Government of India, The Patent Office, 214, Acharya Jagadish Bose Road, Calcutta-17. Complete specification No.142706 dated 8th July 1975. Application and Provisional Specification No.1960/Cal/1974 dated 6th June 1974. Acceptance of the complete specification advertised on 20th August 1977.

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"IMPROVEMENTS IN OR RELATING TO RECOVERY OF ZINC FROM ZINC BY-PRODUCT COMPOUNDS; SUCH AS THE SKIMMINGS FROM GALVANISING INDUSTRY, WASTES FROM THE ZINC OXIDE MANUFACTURING M PLANTS AND BY-PRODUCT ZINC-HYDROXIDE OR ZINC OXIDE FROM THE CHEMICAL INDUSTRY"

COUNCIL OF ~~XXX~~ SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian Registered Body incorporated under the Registration of Societies Act (Act XXI of 1860).

This is an invention by Handady Venkatakrishna Udupa, ~~XXXXXXXXXXXX~~ Pennagaram Vyasa Rao Vasudeva Rao, Rangaswamy Vijayavalli all Scientist, Alagappan Alagappan Junior Scientific Assistant and Ramiah Alagusundaram, Senior Laboratory Assistant all Indians, all of Central Electrochemical Research Institute, Karaikudi, S.Rly, Tamil Nadu, India.

Price-Rs.2.00

This invention relates to improvements in or relating to recovery of zinc from by-product zinc compounds such as the skimmings from galvanising industry, wastes from the zinc oxide manufacturing plants and by-product zinc hydroxide or zinc oxide from the chemical industry.

Hitherto it has been proposed to recover zinc from galvaniser's waste by electrodeposition from an aqueous solution of the zinc values after a suitable purification step to avoid any contamination. Electrolysis of a suspension of the waste zinc compound in alkaline solution has earlier been patented under Indian Patent No.99591, whereby the zinc compounds are kept in uniform suspension in alkali of suitable concentration from which zinc is deposited on the cathode either in the form of sheet or powder.

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In the former method mentioned above, a number of intermediate steps such as dissolution of Zinc values and purification of the solution in order to avoid co.deposition of impurities along with Zinc, are involved. Furthermore, the preparation of a homogeneous solution of zinc valves from galvaniser's waste was found to present a number of difficulties. In the alkaline suspension electrolysis method, it was observed that the deposit was sheet like and contained solid inclusions to the maximum extent of about 1%. Efficiency of melting such deposits was found to be low, when compared to the zinc obtained from an acid elctrolyte. The object of this invention is to obviate these disadvantages by an improvement in the electrolysis of suspension of galvaniser's ash.

To these ends the invention broadly consists in the electrolysis of a suspension of finely powdered galvaniser's waste in a solution of dilute sulphric acid using suitable electrodes, wherein metallic zinc gets deposited on the cathode in the form of sheet which can be melted and cast in the form of ingots.

EXAMPLE.I

Raw material-Zinc ash analyzing as follows:

Zinc	...	...	78.23%
Iron	...	...	Traces
Chloride	...	...	1.11
Acid insolubles		...	negligible
Electrolyte		...	$2N_gH_2SO_4$
Current denzity		...	$5A/dm^2$

Slurry ratio	1:10
Current passed	0.7 Amp
Duration of the Electrolysis	3 hrs
Nature of deposit	Metallic sheet
Current efficiency	81.0%
Purity of deposit	98.5%

EXAMPLE. II.

Raw material	Same as in 1
Electrolyte, current density and slurry ratio	Same as in I
Current passed	11.5amps.

The cell was run continuously removing the deposit at every 6 hrs of electrolysis. Periodic replenishment of the bath by adding calculated amount of mh was also done. Total number of hours of Electrolysis - 110

Average current efficiency	73-80%
Purity of deposit	98.5-99.1%

EXAMPLE III

Raw Material	Same as in 1
Electrolyte	200 l of $2NH_2SO_4$
Current density	5 Amps/dm^2
Current passed	600 amps
Slurry ratio	1:10
cell voltage	4.8V
Current efficiency	66%
Purity of deposit	99%
Duration	4 hours

EXAMPLE IV

Raw Material — Galvaniser's ash analysing

Zinc	60.38%
iron	1.54%
Chloride	1.815%
Acid insoluble	6.18%

Conditions same as in II

Total number of hours of electrolysis	180
Average current efficiency	71-75%
Purity of deposit	99%

EXAMPLE V

Raw material — By product zinc compound obtained from Sodium hydrosulphite plant analysing,

Zinc oxide	84.6%
Zinc sulphate	15.17%
Acid insoluble	0.226%

Conditions — Same as in I

Nature of deposit: Metallic sheet

Current efficiency	85%
Purity of deposit.	99%

The following are among the main advantages:

1. The zinc can be recovered in the form of uniform sheet from galvaniser's waste and the waste need not be separately converted to a soluble salt solution for electrolysis, thus avoiding the handling operations such as filtration, etc.

