

A method for recycling tin-stripping solution and electrolytic tin from waste tin-stripping solution

TECHNICAL FIELD

[1] The present invention relates to a method for recycling both tin-stripping
5 solution and electrolytic tin from waste tin-stripping solution of the print circuit
board (PCB) industries.

BACKGROUND OF INVENTION

[2] Tin-stripping solution is one of the high-volume consumed chemical products
in PCB industries, whose major function is to etch away unwanted tin from the
10 plated copper layer or copper substrate selectively by using a certain pattern but to
avoid corrosion of the copper substrate of the PCB. Traditionally, nitric acid type
tin-stripping solution is the most widely used stripping agent in the field. With the
ongoing of stripping process, tin concentration in the stripping solution is
continuously increasing. The stripping efficiency is lowered dramatically when the
15 tin concentration is over a threshold value, whereby the tin-stripping solution has to
be refilled and the waste tin-stripping solution is therefore produced. Generally, a
tin concentration of more than 100g / L and a concentration of nitric acid of 20%
-30% are presented in the waste tin-stripping solution. The waste tin-stripping
solution also contains small amounts of polymeric surfactant and polycyclic,
20 heterocyclic and other organic chemicals.

[3] Therefore, the waste tin-stripping solution is of a metal rich and high pollution
waste. Developing economic method for recycling the waste tin-stripping solution
can not only achieve zero-pollutant-discharge or close to zero-pollutant-discharge
but also recover high value-added metal products such as metallic tin or electrolytic

tin.

[4] Presently, the methods for recycling waste tin-stripping solution can be divided into the following three categories:

[5] (1) Chemical neutralization method. An alkaline substance is added into the waste tin-stripping solution to precipitate the heavy metal ions and destruct the waste solution exhaustively, which results in the generation of sewage sludge whereby tin resource is not recycled. The disadvantage of this method is that the consumption volume of alkaline substance is large, the produced waste water requests additional treatment before discharging and the separation of produced sludge calls for high processing workload and high cost.

[6] (2) Distillation recovery resource recycling method. This method roots in the recycling the tin resource, see for example the prior art document of Chinese Patent CN 03118158.9, where Tan et al. recovers electrolytic tin from the waste tin-stripping or waste tin-lead solution. In their method, the nitric acid was recovered for reproducing the stripping solution by low pressure distillation, and the residue was neutralized to a pH value of 6-10 to generate tin and iron related precipitates. The resulted precipitates were dissolved completely in alkaline by heating the solution up to a temperature between 100°C -300°C and then the solution was hot dipped, cooled to temperature and centrifugally separated to obtain the tin-related compounds and ferric nitrate (or iron red). Ferric nitrate can be directly reused during the reproduction of stripping solution. The disadvantage of this method is that the large consumption volume of alkaline substance, the large energy consumption during the distillation and the complication of the recycling processes.

[7] (3) Tin-related compounds recycling method. A typical recycling method can be referred to prior art document Chinese Patent CN 1569644A, where Liao et al. make barium stannate from waste tin-stripping solution. In this method,

metastannate precipitates were firstly obtained by adding anionic surfactant and polymer flocculant into the waste solution, and such precipitates were then dissolved in sodium hydroxide or potassium hydroxide solution at high temperature to obtain soluble sodium stannate or potassium stannate. Secondly, the sodium
5 stannate or potassium stannate were then extracted with addition of sufficient water. Finally, BaCl_2 were added into the solution of sodium stannate or potassium stannate to generate barium stannate trihydrate. The disadvantage of this method is that a large amount of acid and other heavy metal ions was not recycled which decrease the utilization efficiency of waste resource, and a large amount of waste
10 water and sludge was resulted during the generation of barium stannate trihydrate which increases the cost of waste treatment.

[8] Conclusively, there still are some challenges presented in the treatment of waste tin-stripping solution and environmental-friendly approaches for recycling the resources from the waste tin-stripping solution are highly demanded. The present
15 invention is directed to a green approach for treating the waste tin-stripping solution from the PCB industry.

DISCLOSURE

[9] The purpose of the present invention is to provide a method for recycling both tin-stripping solution and electrolytic tin from waste tin-stripping solution produced
20 in the PCB industry.

