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ELECTROLYTIC SEPARATION OF PURE LEAD FROM HIGH-ANTIMONY LEAD ALLOYS.

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 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 and Palamuthi Ramaswami Rajagopalan, Both of the Central Electrochemical Research Institute, Karaikudi, India, Both Indian Citizens.

This invention relates to the electrolytic separation of pure lead from high-antimony lead alloys.

Lead-antimony alloys employed for battery grid production contain up to 10 per cent. of antimony. Electrorefining of crude lead is done commercially employing fluosilicic acid as electrolyte, but with lead alloys of high-antimony content, there is co-deposition of antimony, necessitating further thermal refining. (Tarnawiecki, A. Actas Y-Trabayos Congr. Peruano Quim. *2*, II 221-37 (1943.) Impure lead containing up to 5 per cent. of impurity, including antimony, has been successfully refined on a pilot-plant scale by Piontelli in Italy, employing the sulphamate bath. However, the susceptibility of sulphamic acid to decomposition is a disadvantage.

According to the invented process for the electrolytic separation of pure lead from high-antimony alloys by electrolysis, a mixture of lead fluoborate, fluoboric acid and boric acid contained in a concrete cell lined with bitumen, is employed as electrolyte, and the high-antimony lead alloy is used as the anode from which lead preferentially dissolves during electrolysis and deposits at the cathode as pure lead, the antimony being left behind as anode mud.

By employing the electrolyte mentioned above, good and adherent deposits are obtained in a peelable form, on stainless steel cathode.

The electrolysis is conducted advantageously by employing a diaphragm made of drill cloth or the like, with a view to eliminate the pollution of the electrolyte.

"Treeing" is eliminated completely by having a perspex frame for the stainless steel cathode and employing glue as addition agent in a concentration of 0·05 per cent. in the electrolyte.

A current density of 12-15 amps./sq. ft. is found to be optimum depending upon the anode composition.

Under the conditions specified above, a current efficiency of 95 per cent. is obtained.

The anode mud obtained containes 85 to 90 per cent. antimony. The lead deposited at the cathode is free from antimony (analysed spectrographically).

The cell voltage varies from 0·35 to 0·45 or more depending on the composition of the anode and the nature of the electrolyte. Power consumption is about 0·05 K. W. H./lb. of lead produced.

The invented process is suitable for the electrolytic separation of lead in a state of high purity from high-antimony lead alloys, containing upto 10 per cent. of antimony, and in particular for the secondary recovery of lead from battery lead.

The anode material is obtained from discarded lead-acid batteries. These are melted at 400°—500°C and the impure alloy is cast into anodes of the 7″ × 6″× ¼″ size, from which pure lead is separated by a process of electrolytic refining. A mixture of lead fluoborate, fluoboric acid and boric acid is employed as the electrolyte. On electrolysing, the pure lead is dissolved out and deposits at the cathode, while the antimony is left at the anode as anode mud. Laboratory scale experiments were carried out in the set-up described below.

The invention will now be illustrated with the help of accompanying drawings wherein Fig. 1 shows an electrolytic cell and the electrode assembly (sectional elevation), Fig. 2 shows the electrolytic cell and electrode assembly (plan) and Fig. 3 shows the arrangement of anode and diaphragm in the electrolytic cell.

An R. C. tank 1 (10″ × 8″×8″) (I. d.), lined with bitumen 2 constitutes the cell. The anodes 3 (7″ × 6″× ⅛″) are obtained from the melting of battery wastes at 400°—500°C. The cathode 4 is of stainless steel (8″ × 6″× 1/16″) with a perspex lining 5 of 1/16″ all round the edges, in order to minimize 'treeing'. The electrodes 3 and 4 are held in position by means of copper busbars 6 at a distance of 1·5″ from one another. The anodes 3 are surrounded by white drill diaphragms 7, lest the anode slime should pollute the electrolyte 8.

Auxilliary equipment.

For maintaining vigorous agitation, stirring is done mechanically by stirrer 9.

Operating data : Optimum conditions.

