TECHINT INSOLUBLE ANODES TECHNOLOGY WITH AN IMPROVED TIN DISSOLUTION PROCESS.

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ABSTRACT

The application of Techint insoluble anode technology in new or existing tinning lines brings considerable benefits in tinplating such as:

- minimizing the amount of sludge and hence the loss of tin;
- reduction of manpower for anode handling
- improved coating quality
- better process control
- elimination of phenol vapors inside the building.

The paper describes into details such improvements as well as the very satisfactory results reached in tinplate produced with insoluble anodes. In fact, with conventional electroplating technology the homogeneity of tin coating thickness decreases as the coating weight decreases, due to the particular geometry of the tin anodes and due to non-uniform consumption of tin bars.

The critical point of the process is the high production of sludge in the present tin dissolution systems used in the electrotinning lines with insoluble anodes. The tin lost in sludge is higher than 10% of the dissolved tin. This is the reason why the tinplate process with insoluble anodes is not yet used worldwide.

Because of that, Techint Technologies, a division of TECHINT Group, and its connected Research Center, Centro Sviluppo Materiali (CSM) have developed a new low-sludge tin dissolution process successfully proven through extensive tests on Siderar's tinning line (Argentina).

The process is based on the oxidation of metallic tin granules by the tinning electrolyte flowing in a dissolution reactor, which has well defined process and technological settings to reduce sludge under 4% (as tin lost vs. dissolved tin). The electrolyte is saturated with pure oxygen by means of a system for oxygen dissolution designed and realized to this purpose.

Interesting results were achieved on the PSA electrolyte. After dedicated tests looking for the best process parameters, finally the sludge produced by the process was less than 4 % as tin lost vs. dissolved tin. The tin dissolution rate can be easily controlled by setting the oxygen flow properly.

Further trials carried out on a pilot dissolution reactor at CSM laboratories showed that the process is insensitive to the type of tinplating electrolyte. In fact, there were no significant differences between the amounts of sludge generated with phenolsulphonic acid (PSA) either with addition of DIPHONE or ENSA, and methansulphonic acid (MSA).

The pilot plant was able to produce more than 4 kg/h of dissolved tin.

The trials were carried out at different dissolution rates and with different electrolytes, monitoring the total amount of generated sludge, the consumptions of the additives and the quality of tinplate by the Hull cell test.

These successful tests demonstrate that Techint insoluble anodes technology is applicable either in new or existing tinning lines whatever is the type of electrolyte used.

INTRODUCTION

Techint has recently developed and realised two modern and fast tinning lines. The Basic design parameters are summarized in Table 1.

The ETL/TFSL are capable of tin coating from 1.12 g/m² to 11.2 g/m². All combinations of differential coatings from 1.12 / 2.24 g/m² to 8.4 / 11.2 g/m² are producible.

The most common product of the equal coating per side is 2.8 / 2.8 g/m². The most common differential coated strip is 2.8/8.4 g/m². Lower tin coatings <1.12 g/m^2 are also feasible.

The process is based on the use of soluble anodes and either PSA or MSA baths. Anyway, Techint and CSM are making considerable efforts to develop the insoluble-anode technology provided with an improved tin dissolution process able to produce very low amount of sludge.

BASIC DESIGN PARAMETERS	
Electrolyte: either	Phenol sulphonic acid (PSA)
or	Methane Sulphonic Acid (MSA)
Production Capacity	
Tinplate:	200,000 t/y and over depending on the mix
TFS:	50,000 t/y
Total:	250,000 t/y
Line Reference Length	140 m
Material Specification	
Thickness:	0.10 to 0.60 mm
Width:	508 to 1250 mm
Coil Weight:	25,000 kg maximum
Coil OD:	up to 2100 mm
Line Speeds	
Entry & Exit Sections:	700 m/min maximum
Process Section:	550 m/min maximum 450 m/min maximum for TFS
Threading Speed:	30 m/min
Exit Section Shear Speed:	120 m/min maximum
Coating Thickness Range (per side)	
Tin Coating:	11.2 g/m^2 maximum 1.12 g/m^2 minimum
Chrome Coating as Metal	100 mg/m^2 maximum 30 mg/m^2 minimum
Chrome as Oxide:	25 mg/m^2 maximum 10 mg/m^2 minimum
Oil Type	DOS and ATBC 2.5-20 mg/m^2/side

Table 1 – Design parameters of ETL/TFS line

The Ferrostan process, based on the use of soluble tin anodes in Phenolsulphonate solution, is well consolidated in electro tinning lines. The use of soluble anodes is advantageous because the tin plated-out on the strip can be automatically produced by the dissolution of tin from the anodes; but there are disadvantages.

