

NEW TENOVA ELECTROLYTIC TINNING LINES WITH INSOLUBLE ANODES

*Giovanni Astengo
Tenova, Strip Processing
Torre Shipping, Via De Marini 53
16149 Genova, Italy
Tel.: 39 010 605 4591
E-mail: stripprocessing@it.tenovagroup.com*

Key words: Electrolytic Plating, Tinning Lines, Insoluble Anodes, Tin dissolution

Abstract

Traditionally the electrolytic tinning lines are with soluble tin anodes because of the high generation of sludge produced by the tin dissolution process.

Tenova has developed a new low-sludge tin dissolution process.

The application of Tenova technology minimizes the amount of sludge produced and hence the loss of tin. Other benefits of tinplate with insoluble anode are the reduction of manpower for anode handling and therefore increase in safety during operation, improved coating quality, better process control and elimination of phenol vapors in the working environment.

The tin dissolution process is based on the oxidation of metallic tin granules by the tinning electrolyte flowing in a dissolution reactor. The electrolyte is saturated with pure oxygen in a proper mixer before entering the reactor.

The new technology was developed on the Electrolytic Tinning Line at Ternium Siderar.

The paper describes in detail the new plant configuration, the equipment and the very satisfactory results reached during a long period continuous operation with insoluble anodes.

Among the most significant results it has been possible to optimize the anode and edge mask design, for the best quality of strip coating and the best access to the cell for maintenance and operation activities. The oxygen and tin dissolution rates were confirmed, as well as the dissolution plant efficiency and productivity. Moreover, important operational and maintenance practices have been finally defined.

A new installation, using the process with insoluble anodes, will be a tinning line able to produce more than 250,000 TPY, located in China, in operation from 2009.

Introduction

There are many good reasons to definitively choose Insoluble Anode Technology in the tin dissolution process, both for new plants or upgrading of existing process sections.

While 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, on the other hand, there are many 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.

Other disadvantages in the conventional lines 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/m² 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.

The solution to these problems is to equip the entire tinning line with insoluble anodes. The main advantages of tinplating with insoluble anodes are summarized in table 1.

PARAMETER	BENEFIT
Constant tin covering on strip	Less tin consumed
Better edges	Coating thickness less than 1 g/m ²
No anode handling	Reduced labour costs, higher productivity and flexibility, safer and better working environment
No anode melting plant	Reduced labour costs
Covering on tanks	Less fumes inside building
Electrolyte always under control	Lower electrolyte discharge, consumption and pollution
Anodes closer to strip	Reduced electricity consumption

Table 1. Advantages of Insoluble Anodes

The main drawback is that tinplating with insoluble anodes requires a tin dissolution reactor connected to the electrolytic tinning line to replenish the amount of tin deposited on the strip. Tin is not easily dissolved.

Considerable research was done to dissolve tin (chemically or electrochemically) in the plating solution. An industrial chemical process was set up many years ago based on the oxidation of the metallic tin granules by the tinning electrolyte flowing in a dissolution reactor, but, unfortunately, the chemical process of tin dissolution also produces a Sn(IV)-based sludge.

The critical point of the existing electrolytic tinning lines with insoluble anodes is the tin loss, that is the reason why, even if a few plants are working with insoluble anodes, the tinplate process with insoluble anodes is not yet used worldwide.

Technology developed together with Ternium

Tenova, in strict cooperation with his connected Italian research centre CSM (Centro Sviluppo Materiali), developed years ago an innovative process for dissolving tin.

The process is based on the oxidation of metallic tin granules by the tinning electrolyte flowing in a dissolution reactor. The electrolyte is then saturated with pure oxygen to accelerate the oxidation reaction of metallic tin to ionic tin.

The new tin dissolution process, was developed and tuned-up years ago on the Electrolytic Tinning Line at Ternium Siderar (Techint Group) over an extensive operational period. The campaigns

confirmed that the developed tin dissolution process considerably reduces the quantity of generated sludge and consequently the loss of tin.