Electrolyte	A mixture of fluoboric acid, lead fluoborate and boric acid. A 10 cc. sample must analyse : Free HBF_4: Not exceeding 5 cc. of *N*-KOH Total HBF_4: Not exceeding 25 cc. of *N*-KOH. Boric acid in large excess.
Addition agent	0·05 per cent. glue.
Anode	Impure lead-antimony alloy containing upto 10 per cent. of antimony and other impurities.
Cathode	Stainless Steel.
Voltage	0·45 depending on the anode composition.
Current density	12-15 amps./sq. ft. depending on the anode composition.
Current efficiency	95 per cent.
Power consumption	0·05 K. W. H./lb.

Advantages of the new process.

(1) *Complete recovery of antimony.*—Lead is generally recovered from secondary sources by the thermal method. In this method, not only is a large proportion of the antimony lost, by volatilization, but the resultant product is impure and has to be subjected to a further process of refining. The small proportion of the antimony which is recovered is obtained as sodium antimonate and *not as metal.*

By the electrolytic process, practically, all the antimony is present in the anode mud together with the entrained lead sulphate, etc., present in the anode material. From the enriched anode mud, (85-90 per cent.), antimony metal can be recovered by treating with sulphuric acid, and subsequent electrolysis of antimony trifluoride (SbF_3), obtained by leaching the sulphuric acid-treated anode mud with spent electrolyte containing hydrofluoric acid (*vide* co-pending application No. 59978).

2. Secondly, lead is obtained in a state of high purity in one stage unlike in the thermal reclamation process.

3. The process of electrolytic separation is of special interest and significance for applications to commercial

lead-antimony alloys, *viz.*, battery lead, from which *both* lead and antimony can be obtained in a pure form.

4. The percentage recovery of both lead and antimony is very high, well above 95 per cent.

5. The metals recovered, being very pure, can well be utilised for building new batteries having longer life and better performance-characteristics.

We claim :

1. A process for the electrolytic separation of pure lead from high-antimony lead alloys by electrolysis wherein a mixture of lead fluoborate, fluoboric acid and boric acid contained in a concrete cell lined with bitumen, is employed as electrolyte and wherein high antimony lead alloy is used as the anode from which lead preferentially dissolves during electrolysis and deposits at the cathode as pure lead, the antimony being left at the anode as anode mud.

2. A process as claimed in Claim 1 wherein anode consists of impure lead-antimony alloy containing upto 10 per cent. of antimony and other impurities.

3. A process as claimed in Claim 1 and 2 wherein a stainless steel cathode is employed.

4. A process as claimed in any of the preceding claims wherein anodes are surrounded by white drill diaphragms.

5. A process as claimed in any of the preceding claims wherein perspex frame is provided for the stainless steel cathode.

6. A process as claimed in any of the preceding claims wherein glue is added to the electrolyte in concentration of 0·05 per cent.

7. A process as claimed in any of the preceding claims wherein a current density of 12 to 15 amps./ sq. ft. is employed.

8. A process as claimed in any of the preceding claims wherein current efficiency is 95 per cent.

9. A process as claimed in any of the preceding claims wherein the anode mud containing 85 to 90 per cent. antimony is deposited.

10. A process as claimed in any of the preceding claims wherein a cell voltage varying from 0·35 to 0·45 or more is employed.

11. A process as claimed in any of the preceding claims wherein power consumption is about 0·05 K.W. H./lb. of lead produced.

12. A process for the electrolytic separation of lead in a state of high purity from high antimony lead alloys, containing upto 10 per cent. of antimony, and in particular for the secondary recovery of lead from battery lead, substantially as herein-before described.

13. Pure lead separated from high antimony lead alloys according to a process substantially as herein-before described.

R BHASKAR PAI,
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Council of Scientific & Industrial Research.
Dated this 12th day of February 1957.

MGIPC—86—11 Patent/58—28-1-59—100.