The most important one is the necessity to drain off the plating solution because of the different electrochemical efficiency in plating and dissolution. An increase of tin concentration in the plating solution is unavoidable with the use of tin anodes, and dilution of the solution generates overflow and discharge, with loss of expensive material and possible water pollution, unless adequately treated.

The conventional equipment used worldwide for the removal of excess tin is the insoluble anode and many customers today have one half cell equipped with insoluble anodes, but the control of the solution is very difficult and concerns about a rapid decrease of tin and an increase of free acid in the plating solution make the use of insoluble anodes in this way less practical. Other disadvantages with the Ferrostan process are the fumes exiting the plating tanks, the labour requirements for handling the tin anodes and the low productivity.

Additionally, market demand is towards tinplate with thinner coatings; indeed for some uses tin coatings down to 0.2-0.4 g/m^2 are required, causing production problems.

With conventional electroplating technology the homogeneity of tin coating thickness decreases as the coating weight decreases, due to the particular geometry of the tin anodes, which do not present a continuous surface. In fact, each anode is formed by a series of vertical bars drawn against each other so as to leave only a minimum space between the bars, which may produce a lower tin thickness.

Another cause of irregular tin coating derives from non-uniform consumption of tin bars, which in turn gives rise to preferential current distribution. For thicker coatings such situations are alleviated since more cells are employed in the sequence of electroplating steps, thus allowing the tin coating to grow more uniformly. In thin coatings this will not be allowed anymore; for instance, in tinplate for the fabrication of two-piece DWI cans where, owing to wall ironing, the tin coating is reduced and could disappear in those areas where the coating thickness is not homogeneous.

One solution to these problems is to equip an entire tinning line with insoluble anodes, the anode then has a continuous surface and very thin tin coating layers can be produced with high thickness homogeneity.

The main advantages of tin-plating with insoluble anodes are summarized in table 2.

Nevertheless, the use of non-soluble anodes still requires a tin dissolution reactor, connected to the electro tinning line to replenish the amount of tin deposited on the strip.

Considerable research was done to dissolve tin (chemically or electrochemically) in the plating solution [1-10]. An industrial process was set up many years ago and a few plants, mainly in Japan, are working with insoluble anodes.

PARAMETER	BENEFIT
Constant tin covering on strip	Less tin consumed
Better edges	Better strip quality, particularly important for thin coatings
No anode handling	Reduced labour costs, higher productivity and flexibility, safer and better working environment
No anode melting plant	Reduced labour
Covering on tanks	Less fumes
Electrolyte always under control	Lower electrolyte discharge, consumption and pollution
Anodes closer to strip	Reduced electricity consumption

Table 2 – Advantages of insoluble-anode process

The process of chemical tin dissolution, using oxygen to accelerate the oxidation reaction of metallic tin to ionic tin, cannot avoid the formation of a Sn(IV)-based sludge.

The critical point of the process is the high production of sludge in the present tin dissolution systems used in the electrotinning lines with insoluble anodes.

The tin lost in sludge is higher than 10% of the dissolved tin. This is the reason why the tinplate process with insoluble anodes is not yet used worldwide.

Techint, in cooperation with CSM, developed an innovative process for dissolving tin.

This process is able to minimize the amount of sludge and loss of Sn and has been successfully proven through extensive tests on Siderar's tinning line.

MECHANISM OF DISSOLUTION DEPOSITION PROCESS

The process is based on the oxidation of metallic tin granules in the tinning electrolyte saturated with pure oxygen.

