution is stirred

for 1-3h and to filter out cuprous oxide, whose purity is around 95%. The filtrate is recycled to the waste microetching solution for recovering a blister copper compound for next round treatment.

Embodiment 6

- 5 [34]In the embodiment 1, the blister copper compounds E1-E4 are mixed by mass at a ratio of 1: 1: 2: 4to form the blister copper compound mixture E and dissolve it with water to form an aqueous solution. Take the said solution 500L and pump into an electrolysis cell, control the pH value to be 1-3, the current density at $0.5-3\text{A} / \text{dm}^2$ for electrolysis, the copper foil with a recovery rate of 95% is then obtained.
- 10 The residue is then recycled to the waste copper deposition solution for recovering a blister copper compound for next round treatment.

CLAIMS

1. A method for regeneration of copper compounds from waste copper containing solution from a PCB production line, characterized in that the said method comprises the following steps of:

5 (1) collect waste copper containing solution according to four categories of waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D;

(2) distill the waste alkaline etching solution A and the acid etching solution B separately to recover alkali or acidic distillate and cool their residue to crystallize
10 blister copper compounds E1 and E2;

(3) distill the copper deposition solution C and waste microetching solution D separately to remove water fraction and cool their residue to crystallize blister copper compounds E3 and E4;

(4) mix the blister copper compounds E1-E4 into blister copper compound mixture
15 E, prepare an aqueous solution from the said mixture E, recover copper compounds after purification of the said aqueous solution, and recycle its residue F into any one of the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D for further treatment.

20 2. A method for regeneration of copper compounds from waste copper containing solution from a PCB production line according to claim 1, characterized in that, purities of the said blister copper compounds E1-E4 are not less than 65% when copper concentrations in the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching
25 solution D are not less than 30g / L.

3. A method for regeneration of copper compounds from waste copper containing solution from a PCB production line according to claim 2, characterized in that, the said blister copper compounds E1:E2:E3:E4 are mixed in a mass ratio of 1: 1: 1: 1-1: 1: 2: 4 to form a blister copper compound mixture E.
- 5 4. A method for regeneration of copper compounds from waste copper containing solution from a PCB production line according to claim 3, characterized in that, the said recovered copper compounds from the blister copper compound mixture E includes at least one selected from the group consisting of copper sulfate or copper nitrate, alkali copper carbonate, copper oxide and cuprous oxide.
- 10 5. A method for regeneration of copper compounds from waste copper containing solution from a PCB production line according to claim 4, wherein the recovery process of copper sulfate is characterized in that, after the said blister copper compound E is dissolved in an aqueous solution, a sulfuric acid is added into the said solution to supersaturate SO_4^{2-} , and then the said solution is distilled to
- 15 crystallize CuSO_4 .
6. A method for regeneration of copper compounds from waste copper containing solution from a PCB production line according to claim 4, wherein the recovery process of copper nitrate is characterized in that, after the said blister copper compound E is dissolved in an aqueous solution, a nitric acid is added into the said
- 20 solution to supersaturate NO_3^- , and then the said solution is distilled to crystallize $\text{Cu}(\text{NO}_3)_2$.
7. A method for regeneration of copper compounds from waste copper containing solution from a PCB production line according to claim 4, wherein the recovery process of alkali copper carbonate is characterized in that, after the said blister
- 25 copper compound E is dissolved in an aqueous solution, at least one from the group comprising sodium carbonate, ammonium carbonate, ammonium bicarbonate is added into the said solution, and the alkali copper carbonate is then recovered by

stirring for 2-3 hours under a condition of a pH value of 7-10 and a reaction temperature of 70- 85°C.

8. A method for regeneration of copper compounds from waste copper containing solution from a PCB production line according to claim 4, wherein the recovery
5 process of copper oxide is characterized in that, after the said blister copper compound E is dissolved in an aqueous solution, a caustic soda is added into the said solution, and the copper oxide is then recovered by stirring for 1-4 hours under a condition of a pH value larger than 12 and a reaction temperature of 70- 85°C.

9. A method for regeneration of copper compounds from waste copper containing
10 solution from a PCB production line according to claim 4, wherein the recovery process of cuprous oxide is characterized in that, at least one agent selected from the group consisting of glucose, hydrazine hydrate, sodium hypophosphite is dissolved in an aqueous solution, a pH value larger than 12 is then controlled when an amount of 0.75-1 times of theoretical reductant amount of the said blister copper
15 compound mixture E is added into the said solution, and the cuprous oxide is then recovered by stirring for 1-4 hours under room temperature.

10. A method for regeneration of metallic copper from waste copper containing solution from a PCB production line, characterized in that the said method comprises the following steps of:

20 (1) collect waste copper containing solution according to four categories of waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D from a PCB production line;

(2) distill the waste alkaline etching solution A and the acid etching solution B separately to recover alkali or acidic distillate and cool the residue to crystallize
25 blister copper compounds E1 and E2;

(3) distill the copper deposition solution C and waste microetching solution D

separately to remove water fraction and cool the residue to crystallize blister copper compounds E3 and E4;

(4) mix the blister copper compounds E1-E4 into blister copper compound mixture E, prepare an aqueous solution from the said mixture E, recover metallic copper by electrolysis after purification of the said aqueous solution, and recycle its residue G into any one of the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D for further treatment.

11. A method for regeneration of metallic copper from waste copper containing solution from a PCB production line according to claim 10, characterized in that, purities of the said blister copper compounds E1-E4 are not less than 65% when copper concentrations in the said waste alkaline etching solution A, waste acid etching solution B, waste copper deposition solution C and waste microetching solution D are not less than 30g / L.

12. A method for regeneration of metallic copper from waste copper containing solution from a PCB production line according to claim 11, characterized in that, the said blister copper compounds E1:E2:E3:E4 are mixed in a mass ratio of 1: 1: 1: 1-1: 1: 2: 4 to form a blister copper compound mixture E.

13. A method for regeneration of metallic copper from waste copper containing solution from a PCB production line according to claim 12, wherein the recovered metallic copper by electrolytic is characterized in that, after the said blister copper compound E is dissolved in an aqueous solution, a pH value of 1-3 is then controlled in the said solution, a current density of 0.5-3A /dm² is selected to pump into an electrolytic cell to recover the metallic copper foil.