

“A METHOD FOR RECOVERING METAL VALUES FROM SOLDER DROSS”

FIELD OF THE INVENTION

5 The present invention relates to the field of recovering metal values from solder dross. More particularly, the present invention relates to a method of recovering metal values from solder dross of electronic manufacturing services in an economical manner.

BACKGROUND OF THE INVENTION

10 Wave soldering processes are usually carried out in the presence of air, owing to which there are always chances of the metal alloy being rendered unusable because of oxidation. This unusable alloy is known as solder dross that is generally thrown away as process waste. Since, dross is more than 75% pure alloy, therefore, it just needs processing and refining to render it reusable again.

15 The benefit of recycling solder dross is the reduced strain on the Earth's natural resources. When manufacturing processes are optimized for maximum consumption of raw materials through dross recycling, the need for further mining of natural ores is reduced drastically and hence, making these operations easier on the planet. Dross recycling offers additional revenue to the manufacturer as the unusable solder waste can be sold off at
20 reasonable process to recycling companies. The process also helps to reduce the amount of electronic waste that makes its way into landfills and garbage dumps in the form of solder dross.

TWI394846 discloses a recycling means for lead-free silver containing tin solder dross. In this patent, the dross was ground to a size of -50 mesh and subjected to a leaching
25 condition of 4N HNO₃, 70 DEG C, 2 hours and 5g/50ml to reach leaching recovery of 100% and 0.027% for Ag and Sn, respectively. After filtration, the solid obtained is high purity tin oxide. The pH of obtained leaching solution is adjusted to 2 by adding NH₄ to precipitate all the tin (Sn) which contained in the solution. Then, 100% silver (Ag) which
30 remained in the solution are precipitated by adding N₂H₄. H₂O. The collected Ag containing precipitate was washed by 5M HCl at 70 DEG C for 15 minutes and by water

in 27 DEG C for another 15 minutes. The washed precipitate was then melted at 1000 DEG C together with boric acid (H_3BO_3) to obtain a marketable silver ingot. However, nitric consumption is high, effluent treatment is tough. Tin is recovered from residue as well as from precipitate, hydrazine used for silver precipitation is costly.

5 **WO2019180642A1** discloses a method for the selective recovery of tin from a tin-containing material, preferably the electronic scrap and particularly, printed-circuit boards, the method comprising: the pre-treatment of the tin containing material, selective solubilization of the pretreated material to precipitate selectively the tin-containing compounds, comprising exposing of the pretreated tin-containing material to the
10 operation of a washing bath containing nitric (V) acid and isolation of tin from the washing bath as tin (IV) oxide. A reactor is provided that is useful for the selective solubilization of the tin- containing material. This citation further provides a method for the purification of tin dioxide contaminated with lead oxide to give metallic tin by thermal treatment conducted in the presence of a novel fluxing agent and use of a novel fluxing agent as an
15 environment or conducting thermal reduction of tin dioxide to metallic tin.

Syarifah Aminah Ismail et. al., (Applied Mechanics and Materials, ISSN: 1662-7482, Vols. 754-755, pp 567-570), reported the experimental results of leaching of tin (Sn) from solder dross by means of leaching using different concentration of hydrochloric acid (HCl). Solder dross was sieved to obtain a mean particle size of 75 μm . The solder dross powder
20 obtained was leached by using hydrochloric acid (HCl) aqueous solution. To optimize the parameter required for recovery of Sn from solder dross, initially the bench scale studies were carried out using varying acid concentration, stirring time and temperature. The experimental data indicate that 98.7% of Sn was leached out from solder dross using 0.1 M of HCl, 24 hours of stirring at 60°C solution temperature. However, this process is focused
25 on leaching of tin only.

Over the past, many other methods for recovering tin oxide from solder dross are known, however, these methods involve high consumption of concentrated acids, greater processing time, effluent treatments and use of costly chemicals.

Therefore, there is a need to develop a technology to overcome the above mentioned
30 drawbacks. The present invention is an endeavor in this direction.

OBJECT OF THE INVENTION

The main object of the present invention is to provide a method for recovering metal values from solder dross.

5 Another object of the present invention is to provide a method that recovers metals values by selective precipitation.

Yet another object of the present invention is to provide percentage recovery of tin (>98%), silver (95%) and copper (98%).

10 Yet another object of the present invention is to provide percentage purity of tin oxide, silver and copper carbonate in a range of 99.5-99.8%, 99.8-99.9% and 99.5-99.8%, respectively.

Still another object of the present invention is to provide a clean, green and economical method for recovery of metal values from solder dross.

15 **SUMMARY OF THE INVENTION**

The present invention relates to a method for recovering metal values from solder dross. This process involves selective recovery of metal values by selective precipitation at a suitable pH. The method of recovering metal values from solder dross is clean, green and economical.