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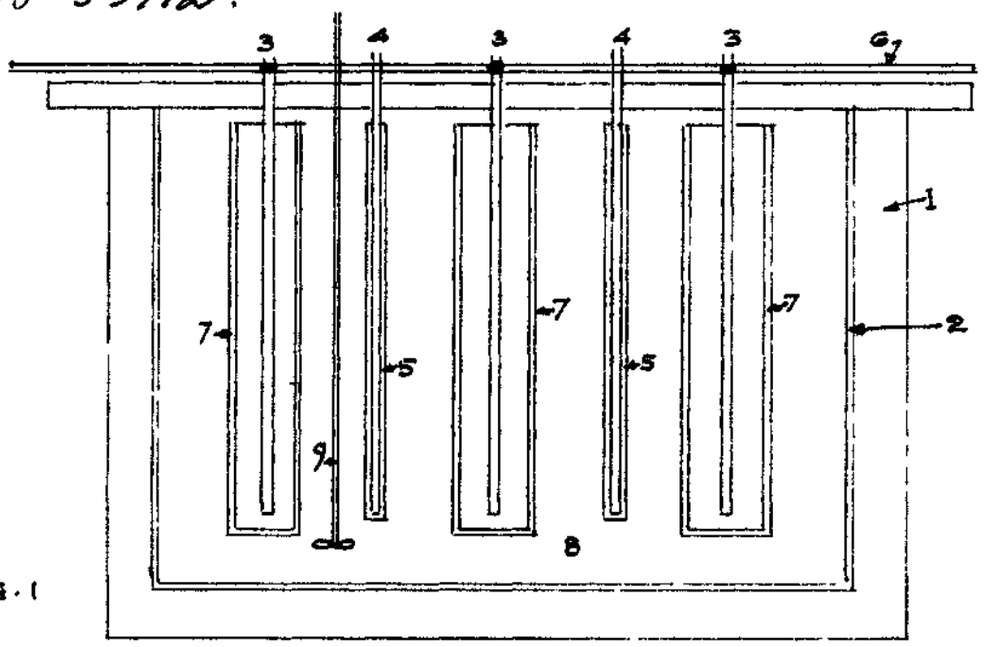

FIG. 1

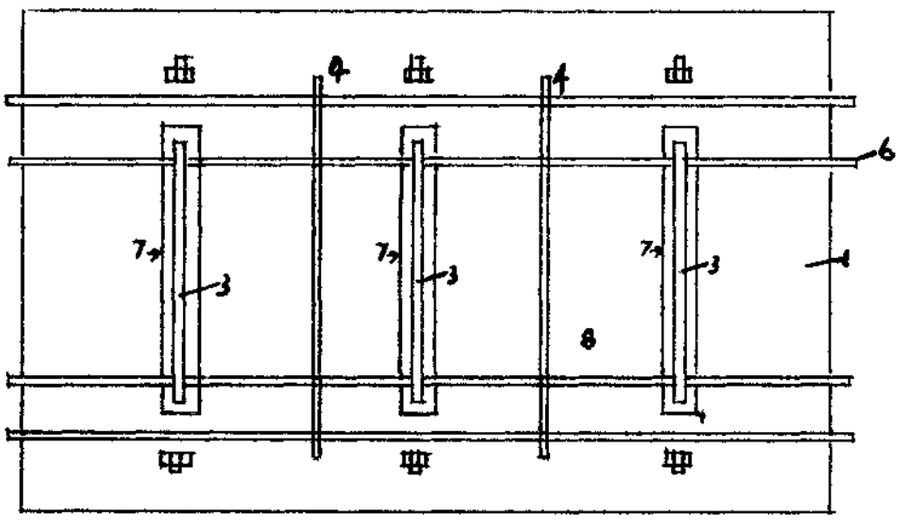

FIG. 2

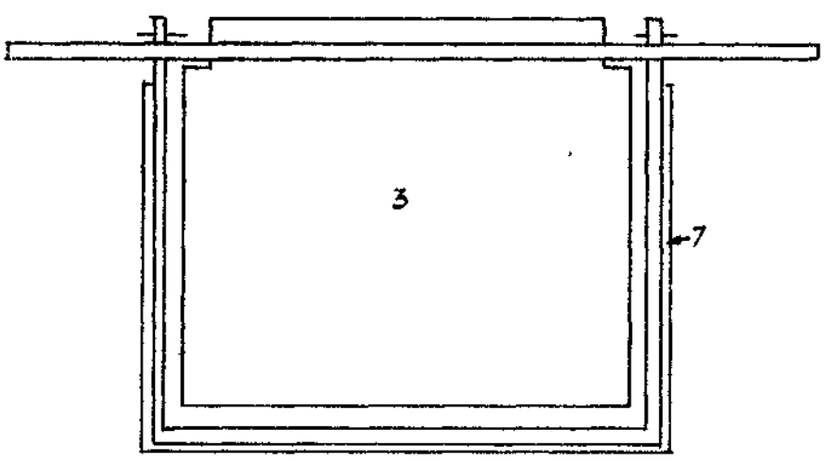

FIG. 3

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