

Specification No. 62293. Application No. 62293, dated 16th November 1957. Complete Specification left on 8th September 1958. Application (Accepted 7th May 1959.)

PROVISIONAL SPECIFICATION.

ELECTROWINNING OF ZINC BY ELECTROLYSIS OF ZINC CHLORIDE SOLUTIONS.

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 VEERARAGAVA ARAVAMUTHAN AND RANGACHARI SRINIVASAN, BOTH OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIAN CITIZENS.

OUTLINE OF THE PROCESS.

Pure zinc chloride solution containing 100-120 grams of zinc and 1 to 1.5 grams of sodium fluoride per litre of solution is electrolysed in a two compartment cell employing graphite as anodes and stainless steel or aluminium as cathodes. The composition of the anolyte and volume are the same as the catholyte. The anode area is the same as the cathode area. The pH of the solution is kept between 1 to 3.5. Electrolysis is conducted at room temperature. A current density of 30 amps. per square foot is employed. The voltage across the cell is 2.9. The current efficiency is not less than 90 per cent.

NOVELTY IN THE PROCESS.

Although it is known that zinc chloride solution can be electrolysed in admixture with sodium chloride, sodium acetate, etc., yet no method has been reported so far indicating the beneficial effects of sodium fluoride when added in small quantities to pure zinc chloride solutions for getting an uniformly smooth and easily peelable sheet form of zinc deposits as found out by us. On the other hand the bad effects of fluoride ion concentration and its tolerance in zinc sulphate electrolysis for electrowinning of zinc is well known.

ADVANTAGES OF THIS PROCESS.

(1) In comparison with the zinc sulphate electrolysis for the electrowinning of zinc in the form of uniformly smooth and easily peelable sheets there is a considerable reduction in cell voltage. The cell voltage for a current density of 30 amps. per square foot at temperatures of about 30° C., with a zinc concentration of 100-120 grams per litre is 2.9 for the chloride bath whereas under the same conditions the voltage across the cell in zinc sulphate bath is 3.6.

(2) Sulphur from zinc ore can be recovered as elemental sulphur by utilising the chlorine evolved at the anode during electrolysis of zinc chloride solutions in a cyclic process. This elemental sulphur and zinc metal can be got, whereas in the electrowinning of zinc from zinc sulphate bath, the ore has to be converted into zinc oxide and sulphur dioxide. In most plants the sulphur dioxide cannot be economically utilised for want of required concentration and purity and hence there is a possibility of not realising the full value of the sulphur content of the ore in zinc sulphate electrolytic process.

(3) Zinc dross available from melting and casting operations of zinc metal can be converted in a cyclic

process to electrolytic zinc metal by the process indicated by us whereas it cannot be used as the raw material for electrowinning of zinc from zinc sulphate bath owing to the presence of chlorides in the dross, which are classified as harmful impurities for sulphate bath.

The following is the typical data obtained on a laboratory scale for the electrowinning of zinc.

Volume and composition of anolyte or catholyte:	500 cc containing 120 grams of zinc chloride and 0.5 to 0.75 grams of sodium fluoride.
Electrolytic vessel made of perspex:	7" × 3½" × 4".
Diaphragm	Two porcelain or microporous rubber diaphragms each of 3" diameter and 4" height.
Anodes	Two graphite plates dipping to the extent 2" × 3" in solutions.
Cathode	Aluminium or stainless steel 2" × 3" dipping in solution and kept between two porous pots.
pH	1 to 3.5.
Temperature of electrolysis:	30° C.
Voltage across the cell	2.9 volts.
Current density	30 amps./sq. ft. (2.5 amps. current passed).
Duration of electrolysis	4 hours.
Amount of zinc	10.9 grams.

R. BHASKAR PAI.

Patents Officer,

Council of Scientific & Industrial Research.

Dated this 13th day of November 1957.

COMPLETE SPECIFICATION.

ELECTROWINNING OF ZINC BY ELECTROLYSIS OF ZINC CHLORIDE SOLUTIONS.

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).

This 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 VEERARAGAVA ARAVAMUTHAN AND RANGACHARI SRINIVASAN, BOTH OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIAN CITIZENS.

OUTLINE OF THE PROCESS.

Pure zinc chloride solution containing 100-120 grams of zinc and 0.5 to 1.5 grams of sodium fluoride per litre of solution is electrolysed in a two compartment cell

employing graphite as anode and stainless steel or aluminium as cathode. The composition of the anolyte is the same as catholyte. The volume ratio of catholyte to anolyte can be 1:1 to 2:1. This volume is not very critical especially when continuous flow of catholyte is maintained. The anode area is the same as the cathode

area. The pH of the solution is kept between 1.5 to 3.5. Electrolysis is conducted at room temperature 25-35° C. The chlorine formed at the anode chamber is sucked off. A current density of 30 amps. per square foot is employed. The voltage across the cell is 2.9. The current efficiency is not less than 90 per cent.

NOVELTY IN THE PROCESS.

Although it is known that zinc chloride solutions can be electrolysed in admixture with sodium chloride, sodium acetate, etc., yet no method has been reported so far indicating the beneficial effects of sodium fluoride when added in small quantities to pure zinc chloride solutions for getting a uniformly smooth and easily peelable sheet form of zinc deposits as found out by us. On the other hand, the bad effects of fluoride ion and its tolerance in zinc sulphate electrolysis for electro-winning of zinc is well known.

ADVANTAGES OF THIS PROCESS.