Since the plant was run continuously, it has been possible to optimize the anode and edge mask design and confirm the dissolution plant efficiency and productivity.

Insoluble Anodes

The main requirements any insoluble anode must fulfil in order to be employed in an electroplating line are:

- a) High surface area
- b) High electrical conductivity
- c) Good electro-catalytic properties
- d) High chemical and mechanical stability
- e) Reduced problems of gas bubbles
- f) Selectivity
- g) Availability and low-cost

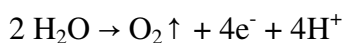
All these characteristics strongly depend on the surface chemistry and morphology of the electrodes, which for this application generally consists of coating layer of Ru, Ir, Sn and/or Ta oxides, applied on a Ti substrate. From a practical point of view the most relevant issues are those related to lifetime, particularly the need of a high electrical conductivity and high chemical and mechanical stability.



Inert Titanium based anodes with an active precious metal coating have been used for this application. The reason is that Titanium is resistant to chemical attack in acid electrolyte, such as PSA, because it has an extremely adherent and inert surface oxide film. Because of this thin surface Ti oxide film, which is electrically non-conducting, Ti by itself will not pass current and will therefore not act as an anode just by itself. The application of the Mixed Metal Oxide coating to the active area of the Ti anode allows the current to flow from the Ti anode through the coated areas into the electrolyte, while the non-coated areas of the Ti anode remain inactive.

Figure 1 - Insoluble anodes at Ternium Siderar

In order to optimise anode and cell design, fluid dynamic studies have been carried out to analyse the velocity distribution of the electrolyte within the cell as a consequence of the movement of the strip as well as the effect of oxygen generation at the anode surface, where the following reaction takes place:



The insoluble anodes are vertically positioned in a vertical cell containing a plating solution, and spaced from a strip running through a down-pass and an up-pass.

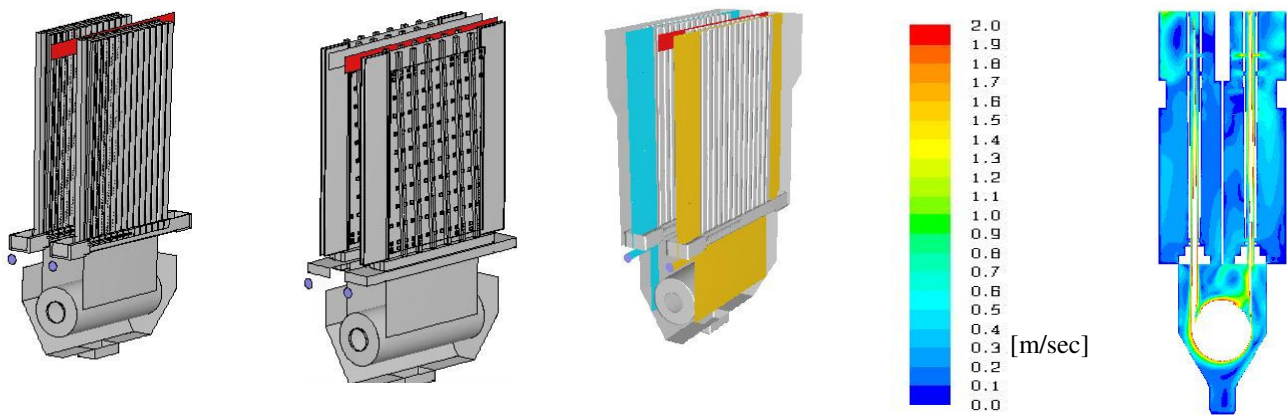


Figure 2 – Plating cell configurations and speed distribution within the cell

The insoluble anodes are spaced from the strip by a distance of less than 50 mm, and the plating solution is blown into the gap between said anode and said strip. Due to the very high speed of the strip, the fluid dynamics of the cell tends to create a so called Venturi effect in the region between the strip and the anode which promotes undesired contact between the anodes and the strip and there-fore marks of anodes on the strip. For these reasons, anodes have been designed with a regular array of orifices, with the aim of reducing such effect. While reducing the level gap between ascending and descending zone of the plating cell, the orifice distribution has also been conceived to maintain transversally evenness in current density distribution.