2. The process is made continuous by suitable arrangement to feed the zinc compounds at pre-determined intervals.

3. The deposit obtained is metallic in character, completely free from iron and has a high purity. The ~~The~~ only impurity being oxide of zinc.

4. Due to the metallic character of the deposit higher efficiencies can be obtained for melting than in the case of deposits from alkaline suspension electrolysis method.

5. The electrolyte can be used over and over again for considerable length of electrolysis with occasional making up for loss of water due to evaporation and acid by spray without any detrimental effect either on the efficiency of recovery or purity of the metal obtained. The solid inclusions which might have accumulated are removed by passing the suspension at one stage through a filter bed and the electrolyte can again be used for further electrolysis.

Dated this 31st day of May, 1974.

THE PATENT ACT,1970

COMPLETE SPECIFICATION

(SECTION 10)

"IMPROVEMENTS IN OR RELATING TO RECOVERY OF ZINC FROM ZINC BYPRODUCT COMPOUNDS, SUCH AS THE SKIMMINGS FROM GALVANIZING INDUSTRY,WASTE FROM THE ZINC OXIDE MANUFACTURING PLANTS AND BYPRODUCT ZINC HYDROXIDE OR & ZINC OXIDE FROM THE CHEMICAL INDUSTRY"

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH,Rafi Marg, 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 HANDADY VENKATAKRISHNA UDUPA, PENNAGARAM VYASARAO VASUDEVARAO, RANGASWAMY VIJAYAVALLI, all Scientists, ALAGAPPAN ALAGAPPAN, Junior Scientific Assistant and RAMIAH ALAGUSUNDARAM, Senior Laboratory Assistant, all of the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indian citizens.

This invention relates to the improvements in or relating to the recovery of zinc from byproduct zinc compounds such as the skimmings from galvanising industry, wastes from the zinc oxide manufacturing plants and byproduct zinc hydroxide or zinc oxide from the chemical industry.

Hitherto, it has been proposed to recover zinc from galvaniser's waste by electrodeposition from aqueous solution of the zinc values after a suitable purification step to avoid any contamination. Electrolysis of a suspension of the waste zinc compounds in alkaline solution has earlier been patented under Indian patent No.99591 whereby the zinc compounds are kept in uniform suspension in alkali of suitable concentration from which zinc is deposited on the cathode either in the form of sheet or powder.

In the hitherto known processes, the following disadvantages were experienced: In the former method mentioned above a number of intermediate steps such as dissolution of zinc values and purification of solution in order to avoid codeposition of impurities along with the zinc are involved. Furthermore, the preparation of a homogeneous solution of zinc values from galvaniser's waste was found to present a number of difficulties. Handling large volumes of solutions, was found to be an additional disadvantage in the process. In the alkaline suspension electrolysis method it was observed that the deposit was sheet-like and contained solid inclusions to an extent of about 1%. Efficiency of melting such deposits was found to be low when compared to the zinc obtained from an acid electrolyte.

The object of this invention is to obviate these disadvantages by an improvement in the electrolysis of suspension of galvaniser's ash.

The main finding underlying the invention relates to the recovery of zinc metal either in the form of sheet or powder by the electrolysis of a suspension of finely powdered zinc compounds in dilute sulphuric acid solution.

According to the present invention, there is provided a process for the recovery ofzinc from zinc bearing materials by electrolysis of a suspension of waste zinc compounds such as Galvaniser's ash and skimmings, zinc hydroxide or oxide from chemical industry and paint industry in an electrolytic solution with lead alloy anodes and aluminium cathodes from which zinc is deposited on the cathode and wherein the zinc compound is continuously added to the slurry to replenish the metal concentration characterised in that the electrolysis of the waste zinc compounds is carried out in an electrolytic medium of aqueous sulphuric acid of strength 5 to 25% (W/V) and the electrolysis of the suspension is carried out at a current density of 2.5 to 20 A/dm^2 the temperature of electrolysis 25 to 60°C, the concentration of zinc in the electrolyte between 20 and 100 g/l.

