

PROVISIONAL SPECIFICATION.

ELECTROWINNING OF ANTIMONY.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification describes the nature of this invention.

This is an invention by Biman Behari Dey, Veeraragava Aravamuthan and Palamuthi Ramaswami Rajagopalan, all of the Central Electrochemical Research Institute, Kara kudi, India, all Indian citizens.

This invention relates to a process for the electrowinning of antimony

Attempts for the electrowinning of antimony from Stibnite ores have been made in Germany and later on a commercial scale in the U. S. A. employing sodium thioantimonate, obtained by leaching antimony concentrates with sodium sulphide solution. However, no plant is known to be in commercial operation at present employing this method for electrowinning, on account of the operational and other technical difficulties.

In Germany, electrorefining of crude antimony regulus was practised employing fluoride-sulphate bath. Schlain and coworkers attempted the electro refining of crude antimony bullion, employing a fluoride sulphate bath and copper cathodes, but were not successful. (Schlain D, Prater J. D. and Ravitz S. F., Tran. Am. Elect. Chem. Soc. 95, 145-160 (1949) The fluoride-sulphate bath has not been used for electrowinning, on account of the silica present in the primary sources. The process invented by us makes use of hydrofluoric acid containing a very high percentage of sulphuric acid as the leaching agent, the raw material for the antimony being free from silica.

"The process for the electrowinning of pure antimony metal consists in treating (i) the anode mud from the electrolytic separation of lead from high-antimony lead alloys like battery lead or (ii) battery dust and battery wastes obtained from discarded lead acid batteries and during the process of manufacture of lead acid batteries, by a process consisting of the following steps:

- (1) Treating the powdered material (-200 mesh) with concentrated sulphuric acid at 100-120°C in a ceramic or lead vessel to convert the lead and antimony into lead sulphate and basic antimony sulphate respectively,
- (2) leaching the mixture of lead sulphate and basic antimony sulphate so obtained with the spent electrolyte containing hydrofluoric acid and sulphuric acid (from Step 3) to get the antimony in solution, the lead sulphate remaining undissolved.
- (3) Electrolysing the solution obtained in Step (2) to get pure antimony metal".

The battery wastes, battery dust and similar material for processing are powdered to 200 mesh and treated with concentrated sulphuric acid at 100-120°C to convert the lead and antimony into lead sulphate and antimony basic sulphates respectively. This can be done in a lead or ceramic vessel.

The electrolyte is a mixture of antimony fluoride and sulphuric acid. After electrolysis, the spent electrolyte containing hydrofluoric acid and sulphuric acid is used for leaching the antimony. The basic sulphate of antimony formed by pre-treatment with sulphuric acid, readily goes into solution as antimony trifluoride. This is the electrolyte for electrowinning. Lead is left behind as insoluble lead sulphate.

The apparatus used in the process is illustrated with the help of accompanying drawings wherein Figure I shows an electrolytic cell and electrode assembly.

A lead lined wooden tank 1 (7" × 6" × 6" I D) constitutes the cell. The graphite anodes 3, two in number (6" × 4" × 1/4"), are suspended from copper busbars. A monel cathode 4 (5" × 4 1/2" × 1/32") is kept in between the anodes. The cathode is well polished and degreased

with trichloroethylene and given a dip in 2 per cent sodium silicate solution, prior to introduction into the cell. The inter electrode distance is 1.5". Since sulphuric acid is in large excess, the cell voltage is not affected by slight changes in current density, above a critical value of antimony concentration viz., 50 gpl of Sb.

0.05 gms. of B naphthol and 0.3 cc of clove oil are used as addition agents for 3.5 litres of electrolyte.

Several cathode materials, like stainless steel, copper and lead have been tried, but monel (K) is found to be the best from several considerations like tensile strength (to withstand repeated strippings), corrosion resistance to the electrolyte, etc.

Operating data.	Optimum conditions:
Electrolyte:	A mixture of antimony trifluoride hydrofluoric acid and sulphuric acid.
	Sb : 120 gms/litre (minimum 50 gpl).
	H ₂ SO ₄ : 600 gms/litre.
Anode:	Acheson graphite.
Cathode:	Monel (K)
Current Density:	12 amps./sq. ft.
Voltage:	1.7
Current Efficiency:	85 per cent
Power consumption:	0.58 K. W. H./lb.
Purity of the product:	Spectrographically pure.