(1) In comparison with the zinc sulphate electrolysis for the electrowinning of zinc, there is a considerable reduction in cell voltage. The cell voltage for a current density of 30 amps. per square foot at temperatures ranging from 25 to 35° C., with a zinc concentration of 100-120 grams per litre is 2.9 for the chloride bath whereas under the same conditions the voltage across the cell in the sulphate bath is 3.6.

(2) Sulphur from zinc ore can be recovered as elemental sulphur, by utilising the chlorine evolved at the anode during electrolysis of zinc chloride solutions in a cyclic process. The anodic chlorine can be directly used to chlorinate the ore or indirectly through a carrier like ferric chloride solution. Thus elemental sulphur and zinc metal can be got by this process whereas in the electrowinning of zinc from zinc sulphate bath, the ore has to be converted into zinc oxide and sulphur dioxide. In most places the sulphur dioxide cannot be economically utilised for want of required concentration and purity. Hence, there is a possibility of realising the value of the sulphur content of the ore better in this process than in zinc sulphate electrolytic process.

(3) Zinc dross available from melting and casting operations of zinc metal can be converted to electrolytic zinc metal by this process without any difficulty. But it cannot be recycled in electrowinning of zinc by the sulphate route owing to the presence of chlorides in the dross, which are classified as harmful impurities for sulphate bath.

Thus in the invented process, zinc dross is roasted in air to get zinc oxide, which is then added to mixed chloride solutions (leach liquor), and iron is eliminated from the said leach liquor as ferric oxide, and the zinc chloride solution thus obtained is subjected to electrolysis according to the present invention.

(4) This process is also valuable for utilising iron zinc alloy containing entrapped zinc usually termed as "dross" available from galvanising operations. This dross contains about 4-6 per cent. iron. It is stated that for every 100 tons of zinc used in galvanising operations, 25 tons of dross are formed. To utilise this dross by this process, pure zinc chloride solution is electrolysed and the anodic chlorine serves to dissolve out zinc and iron in the form of chlorides. By the addition of zinc oxide in required amount, iron is eliminated as hydroxide.

The following is the typical data obtained on a laboratory scale for the electrowinning of zinc from zinc chloride solution.

Volume and composition of anolyte or catholyte.	500 cc containing 120 grams of zinc as chloride and 0.5 to 0.75 grams of sodium fluoride per litre.
Electrolytic vessel made of perspex	7" x 3½" x 4".
Diaphragm	Two porcelain or microporous rubber diaphragms each of 2½" diameter and 4" height.

Anodes	Two graphite plates dipping to the extent 2" x 3" in solutions.
Cathode	Aluminium or stainless steel 2" x 3" dipping in solution and kept between two porous pots.
pH	1.5 to 3.5.
Temperature of electrolysis	30° C.
Voltage across the cell	2.9 volts.
Current density	30 amps./sq. ft. (2.5 amps. current passed).
Duration of electrolysis	4 hours.
Amount of zinc	10.9 grams.

The following are some of the important features and advantages of this invention.

(1) Zinc in the form of easily peelable uniform sheets can be produced by the electrolysis of zinc chloride solutions at 25-35° C., containing 100-120 grams of zinc per litre and 0.5 to 1.5 grams of sodium fluoride;

(2) that a current density of 30 amps./sq. ft. can be employed in a two compartment cell wherein graphite is employed as anode and stainless steel or aluminium as cathode. Porcelain, microporous, rubber, PVC, etc., diaphragms are employed;

(3) that elemental sulphur can be recovered from zinc sulphide ore as a useful by-product in the electrowinning of zinc by the chloride process in which the anodic chlorine is recycled to react with the ore either directly or through a carrier;

(4) that zinc dross available from melting and casting operations of zinc metal or from galvanising plants can be better utilised in this process for the recovery of zinc than in the conventional sulphate bath for the electrolytic production of zinc metal, and

(5) that a distinct advantage of this process over the sulphate bath is the reduction in total energy consumption in the electrowinning of zinc under identical conditions, viz., (a) zinc concentration of 100-120 grams per litre, (b) temperature of 25-35° C., (c) current density of 30 amps. per square foot and (d) current efficiency of not less than 90 per cent. The voltage across the cell in zinc chloride electrolysis is 2.9 whereas in sulphate electrolysis it is 3.6.

We claim:

1. An electrolytic process for the production of zinc in the form of easily peelable uniform sheets which consists in electrolysing at 25-35° C. zinc chloride solutions containing 100-120 grams of zinc per litre and 0.5 to 1.5 grams of sodium fluoride.

2. A process as claimed in Claim 1, wherein a current density of 30 amps./sq. ft. can be employed in a two compartment cell wherein graphite is employed as anode and stainless steel or aluminium as cathode, and porcelain, microporous, rubber, PVC or the like, diaphragms are employed.

3. A process as claimed in Claim 1 or 2, wherein elemental sulphur can be recovered from zinc sulphide or as a useful by-product in the electrowinning of zinc by the chloride process in which the anodic chlorine is recycled to react with the ore either directly or through a carrier.

4. A process as claimed in any of the preceding claims, wherein the zinc chloride solution used for electrolysis is obtained by roasting in air zinc dross obtained from melting and casting operations of zinc metal or from galvanising plants, and adding the zinc oxide thus obtained to mixed chloride solutions (leach liquor) thereby eliminating iron as ferric hydroxide from the said leach liquor.

5. A process as claimed in any of the preceding claims, wherein the conditions for the electrowinning of zinc are as under :

- (a) zinc concentration of 100-120 grams per litre ;
- (b) temperature of 24-35° C. ;
- (c) current density of 30 amps. per square foot ;
and

- (d) current efficiency of not less than 90 per cent. and voltage across the cell for zinc chloride electrolysis is 2.9.

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Dated this 30th day of August 1955.