20 In an embodiment, the present invention provides a method for recovering metal values from solder dross, characterized in that, the method comprising the steps of: (a) leaching of solder dross with a suitable reagent for a predefined time at a pre-determined range of temperature to obtain a leach liquor-I and a leach residue; (b) precipitating selectively tin from the leach liquor-I obtained in step (a) between a pre-defined pH range to obtain a
25 precipitated tin and a tin-free solution; (c) washing the precipitated tin of step (b) with water and drying to obtain pure tin oxide; (d) evaporating the tin-free solution obtained in step (b) to recover sodium chloride; (e) smelting the leach residue obtained in step (a) with soda to obtain a metallic part followed by atomization to obtain a plurality of metallic granules; (f) agitating the metallic granules obtained in step (e) with a suitable acid at a

pre-determined temperature range for a predefined time to obtain leach liquor-II; (g) precipitating the leach liquor-II obtained in step (f) with an appropriate solution to obtain a precipitated silver and a silver-free solution; (h) smelting the precipitated silver of step (g) with soda ash at a temperature in a range of 1000-1100°C to recover silver; and (i) adding a suitable base to the silver-free solution obtained in step (g) at a pH in a range of 5.5-6 to recover copper as copper carbonate.

The present invention relates to an economical method for recovering metal values from solder dross. The process provides recovery of tin (>98%), silver (95%), and copper (98%) with percentage purity of tin oxide in a range of 99.5-99.8%, silver in a range of 99.8-99.9% and copper carbonate in a range of 99.5% to 99.8%.

The above objects and advantages of the present invention will become apparent from the hereinafter set forth brief description of the drawings, detailed description of the invention, and claims appended herewith.

BRIEF DESCRIPTION OF THE DRAWING

An understanding of the method for recovering metal values from solder dross of the present invention may be obtained by reference to the following drawings:

Figure 1 is a process flow sheet for the recovery of metal values from solder dross according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described hereinafter with reference to the accompanying drawings in which a preferred embodiment of the invention is shown. This invention may, however, be embodied in many different forms and should not be construed as being limited to the embodiment set forth herein. Rather, the embodiment is provided so that this disclosure will be thorough, and will fully convey the scope of the invention to those skilled in the art.

The present invention now will be described hereinafter with reference to the detailed description, in which some, but not all embodiments of the invention are indicated. Indeed, the invention may be embodied in many different forms and should not be

construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy applicable legal requirements. Like numbers refer to like elements throughout. The present invention is described fully herein with non-limiting embodiments and exemplary experimentation.

5 The present invention provides a method for recovering metal values from solder dross. This process involves selective recovery of metal values by selective precipitation at a suitable pH. The method of recovering metal values is clean and green.

In a preferred embodiment, the present invention provides a method for recovering metal values from solder dross, characterized in that, the method comprises the steps of: (a) 10 leaching of solder dross with a suitable reagent for a predefined time at a pre-determined range of temperature to obtain a leach liquor-I and a leach residue; (b) precipitating selectively tin from the leach liquor-I obtained in step (a) between a pre-defined pH range to obtain a precipitated tin and a tin-free solution; (c) washing the precipitated tin of step (b) with water and drying to obtain pure tin oxide; (d) evaporating the tin-free solution 15 obtained in step (b) to recover sodium chloride; (e) smelting the leach residue obtained in step (a) with soda to obtain a metallic part followed by atomization to obtain a plurality of metallic granules; (f) agitating the metallic granules obtained in step (e) with a suitable acid at a pre-determined temperature range for a predefined time to obtain leach liquor-II; (g) precipitating the leach liquor-II obtained in step (f) with an appropriate solution to 20 obtain a precipitated silver and a silver-free solution; (h) smelting the precipitated silver of step (g) with soda ash at a temperature in a range of 1000-1100°C to recover silver; and (i) adding a suitable base to the silver-free solution obtained in step (g) at a pH in a range of 5.5-6 to recover copper as copper carbonate.

Here, the suitable reagent of step (a) is hydrochloric acid and the predefined time of step 25 (a) is in a range of 3-4 hours and the pre-determined range of temperature is 70-90°C.

Further, the pre-defined pH of step (b) is in a range of 1.5-2.5 and said tin-free solution is a tin hydroxide solution and the suitable acid of step (f) is selected from nitric acid and the pre-determined temperature range of step (f) is 70-80°C and the predefined time of step (f) is in a range of 2-3 hours.

Additionally, the appropriate solution of step (g) is selected from sodium chloride solution and the silver-free solution of step (g) is a leach liquor containing copper. The suitable base of step (i) is sodium carbonate.