[10] To achieve the purpose of the present invention, a method for recycling tin-stripping solution and electrolytic tin from waste tin-stripping solution is disclosed, the said method comprises the following steps in a sequence of:

(1) adding a flocculant of 0.1wt% and a concentrated sulfuric acid to a waste
25 tin-stripping solution, stirring for 1 hour and allowing to stand for 15-30 minutes, and collecting a first supernatant A1 and a first sludge B1, wherein the volume ratio

of flocculant to the waste tin-stripping solution is 1: 9-1: 12 and the volume ratio of concentrated sulfuric acid to the waste tin-stripping solution is 1: 20-1: 30;

(2) adding a mixture of nitric acid, surfactant C1 and nitrogen oxide inhibitor C2 to the said first supernatant A1 recovered from said step (1), filtering out insoluble
5 impurities and obtaining a tin-stripping solution to be reused in stripping process;

(3) placing said first sludge B1 obtained from said step (1) in water, wherein the volume ratio of said first sludge B1 to water is 1: 1, stirring for 1 hour and allowing to stand for 15-30 minutes, and collecting a second supernatant A2 and a second sludge B2;

10 (4) placing said second sludge B2 obtained from said step (3) in water, wherein the volume ratio of said second sludge B2 to water is 1: 1, stirring for 1 hour and allowing to stand for 15-30 minutes, and collecting a third supernatant A3 and a third sludge B3;

(5) placing said third sludge B3 obtained from said step (4) in water, wherein the
15 volume ratio of said third sludge B3 to water is 1: 1, stirring for 1 hour and allowing to stand for 15-30 minutes, and collecting a fourth supernatant A4 and a fourth sludge B4;

(6) placing said fourth sludge B4 obtained from said step (5) in concentrated hydrochloric acid, wherein the volume ratio of said fourth sludge B4 to
20 concentrated hydrochloric acid is 1: 1, stirring for 10 minutes, heating to 100°C and stirring for 1-3 hours until the said fourth sludge B4 completely dissolved and obtaining a dissolved solution D;

(7) electrolyzing said solution D obtained from step (6) using an electrolyzer, recovering metallic tin and obtaining an electrolytic residual E1;

25 (8) placing said metallic tin obtained from step (7) in methyl sulfonic acid-based

solution F for reaction of 8 hours in a reaction still at a temperature of 125°C, wherein the mass ratio of said metallic tin to methyl sulfonic acid-based solution is 1: 5, filtering out methyl stannous sulfonate crystals to be used in tin plating and obtaining an electrolytic residual E2.

5 [11] Preferably, in said step (2), for stabilizing the regenerated tin-stripping solution, the weight ratio of nitric acid, surfactant C1, nitrogen oxide inhibitor C2 to the said first supernatant A1 are, respectively, 3 -15 %, 1-5% and 1-5%; the reaction time before filtering the insoluble impurities is 10 minutes to 1 hour.

[12] Preferably, the said method in step (2) for filtering the insoluble impurities is
10 membrane separation or diffusion dialysis. The said tin-stripping solution obtained from step (2) can be reused in the stripping process alone or by mixing with fresh tin-stripping solution.

[13] Preferably, the said second supernatant A2 obtained from step (3), the said third supernatant A3 obtained from step (4) and the said fourth supernatant A4 obtained
15 from step (5) are mixed, concentrated and recycled to the processing of step (2) to prepare the said tin-tripping solution from step (2). The said tin-stripping solution contains nitric acid, iron ion, hydrochloric acid, corrosion inhibitor and surfactant.

[14] Preferably, the said electrolytic residual E1 obtained from step (7) is mixed with the fourth sludge B4 collected from step (5) and recycled to the processing of
20 step (6) for the preparation of said solution D.

[15] Preferably, the said electrolytic residual E2 obtained from step (8) is mixed with the said solution D obtained from step (7) and recycled to the processing of step (7) for obtaining the said metallic tin.

[16] Preferably, the said flocculant is polyacrylamide flocculant.

25 [17] Preferably, the mass concentration of said concentrated sulfuric acid is 98%.

[18] Preferably, the mass concentration of said concentrated hydrochloric acid is 37%.

