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ELECTROCHEMICAL EXTRACTION AND CHARACTERIZATION OF A RECOVERY TIN

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ABSTRACT

Statistics on the production of a secondary tin show that its use in many countries reaches a significant amount. One of the most important sources of secondary tin is a scrap of white sheet metal formed by stamping various products, waste from used cans, and other obsolete tin products. In the present work, using chemical, electrochemical and physical methods, a technology for dissolving tin from used cans in alkaline solutions with the addition of p-nitroaniline and its electroextraction from solutions is proposed. The optimal conditions of dissolution and extraction (concentration and temperature of the medium, current density, current yield), as well as the chemical composition of the obtained metal tin, are determined.

Keywords: corrosion, mild steel, tinning, recovery tin, electroextraction.

INTRODUCTION

Tin is known to be one of the most valuable metals, used in many sectors of the economy. At the same time, it is one of the scarcest metals due to its low content in the earth's crust and its difficult extraction. For these reasons, the need for its recycling remains a constant important task. The sources of tin-containing waste are very diverse-enrichment installations, production of alloys, tinning, canning, electronics, electrical engineering, etc. [1 - 5].

Tin removal from tinned products, waste, and a scrap of white sheet metal is performed by mechanical, pyrometallurgical, hydrometallurgical, chlorine, and electrochemical methods. The most suitable of these is hydrometallurgical, conducted in sodium - based solutions. The advantages of this method are that the steel substrate is not attacked by the solution, unlike acid solutions and therefore, the purity of the resulting tin will be high, not sensitive to contaminants, does not require special degreasing, and so on. In addition, the use of alkaline tin dissolution allows the manufacture of equipment made of mild steel, which reduces its cost. Dissolution is more intense in the presence of O_2 and a sodium stannate is formed:

$$Sn + NaOH + O_2 \rightarrow Na_2SnO_3 + H_2O$$

In the absence of O_2 (oxidant) a sodium stannite Na_2SnO_2 is formed. The process is slow due to the high overvoltage of H_2 release on Sn. To increase the rate of dissolution of Sn in alkaline solutions, oxidizing additives of organic or inorganic origin are added. Of the latter, $Pb(C_2H_3O_2)_2$, PbO, $NaNO_3$ and others are used [1, 2].

From Na_2SnO_3 solutions, Sn can be separated by electrolysis with insoluble anodes or by precipitation with CO_2, $Ca(OH)_2$, $NaHCO_3$, and H_2SO_4. The precipitation of Sn in the form of compounds has not been widely used due to the complexity of the technological scheme, the significant cost of expensive reagents, and the accumulation of products from the reduction of inorganic oxidants, requiring frequent correction of solutions [6, 7].

The removal of Sn in alkaline solutions using organic oxidants is more widely used in practice. The advantage lies in their regeneration, at the expense of the oxidation of O_2 to the air or to the anodic electrochemical processes taking place in the bath. Nitrogen derivatives of benzene and other aromatic

compounds are used as organic oxidants: m-nitrobenzoic acid ($C_7H_5NO_4$), m-nitrobenzene sulphonic acid ($C_6H_5NO_5S$), m-nitrophthalic acid ($C_8H_5NO_6$). Under these conditions, the tin is dissolved to Sn^{4+}, and subsequent electroextraction of the cathode results in dense tin coatings.

The present paper describes the results obtained by dissolving tin from waste tinned cans in alkaline solutions with the addition of p-nitroaniline and determines the chemical composition of the metal tin electroextracted from these solutions.

EXPERIMENTAL

Subject of investigations

The object of the research is waste from used food packaging made of tinned sheet metal. The weight of one package, together with the cover, is an average 1350 - 1450 g, and the thickness of the sheet metal is 0.3 - 0.4 mm. The solder consumed per package, according to the prescription, is 0.16 g. The white sheet contains an average of 11.2 g m^{-2} tin (on both sides).

To increase the resistance of the tinned sheet, double-sided varnishing is applied. The outer side is covered with varnishes of high mechanical strength (for example, epoxy-phenolic or acrylate base), and the inner side is coated with protein-resistant varnishes (for example, D2422FP, EJ239120, etc.). The variety of varnishes (with different densities, dry residue, resistance, etc.) significantly complicates their removal from waste - an operation that is obligatory before the dissolution of the tin. The regeneration of secondary tin is significantly complicated by the presence of impurities (fats, food residues, soil, etc.), which inevitably accompanies the use of packaging.

