



Improving the quality of tinned steel using a novel technique to study the effect of industrial process parameters

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Synopsis

Tin plating operations are of a complex nature due to the many operational variables that need to be controlled in order to create a product of required quality.

The work in this report lays the basics for the control of a halogen plating operation based on the DuPont tinning set-up with regard to the chemical make-up of the plating solution, as well as operational variables such as temperature and current density.

To evaluate these aspects of the process, a rotating cathode Hull-cell set-up was used.

This allowed for a laboratory scale plating arrangement that simulates industry closely with regard to chemical and hydrodynamic considerations. Typical industry accepted standards were obtained for the values of operational variables and a 'baseline' test was conducted employing these standards. All subsequent tests conducted were benchmarked against this baseline result. A large suite of results was obtained in which it was found that changes could be made to the industry accepted norm which would improve on the stability of the operation and therefore the quality of the final tin-plated product. Examples of these results are: an increase in stannous tin concentration, an increase in sodium chloride concentration and a slightly elevated plating temperature. In addition, conditions were found that must be avoided to prevent instability and poor product quality.

Introduction

There are a number of techniques that have been developed over the years that take advantage of the chemistry of tin electrodeposition. Techniques such as the Ferrostan Process (ITRA Ltd (Tinning Panel) 2000), a methane sulphonic acid (MSA) electrolyte, and the technique that will be discussed in this report, the Du Pont Process, which uses a halogen electrolyte (De-Nemours 1976).

The chemical complexities of the halogen process are herein investigated with a hope that some quantification can be made of the effect that each one of the various components exhibits on the final product. One of the greatest benchmarks of tin plate production is the aesthetics of the final product. Therefore a better understanding of the effect of production variables can lead to a more consistent quality standard, less reject material, and, ultimately, a higher profit margin.

The use of tinning

Due to qualities such as strength, corrosion resistance, good weldability and formability, printable surface and non-toxicity, tinning has found its largest market in the food and beverage packaging industry. (ITRA Ltd (Tinning Panel) 2000). Tinning is, however, also used for many other packaging purposes such as paints, powders, waxes, oils and so on.

Tinning process—Du Pont halogen process

This process, described by E.I Du Pont De Nemours and company in 1967 (Nemours 1967), is designed specifically to produce a high quality tin coating on strip steel substrate at high production speeds (Steinbiecker n.d.). The process is made continuous by welding the tail end of one strip to the leading end of the next strip to be processed (ITRA Ltd (Tinning Panel) 2000). The line also incorporates a pickling section just before the strip is plated, a reflow tower, passivation tank, and oiling station after the strip has been plated.

The horizontal plating bath arrangement allows for differential coatings (Steinbiecker n.d.), i.e. differing coating weights on either side of the plate as the sides are plated separately (Opaskar 1997). Also, less break-off and tearing occur than with vertical setups. High current density and a wide current density operating range with low applied voltages are also of benefit to be gained in the Du Pont process (De-Nemours 1976).

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As can be seen in Figure 1, the tinning line consists of three tiers. The first two decks contain plating cells and the top deck consists of rinsing tanks for electrolyte recovery and drying equipment (ITRA Ltd (Tinplate Panel) 2000). Once the plate has passed through the three tiers it is sent off to the reflow tower for flow brightening and the chemical treatment for chromium passivation (ibid).

Reflow melting, originally used to improve the appearance of the plate only (Nemours 1967), is carried out at a temperature of 475°C to improve the corrosion resistance of the tinplate (ibid).

Substrate steel preparation techniques

The preparation of the steel basis as substrate material is a complicated process about which much literature is available. It will not be discussed in detail here. Given here is a general overview of the various processes that the steel plate undergoes before being fed into the electroplating line, as seen in Figure 2.

Cast steel

Typically, a low carbon steel is utilized in electroplating. (ITRA Ltd (Tinplate Panel) 2000) Today, this steel is largely produced by the basic oxygen steelmaking process and is metallurgically balanced to have good formability and mechanical properties (ibid).

A continuously cast steel slab exhibits less chemical segregation within the structure than that produced in ingot casting. The steel is delivered to the hot rolling section in a fully killed condition.

Hot rolling (not shown in Figure 2)

Cast slabs are reduced in a roughing stage and a finishing stage respectively from an initial 250 mm down to a final gauge thickness of around 1.6–3 mm (ITRA Ltd (Tinplate Panel) 2000). Scale developed during hot rolling needs to be removed before the strip can be passed on to cold rolling. This is achieved as shown in Figure 2 in a pickling stage.

Cold rolling

Modern tinning practices use a cold rolled steel strip as substrate material. During this rolling, up to 90% reduction is carried out. Rolling most often is carried out on a five stand mill, in a four-high roller configuration. There are, however, plants that utilize four and six stand rolling circuits (ITRA Ltd (Tinplate Panel) 2000).

Annealing

The intense reduction steps carried out on the steel strip during rolling has the effect of work hardening of the steel such that the strip becomes harder and less ductile. An annealing process effectively restores this ductility. The

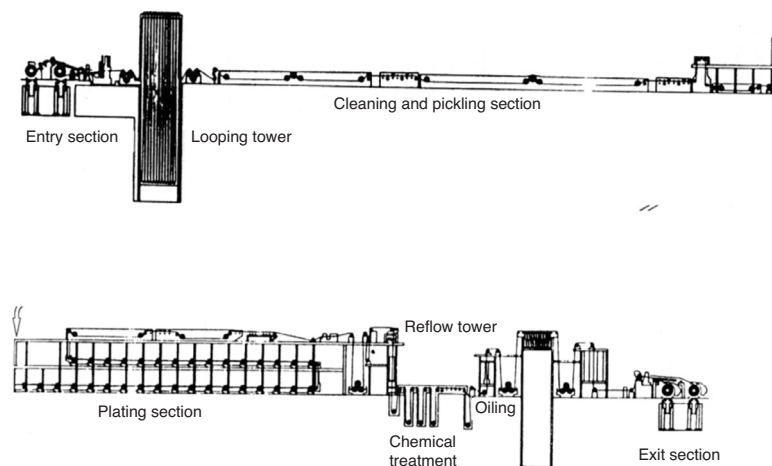


Figure 1—Schematic layout of the Du Pont process halogen tinning line also showing the exit section (ITRA Ltd (Tinplate Panel) 2000)