The main reactions involved in the metallic tin dissolution process are:

1. $2Sn + O_2 + 4H^+ \rightarrow 2Sn^{2+} + 2H_2O$
2. $Sn + O_2 + 4H^+ \rightarrow Sn^{4+} + 2H_2O$
3. $2Sn^{2+} + O_2 + 4H^+ \rightarrow 2Sn^{4+} + 2H_2O$
4. $Sn^{2+} + 2PSA \rightarrow Sn(PSA)_2$
5. $Sn + Sn^{4+} \rightarrow 2Sn^{2+}$

Oxygen is necessary to enhance the reaction rate of the oxidation of tin by the acidity of the bath formed at the insoluble anode.

The electrochemical reactions occurring at the electroplating site with insoluble anodes are:

6. $2Sn^{2+} + 4e^- \rightarrow 2Sn$ (cathode)
7. $2H_2O \rightarrow O_2 + 4e^- + 4H^+$ (anode)

The four moles of hydrogen ions formed at the anode (reaction 7) restore the as many moles of hydrogen ions consumed in the dissolution reactor to dissolve two moles of metallic tin (reaction 1), which, in turn, restore the two moles of tin deposited on the strip (reaction 6). Thus the mass balance is assured.

PILOT LABORATORY LINE

After a first set of laboratory investigations, a 30 l capacity pilot reactor for tin dissolution was initially realised at CSM laboratories (figure 1).

The plant comprises a tin dissolution section and a tin electroplating section. The dissolution section contains the chemical reactor, the pressurizing pump, the oxygen feeder and the tank for the preparation and storage of the solution.

Figure 1 – CSM pilot plant

The PSA electrolyte flows through the reactor by means of a pump operating at a pressure of up to 8 bar. Oxygen is fed into the depleted electrolyte by a special feeder designed to minimize the size of oxygen bubbles and promote their immediate dissolution. The electroplating section has a vertical electrolytic cell with flat parallel electrodes, a pump for solution movement and a recirculation tank.

Since the tin dissolution rate is proportional to oxygen activity, oxygen-saturated electrolyte at pressures higher than 1 bar, are used. A nozzle for feeding oxygen into the solution was specifically developed for this purpose.

The dissolution of metallic tin achieved through oxidation in acidic environment by dissolved oxygen involves two main technological problems: i) to get the maximum solution of gaseous oxygen, possibly up to its saturation, even when working under pressure, ii) to maximize the mass transport coefficient using a fluidized bed reactor, which also minimizes the non-reactive volume of the tin charge.

Preliminary pilot tests

A first series of tests were carried out by varying the following parameters:

- Oxygen flow rate
- Height of the fluidized tin bed
- Surface area of metallic tin
- Electrolytic solution flow rate
- Tin particle size

An additional test was performed at high temperature (~60°C) to evaluate the influence of this parameter on the dissolution kinetics and sludge formation.

The effect of the above parameters on the tin dissolution rate and on the sludge production allowed for the definition of the criteria for designing an industrial tin dissolution plant able to generate a low amount of sludge.

PILOT PLANT CONNECTED TO AN INDUSTRIAL LINE

In a further phase of the work an industrial-scale reactor was realised to feed one insoluble anodes electrolytic cell of the electro tinning line of Siderar Works in S. Nicolas, Argentina (figure 2).

Figure 2 - Tin Dissolving Pilot Plant at Siderar

Techint Technologies decided to design the pre-wetting tank so that it could be used either as a normal pre-wetting tank or as an insoluble anode plating tank connected to a dedicated tin dissolution plant for replenishing the plated-out tin.

The tin dissolution plant was erected, connected to the revamped line and began operation at the beginning of 2001. By the end of the same year the research activity connected to this first industrial campaign was completed.

The schematic flow diagram of the plant is here below shown in figure 3.