Methods

Gravimetrical method

The essence of the gravimetric method consists in measuring the decrease or increase of the mass of the experimental samples for a certain time, after treatment of the latter under a given environment and conditions. The method was used to determine the rate of dissolution of tin from tinned sheets, as well as to calculate the thickness of tin's coating and the current efficiency in the electroextraction of dissolved tin.

Electroextraction

Electroextraction is one of the main methods used in hydrometallurgy, in which the electrolysis process is performed with insoluble anodes, and with appropriately selected polarization, the desired metal is separated on the cathodes. In most cases, less substance is produced by electrolysis than should be following Faraday's law, and for this reason, the concept of *current efficiency* has been introduced. The latter determines that part of the amount of electricity flowing through the system is spent on the reaction of interest.

Analyses

- *Iodometric analysis.* The method was used to determine the amount of a tin in the system [8].
- *Atomic absorption analysis (AAA).* AAA is an analytical method for determining the content of elements based on the absorption of electromagnetic energy by free atoms. It was used to determine the amounts of impurities in the dissolution of Sn from the tinned sheet metal, as well as to determine the purity of the deposited Sn during its electroextraction from the electrolyte. The analysis was performed with a spectrometer SP 191, Pye Unicam, and air/acetylene flame.
- *Mössbauer analysis.* With help of a standard Mössbauer spectrometer (the source is Sn^{119M} in $BaSnO_3$) operating in a transmittance regime and a constant acceleration mode the composition of the precipitate formed by dissolving the tin coatings in an alkaline environment was determined. The average sample thickness was about 10 mg cm^{-2} and the spectra were taken at room temperature (25 ± 2°C).

Apparatus

For the realization of the staged tasks, it was necessary to complete specialized equipment, the characteristic features of which are presented below.

Fig. 1 shows schematically the installation for removing varnish and dissolving tin. In bath 2, with the help of heater 4, the contact thermometer 6, and the electromechanical stirrer 3 the necessary temperature for work is attained. Beaker 8 is used to heat the water with which vessels 9 and 10 are refilled, due to the evaporation of the solutions at high temperatures. At 9, each subsequent working solution is prepared

and thermostated. The removal of the varnish or the dissolution of the tin from the tinned sheet metal 12 is carried out in vessel 10, with the possibility of stirring being provided utilizing the stirrer 7.

The tin electroextraction apparatus is shown schematically in Fig. 2. The working solutions are poured into cell 1 (double-walled), the desired temperature being reached using a thermostat. Anodes 2, made of mild steel, and cathode 3 (of the same material), on which the tin is deposited, are placed in the electrolysis cell.

The process is carried out in a galvanostatic mode, with the help of galvanostat, as the current in the circuit and the voltage between the electrodes are controlled, respectively, with an ammeter and a voltmeter.

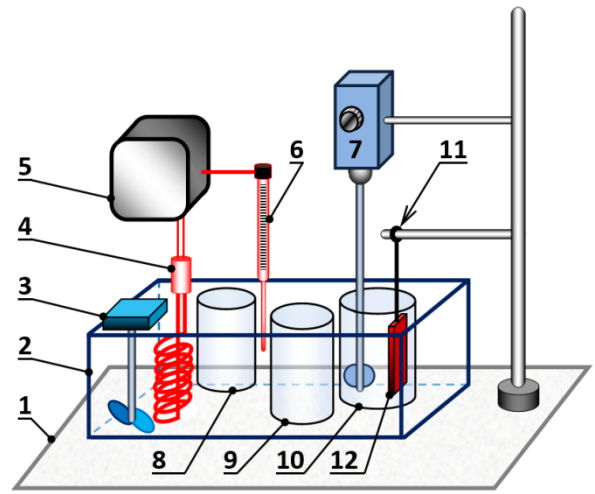

Fig. 1. Scheme of installation for removing the varnish and dissolving the tin coating: 1 - bearing board; 2 - thermostated bath; 3 - stirrer; 4 - heater; 5 - thermal relay; 6 - contact thermometer; 7 - stirrer with a regulator; 8 - tank for topping up with water; 9 - solution preparation tank; 10 - working vessel; 11 - sample holder; 12 - sample.

RESULTS AND DISCUSSION

Pollution removal

Food remains, soil and other contaminants on the waste tinned sheet are removed with hot water (> 80°C) in a container, with stirring. The washing is done in two stages - with a hot and cold water. After removing the contaminants, it is not necessary preliminarily to perform degreasing of wastes, since the subsequent treatment (removal of the varnish) is performed in an alkaline environment.