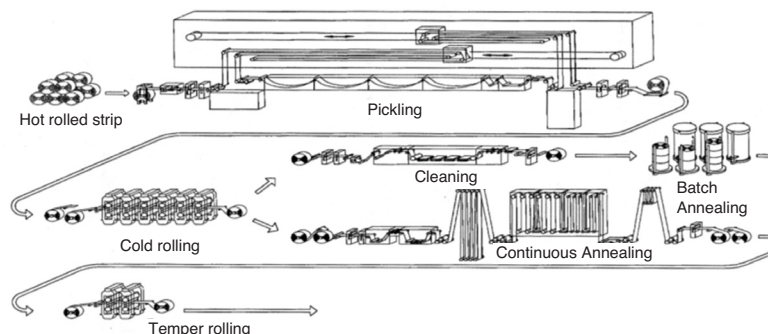


Figure 2—Schematic layout of the steel strip preparation process (ITRA Ltd (Tinplate Panel) 2000)

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annealing process is carried out in a furnace, the interior atmosphere of which is slightly reducing to prevent oxidation of the strip (ITRA Ltd (Tinplate Panel) 2000).

Temper rolling

To reimpart mechanical strength to the steel that has been softened through annealing, as well as creating a required surface finish, the strip is passed through a two stand temper mill. This process is conducted without the use of lubrication and reductions of approximately 0.4 to 5% are obtained (ITRA Ltd (Tinplate Panel) 2000).

Pickling

This process removes any oxides present on the strip as well as etching the steel surface, which allows for better tin deposition (ITRA Ltd (Tinplate Panel) 2000). The pickling is carried out in an acidic medium with the strip being made anodic and then cathodic. Current densities of between 5 and 30 A/dm² are used (ibid).

Electroplating

Figure 3 shows the schematic set-up of a typical electro-chemical plating cell. The part of the circuit of interest is the plating bath itself. In this section of the circuit, electrons are conducted between the cathode and anode by charged metal ions (Hayes 2003) in the plating solution according to the following set of equations:

At the cathode: $M^{n+} + ne^- \rightleftharpoons M \rightleftharpoons$ (This is where plating occurs)

At the anode: $M \rightleftharpoons M^{n+} + ne^-$ (If soluble anodes are used)

$H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$ (If insoluble anodes are used).

There exist two options for the anodic reaction. In the case of the anode being of the same metal with which the cathode is to be plated, the anode is sacrificial and dissolves (Kanani 2004), thus releasing metal cations into solution. In the second option, the anode is dimensionally stable and does not dissolve (ibid). Under such conditions, the metal to be plated at the cathode is supplied directly to the bath in the form of metal salts (ibid).

The plating process can be executed under various kinetic regimes, namely: activation control, diffusion control, or a mixed control regime. This factor will largely determine the quality of the plated surface. This phenomenon can be explained by looking at the kinetics of the system and considering diffusion boundary layer theory (see Figure 4).

As long as diffusion of the metal cations is not the rate limiting step in the plating reaction, i.e. the cations diffuse through the boundary layer and arrive at the cathodic surface faster than they are plated onto the cathode, the system is said to be under activation control and an increase in current density will lead to an increase in plating kinetics. (Kanani 2004). Further, a high quality, homogeneous layer will be deposited. At the point at which the cations are plated onto the cathodic surface faster than the cations can diffuse through the boundary layer and reach the surface, i.e. the area surrounding the surface becomes depleted in metal cations, the system is under diffusion control, thus an increase in current density will have no further effect on the

plating rate. Side reactions such as H₂ evolution, however, will occur on the surface and the deposit will become disrupted in areas, thus decreasing the overall quality of the plated surface (ibid).

Boundary layer thickness plays a crucial role in diffusion rates. This relationship is described by Fick in the formulation of his first law of diffusion (Fogler 1992) and is as follows:

$$j_A = -D_A \frac{\Delta C_A}{\delta} \quad [1]$$

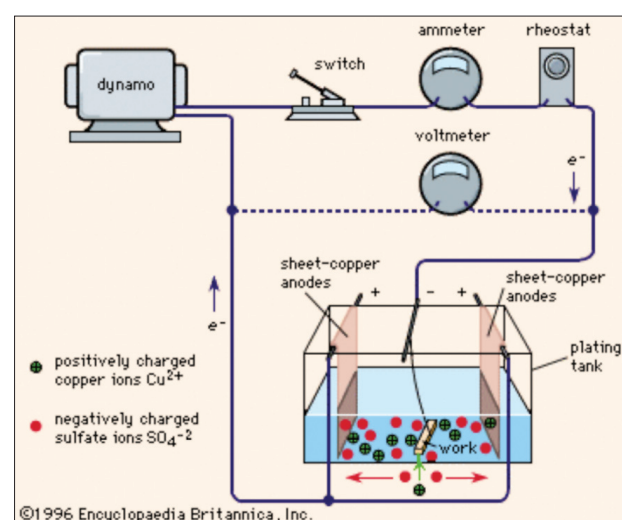


Figure 3—Schematic illustration of a plating cell set-up. (Encyclopaedia-Britannica 2009)

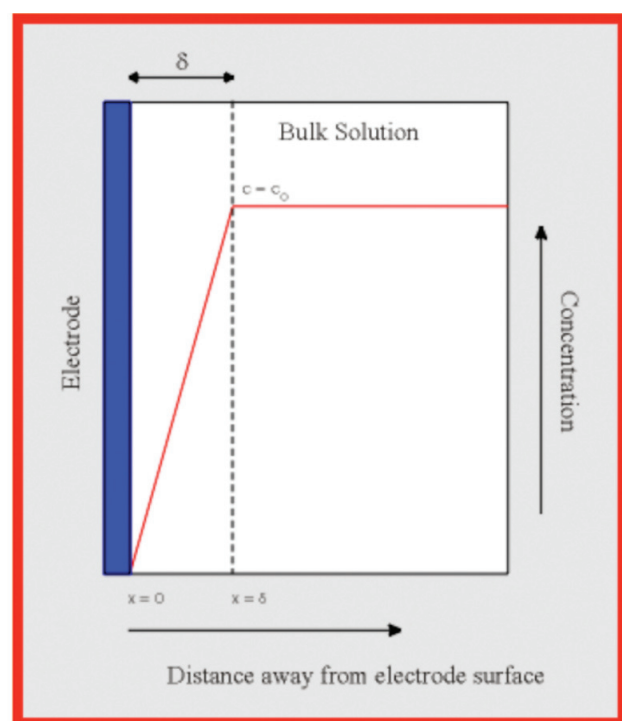


Figure 4—Schematic illustration of the diffusion boundary layer. (University of Paisley 2009)

