Tinplate, and electrolytic tinning at the Iscor works, Vanderbijlpark

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SYNOPSIS
The paper first describes tinplate as a product, dealing with its structure and its advantages to the packaging industry.

It then describes Iscor's electrolytic tinning line, which is one of the largest Halogen units in the world. Details are given of the process and of the equipment used.

Introduction
Tinplate, or tin-coated thin steel strip, is now mostly produced by the electroplating of tin on a steel base in a continuous process. The first modern technique of manufacturing tinplate, by the hot dipping of single sheets of steel in a bath of molten tin, has now been discontinued in this country and accounts for only a very small percentage of world production.

Continuous electrolytic tinning was developed in the thirties and forties in an attempt to reduce the amount of tin required per unit area, as well as to take advantage of the great lengths of strip (coils) that the steel mills could then supply.

The first electrolytic tinning lines began to operate in Germany in 1934 and in the U.S.A. in 1937. Tin shortages in the U.S.A. during the Second World War stimulated a large-scale rise of electrotinning, which soon became the dominant manufacturing technique of tinplate. Some of the factors that gave electrotinning the advantage over hot-tinning can be listed as follows:

— High speed continuous process as opposed to low-speed sheet-by-sheet process.
— Simple and accurate control of the coating thickness over a wide range as opposed to the comparatively high minimum coating thickness obtainable by hot-tinning, which is unnecessary for most end-uses.
— Possibility of producing tinplate with a different coating mass on each side in order to meet the different corrosion conditions existing inside and outside a can.
— Functional and visual consistency of the product obtained.

Apart from a process making use of an alkaline plating solution that could not be developed for very high-speed operation and has therefore been progressively phased out, two processes making use of acid plating solutions now account for most of the tinplate production in the world:

— The Ferrostan process, developed by the U.S. Steel Corporation, accounts for over 70 per cent of world production. This is based on an acid sulphate electrolyte, and features vertical plating passes where both sides of the strip are coated simultaneously.
— The Halogen process, developed by E. I. du Pont de Nemours, accounts for about 20 per cent of world production. This is based on a tin—sodium—halogen electrolyte, and features horizontal plating passes where the two sides of the strip are coated successively.

Iscor's electrolytic tinning line in Vanderbijlpark uses the Halogen process, and this paper, after first describing the main features of tinplate as a product, gives details of this particular process and the equipment used.

Tinplate, the Product
Tinplate is one of the most common flat-steel products in our daily lives. The present South African production, on one single continuous line at the Iscor Works, Vanderbijlpark, is over 250 000 t/a. This figure may seem low when compared with the total tonnage of steel consumed in the Republic, but it is significant when expressed as an area: Iscor produces over 120 000 000 m² of tinplate per year.

This mass-produced material is far more complex in structure than a simple sheet of steel coated with tin on both sides. As Fig. 1 shows, the material consists of five different components in nine different layers.

1. The Steel Base
This is normally a low-carbon steel with a low content of residual elements. The precise chemistry of the steel depends on the desired mechanical properties of the finished tinplate. The total thickness of the base is between 0,17 and 0,60 mm, averaging 0,22 mm, and steel represents 99,5 per cent of the mass of finished tinplate.

2. The Alloy Layer (FeSn₂)
This forms by alloying of the steel and part of the tin when the dull, porous electrolytic deposit is melted during the 'reflow' operation that gives tinplate its
familiar highly reflective surface. Like most inter-metallic compounds, FeSn₂ is chemically very inert and thus contributes to the corrosion resistance of the product.

The alloy mass is normally between 0.4 and 1.2 g/m² (on one side), and only a small fraction of the total tin deposited on the strip is alloyed.

3. The Free Tin
This is the largest fraction of the total tin deposited on the strip and can vary in mass from 1 to 15 g/m² (on one side), the average being about 4 g/m². As most tinplate is used in contact with foodstuffs, only high-purity tin (Sn more than 99.75 per cent) may be plated on the steel. A number of combinations of various coating masses on each side are possible in order to accommodate the end-use requirements.