Removal of the varnish coatings

The different nature of the varnishes used to cover the tinned sheet makes it difficult to remove them from the surface of the waste. A literature review of the problem showed that alkaline media are suitable for removing almost all types of lacquer coatings. In addition, alkaline media will be used to dissolve the tin coating from the waste, and therefore, after removing the varnishes and filtering the solutions, the latter can be used in the following technological operations.

Aqueous solutions of NaOH were used for alkaline media, and to determine the optimal conditions for removing varnishes, solutions with concentrations of 30 - 120 g L^{-1}, in the temperature range 40 - 90°C and with stirring 300 min^{-1}, were tested. It was found that in solutions with higher concentrations and temperatures dissolution of tin begins. Mediums with a concentration of 80 g L^{-1} NaOH, a temperature of 80 - 85°C, and continuous stirring were selected as the most suitable

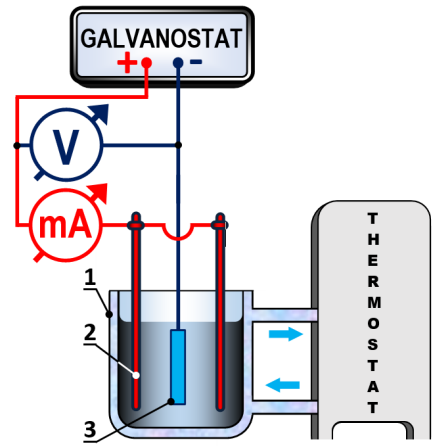

Fig. 2. Scheme of the apparatus for electroextraction of tin from alkaline solutions: 1 - electrolysis cell; 2 - anode; 3 - cathode.

conditions in which the varnishes were removed quickly and completely, without visible dissolution of the tin coating. Peeled varnish coatings make it difficult for the solution to reach the surface of tin's sheet metal, which requires their continuous removal from it.

Dissolving of the tin coatings

As mentioned above, the most widely used in the practice of regeneration of tin from tinned sheets have found hydrometallurgical methods performed in alkaline environments. This is due to a number of their advantages, not at least the possibility of turnover of solutions, after appropriate treatment and correction.

The studies were performed in aqueous sodium-hydroxide solutions. It is known from the literature (as well as from our preliminary studies) that the most common are media with a base concentration between 40 and 50 g L^{-1}, which provides dissolved Sn content up to about 25 g L^{-1} and minimal precipitation from insoluble tin's acids. Another important requirement for alkaline solutions is their temperature - the dissolution of Sn below 70°C is performed at a very low rate.

$NaNO_3$, $NaNO_2$, m-nitrobenzoic acid (m-$O_2NC_6H_4COOH$, m-NBA), and p-nitroaniline (p-$O_2NC_6H_4NH_2$, p-NA) were tested as oxidants. For the first two additives, with a maximum concentration of up to 20 g L^{-1}, dissolution is very slow, and therefore further studies were performed with m-NBA and p-NA. In the tests, it was found that the amount of m-NBA, providing dissolution of tin up to 21 - 25 g L^{-1} is in the range of 15 - 25 g L^{-1}. At higher concentrations of m-NBA, significantly reduces the rate of subsequent electroextraction of tin, due to the enhanced dissolution of tin deposits on the cathode. Since m-NBA is known in the literature and practice as an oxidant in the production of secondary tin by electroextraction, in the present work the studies were performed with the p-nitroaniline.

Table 1 shows the values of the dissolution rate of Sn from the tinned sheet (p-NA-15 g L^{-1}, 80°C), with an increasing concentration of the medium with dissolved Sn. The obtained results show that with increasing the quantity of Sn in the solution to 10.90 g L^{-1}, the dissolution rate of the tin sheet coating increases more than 2 times and then it reduces - at 19.80 g L^{-1} Sn in the solution has the lowest value. Table 1 also shows the effect of stirring on the dissolution rate of Sn, which is significantly higher than that of the unmixed solution, as retaining its character of influence. All this is an indication of a strong intensification of the dissolution of Sn from the tinned sheet by stirring the medium, which can be explained by facilitating the delivery of p-nitroaniline to the surface of the tinned sheet as well as that of the O_2 in the solution.

From the obtained results, for dissolution of Sn from the tinned sheet, the following solution can be recommended as optimal: 40-50 g L^{-1} NaOH; 15 g L^{-1} p-NA and temperature not lower than 80°C.

