INTRODUCTION

Tenova, a long time supplier of Electrolytic Tinning Lines developed a new Insoluble Anode Tin Plating System and Low-Sludge Tin Dissolution Process.

The application of Tenova insoluble anode technology minimizes the amount of sludge produced and hence the loss of tin. Other benefits 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 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.

This tin dissolution process technology was first installed on an industrial line at Ternium Siderar, with testing carried out through 2004. Further refinement to this technology followed in subsequent years, culminating in Tenova’s most recent Tinning Line reference for Jiangsu Sunshine in Dajiang, China, which was commissioned in September of 2011.

The paper describes the start-up and commissioning of the Dajiang Electrolytic Tinning Line as well as the results reached in tinplate produced with Insoluble Anodes and Low Sludge Tin Dissolution.
LAYOUT OF THE LINE

The Dajiang Tinning Line produces 250,000 mt/year of tin plate for sale on both the local and the export markets.

Main Characteristics of the Line
Material to be processed: Cold rolled annealed and tempered low carbon steel, Single Reduced (SR) & Double Reduced (DR)
Final use: Food & Beverage Cans and Packaging
Strip Thickness: 0.15 to 0.55 mm
Strip Width: 700 to 1250 mm
Entry/Exit Section Line Speed: 700 m/min
Process speed: 550 m/min
Tin Coating Weight: 1.1 to 11.2 g/m²
Plating Electrolyte: PSA-ENSA
Oil: DOS 2.0 to 12 mg/m² per side

Entry Section
A double pay-off reel configuration is used with automated coil loading and electromagnetic threading conveyors to eliminate operator contact with the strip. Two thickness gauges with a double cut shear and scrap removal system provide automatic head and tail end strip cropping. A narrow lap seam welder with pre-loader are used to join the tail of the running coil to the new lead end of the next coil. An edge notcher prepares the welded joint for width adjustments at the side trimmer in the case of different strip widths. A side trimmer and edge scrap baller are provided prior to the entry loop tower. The edge trimmed scrap is automatically threaded into the scrap baler without operator intervention.
A double entry loop tower with 52 strands and 17.35 meters carriage travel provide strip storage allowing not only for continuous process operation during coil loading, but also for notching and side trimmer adjustments during width changes. The double loop tower include entry, exit, and intermediate strip steering as well as roll helper drives to reduce strip tension build up due to roll bends.

Overview of the Tinning Line
Process Section
The process section begins with the alkali cleaning section, consisting of two vertical alkali dunk tanks, two grid to grid type electrolytic cleaning tanks and two rinse tanks. The Tension Leveller is located after electrolytic cleaning and prior to the electrolytic pickling section. This location reduces the contamination entering the leveller and extends the leveller roll life.

The tin plating section consists of ten vertical electrolytic tin plating tanks, with eighteen plating passes followed by two drag-out/rinse tanks. Each of the plating passes include insoluble anodes constructed of mixed metal oxide coated titanium and edge masks. Because the insoluble anodes are a fixed width, it is necessary to use an edge masking system to accommodate different widths of strip.

The new generation of edge masks are designed to eliminate the center supports that restrict access to the plating cells. The edge mask supports and positioning mechanism are cantilevered from outside the plating cells and located below removable access plates under the walkway.
The tin reflow section incorporates a combination of conduction and induction to heat the strip above 240°C. The conduction system provides the initial heating exploiting the economic advantage of the conduction heating. The strip then passes through an induction coil for the final heating, quickly bringing the strip through the tin melting point, thereby reducing the chances of wood grain defects on the lighter coating weights. After reflow the strip is then chemically treated with a sodium dichromate solution followed by a vertical electrostatic oiler.

Exit Section
The exit section includes a vertical two side surface inspection system followed by a pin hole detector. A rotary drum shear is provided which allows taking samples from the line without stopping the exit section. TO BE CHECKED
Tin Dissolution Plant

The heart of the Insoluble Anode Tin Plating System is the Tin Dissolution Reactors. This 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. Tenova’s system incorporates a proprietary oxygen injector, and a control which precisely manages the oxygen injection rate, the electrolyte flow rate and pressure, the level of the fluidized bed, and the rate of tin pellet additions. This patented system results in total tin sludge not greater than a conventional soluble anode tin plating system.

