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Operating success of insoluble anodes for tinplate

Conventional electrolytic tinning lines using soluble tin anodes have high maintenance requirements not only to replace consumed anodes but also because the electrolyte has to be periodically drained and diluted as tin dissolves from the anode faster than it is plated onto the strip. Tenova has developed a new low-sludge tin plating process using insoluble anodes and a tin dissolution plant linked to the electrolyte circuit to replenish the plated out tin.

By G Astengo*, L Rombi* & T DeLoia**

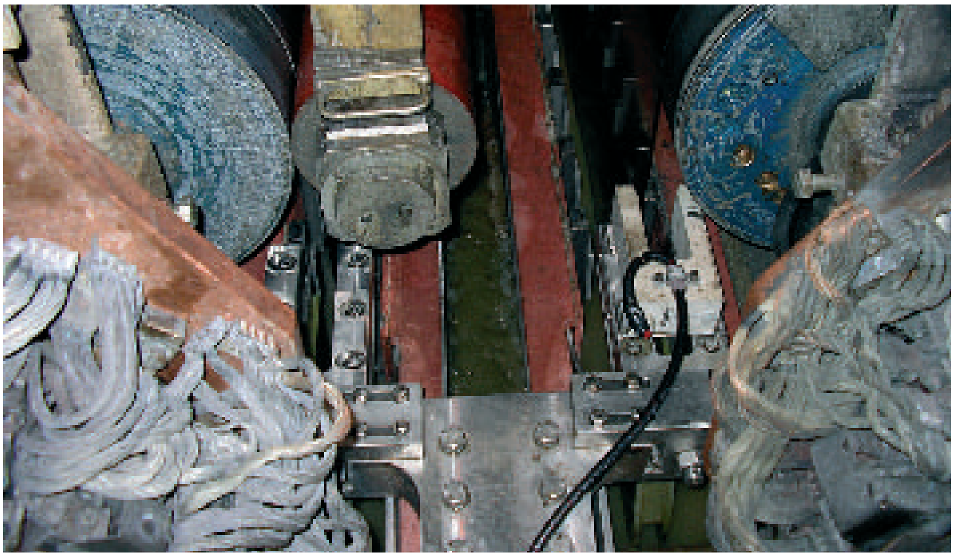

Fig 1 Insoluble Ti anodes at Ternium Siderar, Argentina

THE application of Tenova's insoluble anode technology minimises the amount of sludge produced and hence loss of tin. Other benefits of producing tinplate from insoluble anodes 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 vapours in the working environment.

To replenish the tin plated out from the electrolyte a separate tin dissolution plant is employed, supplied with depleted electrolyte from the tinning line. The electrolyte is saturated with pure oxygen in a mixer before entering the dissolution reactor in order to promote oxidation of the metallic tin granules which aids dissolution. That oxidation, however, generates a large quantity of sludge containing SnO and only the proper design of the plant reduces the formation of Sn^{4+} and consequently the production of sludge. This new technology was developed on the Electrolytic Tinning Line at Ternium Siderar in Argentina.

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

A new installation, using the process with insoluble anodes, will be a tinning line rated at 250kt/y, located in China, to come into operation in 2009.

Sludge problem

The use of soluble anodes in electrolytic tinplating has one advantage in that the tin entering the electrolyte from the anode to replenish that plated out at the cathode (the strip) is produced in ionic form by electrolysis of the tin anodes in the plating tank, thus avoiding the difficult task of chemically taking tin into solution and oxidising it to an ionic form. However, on the down-side, there are several disadvantages. The most important is the necessity to drain off the plating solution periodically because of the difference in electrochemical efficiency between plating and dissolution when using soluble tin anodes. This causes an increase in the concentration of tin in the electrolyte. The subsequent dilution of the solution generates overflow and discharge resulting not only in the loss of expensive tin but also the possibility of water pollution, unless adequately treated.

Other disadvantages in conventional tinplate lines are fumes from the plating tanks, the labour requirements for the frequent replacement of the consumable tin anodes and lower productivity.

Additionally, market demand is towards tinplate with thinner coatings; indeed for some uses tin coatings down to 0.2-0.4g/m^2 are now required, causing production problems. With conventional electroplating technology the uniformity in the thickness of the tin coating decreases as the coating weight decreases due to the particular geometry of the tin anodes which do not present a continuous surface, instead, each anode is formed by a series of vertical bars drawn against each other leaving a minimum space between the bars, which may result in a reduced thickness of tin corresponding to these discontinuities.