Electroextraction of the dissolved tin

The electroextraction of the metal dissolved from the tinned sheet was performed using the apparatus shown schematically in Fig. 2. The insoluble anodes and the cathode on which the tin dissolved by the tinned sheet is deposited, are made of mild steel. Solutions containing different amounts of dissolved tin are subjected to electroextraction. Saturation is achieved by placing pieces of a tinned sheet (after removing the varnish) in a solution containing 40 g L^{-1} NaOH, 15 g L^{-1} p-NA, at a temperature of 80°C. The concentration of dissolved tin was determined iodometrically. The volume of the electrolyte from which the tin is extracted is 150 mL.

Fig. 3 presents the results obtained by electroextraction of a solution containing 19.5 g L^{-1} Sn, 15 g L^{-1} p-NA, at a temperature of 80°C and current densities of 1.0, 2.0, and 3.0 A dm^{-2}. From the course of the kinetic curves, it follows that with increasing current density, the time for extraction of tin from the solution decreases, and the difference from the results obtained at 1.0 and 2.0 A dm^{-2} is relatively small. The process was performed up to 80 ± 5 % tin extraction from the solution.

Table 1. Values of the dissolution rate of Sn from the tinned sheet.

Tin in the solution, g L^{-1}	Coating dissolution rate, g $(m^2 h)^{-1}$	
	without stirring	with stirring, 300 min^{-1}
2.70	921.20	1800.00
7.00	1422.00	2460.00
10.90	1920.30	3400.00
14.80	1299.10	3240.10
17.50	696.00	1496.80
18.60	327.60	765.00
19.10	145.70	414.10
19.80	16.31	43.30

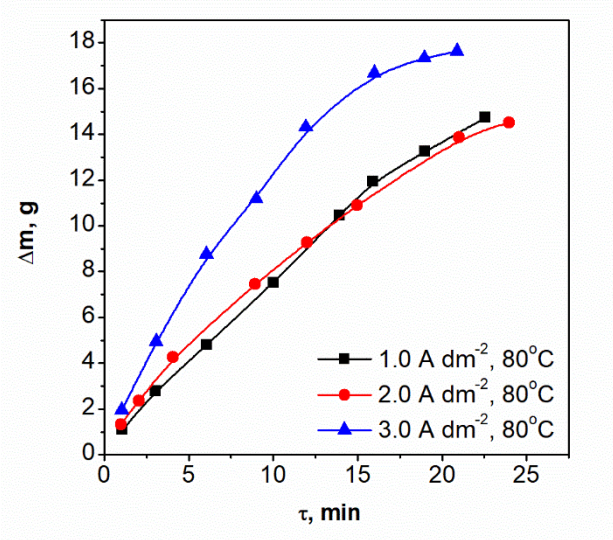

Fig. 3. The effect of current density on the amount of tin, extracted from a solution with composition: 40 g L^{-1} NaOH, 15 g L^{-1} p-NA, 19.5 g L^{-1} Sn, 80°C.

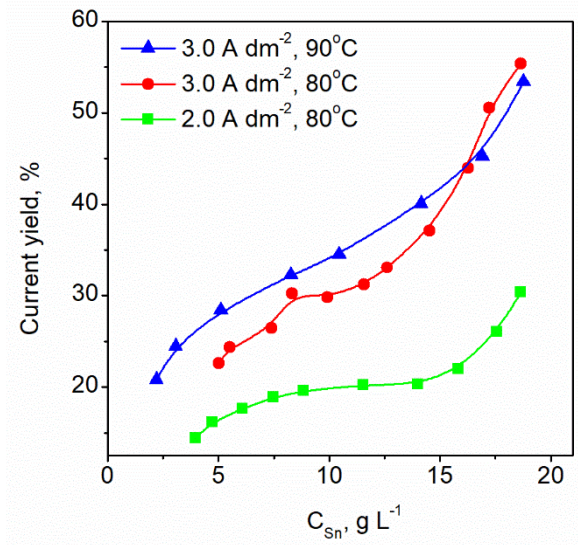

Fig. 4. Relationships of the current yield, on the concentration of dissolved tin, in a solution with composition: 40 g L^{-1} NaOH, 15 g L^{-1} p-NA.

Table 2. Values of the measured voltage.