Advantages claimed for the new process:

The process employs anode mud, containing 85-90 per cent of antimony obtained in the electrolytic separation of lead from high-antimony lead alloys recovered from secondary battery wastes and also battery dust, process waste and the like, as raw materials. There is no loss of antimony as in the thermal process. The product obtained is also found to be of high purity. Moreover unlike in the sodium thioantimonate bath the metal is recovered in good yield and in a high state of purity. This method involves only two stages, viz., leaching and electrolysis. The cathode, monel, is quite corrosion-resistant. The graphite anode does not develop any passivity, as reported in other methods, with the result that the voltage in the electrowinning bath is maintained uniformly at 1.7 as compared with the voltage of 3.6 in the thioantimonate bath. Since the raw materials for preparing the electrolyte are given a preliminary treatment with H₂SO₄, all impurities forming soluble sulphates, such as Ag, Cu, Fe, Zn etc., are removed. When the scrap arising from lead acid batteries containing silver alloy grids are employed for this purpose, silver recovery is also possible.

The following are among the noteworthy features of the invented process:

(1) it is a process for the electrowinning of antimony from battery, dust, battery wastes, anode mud from electrolytic separation of lead from high-antimony lead alloys.

(2) a bath containing antimony trifluoride and sulphuric acid has been found to be suitable for the electrowinning of antimony.

(3) a lead-lined wooden tank fitted with Acheson graphite anodes forms a suitable cell for electrowinning, employing the bath mentioned in (2), from the raw materials mentioned in (1).

(4) monel, well polished and dipped in sodium silicate solution, is the most suitable cathode material.

(5) the optimum current density, employing conditions described in 1 to 4, for electrowinning of antimony is 10-12 amps./sq. ft.

(6) under the conditions described in 1 to 5, the cell voltage for electrowinning of antimony is 1.7.

(7) a mixture of B-naphthol and clove oil is a suitable addition agent for the electrowinning of antimony under conditions mentioned in items 1 to 6 above.

(8) under the condition described in 1 to 7, the power consumption per pound of antimony is 0.58 K. W. H.

(9) a "strip" of not less than 60 gpl of antimony is obtained under the conditions of electrowinning mentioned in items 1 to 8 above.

(10) the product obtained under the conditions described in 1 to 9 is found to be spectrographically pure.

R. BHASKAR PAI.

Patents Officer,

Council of Scientific and Industrial Research.

Dated this 20th day of March, 1957.

COMPLETE SPECIFICATION.

ELECTROWINNING OF ANTIMONY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This is an invention by Biman Behari Dey, Veeraragava Aravamuthan and Palamuthi Ramaswami Rajagopalan, all of the Central Electrochemical Research Institute, Karaikudi, India, all Indian citizens.

This invention relates to a process for the electrowinning of antimony.

Attempts for the electrowinning of antimony from Stibnite ores have been made in Germany and later on a commercial scale in the U. S. A., employing sodium thioantimonate, obtained by leaching antimony concentrates with sodium sulphide solution. However, no plant is known to be in commercial operation at present employing this method for electrowinning, on account of the operational and other technical difficulties.

In Germany, electrorefining of crude antimony regulus was practised employing fluoride-sulphate bath. Schlain and coworkers attempted the electrorefining of crude antimony bullion, employing a fluoride-sulphate bath and copper cathodes, but were not successful. (Schlain, D, Prater J. D. and Ravitz, S. F., *Tran. Am. Electrochem. Soc.*, 95, 145-160 (1949). The fluoride-sulphate bath has not been used for electrowinning, on account of the silica present in the primary sources. The process invented by us makes use of hydrofluoric acid containing a very high percentage of sulphuric acid as the leaching agent, the raw material for the antimony being free from silica.

The invented process for the electrowinning of pure antimony metal consists in reacting (i) the anode mud from the electrolytic separation of lead from high-antimony lead alloys like battery lead or (ii) battery dust and battery wastes obtained from discarded lead-acid batteries and during the process of manufacture of lead acid batteries with concentrated sulphuric acid to obtain a mixture of lead sulphate and basic antimony sulphate and leaching the mixture thus obtained with spent electrolyte containing hydrofluoric acid and sulphuric acid to obtain the antimony in solution, and electrolysis the said solution to get pure antimony metal.

Thus according to an embodiment of the invention, the process consists of the following steps:

- (1) treating the powdered material (-200 mesh) with concentrated sulphuric acid at 100-120°C in a ceramic or lead vessel to convert the lead and antimony into lead sulphate and basic antimony sulphate respectively;
- (2) leaching the mixture of lead sulphate and basic antimony sulphate so obtained with the spent electrolyte containing hydrofluoric acid and sulphuric acid (from Step 3) to get the antimony in solution, the lead sulphate remaining undissolved;

- (3) electrolysis the solution obtained in Step (2) to get pure antimony metal.

The battery wastes, battery dust and similar material for processing are powdered to -200 mesh and treated with concentrated sulphuric acid at 100-120°C to convert the lead and antimony into lead sulphate and antimony basic sulphates respectively. This can be done in a lead or ceramic vessel.