A solution to these problems is to equip the entire tinning line with insoluble anodes. The main advantages of tinplating with insoluble anodes are summarised in **Table1**.

The main drawback of insoluble anodes is that a tin dissolution reactor connected to the electrolytic tinning line is required to replenish the tin deposited on the strip; and tin is not easily dissolved and tends to form ions Sn^{4+} and consequently sludge. In the dissolution reactor Sn^{2+} and Sn^{4+} are formed. Compound formation by the Sn^{2+} ion is prevented by the acidity of the electrolyte and it remains in solution available for plating out in the electrolysis line. The Sn^{4+} ion, however, forms stable SnO_2 which creates the sludge. A good design of the dissolution plant is selective in favour of Sn^{2+} formation so minimising the Sn^{4+} and thus sludge formation.

Considerable research has been carried out in the past into ways of dissolving tin (chemically or electrochemically) in the plating solution. An industrial chemical process was set up many years ago based on the oxidation of metallic tin granules by the tinning electrolyte flowing in a dissolution reactor, but, unfortunately, the chemical process of tin dissolution also produces a Sn^{4+} based sludge. While Tenova's process uses this same mechanism it is selective in minimising the generation of Sn^{4+} ions and hence sludge. A critical disadvantage of

Parameter	Benefit
Constant tin covering on strip	Less tin consumed
Better edges	Coating thickness less than 1g/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

Table 1 Advantages of insoluble anodes

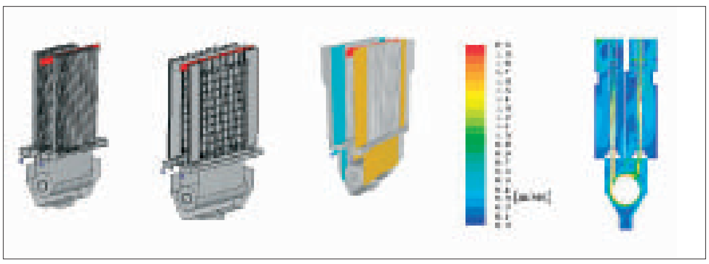

Fig 2 Plating cell configurations and speed distribution within the cell

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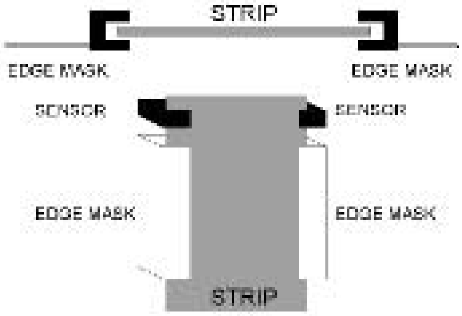

Fig 3 Principle of edge masks

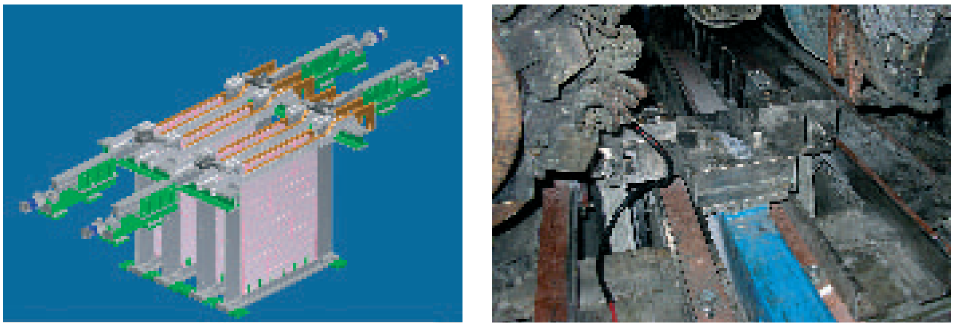

Fig 4 a & b Edge masks in position in plating cells

present-day electrolytic tinning lines employing insoluble anodes is this loss of valuable tin as SnO_2 by this sludge formation and this is the reason why few plants are working with insoluble anodes anywhere in the world.

Tenova insoluble technology

Tenova, in cooperation with the Italian research centre CSM (Centro Sviluppo Materiali), some years ago developed an innovative process for dissolving tin without forming excess sludge. The process is based on the oxidation of metallic tin granules by the tinning electrolyte flowing in a dissolution reactor. The electrolyte is first saturated with pure oxygen to accelerate the oxidation reaction of metallic tin to ionic tin.