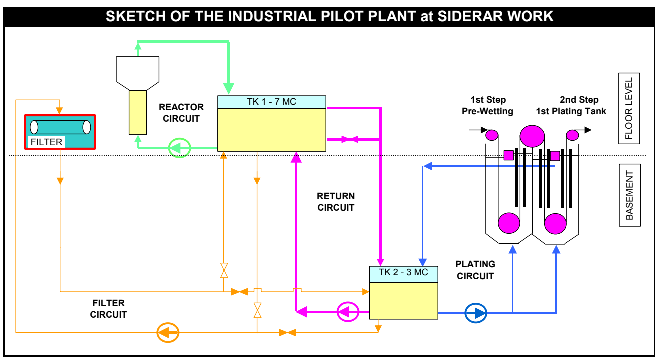

Figure 3 – Scheme of the industrial-scale reactor

The plant consists of a reactor into which irregular sized tin pellets of about 2 mm diameter, are charged into the metallic tin bed from the top of the reactor, four recirculating circuits and two recirculating tanks, one of which was already existing in the old line.

The first circuit feeds the plating tank from which the low tin ion content solution is returned because of the deposition of tin on the running strip; and a second circuit connects the two recirculation tanks.

A third, and most import circuit, feeds the tin dissolution reactor. This circuit works at high pressure (5-6 bar) in order to provide high solubility of oxygen in the solution. The fourth circuit removes the sludge from the solution. The tin dissolution plant has a design capacity of 30 kg/h of dissolved tin.

The charging system was designed with proper automatic valves to maintain the recirculation inside the reactor during the charging operation. The tin is charged in the reactor once every two to three hours depending on the tin dissolution rate set in the plant, and the call for charging is performed by the plant automatic system when the quantity inside the reactor has reached a minimum value.

The reactor is a vertical cylindrical vessel, divided in two parts: the upper part has a large diameter to avoid small tin particles to escape from the reactor. The total volume is about 1 m^3.

The plating solution is fed from the bottom into the reactor through a distributor that supports the metallic tin particles and distributes the solution. Before entering the reactor the solution is enriched in dissolved oxygen.

Suitable heat exchangers are installed in the circuits in order to maintain the plating solution at a constant temperature and, because of the drag-out from the plating tanks in order to keep the level constant in the two recirculating tanks, a refilling of solution from the normal line is available. The plating tank is equipped with insoluble anodes located in the tank as shown in figure 4.

Figure 4 - Insoluble anodes in industrial plant

The Iridium Mixed Metal Oxide covered titanium anodes are connected to two rectifiers each having a capacity of 4,000 A. The replenishing rate of the plant is controlled by the flow rate of the oxygen.

The plant can work in three modes:

- at constant oxygen flow rate (manual)
- at constant tin dissolution rate (auto 1 mode)
- at a rate proportional to the current given by the rectifiers (auto 2 mode).

This last mode permits working at constant tin concentration in the solution because the replenishing rate is calculated taking into consideration the tin plated out at any given moment.

A simulation model was developed to providing a continuous on-line calculated value of actual dissolution rate, based on the following main process parameters: the tin charge, pressure, temperature, injected oxygen and recirculating solution flow rate.

FIRST INDUSTRIAL TIN DISSOLUTION AND DEPOSITION TESTS

Continuous weekly tests with simultaneous dissolution and tin-plating were performed. No problems were encountered with the line operation or product quality and during the test operation the plant mainly worked at constant tin dissolution rate for calibration purposes.

The dissolution rate was found to always depend on the oxygen flow rate while working in conditions of full solubility of oxygen according to Henry`s law. This was demonstrated at reactor pressures of 2, 3 and 4 bar.

At each test the quantity of generated sludge was weighed and correlated with the dissolved tin. The sludge can be generated both in the dissolution and plating circuits. The weighed amount is the total from the two circuits.

Depending on the operating conditions (pressure, injection of oxygen, tin charge, solution flow rates, and so on) different quantities of tin lost in the sludge were measured.

Two main test campaigns were performed (in summer and in autumn). In the first one, performed during summer 2001, the behavior of the plant was tested in different operating conditions by varying one parameter at a time and keeping the others constant.

Then the plant was set up in the best operating condition working out from the results of the first campaign. A second industrial campaign was carried out in the autumn 2001.