A particular design of the lower guide allows the possibility to control both the distance of the anodes from the strip, as well as to regulate the anodes lower position in order to be equal-distant to the strip after a sink roll grinding.

One of the most essential operating conditions stated by the manufacturer is to maintain the anodes anodically polarised at any time as long as they were immersed in the electrolyte. The reason for this is that the PSA is a reducing acid. As long as the anode is polarised the protective Ti oxide film will be maintained and the Ti anode will not be corroded. On the contrary if the anodes are not kept anodically polarised the reducing acid will attack the Ti oxide film and the anode will suffer from some corrosion. Finally the Ti metal will dissolve, forming a thicker insulating Ti oxide film between the MMO coating and the Ti substrate. This mechanism leads to a significant increase in the operating anodic potential due to passivation by the non-conductive Ti oxide film. Eventually the anode will be totally passivated and it will cease to pass the current.

During the validation of this new technology insoluble anodes have replaced soluble anodes on the first plating cells of the ETL of Ternium Siderar. The first plating tank equipped with insoluble anodes is shown in figure 1.

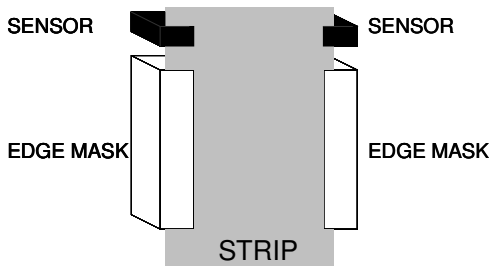
No defects to the strip which could be related to the use of insoluble anodes have occurred. Although no particular attention has been paid to the system, since the anodes have been often working without edge masks and without stand-by current, the MMO coated Titanium, anodes have shown excellent behaviour and no significant increase in the operating anodic potential due to anode passivation has been observed.

After removal of the anodes from the cell and accurate flushing with water at elevated temperature to remove the sludge, no damage to the coating could be observed.

Edge Masks

Insoluble anodes are of a fixed width. In order to process strips of different widths, electrically insulating plates so called edge masks are used to prevent the current from flowing between the two anodes next to the strip, thus avoiding so called white border defects.

The strip edges engage in U-shaped sections arranged at the end faces of the electrically insulating plates. The degree of edge galvanization depends on the insertion depth of the strip edges into the U-shaped sections. Accordingly, it is necessary that the U-shaped sections accurately follow the strip travel.



The edge masks must follow the strip very exactly, the expected accuracy being less than 1 mm. Inductive sensors moving jointly to the masks are used to detect the strip penetration and vary the edge mask position accordingly. The working principle of the system is depicted in figure 3.

Figure 3 - Edge masks principle

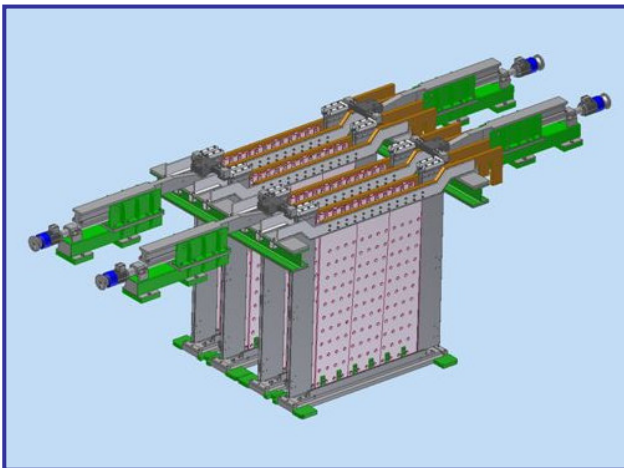


Figure 4a,b - Edge masks in plating cells

The edge mask system, in any cell) mainly consists of:

- Two pairs of edge masks (1 at operator side, 1 at motor side), made of epoxy glass, each pair driven by one servo-cylinder. The masks are held from the top and guided at the bottom by the anodes guides. They are supported by a stainless steel structure with slide bearings, both located outside the plating tanks for the best accessibility.
- Two servo-cylinders with linear transducers.
- Two strip edge detection sensors designed to resist at a maximum temperature of 80 °C, not affected by dirt, humidity, metallic particles.