To these ends, the invention broadly consists in the electrolysis of a suspension of finely powdered galvaniser's waste in a solution of dilute sulphuric acid using suitable electrodes, wherein metallic zinc gets deposited on the cathode in the form of a sheet, which can be melted and cast in the form of ingots. The galvaniser's waste is ground to a very fine powder suspended in dilute sulphuric acid and electrolysed. By this process, zinc can be obtained in the form of sheet deposited on the cathode which could be peeled off from the same. The larger impurities like iron, do not go into solution to a considerable extent and only very low concentration of iron has been found in the electrolyte. The rest gets precipitated in the form of hydroxide under the conditions of electrolysis. Zinc compounds go into solution in the form of zinc sulphate

which serves as the electrolyte. The iron in the deposited zinc is as low as 0.002 to 0.005 percent. It has been established that the cell could be run continuously by frequent addition of powdered material in order to maintain the concentration of zinc in the suspension at a desired level. The accumulation of iron in the suspension was not found to affect either the purity of the zinc or the efficiency of the process.

Thus, zinc is recovered from industrial byproduct zinc compounds such as Galvaniser's ash and skimmings zinc hydroxide or oxide from industries, e.g., from the chemical or paint industry by electrolysis of a suspension of the powdered zinc compound in an electrolyte. The suspension is made in a medium of aqueous sulphuric acid of strength 5 to 25% (W/V) and the electrolysis of the suspension is carried out at a current density of 2.5 to 20 A/dm^2, the temperature of the electrolysis 25 to 60°C, the concentration of zinc in the electrolyte between 20 and 100 g/l, with lead alloy anodes and aluminium cathodes, the electrolysis being carried out continuously by periodic additions of the powdered material. During the electrolysis the finely powdered material is kept in uniform suspension by effective stirring. The zinc is obtained as uniform sheet deposit containing iron to the extent of 0.002 to 0.005%. The recovery efficiency was found to be 95% at an average current efficiency of 80 to 85 per cent.

LABORATORY SCALE EXPERIMENTS

Rectangular cells made of PVC were used for the laboratory scale experiments. The cell was run continuously removing the deposit at intervals and periodic replenishment of the bath was done by adding calculated quantity of ash to the bath at predetermined intervals. One aluminium cathode and two lead anodes on either side of the cathode were used. The electrodes were tightly held in their position by proper arrangement and PVC spacers in between. The total number of hours of electrolysis was 110 stretched over a period of 20

days. Large scale experiments were carried out with a 100 A cell. This was further scaled upto 600 A and 1000 A. The cell used was made of alkathene and the 1000 A cell contained a total of 11 electrodes. The inter-electrode distances were maintained at 5 cms by using PVC spacers. The electrodes were connected to busbars which were fixed on to insulating PVC strip fitted among the edge of the top of the cell container. Effective agitation of the solution was done by compressed air by using a specially designed distributor system made of PVC. The deposit obtained was analysing 99.8% zinc and contained very small quantities of lead and iron. Raw materials from different sources were tried in the lab. scale and found to be satisfactory.

The following typical examples illustrate the invention.

EXAMPLE - I

Raw materials: Zinc ash analysing as follows

Zinc	78.23%
Iron	trace
Chloride	1.1%
Acid insolubles	Negligible
Electrolyte	2N H_2SO_4
Current density	5 A/sq.dm.
Current passed	0.7 A
Duration of electrolysis	3 hrs
Nature of deposit	Metallic sheets
Current efficiency	81%
Purity of the deposit	99.5 to 99.8%

EXAMPLE - II

Galvanizer's ash analyzing

Zinc	60.38%
Iron	1.54%
Chloride	1.815%

Acid insoluble	6.18%
Conditions same as in I	
Current efficiency	80%
Purity of deposit	99%

EXAMPLE - III

Raw material same as in I

Electrolyte, current density same as in I

Current passed	11.5 A

The cell was continuously run removing the deposit at every 6 hours of electrolysis.

Periodic replenishment of the bath by adding calculated amount of ash was also done. The total number of hours of electrolysis 110.

Average current efficiency	73-80%
Purity of deposit	99.5 to 99.8%

EXAMPLE - IV

Raw material: Byproduct zinc compound obtained from sodium hydrosulphite plant analysing zinc oxide 84.6%.

Zinc sulphate	15.17%
Acid insolubles conditions same as in I	0.2%
Current efficiency	85%
Purity of deposit	99.2%

EXAMPLE - V

Raw material same as in I

Current density	2.5 A/sq.dm.
Current passed	600 A
Cell voltage	3.5-4 V duration 8 hrs.
Current efficiency	75%
Purity of deposit	99.8%

The following are the main advantages of the invention.