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where:

- j_A = Molar flux
- D_A = Diffusion coefficient of diffusing species
- $C_A = (C_b - C_s)$ concentration of diffusing species (C_b = bulk, C_s = surface)
- δ = Diffusion layer thickness

So, a decrease in diffusion layer thickness will result in a greater molar flux, or otherwise for constant molar flux, a greater concentration of diffusing species at the reaction surface. As the cathode moves through the electrolyte, which is continually pumped through the plating cells, relative movement between the bulk solution and the cathode surface is imparted (ITRA Ltd (Tinplate Panel) 2000). This solution movement effectively reduces the boundary layer thickness (Landolt 1994) and by the above description, increases the concentration of the diffusing species at the plating surface. This will allow higher current densities to be employed while still maintaining plating under activation control.

The halogen process

The aim of this paper is to investigate the effects that the chemistry and operational variables of such a plating bath have on the quality of a tinned steel substrate. The effect that each chemical constituent has on the overall performance of the plating cell will also be listed as other research has revealed.

The halogen tinning operation is a very complex one and much attention must be given to the chemical composition and condition of the plating electrolyte. (Steinbiecker n.d.) The electrolyte consists of the following chemicals (De-Nemours 1976):

- Stannous/stannic tin
- Sodium ferrocyanide
- Sodium bifluoride
- Sodium chloride
- Hydrochloric acid
- Flow-brightening agents.

Stannous tin

The source of tin for electrodeposition within the plating bath comes from the stannous tin ion (De-Nemours 1976). Low levels result in quality defects such as porosity and/or poor surface coverage of the tinned steel substrate. The stannous tin originates from the dissolution of the sacrificial tin anode. Due to differences in the cathode and anode current efficiencies, a slight excess of stannous tin will be maintained in the plating bath (ibid). Additions of stannous chloride can be made if required (ibid).

The stannous tin undergoes an unwanted oxidation reaction with ferric ions present in solution to form the stannic tin ion (Steinbiecker n.d.). This is discussed in more detail under the section on sodium ferrocyanide. The stannic tin ion forms a metastannic acid, which precipitates out of solution as an insoluble tin compound and is therefore unavailable for tin electrodeposition (Opaskar 1997).

Sodium bifluoride

As the steel strip enters the lower plating tier, the bottom of the strip is plated while the top strip is wet with plating solution and exposed to the air (Opaskar 1997). This results in the oxidation of iron from the top side of the strip before it

is in turn plated on the second plating tier (Steinbiecker n.d.). To minimize the iron oxidation, the bath is operated at a relatively low pH i.e. approximately pH = 3.8. This, however, results in a further problem. At these low pH levels, hydrolysis of the components and subsequent solid precipitation becomes a major issue (ibid). To stabilize the bath, large amounts of fluoride salts are added to the bath. These fluoride salts form complex ions as follows:

- $\text{Sn}^{2+} + 2\text{HF}_2^- \rightleftharpoons \text{SnF}_3^- + \text{H}^+$
- $2\text{Sn}^{2+} + 3\text{HF}_2^- \rightleftharpoons \text{Sn}_2\text{F}_5^- + \text{HF}^- + 2\text{H}^+$

The complex tin ions then no longer hydrolyze, rather remaining in solution, available for electrodeposition (ibid).

Sodium ferrocyanide

The stannous oxidation reaction is catalyzed by any ferrous ions present in the solution (Steinbiecker n.d.). Thus, to remove any ferrous ions, sodium ferrocyanide additions are made to the bath to form iron precipitates (Opaskar 1997) according to:

- $\text{Fe}^{2+} + 2\text{Na}^+ + \text{Fe}(\text{CN})_6^{4-} \rightleftharpoons \text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$
- $\text{Fe}^{3+} + \text{Na}^+ + \text{Fe}(\text{CN})_6^{4-} \rightleftharpoons \text{NaFe}[\text{Fe}(\text{CN})_6]$ (known as Prussian Blue).

It is noted that the colloidal 'Prussian blue' ferrous solids are still able to take part in the oxidation reaction of tin but at a notably lower rate than would otherwise be observed. (Steinbiecker n.d.).

Sodium chloride

The role of sodium chloride in the plating bath is to ensure adequate solution conductivity (De-Nemours 1976). It also aids in the effective dissolution of the anodes (ibid). Finally, maintaining the correct chloride concentration in the bath will also maintain the stannic tin content at acceptable levels as the chloride concentration ensures proper dissolution of the soluble tin anodes (Steinbiecker n.d.).

Hydrochloric acid

The pH of the solution will increase slightly if no stannous chloride additions are made (De-Nemours 1976). However, under normal operation stannous chloride additions made to replenish stannous tin will decrease the pH sufficiently (ibid). In such situations where the pH is too high and the stannous tin concentration is within specification, hydrochloric acid additions are made to readjust the pH to acceptable levels.

Flow-brightening agents (polyethylene glycol)

The addition of a flow-brightening agent is to ensure that semi-bright deposits are made, which can then be brightened through flow-brightening (De-Nemours 1976). Without this addition, the deposits are found to be dull, granular, and exhibit poor coverage.

Other considerations

Two other operating variables that will be considered in this report are the plating bath solution temperature and the current density experienced by the moving steel strip cathode. Typically, the halogen tin lines operate with current densities as high as 65 A/dm² (ITRA Ltd (Tinplate Panel) 2000) and temperatures in the order of 58°C.

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Experimentation planning

Autolab Rotahull

Figure 5 below illustrates the Autolab rotating hull cell setup that was used for the experiments detailed below. The rotating cathode simulates the hydrodynamic nature of a typical industry sized plating operation.

Various current densities were measured along the length of the cathode with each run of the cell due to the varying distance from the anode to the cathode surface. Figure 6 demonstrates the relationship of current density and distance along the length of the cathode.