The electrolyte is a mixture of antimony fluoride and sulphuric acid. After electrolysis, the spent electrolyte containing hydrofluoric acid and sulphuric acid is used for leaching the antimony. The basic sulphate of antimony formed by pre-treatment with sulphuric acid, readily goes into solution as antimony trifluoride. This is the electrolyte for electrowinning. Lead is left behind as insoluble lead sulphate.

The apparatus used in the process is illustrated with the help of drawings accompanying the provisional specification wherein Figure I shows an electrolytic cell and electrode assembly.

A lead (2) lined wooden tank (1) (7" × 6" × 6" I. D.) constitutes the cell. The graphite anodes (3), two in number (6" × 4" × 1/4"), are suspended from copper busbars. A monel cathode (4) (5" × 4 1/2" × 1/32") is kept in between the anodes. The cathode is well polished and degreased with trichloroethylene and given a dip in 2 per cent. sodium silicate solution, prior to introduction into the cell. The inter electrode distance is 1.5". Since sulphuric acid is in large excess, the cell voltage is not affected by slight changes in current density, above a critical value of antimony concentration *viz.*, 50 gpl of Sb.

0.05 gms. of B-naphthol and 0.3 cc of clove oil are used as addition agents for 3.5 litres of electrolyte.

Several cathode materials, like stainless steel, copper and lead have been tried, but monel (K) is found to be the best from several considerations like tensile strength (to withstand repeated strippings), corrosion resistance to the electrolyte.

Operating data :	Optimum conditions :
Electrolyte :	A mixture of antimony trifluoride hydrofluoric acid and sulphuric acid.
	Sb : 120 gms/litre (minimum 50 gpl)
	H ₂ SO ₄ : 600 gms/litre
Anode :	Acheson graphite
Cathode :	Monel (K)
Current density :	12 amps/sq. ft.
Voltage :	1.7
Current efficiency :	85 per cent.
Power consumption :	0.58 kwh/lb.
Purity of the product :	Spectrographically pure.

Advantages claimed for the new process:

The process employs anode mud, containing 85-90 per cent. of antimony obtained in the electrolytic separation of lead from high-antimony lead alloys recovered from secondary battery wastes and also battery dust, process waste and the like, as raw materials. There is no loss of antimony as in the thermal process. The product obtained is also found to be of high purity. Moreover, unlike in the sodium thio-antimonate bath, the metal is recovered in good yield and in a high state of purity. This method involves only two stages, viz., leaching and electrolysis. The cathode, monel, is quite corrosion-resistant. The graphite anode does not develop any passivity, as reported in other methods, with the result that the voltage in the electrowinning bath is maintained uniformly at 1.7 as compared with the voltage of 3.6 in the thioantimonate bath. Since the raw materials for preparing the electrolyte are given a preliminary treatment with H_2SO_4 , all impurities forming soluble sulphates, such as Ag, Cu, Fe, Zn, are removed. When the scrap arising from lead acid batteries containing silver alloy grids are employed for this purpose, silver recovery is also possible.

The following are among the noteworthy features of the invented process:

(1) it is a process for the electrowinning of antimony from battery dust, battery wastes, anode mud from electrolytic separation of lead from high-antimony lead alloys;

(2) a bath containing antimony trifluoride and sulphuric acid has been found to be suitable for the electrowinning of antimony;

(3) a lead lined wooden tank fitted with Acheson graphite anodes forms a suitable cell for electrowinning, employing the bath mentioned in (2), from the raw materials mentioned in (1);

(4) monel, well polished and dipped in sodium silicate solution, is the most suitable cathode material;

(5) the optimum current density, employing conditions described in 1 to 4, for electrowinning of antimony is 10-12 amps/sq. ft;

(6) under the conditions described in 1 to 5, the cell voltage for electrowinning of antimony is 1.7;

(7) a mixture of B-naphthol and clove oil is a suitable, addition agent for the electrowinning of antimony under conditions mentioned in items 1 to 6 above.

(8) under the condition described in 1 to 7, the power consumption per pound of antimony is 0.58 kwh;

(9) a "strip" of not less than 60 gpl of antimony is obtained under the conditions of electrowinning mentioned in items 1 to 8 above;

(10) the product obtained under the conditions described in 1 to 9 is found to be spectrographically pure.

We claim:

1. A process for the electrowinning of pure antimony metal which consists in reacting (i) the anode mud from the electrolytic separation of lead from high-antimony lead alloys like battery lead or (ii) battery dust and battery wastes obtained from discarded lead-acid batteries and

during the process of manufacture of lead acid batteries, with concentrated sulphuric acid to obtain a mixture of lead sulphate and basic antimony sulphate and leaching the mixture thus obtained with spent electrolyte containing hydrofluoric acid and sulphuric acid to obtain the antimony in solution, and electrolysis of the said solution to get pure antimony metal.