The results were very good (see figure 5); the plant was able to reach a dissolution rate higher than 40 kg/h without loss in efficiency and without higher generation of sludge.

In the Autumn campaign the sludge percentage was very low with a maximum rate of 4%, expressed as tin lost in sludge vs. dissolved tin; the only exception being in the fifth test when the plant was set outside the standard conditions for a final check.

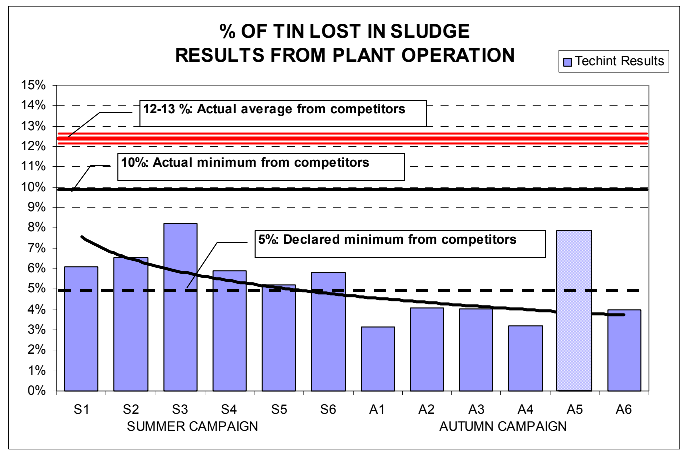

Figure 5 – Tin losses during summer and autumn campaigns

During the autumn tests, tinplate with a coating weight of ≈ 2 g/m^2 for each side was produced using only the first electrolytic cell equipped with insoluble anodes and fed with the electrolyte coming from the tin dissolution reactor.

Then, tinplate with the same tin weight was produced, for comparison, using only the second electrolytic cell, equipped with soluble anodes and fed with classic electrolyte coming from the storage tanks.

No difference was seen as far the visual appearance of the two products. SEM (Scanning Electron Microscope) and GDOES (Glow Discharge Optical Emission Spectroscopy) investigations (figures 6-9) confirmed that the tinplate produced with insoluble anodes is quite equal to that produced with soluble anodes.