[19] Preferably, the said surfactant C1 is one or mixture of etidronic acid, polyacrylic acid and zinc sulfate.

5 [20] Preferably, the said nitrogen oxide inhibitor C2 is one or mixture of 2,2,6,6-tetramethyl piperidine, 2,2,6,6-tetramethyl-piperidine amine and 2,2,6,6-tetramethyl piperidine.

[21] Preferably, the said methyl sulfonic acid-based solution F is 4-pyridine-carboxylic acid or nonylphenol polyoxyethylene or their mixture.

10 [22] Preferably, the volume concentration of nitrate in the said third supernatant A3 obtained from said step (4) is not less than 5%, and more preferably, not less than 10%; the volume concentration of nitrate in the said fourth supernatant A4 obtained from said step (5) is not less than 3%, and more preferably, not less than 7%.

15 [23] Preferably, the mass concentration of stannic compounds in the said third sludge B3 obtained from said step (4) is not less than 30%, and more preferably, not less than 50%; the mass concentration of stannic compounds in the said fourth sludge B4 obtained from said step obtained from said step (5) is not less than 50%, and more preferably, not less than 70%.

20 [24] Preferably, the purity of said methyl stannous sulfonate crystals obtained from said step (9) is 5N, and more preferably, more than 6N.

[25] On the first aspect, the present invention discloses a process for preparing a tin-stripping solution and recycling electrolytic tin for reusing in plating process from waste tin-stripping solution. The present invention is to recycle the waste tin-stripping solution by using a combination of processing including the separation
25 after flocculation, dissolution of sludge, electrolysis and preparation of electrolytic

tin for plating process, whereby all components in the waste tin-stripping solution is recycled and high quality of methyl stannous sulfonate crystals for tinplating can be obtained.

5 [26]On the second aspect, the inventor surprisingly found that a mixture of the regenerated tin-stripping solution from step (2) and a fresh tin-stripping solution with a volume ratio range of 1:1-1:10 reused in the stripping process yields 5-10% more cycles than the fresh tin-stripping solution or the regenerated tin-stripping solution alone. Such a lifespan extension of the tin-stripping solution might be contributed to the introduction of the surfactant and/or the nitrogen oxide inhibitor.

10 [27]On the third aspect, the treatment process disclosed in the present invention is relatively simple, and more important, the said process can recycle and reuse all materials while reducing waste discharge and having good economic returns. This invention provides a technical solution that overcomes the disadvantages of the prior art technologies.

15 DESCRIPTION OF FIGURE

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

EMBODIMENTS

Embodiment 1

20 [29]Select 300 ml waste tin-stripping solution from a PCB manufacturer production line and add 30 ml 0.1wt% polyacrylamide flocculant and 15 ml 98% concentrated sulfuric acid into the said solution. Stir the said solution for 1 hour and then allow to stand for 20 minutes. The supernatant after stratification of the said solution is supplemented with 16 ml nitrate, 4 ml etidronic acid and 3 ml 2,2,6,6-
25 tetramethylpiperidine, then filtered out the insoluble impurities, and the obtained

solution was returned to use in the production line. Take 140 ml water to dissolve the sludge, stir for 1 hour, allow to stand for 20 minutes and then separate the supernatant and sludge after stratification. Repeat the said process twice. All the supernatants are mixed, concentrated and supplemented with 40 ml nitric acid, 10 ml etidronic acid and 11 ml 2,2,6,6- tetramethylpiperidine, then filter out the insoluble impurities, and the resulting solution mixed with the fresh tin-stripping solution is returned to reuse in the same production line. Take 140 ml 37% concentrated hydrochloric acid to dissolve the sludge by stirring for 10 minutes and heating to 100°C for 2 hours and obtain the dissolved solution. The said dissolved solution is then placed in an electrolyzer cell to obtain the electrolytic tin by electrolysis. The electrolytic residual is then returned to the processing step for dissolving the sludge. The metallic tin obtained from electrolysis is then placed in 1 L methyl sulfonic acid solution for 8 hours in a reactor at 125°C. After crystallization, the methyl stannous sulfonate crystals can be claimed and used in tin plating process while the residual is returned to the processing step for electrolysis.