2. A process as claimed in Claim 1 wherein the anode mud or the like is powdered to -200 mesh before it is reacted with sulphuric acid.

3. A process as claimed in Claim 1 or 2, which consists of the following steps:—

(1) treating the powdered material (-200 mesh) with concentrated sulphuric acid at 100-120°C in a ceramic or lead vessel to convert the lead and antimony into lead sulphate and basic antimony sulphate respectively;

(2) leaching the mixture of lead sulphate and basic antimony sulphate so obtained with the spent electrolyte containing hydrofluoric acid and sulphuric acid (from Step 3) to get the antimony in solution, the lead sulphate remaining undissolved;

(3) electrolysis of the solution obtained in Step (2) to get pure antimony metal.

4. A process as claimed in any of the preceding claims wherein a bath containing antimony trifluoride and sulphuric acid is used for the electrolysis.

5. A process as claimed in any of the preceding claims wherein the electrolysis is carried out in a cell consisting of lead-lined wooden tank fitted with Acheson graphite anodes.

6. A process as claimed in any of the preceding claims wherein monel, well polished and dipped in sodium silicate solution is used as a cathode material for the electrolysis.

7. A process as claimed in any of the preceding claims wherein optimum current density for the electrolysis is 10-12 amps/sq. ft.

8. A process as claimed in any of the preceding claims wherein the cell voltage employed for the electrolysis is 1.7.

9. A process as claimed in any of the preceding claims wherein a mixture of B-naphthol and clove oil are added to the electrolyte.

10. A process as claimed in any of the preceding claims wherein the power consumption per pound of antimony is 0.58 kwh.

11. A process as claimed in any of the preceding claims wherein a "strip" of not less than 60 gpl of antimony is obtained.

12. Pure antimony metal whenever obtained according to a process substantially as hereinbefore described.

R. BHASKAR Pai,
Patents Officer,

Council of Scientific and Industrial Research.

Dated this 16th day of December 1957.

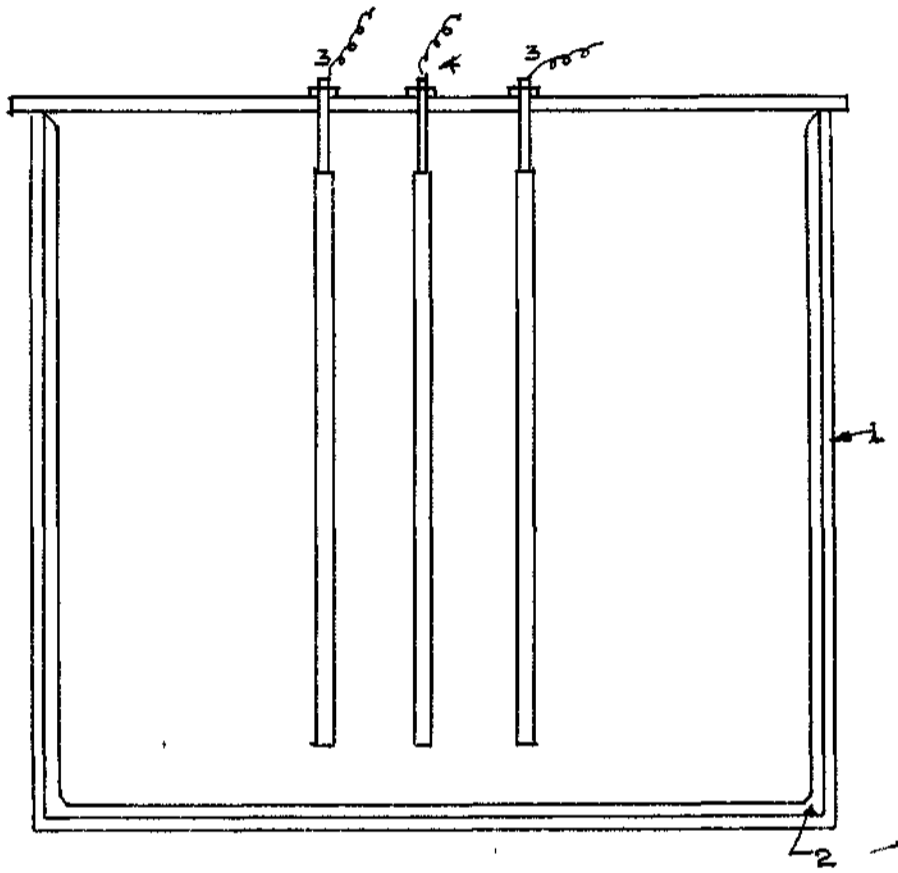


Fig 1

R. B. PAI
PATENTS OFFICER
C. S. I. R