5 The percentage recovery of tin is in a range of 98-98.5%, silver is in a range of 95-96% and copper is in a range of 98-98.5%. The percentage purity of tin oxide, silver and copper carbonate is in a range of 99.5-99.8%, 99.8-99.9% and 99.5-99.8%, respectively.

Figure 1 shows the process flow sheet for the recovery of metal values from solder dross.

EXAMPLE 1

BATCH ANALYSIS

10 **Batch 1**

In a 50 kg batch-1, solder dross was agitated with 150 L of HCl and 150 L of water for 4 hours at 85°C to obtain a slurry. Then the slurry was cooled and filtered to get the leach liquor-1(300 L) and residue-1(6.1 kg). To the leach liquor-1, 110 L of sodium hydroxide solution (40%, w/v) was added under agitation, to precipitate tin by increasing the pH of the slurry to 2.7. Then, the slurry was filtered to get tin oxide cake (77.2 kg) and filtrate (388 L). The tin oxide cake was washed with water (150 L) and filtered followed by drying of the washed cake to get 54 kg of pure tin oxide. The analysis of solder dross, leach liquor-1, and residue-1 is shown in Table-1 below:

Table-1: Analysis of solder dross, leach liquor-1, and residue-1

Sample Description	Unit	Analysis of elements		
		Ag	Sn	Cu
Solder dross	%	0.37	84.67	0.85
Residue-1	%	3.3	0.02	7.05
Leach liquor-1	g/L	BDL	141.1	0.015

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The residue-1 (6.1 kg) was mixed with 0.3 kg of soda ash and kept at 1000°C for an hour to melt. The molten liquor was slowly poured over water (50 L) for granulation. Then, the

metal granules (0.61 kg) were agitated with 8 L of nitric acid at 70°C for 3 hours to get the leach liquor-2 (containing silver and copper).

To the leach liquor-2, 0.5 L of 20% (w/v) sodium chloride was added under agitation to precipitate the silver. The slurry was filtered to get silver chloride cake (0.35 kg) and filtrate-2 (8.4 L). The silver chloride cake was washed, dried, and smelted to get the silver metal (0.185 kg). The analysis of leach liquor-2 and filtrate-2 is presented in **Table-2**. To filtrate-2, 0.73 kg of soda ash was added under agitation to precipitate copper. The precipitated copper cake (1.21 kg) was washed with water and dried to get pure copper carbonate (0.83 kg).

Table-2: Analysis of leach liquor-2 and filtrate-2.

Sample Description	Unit	Analysis of elements		
		Ag	Sn	Cu
Leach liquor-2	g/L	23.1250	0.001	53.125
Filtrate-2	g/L	BDL	BDL	50.595

Batch 2

In another batch of 50 kg (batch-2), solder dross was agitated with 150 L of HCl and 150L of water for 4 hours at 85°C. Then, the slurry was cooled and filtered to get the leach liquor-1(302 L) and residue-1(6.23 kg). To the leach liquor-1, 111 L of sodium hydroxide solution (40%, w/v) was added under agitation, to precipitate tin by increasing the pH of the slurry to 2.7. Then, the slurry was filtered to get tin oxide cake (79.3 kg) and filtrate (391 L). The tin oxide cake was washed with water (150 L) and filtered followed by drying of the washed cake to get 54.2 kg of pure tin oxide. The analysis of solder dross, leach liquor-1, and residue-1 is presented in **Table-3** below.

Table-3: Analysis of solder dross, leach liquor-1, and residue-1.

Sample Description	Unit	Analysis of elements		
		Ag	Sn	Cu
Solder dross	%	0.39	86.2	0.78
Residue-1	%	3.13	0.03	6.26

Leach liquor-1	g/L	BDL	142.7	0.011
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The residue-1 (6.23 kg) was mixed with 0.31 kg of soda ash and kept at 1000 °C for an hour to melt. The molten liquor was slowly poured over water (50 L) for granulation. Then, the metal granules (0.62 kg) were agitated with 8 L of nitric acid at 70°C for 3 hours to get the leach liquor-2 (containing silver and copper).

To the leach liquor-2, 0.51 L of 20% (w/v) sodium chloride was added under agitation to precipitate the silver. The slurry was filtered to get silver chloride cake (0.37 kg) and filtrate-2 (8.41 L). The silver chloride cake was washed, dried, and smelted to get the silver metal (0.194 kg). The analysis of leach liquor-2 and filtrate-2 is presented in **Table-4**. To filtrate-2, 0.7 kg of soda ash was added under agitation to precipitate copper. The precipitated copper cake (1.01 kg) was washed with water and dried to get pure copper carbonate (0.68 kg).