Experimental variables and considerations

The plating solution contains fluoride ions which corrode glass at a reasonably fast rate (De-Nemours 1976). So all glass labware was replaced with plastic equivalents. Where this was not possible, glassware that was used was rinsed with distilled water immediately after use.

Temperature control was achieved by using a heated water bath whereas pH control was managed by using a standard laboratory pH meter making adjustments for reading deviations incurred due to the elevated temperatures. Thus industry norm operational variables were effectively re-created and controlled.

Test solutions

Table I details the experiments that were carried out. The first experiment was with a solution identified as 'ideal' and its chemical make-up mirrored that in use in industry. Further experiments would vary the concentration of one chemical compound at a time. One test was in excess of the compound and the following with a lack of the compound of interest. The hydrochloric additions are not shown as their contribution to total volume was found to be negligible.

Rotational speed

All tests were carried out with the variable speed motor drive of the Rotahull test cell set to a value of 350 rpm. This speed, in correlation with the bulk solution stannous concentration and the current density, was selected to ensure that, under the 'ideal' solution chemistry, the plating operation would occur under activation controlled plating where the current density was constant over the entire length of the sample. The calculations were made using equations after Madore *et al.* (Madore 1995) and are shown below.

$$i_{lim} = 0.079 \ln \left(FCU^{0.7} d^{-0.3} \nu^{-0.344} D^{0.644} \right) \quad [2]$$

where:

- F = Faraday's constant (C/mol)
- C = Bulk concentration (mol/l)
- U = Peripheral velocity (cm/s)
- d = Cylinder diameter (cm)
- ν = Kinematic viscosity (cm²/s)
- D = Diffusion coefficient (cm²/s).

The current density to be used was calculated to be 6.67 A/dm². This is a setting of 1 ampere on the Rotahull

controller. Under these conditions, a section at least will be under activation controlled plating whereas other regions near the tip of the sample are likely to experience diffusion controlled plating. Therefore the effect of changing plating regimes could also be investigated.

Pre-plating procedure

This procedure was implemented to ensure that the steel surface to be plated was free of organic material such as grease and cutting fluid, as well as surface oxides that may have formed. Degreasing is accomplished by submerging the unplated sample in an EXTRAN MA 01 solution. Inhibited

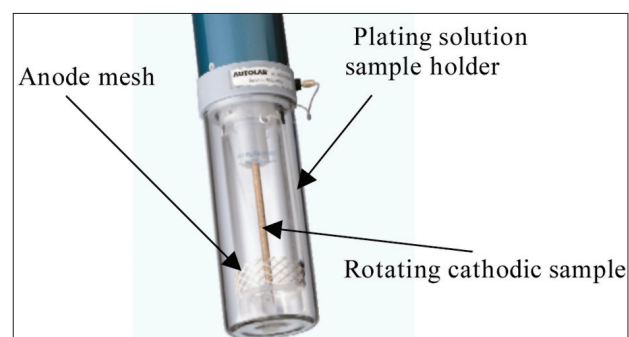


Figure 5—Autolab, rotating hull cell setup (autolab-instruments.com 2009)

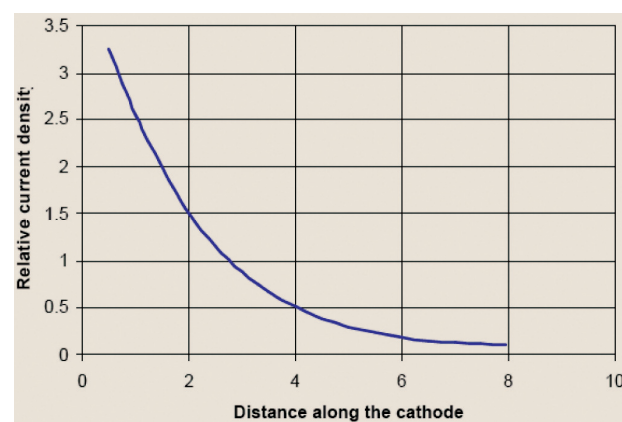


Figure 6—Graphical relationship between the current density and length of the rotating cathode (brinkmann.com, 2009)

	Chemical component Test	Within specs 'ideal' g/l
1	Stannous chloride (Sn ²⁺)	10
2	Sodium bifluoride (F ⁻)	25
3	Sodium ferrocyanide	3
4	Sodium chloride	32
6	Polyethylene glycol	4.3
5	Hydrochloric acid 25% (pH)	3.6
7	Temperature	58

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hydrochloric acid, HIBATEX is used to remove the surface oxides without damaging the underlying steel substrate. The sample was rinsed with distilled water and immediately assembled into the Rotahull for the respective test runs.

Post-plating treatment

Once the samples had been plated, they were removed from the rotating cell, rinsed with distilled water, dried, and stored in a dessicator until required for surface analysis.

General procedure outline

Except when stated otherwise, samples were plated at 58°C, at a current of 1 ampere and for a period of 5 minutes.

For the sake of repeatability, each solution was tested three times.

Surface analysis procedure

A metallographic analysis was carried out on the plated samples making use of microscopes at various magnifications to obtain relevant information.

Further, using a SEM analysis, an idea was gained of the extent of the surface coverage by the tin deposit during a specific run of the experimental set-up as well as phase identification. This allowed a correlation to be made between plating parameters and the type of deposit formed.

Experimentation

To ensure repeatable results, procedures were set up and followed for all major steps in the experimentation. They were: pre-plating, solution preparation, plating, post-plating. The pre- and post-plating procedures have already been discussed above. Solution preparation and the plating procedure are shown below in Table II and Table III respectively.

Analysis

The first analysis was carried out optically, based on the physical characteristics visible to the naked eye. Specific regions developed on the plated samples in which the tin crystal morphology differs.

A microscopic analysis followed which required metallographic sample preparation. Due to the fragile nature of the tin deposits in certain regions, the entire sample had first to

be mounted in cold mounting resin before sections were made at intervals of interest to obtain sub-samples of a size that could be used in a metallographic analysis.

A stereoscopic microscope was used to gain initial insight into the differing morphologies of the different regions along the length of the plated sample.

An SEM analysis was used to obtain results on the phase composition of the various plated components as well as plating thickness data of the regions.

Results

Tests conducted during this investigation were performed so that the effects of various disturbances to the accepted 'normal practice' of tin-plating could be observed. These disturbances are of both a chemical and physical nature. Table IV below indicates the tests conducted with the respective disturbance of interest.