This new tin dissolution process, was developed and optimised some years ago on the electrolytic tinning line at Ternium Siderar (Techint Group) over an extensive operational period. The campaigns confirmed that the dissolution process considerably reduces the quantity of sludge generated and consequently the loss of tin.

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

The main requirements any insoluble anode must fulfil to be employed in an electroplating line are:
- high surface area;
- high electrical conductivity;
- good electro-catalytic properties;
- high chemical and mechanical stability;
- reduced problems of gas bubbles;
- selectivity;
- availability and low-cost.

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

Inert titanium based anodes with an active precious metal coating proved suitable for this application. Titanium is resistant to chemical attack in acid electrolytes, such as PSA (Phenol Sulphonic Acid), because it has an extremely adherent and inert oxide film on its surface. Because of this thin Ti oxide film, which is electrically non-conducting, titanium by itself will not pass current and cannot therefore act as an anode unless modified. The application of the Mixed Metal Oxide (MMO) 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 areas of Ti not treated with MMO remain inactive.

Fig 5 Tin dissolution plant at Ternium Siderar

To optimise anode and cell design, fluid dynamic studies were carried out to analyse the velocity distribution of the electrolyte within the cell as a consequence of the passage of the strip through the tank as well as the effect of oxygen generated at the anode surface, where the following reaction takes place:

$$2H_2O \rightarrow O_2\uparrow + 4e^- + 4H^+$$

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

The distance between an insoluble anode to the moving strip is less than 50mm. The plating solution is dragged into the gap by the passage of the 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 can cause contact between the anodes and the strip which results in undesirable marks on the plated strip. To overcome this, the anodes have been designed with a regular array of large perforations passing completely through the anode to reduce the Venturi effect. Also a bias in alignment of alternate holes (ie to avoid a vertical row of adjacent holes) maintains an even distribution of current density.

The design of the lower guide roll enables the distance between the anode and the strip to be adjusted and also to regulate the lower position of the anode so as to maintain it equidistant from the strip after grinding of the sink roll – the roll at the bottom of the cell around which the strip passes to change from downwards motion to upwards.

An essential operating condition stated by the anode manufacturer is to keep them anodically polarised at all times they are immersed in the electrolyte. The reason for this is that the PSA electrolyte 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 corrode. If the anodes are not kept anodically polarised the reducing acid may attack the Ti oxide film and the anode will suffer corrosion. In such a condition the Ti metal will start to dissolve and form a thicker insulating layer of Ti oxide film between the MMO coating and the Ti substrate. This mechanism leads to a significant increase in the applied anodic potential due to passivation by the non-conductive Ti oxide film. Eventually the anode will be totally passivated and will cease to pass current.

During the validation of this new technology insoluble anodes have replaced soluble anodes on the first plating cells of the electrolytic tinning line at Ternium Siderar. The first plating tank to be equipped with insoluble anodes is shown in **Fig 1.**

No defects to the coating on the strip which could be related to the use of insoluble anodes have occurred.

Although no particular attention has been paid to anodic protection, since the anodes have often been working without edge masks and without stand-by current to protect the coating, the MMO coated titanium, anodes have shown excellent behaviour and no significant increase in operating anodic potential has been required indicating anode passivation has been avoided.

After removal of the anodes from the cell after the working campaign followed by careful flushing with water at elevated temperature to remove the sludge, no damage to the coating was observed.

Edge masks

The insoluble anodes have a fixed width. To process strips with narrower dimensions electrically insulating plates – so called 'edge masks' – are positioned to prevent the current from flowing directly between the outer parts of two anodes where the anode extends beyond the width of the strip being coated. This avoids so called 'white border' defects.

The strip edges pass within U-shaped sections formed on the vertical edges of the edge masks. The degree of coating of the edge of the strip depends on the depth of penetration of the strip edges into the U-shaped sections. Accordingly, it is necessary that the U-shaped sections accurately follow any lateral strip travel.

The edge masks must follow the strip side travel very precisely, the expected accuracy being less than 1mm. Inductive sensors moving with the masks are used to detect the depth of strip penetration and vary the edge mask position accordingly. The working principle of the system is depicted in **Fig 3**.