Edge mask control is obtained by means of a local PLC communicating constantly with the PLC of the line. Communication was needed mainly to track the position of the weld, so that edge masks could open when the weld was passing through the plating cells. Edge masks opens also when the line is stopped or when the line speed is below a threshold value (30m/min).

Communication between the two PLCs also allows information about strip width being sent to the local PLC. Once the information about the strip width is known, only one strip edge sensor is needed to detect the position of the strip edge and virtually to control the masks, since the position

of the other edge of the strip can be easily calculated. However, the system is conceived with two edge sensors to improve system reliability. In case of failure of one of the sensors, an alarm is activated when the absolute distance of the masks is less than the strip width.

The strip edge position is monitored accurately by the inductive sensors and edge mask drives regulated the mask position accordingly.

Two different edge masks configurations were developed in by Tenova in the last year: in comparison with the masks used previously, the current edge mask design was significantly modified to ease inspection and access to the cell for maintenance and operational activities. Thanks to the new design it is possible to remove all supports inside the plating tanks, at the same time permitting easy access to the edge masks and to the anodes for maintenance.

Strip edge sensors with improved design were also re-developed internally to fulfil application requirements.

As expected, the position accuracy, during the tests on the Electrolytic Tinning Line at Ternium Siderar has always been around ± 1 mm on both sides.

Tin dissolution Process

The process is based on the oxidation of metallic tin granules by the tinning electrolyte flowing in a dissolution reactor. The electrolyte is then saturated with pure oxygen to accelerate the oxidation reaction of metallic tin to ionic tin.

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

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

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. $2\text{Sn}^{2+} + 4\text{e}^- \rightarrow 2\text{Sn}$ (cathode)
7. $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$ (anode)

The four moles of hydrogen ions formed at the anode (reaction 7) restore 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.

Dissolution Plant

A Tin dissolution Plant is necessary to replenish the amount of tin deposited on the strip. The dissolution reactor realised to feed the insoluble anodes electrolytic cells of the electro tinning line of Ternium Siderar in S. Nicolas, Argentina is shown in figure 5.



The plant mainly consists of: a chemical reactor, a pressurizing pump, oxygen feeders with improved design and a tank for the preparation and storage of the solution. The reactor is a vertical cylindrical vessel, divided in two parts: the upper part has a large diameter to prevent small tin particles from escaping the reactor.

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 in a proper oxygen feeding station able to guarantee the max oxygen dissolution in accordance with the Henry law.

The tin dissolution rate of the plant is controlled by the flow rate of the oxygen. The plant control system can automatically calculate the oxygen flow rate needed to dissolve the tin which has been plated in the cells depending on the current provided by the rectifiers, thus maintaining a constant tin concentration in the plating solution.

Figure 5 - Tin Dissolving Plant at TERNIUM SIDERAR

Operating results at Ternium Siderar

The electrolyte produced fully complies with the requirements of the tinning line and important operational and maintenance practices have been defined.

According to Ternium Siderar, operating company, the most promising aspects of the system of insoluble anodes are: improved strip quality related to the elimination of chronic defects, such as white edges and marks of anodes, elimination of anode handling, and more flexible campaigns in terms of strip width programming, since the edge masks can adapt to all strip widths. Moreover, the dissolution plant allows controlling the tin concentration in the electrolytic solution of the line.

New Tinning Line with Insoluble Anodes in China



Tenova is currently supplying a complete new Electrolytic Tinning Line in China, with a 250,000 TPY capacity and with a process speed of 550 metres/min, equipped with insoluble anodes and edge masks with associated tin dissolution plant. The plant will start up in the 2009.