Zinc can be recovered in the form of uniform sheet from Galvaniser's ash and byproduct zinc compounds and the same need not be separately converted to a soluble salt solution for electrolysis, thus avoiding the handling operations such as filtration, etc.

2. The impurities such as iron remain in suspension without being included in the deposit and can occasionally be modified over and over again, be removed either by settling and decanting or by passing through suitable filters.

3. The process may be made continuous by suitable arrangement to feed the zinc compounds at pre-determined intervals. The deposit obtained is metallic in character, and is of high purity.

4. Due to the metallic character of the deposit higher efficiencies could be obtained for melting than in the case of deposits from alkaline suspension electrolysis method.

5. The electrolyte can be used over and over again for a considerable time with occasional making up for loss of water due to evaporation and acid by spray without any deterimental effect either on the efficiency of the deposit or the purity of the metal obtained. The solid inclusions that might have accumulated are removed by passing the suspension through a filter bed and the electrolyte can again be used for further electrolysis.

To summarize, zinc may be recovered from byproduct zinc compounds and skimmings and ash obtained in the galvanising industry as well as zinc oxide obtained from chemical and paint industries by the process known as suspension electrolysis. As the name implies, a suspension of finely powdered material in sulphuric acid solution is electrolysed between lead alloy anodes and aluminium cathodes. During electrolysis, zinc goes into solution and gets deposited

on the cathode whereas the impurities such as iron remain in the suspension. Codeposition of iron does not occur under the conditions of electrolysis and the impurity of iron has been estimated to be 0.002 to 0.005% only. The deposited metal is in the form of metallic sheets having a purity of the order of 99 - 99.8%. The process can be made continuous by frequent addition of the powdered material at predetermined intervals. In this process of recovery, some of the unit processes, such as precipitation and filtration of the impurities, purification of the solution, etc., are eliminated and the material is fed direct into the electrolysis tank for electrolysis. The type of the raw material does not influence to any great extent, either the purity of the metal or the efficiency of the process.

We claim: -

1. A process for the recovery of zinc from zinc bearing materials by electrolysis of a suspension of waste zinc compounds such as Galvaniser's ash and skimmings, zinc hydroxide or oxide from chemical industry and paint industry in an electrolytic solution with lead alloy anodes and aluminium cathodes from which zinc is deposited on the cathode and wherein the zinc compound is continuously added to the slurry to replenish the metal concentration characterised in that the electrolysis of the waste zinc compounds is carried out in an electrolytic medium of aqueous sulphuric acid of strength 5 to 25% (W/V) and the electrolysis of the suspension is carried out at a current density of 2.5 to 20 A/dm^2 the temperature of electrolysis 25 to 60°C, the concentration of zinc in the electrolyte between 20 and 100 g/l.

2. A process as claimed in claim 1 wherein the zinc compound is made into a suspension in the electrolyte the ratio of the slurry being 1:5 to 1:20 preferably 1:10.

3. A process as claimed in the preceding claims wherein the particle size of the powdered zinc compound is -100 to 200 mesh.

4. A process as claimed in the preceding claims wherein the electrolyte of aqueous sulphuric acid is of strength 10%.

5. A process as claimed in the preceding claims wherein the electrolysis is carried out with lead or lead alloy anodes containing pure lead or alloy with silver, the ratio of silver being 0.01 to 1% preferably 0.1%.

6. A process as claimed in the preceding claims wherein aluminium sheets of proper purity are used as cathodes.

7. A process as claimed in the preceding claims wherein when aluminium is used as a cathode, a pretreatment in concentrated nitric acid by dipping the same or by brushing or alternately the cathodes are anodised prior to use to facilitate easy removal of the deposit of zinc.

8. A process as claimed in the preceding claims wherein a current density of 2.5 to 20 A/dm^2 preferably 5.0 A/dm^2 is employed.

9. A process as claimed in the preceding claims wherein the temperature of electrolysis is 45°C.

10. A process as claimed in the preceding claims wherein zinc concentration in the electrolyte is maintained between 20 and 100 g/l preferably around 70 g/l of the electrolyte.

11. A process as claimed in the preceding claims wherein the zinc is obtained in the form of sheets which can be peeled off from the cathode.

12. A process as claimed in the preceding claims wherein the cathode sheets obtained as above is melted and ast in the form of slabs exceeding 99.8% in purity.

13. A process as claimed in the preceding claims wherein the process is made continuous with periodical additions of the powdered zinc compounds.

14. A process for recovery of zinc in the form of slabs from byproduct zinc compounds from various industries as substantially described hereinbefore.

G.I.P.P./1980-81/150

Dated this 2nd day of July, 1975

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