The Dajiang Tinning Line utilizes three tin dissolution reactor, each with a nominal capacity of 130 kg/hr. However each reactor can operate between 60 and 160 kg/hr.
COMMISSIONING OF THE LINE

The commissioning of the line started with the calibration of the tin dissolving reactor in terms of Tin charge monitoring. The charge inside the reactor is continuously measured by a differential pressure transmitter being the pressure drop depending on the height of tin level.

### Calibration $\Delta P$-Sn inside reactor

<table>
<thead>
<tr>
<th>Flowrate (m$^3$/h)</th>
<th>Sn in reactor (kg)</th>
<th>$\Delta P$ (mbar)</th>
<th>Flowrate (m$^3$/h)</th>
<th>Sn in reactor (kg)</th>
<th>$\Delta P$ (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_1$</td>
<td></td>
<td></td>
<td>$X_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>200</td>
<td>2000</td>
<td>374</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>370</td>
<td>3090</td>
<td>563</td>
<td></td>
<td></td>
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<tr>
<td>3090</td>
<td>558</td>
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<td>4500</td>
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</tr>
<tr>
<td>$X_2$</td>
<td></td>
<td></td>
<td>$X_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>365</td>
<td>2000</td>
<td>378</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3090</td>
<td>560</td>
<td>3090</td>
<td>565</td>
<td></td>
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<tr>
<td>3990</td>
<td>710</td>
<td>3990</td>
<td>715</td>
<td></td>
<td></td>
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<tr>
<td>4500</td>
<td>800</td>
<td>4500</td>
<td>801</td>
<td></td>
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</tr>
</tbody>
</table>

The first step was the production of the electrolyte because one of the main advantages of the insoluble anodes is the possibility to create the electrolyte at the required concentrations without the necessity to store “already made electrolyte” very often concentrated, with proper recipes representing an incontinence for the operators.

**Utilities necessary:**
- Demineralized Water
- Oxygen
- Commercial PSA
- Commercial ENSA
- Metallic tin in Pellets

**Tinplate electrolyte:**
- $30 \text{ g/l } \text{Sn}^{2+}$
- $15-20 \text{ g/l } \text{H}_2\text{SO}_4$ equivalent
- $5 \text{ g/l ENSA}$

During four working 8-hours shifts, starting from a speed of 60 kg/h approx., 100 m$^3$ of tinplate electrolyte were produced with only one reactor in operation. The details are shown in the following table.

<table>
<thead>
<tr>
<th>$v_{\text{dis}}$ (kg/h)</th>
<th>1$^{\text{a}}$ day</th>
<th>2$^{\text{a}}$ day</th>
<th>3$^{\text{a}}$ day</th>
<th>4$^{\text{a}}$ day</th>
<th>tot</th>
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</thead>
<tbody>
<tr>
<td>60-66</td>
<td>5.67</td>
<td>1.39</td>
<td></td>
<td></td>
<td>7.06</td>
</tr>
<tr>
<td>65-70</td>
<td></td>
<td>0.66</td>
<td></td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>80-88</td>
<td></td>
<td>2.17</td>
<td></td>
<td></td>
<td>2.17</td>
</tr>
<tr>
<td>100-110</td>
<td></td>
<td></td>
<td>3.00</td>
<td>2.06</td>
<td>5.06</td>
</tr>
<tr>
<td>120-130</td>
<td></td>
<td></td>
<td>0.53</td>
<td>5.92</td>
<td>6.45</td>
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<tr>
<td>130-140</td>
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<td></td>
<td>3.91</td>
<td>9.83</td>
<td>13.74</td>
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<tr>
<td>136-150</td>
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<td></td>
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<td>0.21</td>
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<tr>
<td>145-160</td>
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<td></td>
<td>1.73</td>
<td>1.73</td>
<td>3.46</td>
</tr>
<tr>
<td>150-165</td>
<td></td>
<td></td>
<td>0.97</td>
<td>0.97</td>
<td>1.94</td>
</tr>
<tr>
<td>tot</td>
<td>5.67</td>
<td>7.22</td>
<td>8.53</td>
<td>6.82</td>
<td>26.24</td>
</tr>
</tbody>
</table>
A comparison between calculated and real charge inside the reactor during 9 hours of operation is shown here-above. The lines are parallel.