4. The Passivation or 'Oxide' Film
This film is deposited by simple immersion or cathodic treatment of the strip in a sodium dichromate solution. The exact nature of the film is not known, but it appears, in the light of recent research work, that it is a combination of metallic chromium, of tin oxides produced during the reflow operation, and of Cr³⁺ oxides. The thickness of the passivation film is sufficient to ensure adequate protection of the plate against discoloration during stowing operations at the can makers, as well as against sulphide staining by can contents. However, it does not, as a result of excessive thickness, impair the solderability of the material.

5. The Oil Film
A film of oil is deposited on tinplate with the sole purpose of preventing scuffing and assisting the depiling of cut sheets. A virtually monomolecular layer will fulfil this purpose without interfering with the printing operations that may subsequently be carried out by the can makers. Needless to say, the oils used on tinplate have to be safe for food containers.
These five constituents each serve a precise purpose for the main end user of tinplate: the packaging industry. The privileged position held by tinplate in this industry can be explained by the following advantages:

- The mechanical properties of tinplate are those of the steel base, i.e. strength allied to lightness and formability.
- The tin coating provides excellent corrosion resistance or inhibition towards most interior and exterior can environments.
- Tinplate provides an excellent base for decorative purposes, or the application of lacquers when additional protection is required.
- Tinplate is suitable for a number of assembling processes, e.g. crimping, soldering, welding, cementing.
- Tin, being a very soft metal, ensures low wear of the can maker's tooling and can even contribute to lubrication in cases of severe forming.

However, in spite of these advantages, the established position of tinplate as a packaging material could be maintained against the fierce competition from plastics, aluminium, and glass only on account of its low price, which results from the high output and efficiency of its modern production technique: the electrolytic tinning line.

**Electrotinning**

The manufacture of tinplate from 'blackplate', or uncoated steel strip, involves a number of operations and processes that are all performed continuously on an electrolytic tinning line. The succession of these operations is described below, special emphasis being placed on the actual plating process.

**Iscor's line**, one of the largest Halogen units in the world, is schematically represented in Fig. 2.

**Entry Section of the Tinning Line**

This extends up to the entry looping tower and is designed to ensure the continuous running of the centre section.

Coils of blackplate, often over 20 t in mass and up to 940 mm wide, are loaded on either of two expanding mandrel decoilers. Loading and coil preparation take place on one decoiler while the line is supplied by the other. When only a few wraps of strip are left, the entry section is stopped for 15 to 30 seconds and the front end of the new coil is resistance lap welded to the tail end of the finished coil. Upon completion of the weld, the entry section is re-started and supplies strip to the line while a new coil is being loaded on the empty decoiler.

The purpose of the entry looping tower is to store strip to feed the centre section of the line during the necessary stoppages of the entry section. The tower consists of two arrangements of rolls: that at the top is fixed, and that at the bottom is mobile. By varying the length of the strands, strip can either be accumulated from upstream or delivered downstream. After a welding operation, the tower is immediately replenished by over-speeding the decoiler; thus it normally runs 'full' to provide for incidents in the entry section and to ensure the smooth, uninterrupted operation of the centre section.

**Centre Section of the Tinning Line**

The actual manufacture of tinplate takes place in the centre section of the line, which operates at constant speed as the tin coating, the passivation layer, and the oil film must be consistent in quality and within close tolerances.

**Strip Cleaning**

In order to remove all traces of oil or soil that could interfere with pickling or plating, the strip is submitted to successively anodic and cathodic currents while immersed in a hot alkaline solution. The chemical action of the electrolyte, as well as the evolution of gases from the strip surface (H₂ while cathodic, O₂ while anodic), loosens foreign matter from the steel. Cleaning is finished off by scrubbing and rinsing. The strip travels through two successive cleaning units, which are identical in design.