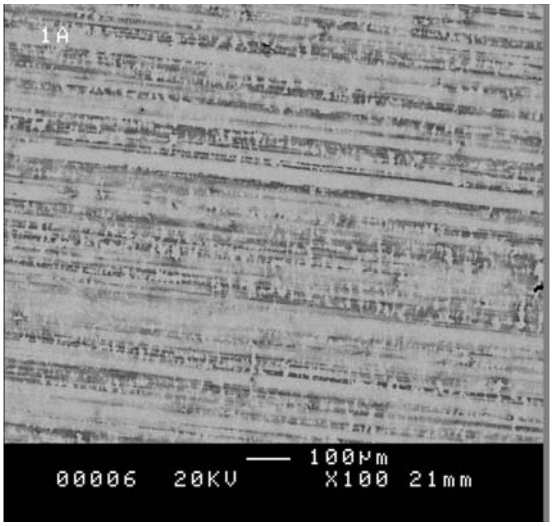

Figure 6 – Tinplate produced with soluble anodes

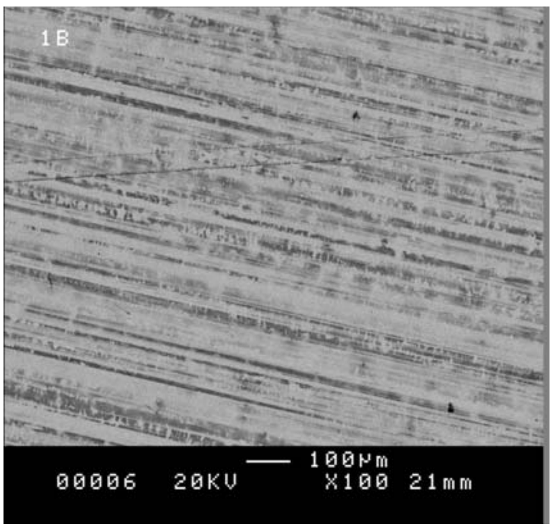

Figure 7 – Tinplate produced with insoluble anodes

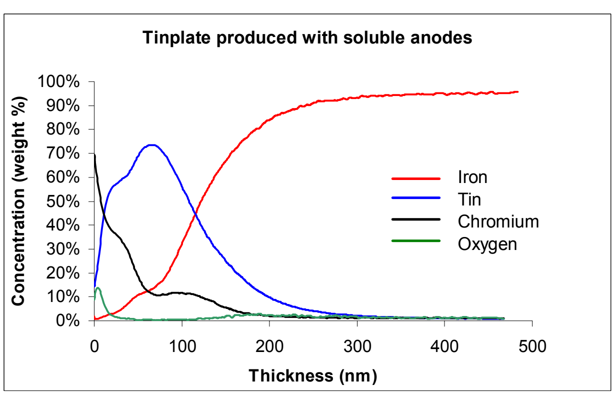

Figure 8 – Element profile, tinplate soluble anodes

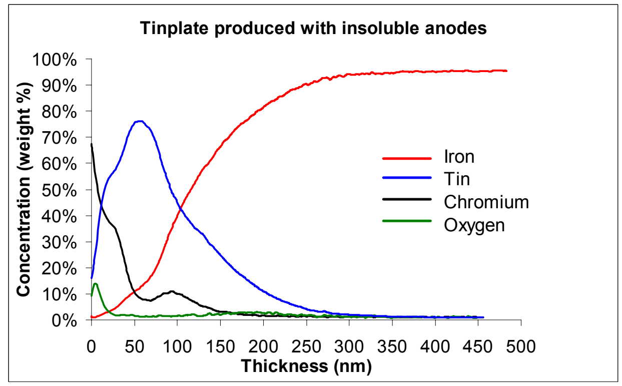

Figure 9 – Element profile, tinplate insoluble anodes

PILOT TESTS WITH DIFFERENT ELECTROLYTES

All the activities and the results described above were performed with PSA-based electrolyte containing Diphone V as additive.

To test the low-sludge tin-dissolution process also with baths having different additives (Diphone VI, ENSA) and with new ecological baths based on MSA system, a new series of tests was carried out on the pilot dissolution plant at CSM laboratories.
The trials were carried out at different dissolution rates and with different electrolytes, monitoring the total amount of generated sludge, the consumptions of the additives and the quality of tinplate by the Hull cell test.

Four types of electrolytes were used in the tests:

– PSA + Diphone 5
– PSA + Diphone 6
– PSA + ENSA 6
– Ronastan® system (MSA + proprietary additives)

The electrolyte volume was 500 l. The tests were made with a flow rate of 5 m^3/h and a pressure of 5 ata.

Also electrolytes containing up to 15 g/l Fe were tested to check the effect of such ion on the loss of tin in sludge. Fe^{++} ion is generally present in tin electrolyte owing to the dissolution of steel strip in the first half cell (pre-dip).

The results were really good with all the electrolytes. Very low percentages of tin loss were detected, with a maximum rate of 4,5 %, no matter the electrolyte used (figure 6).

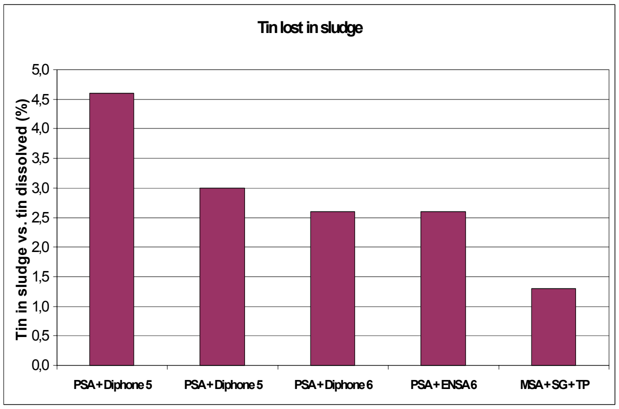

Figure 6 – Tin loss with various electrolytes

As low percentage of tin loss were found even with the same electrolytes containing up to 15 g/l iron (figure 7).