Embodiment 2

[30] Select 500 ml waste tin-stripping solution from a PCB manufacturer production line and add 60ml 0.1wt% polyacrylamide flocculant and 25 ml 98% concentrated sulfuric acid into the said solution. Stir the said solution for 1 hour and then allow to stand for 20 minutes. The supernatant after stratification of the said solution is supplemented with 75 ml nitrate, 20 ml etidronic acid and 25 ml 2,2,6,6-tetramethylpiperidine, then filtered out the insoluble impurities, and the obtained solution mixed with the fresh tin-stripping solution was returned to use in the production line. Take 260ml water to dissolve the sludge, stir for 1 hour, allow to stand for 20 minutes and then separate the supernatant and sludge after stratification. Repeat the said process twice. All the supernatants are mixed, concentrated and supplemented with 40 ml nitric acid, 10 ml etidronic acid and 11 ml 2,2,6,6-tetramethylpiperidine, then filter out the insoluble impurities, and the resulting

solution is returned to reuse in the same production line. Take 260 ml 37% concentrated hydrochloric acid to dissolve the sludge by stirring for 10 minutes and heating to 100°C for 2 hours and obtain the dissolved solution. The said dissolved solution is then placed in an electrolyzer cell to obtain the metallic tin by electrolysis. The electrolytic residual is then returned to the processing step for dissolving the sludge. The metallic tin obtained from electrolysis is then placed in 1.8 L methyl sulfonic acid solution for 8 hours in a reactor at 125°C. After crystallization, the methyl stannous sulfonate crystals can be claimed and used in tin plating process while the residual is returned to the processing step for electrolysis.

10 Embodiment 3

[31]Select 300 ml waste tin-stripping solution from a PCB manufacturer production line and add 30 ml 0.1wt% polyacrylamide flocculant and 20 ml 98% concentrated sulfuric acid into the said solution. Stir the said solution for 1 hour and then allow to stand for 20 minutes. The supernatant after stratification of the said solution is supplemented with 15 ml nitrate, 5 ml etidronic acid and 5 ml 2,2,6,6-tetramethylpiperidine, then filtered out the insoluble impurities, and the obtained solution was returned to use in the production line. Take 150ml water to dissolve the sludge, stir for 1 hour, allow to stand for 20 minutes and then separate the supernatant and sludge after stratification. Repeat the said process twice. All the supernatants are mixed, concentrated and supplemented with 45 ml nitric acid, 15 ml etidronic acid and 15 ml 2,2,6,6- tetramethylpiperidine, then filter out the insoluble impurities, and the resulting solution mixed with the fresh tin-stripping solution is returned to reuse in the same production line. Take 150 ml 37% concentrated hydrochloric acid to dissolve the sludge by stirring for 10 minutes and heating to 100°C for 2 hours and obtain the dissolved solution. The said dissolved solution is then placed in an electrolyzer cell to obtain the metallic tin by electrolysis. The electrolytic residual is then returned to the processing step for dissolving the sludge. The metallic tin obtained from electrolysis is then placed in

1L methyl sulfonic acid solution for 8 hours in a reactor at 125°C. After crystallization, the methyl stannous sulfonate crystals can be claimed and used in tin plating process while the residual is returned to the processing step for electrolysis.

- 5 [32]The above embodiments are only used to illustrate the present invention, not intended to limit the scope thereof. Many modifications of the above embodiments can be made without departing from the spirit of the present invention.

CLAIMS

1. A method for recycling tin-stripping solution and electrolytic tin from waste tin-stripping solution, characterized in that the said method comprises the steps of:

(1) adding a flocculant of 0.1wt% and a concentrated sulfuric acid to a waste

5 tin-stripping solution, stirring for 1 hour and allowing to stand for 15-30 minutes, and collecting a first supernatant A1 and a first sludge B1, wherein the volume ratio of flocculant to the waste tin-stripping solution is 1: 9-1: 12 and the volume ratio of concentrated sulfuric acid to the waste tin-stripping solution is 1: 20-1: 30;

(2) adding a mixture of nitric acid, surfactant C1 and nitrogen oxide inhibitor C2 to

10 the said first supernatant A1 recovered from said step (1), filtering out insoluble impurities and obtaining a tin-stripping solution to be reused in stripping process;