**Pickling**

From the second cleaning scrubber, the strip enters the pickler, which is a vessel containing a 6 per cent solution of H₂SO₄ in water. Acid pickling removes all traces of oxides from the strip surface, and is completed by scrubbing and jet rinsing followed by wringing. Past the wringer rolls, the strip enters the plating section.

**The Halogen Process**

For obvious efficiency reasons, it is preferable to plate out metallic tin (Sn⁺) from stannous ions (Sn²⁺) than from stannic ions (Sn⁴⁺), where double the current would be required for a given amount of tin. Therefore, the Halogen electrolyte is based on stannous compounds; in addition, various constituents inhibit the oxidation of Sn²⁺ to Sn⁴⁺.

The approximate formula of the plating agent is Na₄Sn₁₁Fe₆, which tends, in the presence of unavoidable dissolved O₂, to oxidize into Na₄Sn₁⁴Fe₆. This latter compound has only a low solubility in the plating solution and most of the stannic tin sludges, and is lost from the plating process until recovered in a unit that is auxiliary to the tinning line. Ferric and cupric ions act as catalysts for the oxidation of Sn²⁺ to Sn⁴⁺. The introduction of some iron is, however, unavoidable in an acid solution through which a steel strip travels, and copper contamination can originate from the steel or out of dust from the electrical equipment. Hence, it is necessary to complex the ferric and cupric ions. This is accomplished by the addition of sodium ferrocyanide (Na₄Fe(CN)₁₁·10H₂O) to the plating solution. Chlorides are also present in the electrolyte and ensure a high electrical conductivity while not contributing directly to plating. There are, however, limitations to the maximum permissible concentration of Cl⁻, namely crystallization and the risk of blocked piping, which could occur should the total salt content of the electrolyte become too high.

The last component of the plating solution is an additive that improves the appearance and adhesion of the tin coating to the steel base. This is a proprietary
The typical operating conditions of the electrolyte are:

- \( \text{Sn}^{2+} \): 19 g/l
- \( \text{Sn}^{4+} \): 7 g/l
- \( \text{Sn}_{\text{tot.}} \): 26 g/l
- F\(^-\): 30 g/l
- Cl\(^-\): 26 g/l
- \( \text{Na}_4\text{Fe}((\text{CN})_6)\cdot10\text{H}_2\text{O} \): 1 g/l
- Additive: 3 g/l
- pH: 3.5
- Temperature: 60°C

A number of these values are not very critical and one of the recognized advantages of the Halogen process is the satisfactory operation of the plating solution over a reasonably wide range of concentrations.

Owing to the large volume of electrolyte involved in the process (about 100 kl), the concentrations listed above normally vary smoothly and predictably. Thus, full analyses are carried out only on an 8-hourly basis. Maintenance additions to the electrolyte are monitored by the analytical results.

Tin is supplied as high purity grade cast anodes and as anhydrous stannous chloride (SnCl\(_2\)). It is consumed by plating, sludging of Sn\(^{4+}\), and electrolyte losses (leaks and drag-out).

F\(^-\) is added in the form of sodium bifluoride (NaHF\(_2\)) and/or sodium fluoride (NaF), depending on the desired side effect on pH. Fluorides are lost by sludging of stannic compounds and by electrolyte losses.

Cl\(^-\) is supplied by SnCl\(_2\), additional requirements being normally met by NaCl but, should a sharp drop of pH be desired simultaneously with the addition of Cl\(^-\), HCl also can be used. Chlorides are consumed by electrolyte losses only.

\( \text{Na}_4\text{Fe}((\text{CN})_6)\cdot10\text{H}_2\text{O} \) and the additive are supplied as such to the plating solution. Ferrocyanide losses are mainly the result of thermal decomposition and of the precipitation of the iron or copper complex compounds.

pH is controlled by means of the various options for F\(^-\) or Cl\(^-\) additions: NaF will raise the pH, while NaHF\(_2\) and HCl additions will decrease it.