A final test was conducted to analyse the 'ideal' conditions as described by typical industry practice.

As a rule of thumb, during electrochemical plating operations, no more than 10% of the metal of interest should be removed from the plating solution. This rule was tested based on values obtained from these experiments to ensure the significance of the results. It was found that no more than 6% of the original stannous ion was removed during the plating procedure.

Table II
Solution preparation procedure

Solution preparation		
No.	Action	Comment
1	Heat water	58°C
2	Ferrocyanide	All
3	Bifluoride	Half of.
4	Stir until dissolved	
5	Stannous tin	All
6	Bifluoride	Balance of.
7	Sodium chloride	All
8	Polyethylene glycol	All
9	Stir until dissolved	
10	Check pH and adjust if necessary	3.6

Table III
Plating procedure

Plating procedure		
No.	Action	Comment
1	Check polarity	Cathode
2	Start motor	
3	Set speed	350 rpm
4	Set current	1 Ampere
5	Stop motor	
6	Set timer	5 minutes
7	Pour solution into holder	
8	Insert sample into motor	
9	Attach cathode cylinder	
10	Connect cathode clip	
11	Place assemblage into holder	
12	Start motor	Test starts

Table IV
Test with respective parameter of interest

Test	Parameter
1	Stannous chloride (Sn ²⁺)
2	Sodium bifluoride (F)
3	Sodium ferrocyanide
4	Sodium chloride
5	Hydrochloric acid 25% (pH)
6	Polyethylene glycol
7	Temperature
8	Industry norm

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Morphological regions

There came to the fore the repeated appearance of a maximum of four distinct regions on each plated sample respectively (Figure 7). (In some cases only three regions were present) These regions were defined by optical appearance and variation in colouration of the deposit. Later, further distinction was made on the basis of morphology geometry, layer thickness, and the extent of substrate material coverage.

Optical results

Figure 8 below shows optical microscope photos of the various regions defined above. From these images it is clearly seen that Regions 1 and 2 display deposit growth originating from the steel substrate and subsequently extend outwards.

SEM results

Three phases were identified which were common to all samples analysed. These phases were: the steel substrate, a Fe-Sn alloy layer in continuous contact with the steel substrate, and, finally, in Regions 1 and 2, a seemingly pure Sn deposit initiating on the steel substrate and extending outwards. The spectra are shown for the two latter phases in Figure 9 and Figure 10 respectively.

Table V indicates the atom analysis of the Fe-Sn region and Table VI indicates the atomic analysis for the region of concern, namely, the tin growths.

The Au peak seen in the graphs originate from a conductive layer of gold deposited on the resin sample holder to facilitate conductivity of electrons during the SEM analysis.

The first set of SEM images shown in Figure 11 is that of Region 1 on the plated sample. Most important to note is the branched growths extending away from the steel substrate as well as the thickness of the layer in continuous contact with the steel substrate.

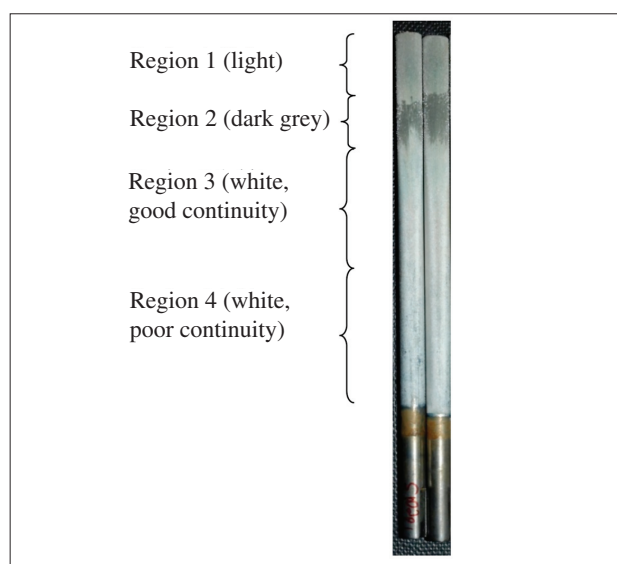


Figure 7—Samples plated under conditions defined by typical industry operation

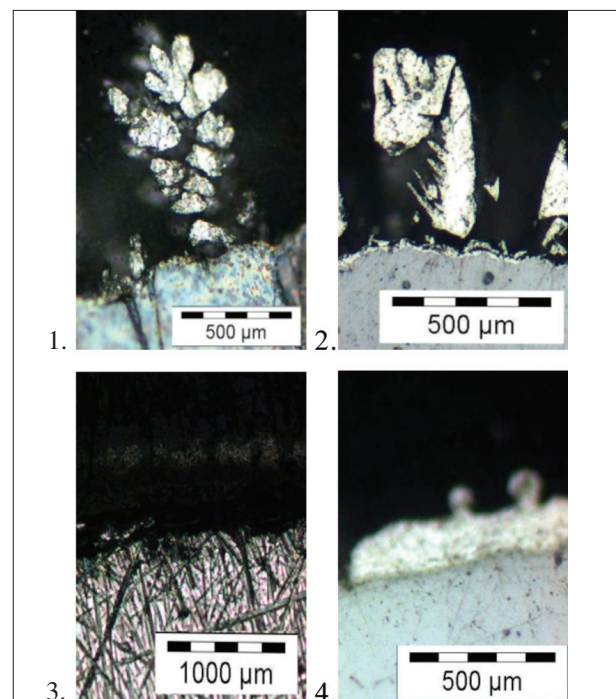


Figure 8—Optical microscope images of tin crystal growth in Regions 1 to 4 respectively

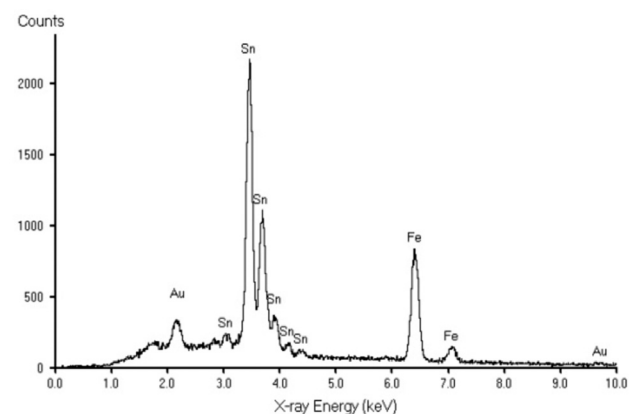


Figure 9—Spectrum and analysis showing composition of continuous Fe-Sn layer deposited on steel substrate