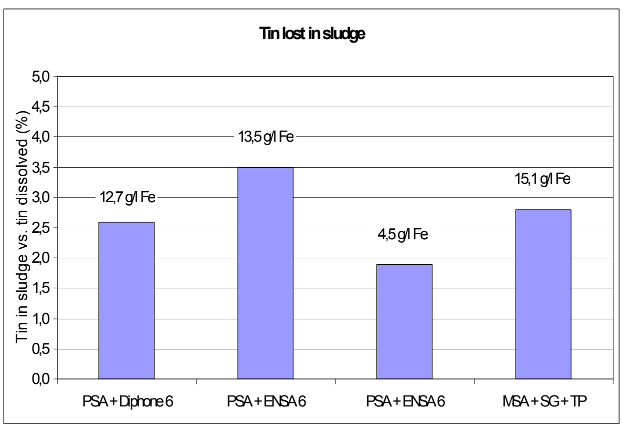

Figure 7 – Tin loss with electrolytes containing Fe

SECOND INDUSTRIAL TIN DISSOLUTION AND DEPOSITION TESTS

In May and June 2004 a second industrial campaign was carried out at Siderar electrotinning line. Both the pre-dip half cell and the second electroplating cell were equipped with insoluble anodes.

An automatic procedure was adopted to set the oxygen flow rate and, consequently, the tin dissolution rate, according to the current applied in the two electrolytic cells equipped with insoluble anodes.

Thus, the amount of tin dissolved at any time is equal to that of tin deposited on the strip, plus the amount of tin to compensate the drag-out.

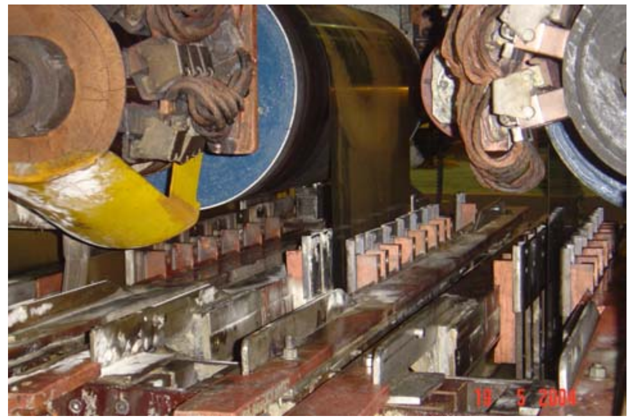

Figure 8 – Insoluble Anodes in 2004 industrial campaign .

Two long-term running tests were carried out. The amount of sludge was measured at the end of each test and correlated to the dissolved tin. The total amount of tin lost resulted less than 4 %.

The insoluble anodes were connected to four rectifiers for a total capacity of 22,000 A. Figure 9 shows the amount of current provided, during normal operating conditions of the line, with insoluble anodes, which is proportional to the tin plated with insoluble anodes. In general more than 30 % is given with insoluble anodes, up to a maximum of 45 % in case of low coating (2.2 g/m^2).

Two commercial coils were also produced only with insoluble anodes.

Figure 10 shows the progressive amount of tin dissolved and plated out during one test.

The very good results obtained in the previous industrial campaign with only the pre-dip cell equipped with insoluble anodes, were confirmed even in this second campaign with one cell and a half equipped with insoluble anodes.