The plating production rate made it necessary to supply 9 plating cells, each having 4 sets of insoluble anodes: on the up and down passes, upper and lower sides.

Each set of anodes consists of three insoluble anodes, designed without bus bars in the back, directly fixed to the anodes bridges. The anodes, fully in Titanium, will have a thickness of 15 mm.

Figure 6 - Tin Insoluble anodes in the rack during coating.

Three tin dissolution reactors are foreseen, each of them as shown in figure 7. The tin granules, coming in box or large bags directly from the tin producers, will be charged on a receiving bin laying on load cells. From that, by means of a star valve (rotating), they will fall by gravity on the reactor. Thanks to two dome valves (fig. 7 right side) the reactor will be charged with pellets without stopping the pumps.

Because of the vicinity of the reactor to the main line recirculating tanks, the two recirculating tanks (one as stand by) properly dimensioned, will act also as dissolution reactor recirculating tanks, that increasing the turbulence in the tanks.

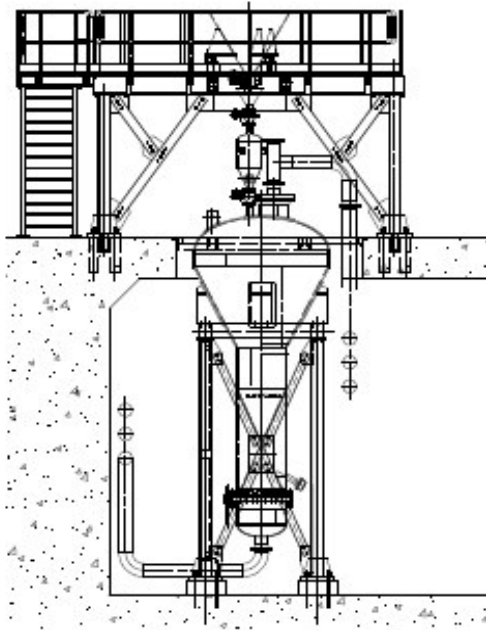


Figure 7 - Tin Dissolving reactor at Dajiang and detail of tin charging system.

A fully automatic filter station will keep the level of solid particles in the electrolyte at a level < 1 g/l (see figure 8)

In terms of capacity, performance, and technology the new plant will be, one of the most important in the World, further enhancing the experience and the technical solutions developed in the high-speed plants supplied recently to Mittal Arcelor (the Avilès facility) in Spain and to Erdemir (Eregli) in Turkey.

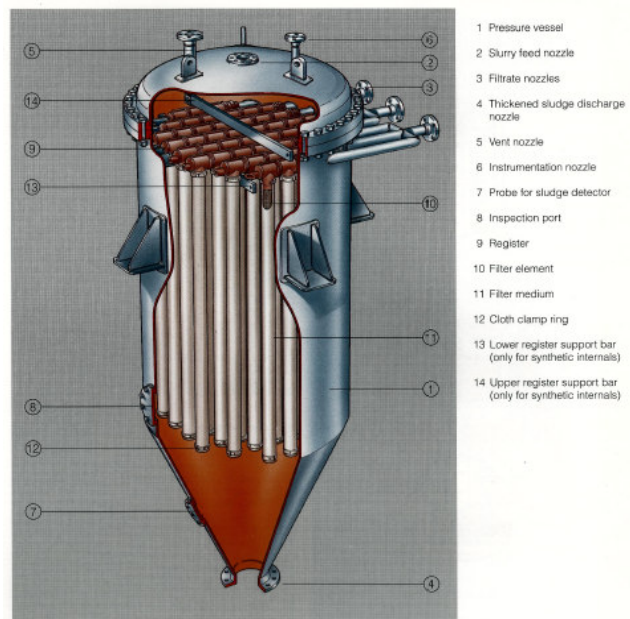


Figure 8 - Filter