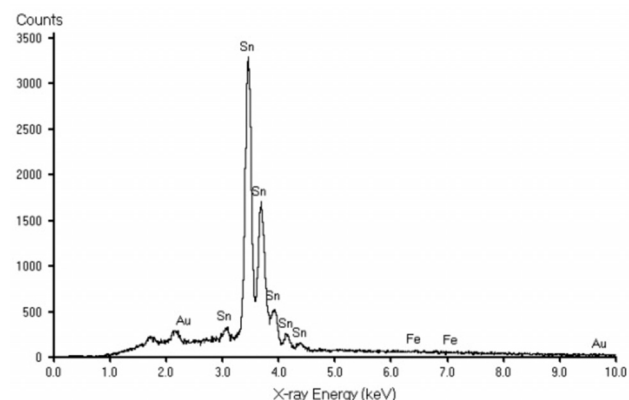


Figure 10—Spectrum showing composition of Sn growths extending from steel substrate

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Table V

Analysis showing composition of continuous Fe-Sn layer deposited on steel substrate

Element	Atom%	Wt%	Error %
Fe-K	58.4	39.8	2.1
Sn-L	41.6	60.2	2.7
Total	100	100	

Table VI

Analysis showing composition of Sn growths extending from steel substrate

Element	Atom%	Wt%	Error %
Fe-K	1.3	0.6	0.6
Sn-L	98.7	99.4	3.3
Total	100	100	

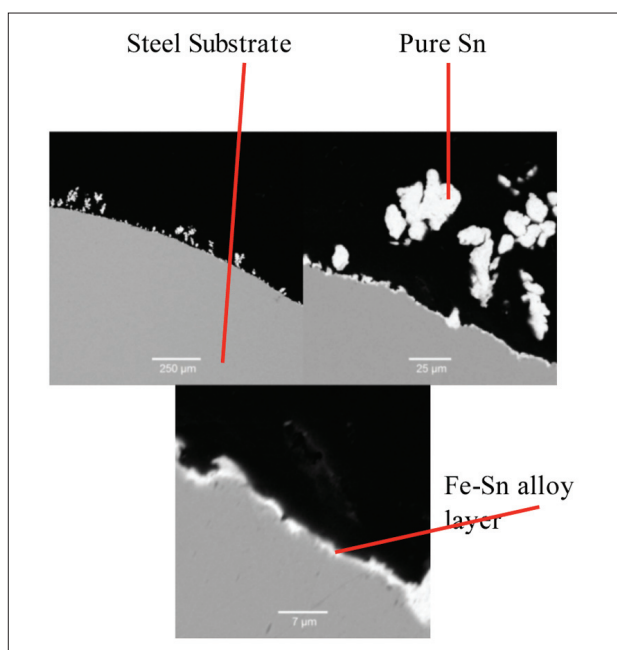


Figure 11—Region 1 SEM images showing deposit morphology and layer thickness

The extended growths appear along the entire length and circumference of Region 1 and extend roughly 100 µm from the plated surface. The continuous layer exhibits an average thickness of around 1.2 µm. Further, this layer disappears completely in small areas along the plated sample.

As with Region 1, Region 2 displays growths extending away from the steel substrate. However, the growths in Region 2 are not branched but exhibit a single blade-like appearance. Also, the growths appear to be slightly longer at an average length of around 120 µm. The continuous layer in Region 2 shows a more consistent coverage behaviour than that of Region 1 as well as being somewhat thicker at 1.4 µm. This is seen in Figure 12.

A number of significant differences come to light when viewing Region 3 in Figure 13. Firstly, no extended growths are observed in this region. The continuous layer nears actual continuity showing almost no breaks and, finally, this layer is much thicker than the first two regions, varying between 5 and 40 µm at the two extremes.

Figure 14 shows Region 4. Similar to Region 3, this region shows no extended tin growths but rather only the layer in direct contact with the substrate steel is present. However, it is noted that the continuity of this layer is greatly diminished compared to Region 3. This indicates poor coverage and thus a product of poorer quality.

Discussion on morphology

The continuous Fe-Sn layer bound directly to the steel substrate is responsible for the typical corrosion resistance characteristics of tin plate. Therefore this layer should be considered most important when one identifies the most attractive region under which plating should occur.

Regions 1 and 2 show very thin layers with intermittent breaks along the circumference of the sample. Region 4 shows a rather thick layer but again with intermittent breaks in the layer. Region 3, on the other hand, shows a mostly continuous layer of appreciable thickness at all viewed sites during this analysis. It is noted that in a typical plant in the industry, the tin plated product is exposed to a further heat

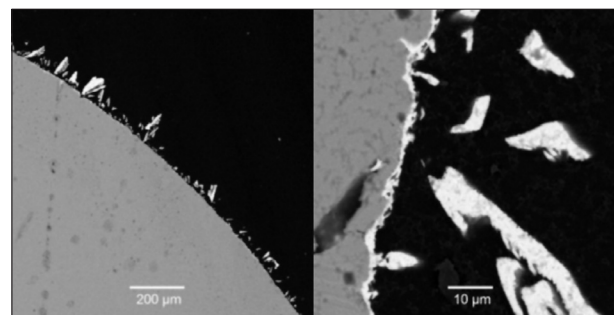


Figure 12—Region 2 SEM images showing deposit morphology and layer thickness

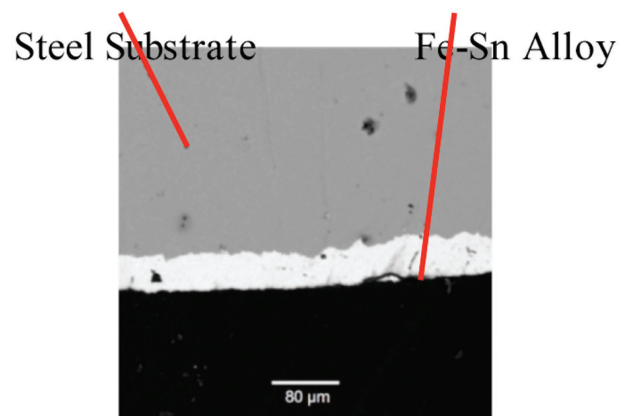


Figure 13—Region 3 SEM images showing layer thickness and lack of elongated growth

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treatment in which the layer of tin crystals is rapidly and partially melted and allowed to 'reflow' as it is known, before being quenched in water. This procedure allows for the 'patching' of any small breaks in the coating as well as producing a smooth, high gloss final product.

