

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 105081, Application No. 105081, dated 29th April 1966. Complete Specification left on 28th January 1967. (Application accepted 16th November 1967.)

Index at acceptance—130G[XXXIII(7)].

CHEMICAL RECOVERY OF TIN METAL FROM THE ACID DETINNING BATH.

### PROVISIONAL SPECIFICATION.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJF MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960).

The following specification describes the nature of this invention.

This is an invention by Dr. PREM BEHARI MATHUR, Dr. ROSHAN LAL SETH and Shri NARASIMHAN VENKATAKRISHNAN, all the three of the Central Electrochemical Research Institute, Karaikudi-3, S. Rly., India, all Indian citizens.

This invention relates to a process of recovery of pure tin metal from the detinning mother liquor obtained during the process of detinning of tin scraps in a mixture of hydrochloric acid and an organic inhibitor as described in the earlier patent.

It is herein proposed to make improvements in the composition of the highly acidic mother liquor with a view to enable the chemical displacement of tin metal by means of minimum quantity of a more basic and cheap metal like aluminium, zinc, etc.

The import of huge quantities of tin metal required for tin plate industry, can be cut at least by 10 per cent. by recovering tin metal from the waste tinned steel scraps accumulating in large quantities in tin box industries. The estimated demand of tin plate by the end of IV plan i.e., in the year 1970-71 is nearly 5 lakhs tons. Since 10 to 15 per cent. of the tinned steel sheets is obtained as scraps and since the tin coating weights nearly 1 per cent. of the total weight of the plate, approximately 500 to 750 tons of tin metal will be recoverable during the year 1970-71 from the then available 50,000 to 75,000 tons of the scraps. The market price of that tin will be nearly 1.5 to 2.25 crores rupees.

In an earlier patent application an economic process for detinning of tin scraps was described. The mother liquor obtained in the last process contained mainly chlorides of tin metal, large quantities of free hydrochloric acid and small quantities of an organic substance (1 per cent.) and traces of iron metal, which come along with tin from the scraps.

The objective of this invention is to recover tin chemically from the mother liquor obtained in earlier described chemical detinning process and thus to enable the recovery of tin economical and industrially feasible.

To these ends, the invention broadly consists in:

(a) Neutralisation of large quantity of free acid present in the mother liquor by a neutral carbonate mineral such as limestone, etc.

(b) Displacement of the metal from the neutralised mother liquor by means of a more basic scrap such as waste aluminium scrap, zinc metal, etc.

(c) Obtaining tin ingots by melting at the melting point of tin in presence of a flux.

(d) Recovery of aluminium or zinc as hydroxides from the treated bath by the action of calculated quantities of quick lime, sodium hydroxide or other alkalis.

The following typical example is given to illustrate the invention:

#### EXAMPLE 1.

One litre of detinned solution was taken in a five litre glass beaker. 300 grams of limestone in the form

of small pieces are added and the beaker is left undisturbed for three hours. Limestone vigorously reacted with free hydrochloric acid present in the mother liquor to produce  $\text{CO}_2$  gas and  $\text{CaCl}_2$  in the solution. The pH of the solution which was initially below 0.5 raised to about 2 to 2.5 after the reaction ceased. About 25 grams of aluminium scraps were put in neutralised mother liquor and the beaker was again left undisturbed for about four hours. The tin powder collected in the bottom of the beaker was separated, washed well with water and dried at a temperature at about  $110^\circ\text{C}$ . The dried powder was weighed, later melted in presence of ammonium chloride as a flux. The filtrate obtained after the removal of tin metal is treated with sodium hydroxide solution till the whole of the aluminium is precipitated as aluminium hydroxide and the pH started rising to higher values above 8. The aluminium hydroxide is washed and dried. This compound is the by-product of this industry.

#### EXAMPLE 2.

One litre of detinned solution was taken in a five litre glass beaker. 300 grams of limestone in the form of small pieces are added and the beaker is left undisturbed for three hours. Limestone vigorously reacted with free hydrochloric acid present in the mother liquor to produce  $\text{CO}_2$  gas and  $\text{CaCl}_2$  in the solution. The pH of the solution which was initially below 0.5 raised to above 2 to 2.5, after the reaction ceased. About 40 grams of zinc granules were put in neutralised mother liquor and the beaker was again left undisturbed for about four hours. The tin powder collected in the bottom of the beaker was separated, washed well with water and dried at a temperature about  $110^\circ\text{C}$ . The dried powder was weighed, later melted in presence of ammonium chloride as a flux. The filtrate obtained after the removal of tin metal is treated with sodium hydroxide solution till the whole of the zinc is precipitated as zinc hydroxide and the pH started rising to higher values, above 8. The zinc hydroxide is washed and dried. This compound is the by-product of this industry.

R. BHASKAR PAI

Patents Officer,

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

Dated this 26th day of April 1966.