Maintaining a constant electrolyte temperature can require cooling when plating at high current densities, or heating when operating at low current densities throughout the plating section. This is achieved by water/steam circulation coils immersed in the plating solution.

Finally, the plating current density, which depends on the desired mass of tin coating and the line speed, is several kA/m\(^2\) at 8 to 10 V for the normal range of commercial coatings. The operating practice is to set the total current at the start of a run of material of given characteristics; it is then coupled to the line speed and does not require further major adjustment for the rest of the run. The direct-current requirements of the plating section are met by MG sets with a maximum output of 280 000 A at 20 V.

In the Halogen process, the anode efficiency is 100 per cent, whereas the cathode efficiency varies between 90 and 98 per cent as the current density decreases. The difference between anode and cathode efficiencies contributes to part of the Sn\(^{2+}\) supply to the electrolyte.
of cavitation. There are 28 plating cells on Iscor's line. These are grouped in 2 decks, each containing 14 cells in line. The strip first travels through the bottom deck, at floor level, where one side is coated, and then folds over onto the upper deck, where plating of the other side occurs. Within each deck, the anode carriers of adjacent cells slope in opposite directions in order to ensure the even coating of the strip from edge to edge. The two decks have independent current supplies and settings to provide for the differential coating of the two sides of the strip.

Rinsing

After plating, the strip is rinsed. It is first dipped in a reclaim tank, where the electrolyte that is dragged out of the plating section is diluted. The tin contained in the overflow of this tank is recovered in a separate unit. After the reclaim tank is a conventional scrubbing and hot-water jet-rinsing unit, ending with wringer rolls. Upon completion of rinsing, the strip is dried by hot-air blowers.

Tin Reflow

The tin deposited on the strip in the plating section is dull and porous, and unsuitable for most end-uses of tinplate. In order to acquire a highly reflective appearance and to have a continuous compact layer providing protection to the steel base, it has to be melted. The melting of electrodeposited tin is known as reflow. This operation requires a temperature in excess of the melting point of tin (232°C), and is performed by high-frequency induction heating of the strip at approximately 260°C. Within a few metres of travel through the induction coils, the strip reaches the required temperature and is then immediately quenched through a water tank to avoid discoloration by oxidation in the air.

Although very compact in size, the reflow induction coils can deliver a maximum energy of 3 MW.

Tinplate Passivation or Chemical Treatment

After quenching, tinplate undergoes a passivation treatment, which is performed by a dilute sodium dichromate solution (approximately 20 g/l) and can be a simple dip. More frequently, the strip is made cathodic while travelling through the electrolyte between vertical steel grids, which act as anodes.

Final Rinse

Once passivated, the tinplate is scrubbed and jet-rinsed by hot steam condensate or de-ionized water, and finally dried between hot-air blowers. The quality of this final rinse is essential to the compatibility of the material with foods. Furthermore, any surface contamination could be detrimental to reflectivity or printing.

Oiling

The clean, dried strip passes through an electrostatic oiler in which the required amount of lubricant is deposited. The working principle of the oiler is as follows: fine particles of oil are accelerated towards the tinplate by a high voltage applied between spray nozzles and thin grids located on either side of the strip.

Exit Section of the Tinning Line

This extends from the exit looping tower to the recoilers.

The purpose of the exit looping tower, which has a very similar design to that of the entry looping tower, is to accumulate strip fed from the centre section of the line while the exit section is standing. This tower normally runs 'empty' to provide for unexpected short delays in the exit section.

Past the looping tower, a cabin is built around a vertical strand where visual inspection of the strip is carried out with the aid of stroboscopic illumination. In spite of the high line speed, a number of appearance defects can be detected on the fly by trained inspectors and are reported to the line operators for corrective action. The defects are also entered into the line's data logger, which issues a visual quality summary for each completed coil. Following the inspection station, the strip travels past a pinhole detector, an X-ray thickness gauge, and a beta-ray backscatter coating-thickness gauge.