(3) placing said first sludge B1 obtained from said step (1) in water, wherein the volume ratio of said first sludge B1 to water is 1: 1, stirring for 1 hour and allowing to stand for 15-30 minutes, and collecting a second supernatant A2 and a second

15 sludge B2;

(4) placing said second sludge B2 obtained from said step (3) in water, wherein the volume ratio of said second sludge B2 to water is 1: 1, stirring for 1 hour and allowing to stand for 15-30 minutes, and collecting a third supernatant A3 and a third sludge B3;

20 (5) placing said third sludge B3 obtained from said step (4) in water, wherein the volume ratio of said third sludge B3 to water is 1: 1, stirring for 1 hour and allowing to stand for 15-30 minutes, and collecting a fourth supernatant A4 and a fourth sludge B4;

(6) placing said fourth sludge B4 obtained from said step (5) in concentrated

25 hydrochloric acid, wherein the volume ratio of said fourth sludge B4 to

concentrated hydrochloric acid is 1: 1, stirring for 10 minutes, heating to 100°C and stirring for 1-3 hours and obtaining a dissolved solution D;

(7) electrolyzing said solution D obtained from step (6) using an electrolyzer, recovering metallic tin and obtaining an electrolytic residual E1;

5 (8) placing said metallic tin obtained from step (7) in a methyl sulfonic acid-based solution F for reaction of 8 hours in a reaction still at a temperature of 125°C, wherein the mass ratio of said metallic tin to methyl sulfonic acid-based solution is 1: 5, filtering out methyl stannous sulfonate crystals to be used in tin plating and obtaining an electrolytic residual E2.

10 2. A method for recycling tin-stripping solution and electrolytic tin from waste tin-stripping solution according to claim 1, characterized in that, in said step (2), the weight ratio of nitric acid, surfactant C1, nitrogen oxide inhibitor C2 to the said first supernatant A1 are, respectively, 3 -15 %, 1-5% and 1-5%.

15 3. A method for recycling tin-stripping solution and electrolytic tin from waste tin-stripping solution according to claims 1 or 2, characterized in that, the said second supernatant A2 obtained from step (3), the said third supernatant A3 obtained from step (4) and the said fourth supernatant A4 obtained from step (5) are mixed, concentrated and recycled to the processing of step (2) to prepare the said tin-tripping solution from step (2).

20 4. A method for recycling tin-stripping solution and electrolytic tin from waste tin-stripping solution according to any of claims 1-3, characterized in that, the said electrolytic residual E1 obtained from step (7) is mixed with the fourth sludge B4 collected from step (5) and recycled to the processing of step (6) for the preparation of said solution D.

25 5. A method for recycling tin-stripping solution and electrolytic tin from waste tin-stripping solution according to any of claims 1-4, characterized in that, the said

electrolytic residual E2 obtained from step (8) is mixed with the said solution D obtained from step (7) and recycled to the processing of step (7) for obtaining the said metallic tin.

6. A method for recycling tin-stripping solution and electrolytic tin from waste
5 tin-stripping solution according to any of claims 1-5, characterized in that, the said surfactant C1 is one or mixture of etidronic acid, polyacrylic acid and zinc sulfate.

7. A method for recycling tin-stripping solution and electrolytic tin from waste
tin-stripping solution according to any of claims 1-5, characterized in that, the said
nitrogen oxide inhibitor C2 is one or mixture of 2,2,6,6-tetramethyl piperidine,
10 2,2,6,6-tetramethyl-piperidine amine and 2,2,6,6-tetramethyl piperidine.

8. A method for recycling tin-stripping solution and electrolytic tin from waste
tin-stripping solution according to any of claims 1-7, characterized in that, the said
tin-stripping solution obtained from step (2) contains nitric acid, iron ion,
hydrochloric acid, corrosion inhibitor and surfactant.

15 9. A method for recycling tin-stripping solution and electrolytic tin from waste
tin-stripping solution according to any of claims 1-8, characterized in that, the said
tin-stripping solution obtained from step (2) is mixed with a fresh tin-stripping
solution with a volume ratio range of 1:1-1:10 to be reused in stripping process.