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

Fig 6 Insoluble anodes in the rack during MMO coating

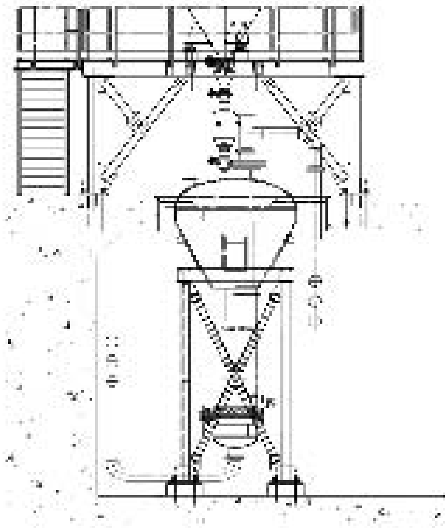

Fig 7 Tin dissolution reactor

– two pairs of edge masks (one at operator side, one at motor side) made of an epoxy glass are driven as a pair by one servo-cylinder. The masks are driven 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 accessibility and corrosion resistance.
– two servo-cylinders with linear transducers;
– two strip edge detection sensors designed to resist a maximum temperature of 80°C, and not affected by dirt, humidity or metallic particles.

Edge mask control is obtained by means of a local PLC communicating constantly with the line's PLC. Communication is needed mainly to track the position of the weld joining the tail of the passing strip to the head of the next, so that edge masks can withdraw as the thicker weld area passes through the plating cells to prevent damage to the mask. The edge mask is also opened when the line is stopped or when the line speed is below a threshold value of 30m/min.

Communication between the two PLCs also provides information on the strip width for the local PLC. Once the strip width is known, only one strip edge sensor is needed to detect the position of the edge of the strip 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 the case of a failure of one of the sensors, an alarm is activated when the absolute distance of the masks is less than the strip width.

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

Two different edge masks configurations were developed by Tenova in the past 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 operation activities. Thanks to the new design it is possible to remove all supports inside the plating tanks and so permit easy access to the edge masks and to the anodes for maintenance.

Strip edge sensors of 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 ±1mm for both sides.

Tin dissolution

The main reactions involved in the dissolution process of metallic tin and its oxidation to ionic form 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 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 built to feed the insoluble anodes electrolytic cells of the electro tinning line of Ternium Siderar in S Nicolas, Argentina is shown in **Fig 5**.

The plant consists of: a chemical reactor, a pressurising pump, oxygen feeders with improved design and a tank for the recirculation and storage of the solution.

The reactor is a vertical cylindrical vessel, divided in two parts: the upper part has a larger 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 via an oxygen feeding station able to guarantee the maximum dissolution of oxygen gas in accordance with Henry's law.

The dissolution rate of the tin is controlled by the flow rate of the oxygen. The plant control system can automatically calculate the oxygen flow rate needed to dissolve the same amount of tin which has been lost to the electrolyte through plating out on the strip in the cells, this depending on the current provided by the rectifiers. Thus a constant concentration of tin is maintained in the plating solution.

Operating results

The electrolyte replenished in the dissolution plant fully complies with the requirements of the tinning line and important operational and maintenance practices have been defined.

According to Ternium Siderar, the most promising aspects of using insoluble anodes are:
– improved strip quality related to the elimination of chronic defects, such as white edge and anode marks;
– elimination of anode handling,
– more flexible campaigns in terms of strip width programming, since the edge masks can adapt to all strip widths.

Moreover, the dissolution plant enables better control of the tin concentration in the electrolytic solution fed to the line.

Insoluble anodes for China

Tenova is currently supplying a complete new electrolytic tinning line in China, with a capacity of 250kt/y which will operate at a process speed of 550m/min. This is equipped with insoluble anodes and associated tin dissolution plant, and also the edge mask system. The plant is expected to start operations in 2009.

The high plating production rate made it necessary to supply nine plating cells, each having four sets of insoluble anodes – on the up and down passes, to coat the top and bottom surfaces of the strip.

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

Three tin dissolution reactors are foreseen, each of them as shown in **Fig 7**. The tin granules, shipped in boxes or large bags directly from the tin producers, will be charged into a receiving bin supported on load cells. From there, by means of a rotating star valve they will fall by gravity into the reactor. Two dome valves open to charge the reactor with the tin pellets without stopping the pumps.

Because of the vicinity of the reactor to the main line recirculation tanks, the two recirculation tanks (one on stand by) properly dimensioned, will double up as dissolution reactor recirculation tanks, thus increasing the turbulence in the tanks.

A fully automatic filter station will keep the level of solid particles in the electrolyte at a level below 1g per litre.

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 ArcelorMittal (the Avilès facility) in Spain and to Erdemir (Eregli) in Turkey. ■

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