Current density, A dm^{-2}	Voltage, V
1.0	3.2 ± 0.2
2.0	3.4 ± 0.2
3.0	3.8 ± 0.2

During the electrolysis, the change of the inter-electrode voltage at different current densities was also monitored. Table 2 presents the values of the measured voltage. In general, it can be said that as the current density increases, the inter-electrode voltage increases, the highest being at 3.0 A dm^{-2}.

The effect of the amount of tin in the solution on the current yield, for the oxidant p-NA, is shown in Fig. 4. It can be seen that the values of the current yield are higher at 3.0 A dm^{-2}, respectively at 80°C and 90°C, that is, the increase of the temperature to 90°C does not lead to a significant increase of the current yield at 3.0 A dm^{-2}.

The effect of p-NA content on the degree of tin extraction from the solution and other conditions being equal is shown in Fig. 5. A comparison of the curves for different concentrations of p-NA shows that as it increases the rate (respectively the degree) of tin extraction increases.

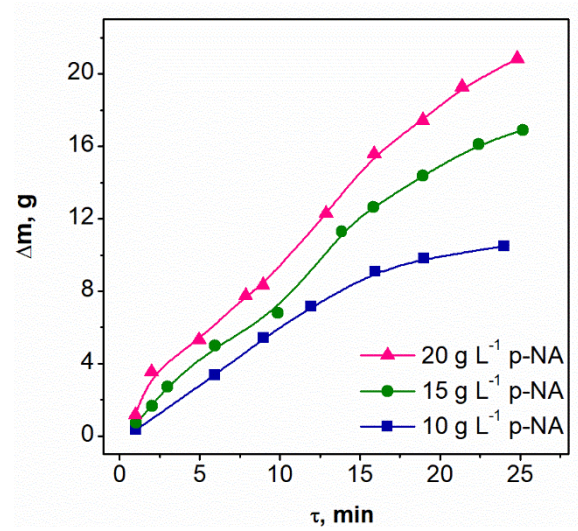

Fig. 5. Effect of the amount of p-NA on the quantity of tin extracted from a solution with a composition: 40 g L^{-1} NaOH, 19.5 g L^{-1} Sn, 80°C, 3.0 A dm^{-2}.

Using Mössbauer spectroscopy, the composition of the solution was determined after dissolving the tin from the tinned sheet metal. The Mössbauer spectrogram in Fig. 6 shows that Sn is of the 4th valency and is a mixture of α- and β-tin acids.

The results of the atomic absorption analysis of the solution from which the tin was extracted, as well as of

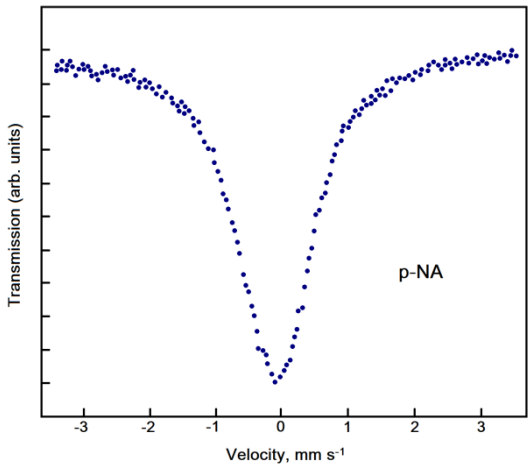

Fig. 6. The Mössbauer spectrum of the medium after tin dissolution in alkaline solution.

Table 3. Atomic absorption analysis of the solution from which the tin was extracted.

Elements	Impurities in the electrolyte, g L^{-1}	Coating composition, %
Pb	1.10^{-3}	0.086
Zn	5.10^{-4}	0.258
Cu	2.10^{-3}	0.258
Sn	2.10^{-3}	99.398

the analysis of the coating on the cathode, are presented in Table 3. The results show that very high purity tin is extracted, which can be widely used in the technique.

CONCLUSIONS

The paper describes the results obtained by removing tin from waste tinned sheet metal. The conditions are determined, ensuring a high degree of removal of contaminants and complete removal of lacquer coatings from the surface of the sheet metal. It was determined that in alkaline solutions containing 40 g L^{-1} NaOH, 15 g L^{-1} p-NA at 80°C about 95 % of the tin coating is removed. Electroextraction of alkaline tin-containing solutions (~ 80°C) carried out at 2 - 3 A dm^{-2} yielded metallic tin with a purity of about 99.5 %.

The regeneration of secondary tin from tinned waste is essential in the overall balance of the tin. Therefore, despite all the difficulties, mainly associated with the collection, the regeneration of tin from these wastes must be expanded.

Acknowledgements

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