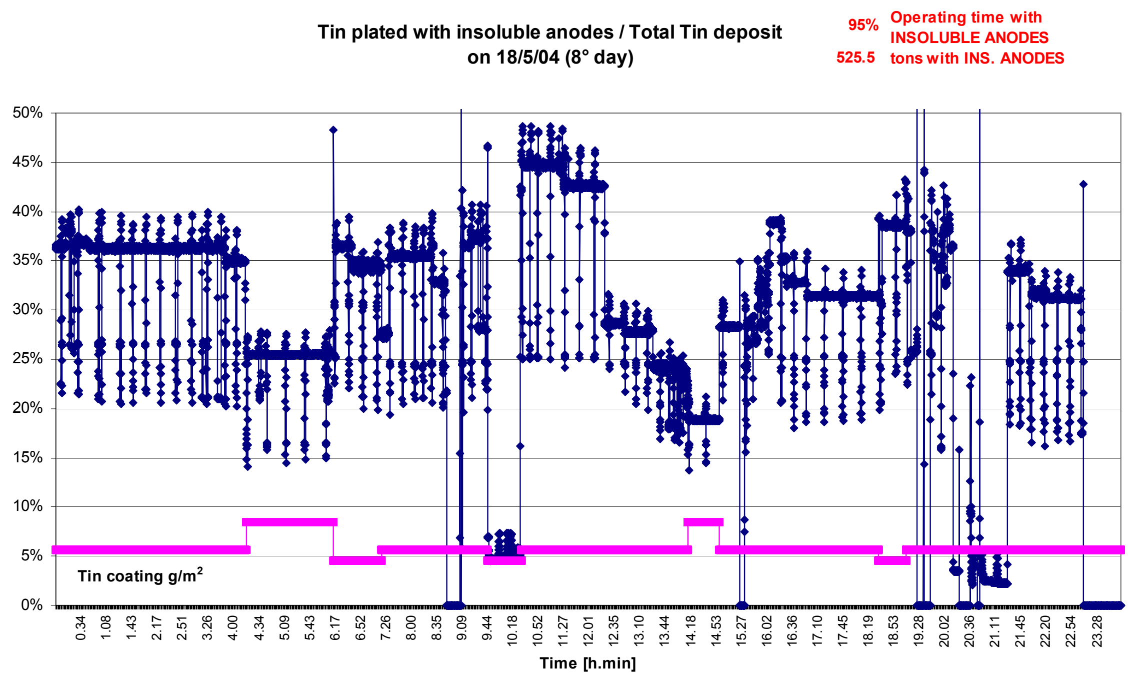

Fig. 9 – Amount of current given with Insoluble Anodes during one typical day

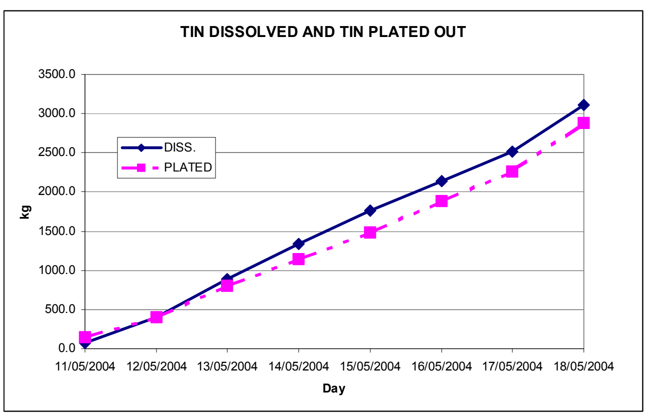

Figure 10 – Tin dissolved and plated out during a test

Electrolytic E1 tinplate was produced by using only the two cells with insoluble anodes. No visual difference in the aspect was seen in comparison to E1 tinplate produced with soluble anodes. Samples of such tinplates are under investigation by SEM and GDOES techniques.

CONCLUSIONS

Last trials carried out on a pilot laboratory plant at CSM showed that the process is insensitive to the type of tinplating electrolyte. In fact, there were no significant differences between the amounts of sludge generated with phenol-sulphonic acid (PSA) either with addition of DIPHONE or ENSA, and methanesulphonic acid (MSA). Moreover also the presence of Fe ions in solutions has been checked. The results showed no influence on the amount of produced sludge.

The second industrial campaign confirmed that the Techint-CSM tin dissolution process is able to produce a tin loss in sludge as great as that of the classic electrotinning process based on the use of soluble anodes.

Thanks to such results, the tinplate process with insoluble anodes is ready for full industrialisation, bringing all the advantages connected to the use of insoluble anodes, which were not exploited so far for the absence of a low sludge dissolution system. A further step in the direction of a full insoluble anodes line is scheduled for the tinning line at Siderar work, where a third plating tank is going to be equipped with insoluble anodes.

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