### COMPLETE SPECIFICATION.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJF MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960).

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 Dr. PREM BEHARI MATHUR, Dr. ROSHAN LAL SETH and Shri NARASIMHAN VENKATAKRISHNAN, all the three of the Central Electrochemical Research Institute, Karaikudi-3, S. Rly., India, all Indian citizens.

This invention relates to a process of recovery of pure tin metal from the detinning mother liquor obtained during the process of detinning of tin scraps

in a mixture of hydrochloric acid and an organic inhibitor as described in the earlier Indian Patent No. 101628.

Price: TWO RUPEES.

It is herein proposed to make improvements in the process of recovery of pure tin metal in a single step from the detinning solution by a chemical process of displacement in place of the electrolytic process described in the earlier Indian Patent No. 101628.

The import of huge quantities of tin metal required for tin-plate industries can be cut at least by 10 per cent. by recovering tin metal from the waste tinned steel scraps, accumulating in large quantities in tin box industries. The estimated demand of tin-plates by the end of Fourth Plan in the year 1970-71 is nearly 8 lakhs tons. Since 10 to 15 per cent. of the tinned steel sheets is obtained as scraps and since the tin coating weights nearly 1 per cent. of the total weight of the plate, approximately 500 to 750 tons of tin metal will be recoverable during the year 1970-71 from the then available 50,000 to 75,000 tons of the scraps. The market price of that tin will be nearly 1.5 to 2.25 crores rupees.

In our earlier Indian Patent No. 101628 an economic process for detinning of tin scraps was described. In our subsequent co-pending Indian Patent Application No. 101628 an electrolytic process of the recovery of tin metal was described. Since the electrolytic process is useful for commercial exploitation at places where electric power is cheap, its universal application may not be economical. Secondly, the electrolytic process involved several engineering aspects and a number of controls.

The object of this invention is to obviate these disadvantages of the electrolytic process by displacing chemically tin metal in the form of sponge from the detinning mother liquor containing hydrochloric acid and inhibitor thus enabling the recovery of tin economical and industrially feasible.

To these ends, the invention broadly consists in:

(a) Displacement of tin metal in the form of sponge by more electro-negative metals such as aluminium, zinc or the like from the detinning mother liquor.

(b) Obtaining the ingots by melting at the melting-point of tin metal sponge in presence of a suitable flux.

(c) Recovery of aluminium or zinc as hydroxides from the treated bath by the action of calculated quantities of quick lime, sodium hydroxide or other alkalis.

The following typical example is given to illustrate the invention:

#### EXAMPLE 1.

One litre of the detinned solution containing tin metal in the dissolved form was taken in a five litre glass beaker and aluminium scraps were put in the solution. Tin metal precipitated out in the form of floating sponge was separated, washed well with water and dried at a temperature at about 110° C. The dried powder was weighed, later melted in presence of a chloride flux. The ingot thus obtained were of the

order of 99 per cent. and more purity. The filtrate obtained after the removal of tin metal is treated with sodium hydroxide solution till the whole of the aluminium is precipitated as aluminium hydroxide. The aluminium hydroxide is washed and dried. This compound is, the by-product of this industry.

#### EXAMPLE 2.

One litre of the detinned solution containing tin metal in the dissolved form was taken in a five litre glass beaker and zinc scraps were put in the solution. Tin metal precipitated out in the form of floating sponge was separated, washed well with water and dried at a temperature at about 110° C. The dried powder was weighed, later melted in presence of a chloride flux. The ingot thus obtained were of the order of 99 per cent. and more purity. The filtrate obtained after the removal of tin metal is treated with sodium hydroxide solution till the whole of the zinc is precipitated as zinc hydroxide. The zinc hydroxide is washed and dried. This compound is the by-product of this industry.

We claim:

1. A process for the recovery of highly pure tin metal from the acid detinning bath which consists in:

(a) Chemical displacement of the tin metal from the detinning solution containing mineral acid and organic inhibitor along with the tin metal by means of a more basis metal scrap such as waste aluminium scrap, zinc metal, or the like.

(b) Obtaining tin ingots by melting of tin sponge at the melting point of tin in the presence of a chloride flux.

(c) Recovery of aluminium or zinc as hydroxides from the treated bath by the action of calculated quantities of quick lime, sodium hydroxide or other alkalis.

2. A process as claimed in Claim 1 wherein pure tin metal is recovered from the detinning liquor obtained during the process of detinning of tin scraps in a mixture of hydrochloric acid and an organic inhibitor as described in our earlier Indian Patent No. 101628.

3. A process for the recovery of tin metal from the acid detinning bath substantially as described in the examples.

4. A process for the recovery of tin metal substantially as hereinbefore described.

5. Tin metal whenever recovered according to a process substantially as hereinbefore described.

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Dated this 24th day of January 1967.