Table-4: Analysis of leach liquor-2 and filtrate-2

Sample Description	Unit	Analysis of elements		
		Ag	Sn	Cu
Leach liquor-2	g/L	24.3750	0.001	48.750
Filtrate-2	g/L	BDL	BDL	46.373

The analysis of the impurity profile and assay of pure tin oxide, silver metal, and copper carbonate obtained in batches 1 & 2 was done by Microwave Plasma Atomic Emission Spectrophotometer and titration, respectively as shown in **Tables-5, 6 & 7**.

Table 5: Analysis of silver metal

Elements, %	Silver Metal	
	Batch-1	Batch-2
Fe	0.0001	0.0001
Cu	0.032	0.04
Sn	0.04	0.07
Na	0.0001	0.0001

Ca	0.0001	0.0001
Mg	0.0001	0.0001
Pb	0.0001	0.0001
Assay	99.93	99.89

Table 6: Analysis of Tin oxide

Elements, %	Tin oxide	
	Batch-1	Batch-2
Fe	0.001	0.001
Cu	0.03	0.05
Ag	0.0001	0.0001
Na	0.23	0.37
Ca	0.011	0.018
Mg	0.005	0.005
Pb	0.0001	0.0001
Assay	99.72	99.56

Table 7: Analysis of copper carbonate

Elements, %	Copper carbonate	
	Batch-1	Batch-2
Fe	0.001	0.001
Ag	0.0001	0.0001
Sn	0.002	0.012
Na	0.29	0.14
Ca	0.01	0.036
Mg	0.012	0.009
Pb	0.001	0.001
Assay	99.68	99.80

Therefore, the present invention provides a method for recovering metal values from solder dross. The process recovers all the metal values economically and hence, this process is attractive for the recycling industry.

Many modifications and other embodiments of the invention set forth herein will readily
5 occur to one skilled in the art to which the invention pertain having the benefit of the
teachings presented in the foregoing descriptions and the associated drawings. Therefore,
it is to be understood that the invention is not to be limited to the specific embodiments
disclosed and that modifications and other embodiments are intended to be included
within the scope of the appended claims. Although specific terms are employed herein,
10 they are used in a generic and descriptive sense only and not for purposes of limitation.

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CLAIMS

We claim:

1. A method for recovering metal values from solder dross, characterized in that, the method comprises the steps of:
 - a) leaching of solder dross with a suitable reagent for a predefined time at a pre-determined range of temperature to obtain a leach liquor-I and a leach residue;
 - b) precipitating selectively tin from the leach liquor-I obtained in step (a) between a pre-defined pH range to obtain a precipitated tin and a tin-free solution;
 - c) washing the precipitated tin of step (b) with water and drying to obtain pure tin oxide;
 - d) evaporating the tin-free solution obtained in step (b) to recover sodium chloride;
 - e) smelting the leach residue obtained in step (a) with soda to obtain a metallic part followed by atomization to obtain a plurality of metallic granules;
 - f) agitating the metallic granules obtained in step (e) with a suitable acid at a pre-determined temperature range for a predefined time to obtain leach liquor-II;
 - g) precipitating the leach liquor-II obtained in step (f) with an appropriate solution to obtain a precipitated silver and a silver-free solution;
 - h) smelting the precipitated silver of step (g) with soda ash at a temperature in a range of 1000-1100°C to recover silver; and
 - i) adding a suitable base to the silver-free solution obtained in step (g) at a pH in a range of 5.5-6 to recover copper as copper carbonate.
2. The method as claimed in claim 1, wherein the suitable reagent of step (a) is hydrochloric acid.
3. The method as claimed in claim 1, wherein the predefined time of step (a) is in a range of 3-4 hours and the pre-determined range of temperature is 70-90°C.
4. The method as claimed in claim 1, wherein the pre-defined pH of step (b) is in a range of 1.5-2.5 and said tin-free solution is a tin hydroxide solution.

5. The method as claimed in claim 1, wherein the suitable acid of step (f) is nitric acid.
- 5 6. The method as claimed in claim 1, wherein the pre-determined temperature range of step (f) is 70-80°C and the predefined time of step (f) is in a range of 2-3 hours.
7. The method as claimed in claim 1, wherein the appropriate solution of step (g) is sodium chloride solution.
- 10 8. The method as claimed in claim 1, wherein said silver-free solution of step (g) is a leach liquor containing copper.
9. The method as claimed in claim 1, wherein the suitable base of step (i) is sodium carbonate.
- 15 10. The method as claimed in claim 1, wherein the percentage recovery of tin is in a range of 98-98.5%, silver is in a range of 95-96% and copper is in a range of 98-98.5%.
- 20 11. The method as claimed in claim 1, wherein the percentage purity of tin oxide, silver and copper carbonate is in a range of 99.5-99.8%, 99.8-99.9% and 99.5-99.8%, respectively.