Laboratory analyses for Sn$^{2+}$ and PSA in the electrolyte were carried out every 1-2 hours. The production was stopped when 30 g/l of Sn$^{2+}$ were reached.

The filter was ready to start but no need of it both during the preparation of the electrolyte and the first weeks of production. Always the electrolyte was seen with very negligible amount of sludge in the bottles of samples, even after hours of settling.

The tin pellets were available in large bags, 1 mt capacity each, lifted by crane on the top of the reactor and charged inside the hopper on the top of the reactor. The cut of the bag is the only manual operation to be performed on the plant.

A proper warning advices the operator of the necessity to make a tin charge: the operator at the pulpit has only to push the “charging” pushbutton.

When the line was ready for the operation, the first coil was charged obtaining tinplate of commercial quality.
ADVANTAGES OF INSOLUBLE ANODES VERSES SOLUBLE TIN ANODES

With conventional soluble tin anodes it 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 control of the tin concentration in the plating solution is the insoluble anode and many producers 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 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.

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.

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Anodes & Current Distribution

Soluble Sn anodes

Insoluble Ti anodes

Coating Weight Distribution along Strip Width

Coating Weight Distribution along Strip Width
The solution to these problems is to equip the tinning line with insoluble anodes. They have a continuous surface and therefore very thin tin coating layers can be produced with high thickness homogeneity.

Very much higher tinplate production is possible with insoluble anodes mainly in countries where unions impose to slowdown or stop the line while inserting and regulating the tin anodes in the cells.

No operators are anymore necessary continuously along the plating section and no people for tin anodes casting.

Some figures are shown herebelow

**NEEDS for SOLUBLE & INSOLUBLE Technologies**

**NECESSARY FOR SOLUBLE**
- Tin anodes casting
- Tin anodes handling
- 2 people / Shift for tin anodes handling
- 2 people - one shift/day to make anodes
- 60325 anodes brought to the line
- 60325 anodes brought back to tin casting
- 10,7 min/h spent by operators around the line (TOSSIC FUMES) as minimum
- 18% less production if stop the line during changing anodes (SAFETY) (-44747 t/y)
- 14% less production if slow done the line up to 120 m/min during changing anodes (SAFETY) (-34006 t/y)

**NECESSARY FOR INSOLUBLE**
- Tin dissolving reactor
- Tin pellets handling
  - (1500 bags/y – 1,7 bags/shift)
- No additional person for Tin pellets handling –
- No operators around the line (only for check)
- From 7 to 11 people less

A healthy and safety operation is much easier with insoluble anodes

Tinning with insoluble anodes requires a tin dissolution reactor connected to the electro tinning line to replenish the amount of tin deposited on the strip.

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.
Unfortunately, the chemical process of tin dissolution also produces a Sn$^{(IV)}$-based sludge. The critical point of the electrolytic lines with insoluble anodes is the tin loss, in the past higher than 10% of the dissolved tin. This is the reason why the tinplate process with insoluble anodes found resistances.

Tenova, in strict cooperation with his connected Italian research centre CSM (Centro Sviluppo Materiali), developed an innovative process for dissolving tin which is able to minimize the amount of sludge and loss of Sn.

**INSOLUBLE ANODES**

Inert Titanium based anodes with an active precious metal coating (of Ru, Ir, Sn and/or Ta oxides) have been used for this application.

The insoluble anodes are vertically positioned in a vertical cell containing the 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](image)

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 therefore 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.

**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](image)

Edge mask control is obtained by means of a local PLC communicating constantly with the PLC of the line. Edge masks open also when the line was stopped or when the line speed was below a threshold value (30m/min). The strip edge position was monitored accurately by the inductive sensors and edge mask drives regulated the mask position accordingly.