Further, any tin deposited elsewhere than in the continuous layer is lost due to further processing. This results in a lowered plating efficiency.

Occurrence of regions

For Figure 15 below, a greater length reading in any given region would indicate a higher stability for that specific region under given conditions. So, during all tests it is clear that Regions 3 and 4 are more stable than the other regions for any given set of conditions.

Figure 16 below gives the length of Region 3 as it appears on each plated sample respectively, relative to the length observed on the sample produced under typical industry operations. The last is represented by the value 1. In this way the effect of various changes to the plating procedure results in a Region 3 length being either less than or greater than 1.

Current density considerations

Figure 17 shows the current densities over which a plating operation could be conducted to ensure the formation of Region 3 type deposits. To obtain a better perspective, Figure 18 shows these current density ranges relative to the 'ideal' plating conditions. Differing current densities are

required to change the thickness of the deposit on a given substrate strip. That is, a higher current density will result in a thicker deposit. Conversely, a lower current density will result in a thinner deposit. Therefore, a greater current density range over which acceptable tin deposits can be produced results in a wider range of thicknesses, and so a larger range of products from the manufacturer.

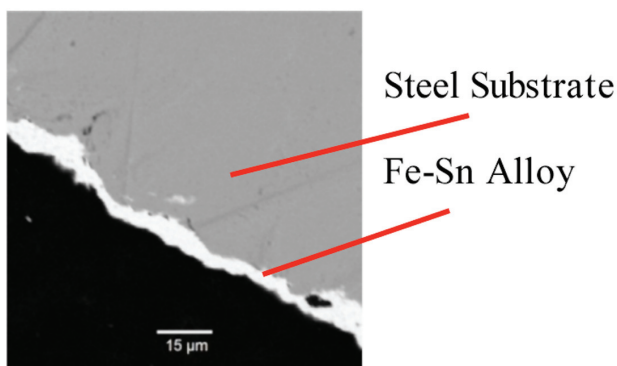


Figure 14—Region 4 SEM images showing layer thickness and lack of elongated growth

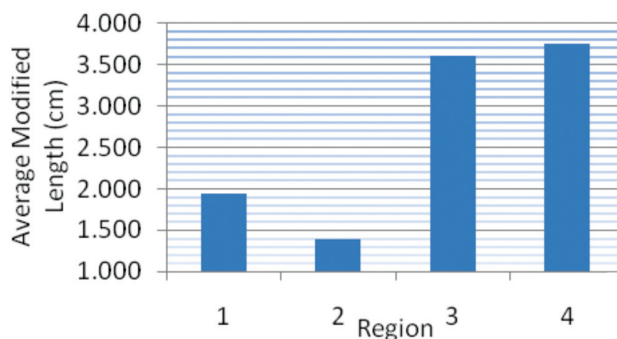


Figure 15—Average modified lengths of regions

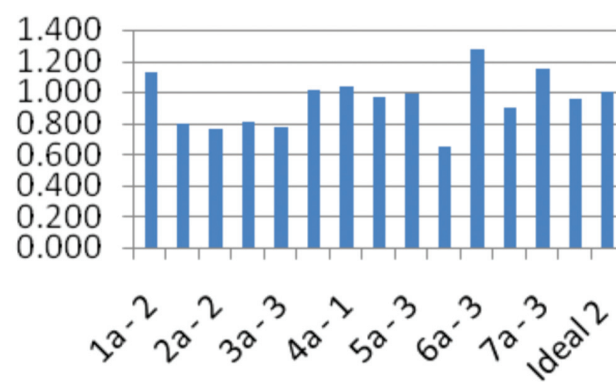


Figure 16—Region 3 length per sample relative to that observed on the 'ideal' sample

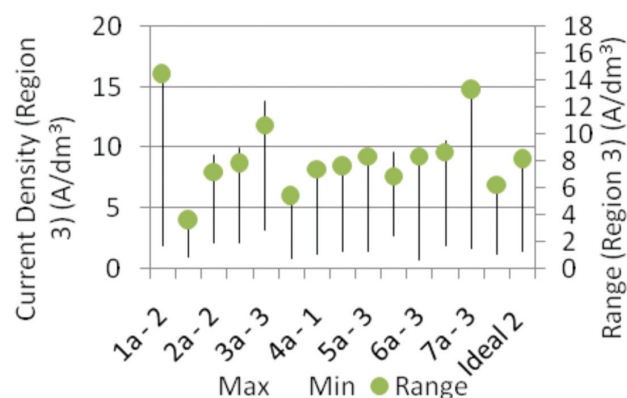


Figure 17—Current density range over which Region 3 is present on each sample respectively

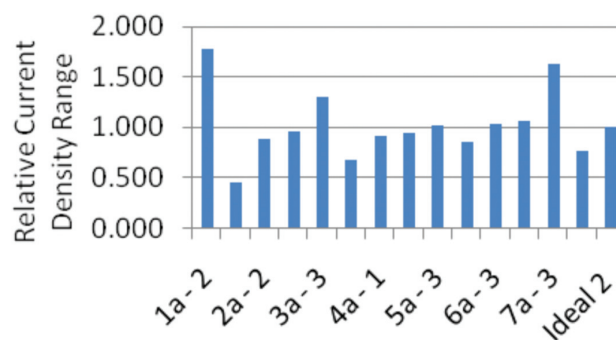


Figure 18—'Window' of current density over which Region 3 appears relative to 'Ideal' sample

Improving the quality of tinned steel using a novel technique

Table VII

Effect of plating bath components on Region 3 type deposits

Component	State	Relative Region 3 type deposit	Relative current density range
Stannous tin	Excess	1.126	1.77
Sodium bifluoride	Excess		
Sodium ferrocyanide	Excess		1.301
Sodium chloride	Excess	1.036	
pH	Excess		1.019
Polyethylene glycol	Excess	1.271	1.024
	Lack		1.058
Temperature	Excess	1.149	1.626

Discussion on plating variables

Setting the industry norm conditions as a benchmark against which the other results were compared allows one to make the following observations about the chemical constituents that make up the typical halogen tin plating bath solution.

A solution with an excess of stannous tin, sodium chloride or polyethylene glycol shows improved plating characteristics, i.e. a larger portion of the plated sample shows Region 3 type deposits. The excess of stannous tin also allows for a greater current density range to be employed. This makes sense from an electrochemical point of view as the tin concentration is increased. The polyethylene glycol has little to no effect on the current density range, whereas the sodium chloride decreases the 'safe' range over which Region 3 type deposits can be formed. Further, an increase in temperature has the effect of increasing the likelihood of Region 3 formation and allows a greater 'window' of current densities to be used to achieve the plating operation.

A final point to be made is that except for test 6b, generally, a lack of any constituent resulted in a lower stability of Region 3 type deposits and a decreased current density range over which the operation could occur. The worst performance was noted with a lack of stannous tin, and an exceptionally low pH value.

Table VII summarizes the beneficial effect that each component has on the plating procedure with respect to Region 3 type deposits and current density range.

Conclusion

The work in this report shows that it is possible to conduct experiments on a laboratory scale that effectively simulates the industry process of halogen tinning. The complex chemistry and operational variables can be manipulated to give satisfactory results, which can be drawn on when one considers the tinning process on any scale. From an experimentation point of view, this was achieved using a modified Hull cell set-up known as the RotaHull. The cell in question makes use of a rotating cathode to simulate the hydrodynamic nature of a continuous tinning line. The chemistry, temperature, and current density can also be accurately altered and controlled. In this way, not only can industry accepted norms be tested and analysed but also results can be obtained in which deviations are incurred to industry norms and comprehensive comparisons can be made on the differences that result. Using this approach, a broad idea was obtained as to the effect that each of the constituent plating variables has on the final product.

References

1. ITRA Ltd (Tinplate Panel). Guide to Tinplate. Middlesex: ITRA Ltd, 2000.
2. Du Pont De-Nemours El. The Du Pont Process Operating Manual. The Du Pont Company, 1976.
3. STEINBECKER, R.N. Some effects of plating bath variables on the quality performance of a halogen tinning line. The British Library—The world's knowledge.
4. OPASKAR, V.C. Halogen tin composition and electrolytic plating process. United States of America Patent 5,628,893. 13 May 1997.
5. HAYES, P. *Process principles in minerals and material production*, 3rd edition. Queensland, Hayes Publishing, 2003.
6. KANANI, N. *Electroplating, Basic Principles, Processes and Practice*. Germany, Elsevier Ltd, 2004.
7. FOGLER, H.S. *Elements of chemical reaction engineering*. Michigan, Prentice-Hall, 1992.
8. LANDOLT, D. Electrochemical and materials science aspects of alloy deposition. *Electrochimica Acta*, vol. 39, 1994, pp. 1075–1090.
9. Brinkmann Instruments. Products. Brinkmann. 2009. www.brinkmann.com (accessed April 3, 2009).
10. Du Pont De Nemours, E.I. Tin Plate. Patent Specification, 1055762. United Kingdom: The Patent Office, London, 18 January 1967.
11. Encyclopaedia-Britannica. *Encyclopaedia Britannica*. 2009. <http://www.britannica.com/> (accessed April–May 2009).
12. Fast Comtec. Fast Comtec. 2009. www.fastcomtec.com (accessed May 5, 2009).
13. LEWIS, A.E. and ROBERTS, M. Quantifying morphology of nickel crystals. *The Journal of the South African Institute of Mining and Metallurgy*, Nov/Dec, 2001, pp. 421–426.
14. LOW, C.T.J. and WALSH, F.C. The influence of a perfluorinated cationic surfactant on the electrodeposition of tin from a methanesulfonic acid bath. *Journal of electroanalytical chemistry*, Elsevier, 2008, pp. 91–102.
15. MADORE, C., LANDOLT, D., HASSENPLUG, C., and HERMANN, J.A. Application of the rotating cylinder Hull cell to the measurement of throwing power and the monitoring of copper plating baths. *Plating and Surface Finishing*, 1995, pp. 36–41.
16. MERCK. Merck Chemicals. 2009. <http://www.merck.de/en/index.html> (accessed May 3, 2009).
17. OGATA, H., KIKUCHI, T., MORITO, N., and ICHIDA, T. Morphological investigation of a tin-plated surface with an atomic force microscope. *5th International tinplate conference*. London: ITRI Ltd, 1992. pp. 316–327.
18. Purdue University. Scanning Electron Microscope. 2009. <http://www.purdue.edu/REM/rs/sem.htm> (accessed May 10, 2009).
19. SHINJO, T., HOSOTO, N., HINE, S., and TAKADA, T. Reaction at Fe-Sn interface studied by Mossbauer spectroscopy. *Japanese journal of applied physics*, September 1980, vol. 19, no. 9. pp. L531–L533.
20. The Engineering toolbox. Water—Dynamic and Kinematic viscosity. 2009. http://www.engineeringtoolbox.com/water-dynamic-kinematic-viscosity-d_596.html (accessed May 8, 2009).
21. Thermo Scientific. NITON XRF Analyzers. 2009. www.niton.com (accessed May 5, 2009).
22. UNIVERSITY OF CAMBRIDGE. Tin can processing. 2009. http://www.doitpoms.ac.uk/tlplib/recycling-metals/tin_cans.php (accessed May 7, 2009).
23. UNIVERSITY OF MINNESOTA. Theory. 2009. <http://mxp.physics.umn.edu/s04/Projects/s04xrf/theory.htm> (accessed May 11, 2009).
24. UNIVERSITY OF PAISLEY. The concept of the Nernst Diffusion Layer. 2009. http://www-biol.paisley.ac.uk/marco/Enzyme_Electrode/Chapter2/Chapter2_page3.htm (accessed May 14, 2009).
25. ZUBIMENDI, J.L. and BAIELI, C. The influence of operating conditions on the morphology of tin electrodeposits and tinplate quality. *Sixth international tinplate conference*. London: ITRI Ltd, 1996. pp. 85–94. ◆