Finally, ahead of the two expanding mandrel recoilers, the line is equipped with a shear. Upon completion of an output coil, the exit section is stopped for 5 to 10 seconds, the strip is sheared, and its leading edge is automatically transferred to the empty recoiler, where the new coil will be built up and the exit section is restarted. The completed coil is then unloaded from its mandrel, which becomes available for the next transfer operation.

The mass of output coils varies from a few tons for direct despatch to customers to over 20 t for shearing into sheets on either of the two tinplate shearing lines installed at Iscor.

Line Speed and Auxiliary Equipment

The maximum operating speed of the tinning line centre section is 650 m/min. The entry and exit sections can, when filling or emptying the corresponding looping tower, operate at slightly higher speeds. Other than mechanical factors, the speed-limiting factors in the centre section are:

- The maximum plating current when thick coatings have to be applied to wide strip.
- The maximum power available for tin reflow when thick and/or wide tinplate is processed.

Most of the tinplate can, however, be produced at speeds in excess of 500 m/min.

It is quite obvious, from the multiplicity of processes undergone by the strip for preparation, coating, and finishing at the above speeds, that an electrolytic tinning line is a very large and complex unit. A few examples of the ancillary equipment might give the reader further insight into this complexity.

- There are over 250 rolls in the line that are in contact with the strip. Most of these are driven at speeds that have to accurately match that of the strip from 0 to 650 m/min if friction and scoring of the material are to be avoided.
- Accurately controlled tension has to be applied to the strip for proper tracking, which also has to be corrected automatically by steering rolls.

Finally, the following monthly figures relating to Iscor's line will show the scale of a large electrolytic tinning operation.
Evolution of Electrotinning and Tinplate

Although improved in details, the electrolytic tin-plating processes as used at present show little difference from those first implemented thirty to forty years ago. Most significant advancements are primarily related to the equipment and the tinplate itself. Trends are set towards tin and steel savings as well as higher line output and efficiency.

The need to conserve tin has led to the discovery of new additives for the Halogen plating solution that aim at reducing further the losses of stannic tin. Accurate on-line coating gauges have been developed in the past five years that assist in keeping closer coating mass tolerances and, therefore, in avoiding unnecessary 'overcoating'. Improving the continuity of the alloy layer at the steel-free tin interface and, consequently, the additional corrosion protection it offers have made it possible to specify lighter tin coatings for the same end-uses. Similar results are also achieved with the improved lacquers applied by the can makers.

Steel savings are made by reducing the thickness of the tinplate. This results from constant development of can maker's manufacturing techniques and from new can designs.

Finally, electrolytic tinning lines have greatly benefited from a number of developments in electrical controls and electronics. Over the years, these have enabled safe increases of line speeds (up to 700 m/min), resulting in higher outputs. Also, automation has reduced the size of the crews required to operate large lines (5 to 7 men).

It can be concluded, in the light of the above, that the dominant position of electrolytic tinplate in the food-packaging industry appears firm against competition from other products. This position is ensured by the efficiency of the production units, which results in a competitive price, and by the proven record of adaptability to new developments in both the manufacturing and consuming industries.

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Bibliography


Book review

Doyle, William S. Strip Mining of Coal; Environmental solutions. Park Ridge (New Jersey), 1976. 352 pp. $32.

Surface mining of coal is still in its infancy in South Africa. The environmental repercussions following large-scale disturbance of the land surface, and the secondary effects of the disposal of waste products and effluents from mining, have not yet become apparent. In other parts of the world where the surface mining of coal has been practised for decades, the deleterious effects on the environment of earlier mistakes, carelessness, or ignorance have aroused such public and civic indignation that far-reaching legislation has now been enacted to protect the immediate and contiguous land surfaces, both in the short term and in the long term. In the light of the experience of these countries, especially Europe and the United States of America, there can be no excuse for making the same mistakes in South Africa.

William S. Doyle examines the various methods of surface mining for coal, analyses the various sources of environmental pollution, and details the measures that can be and have been taken in practice to counteract the undesirable consequences. The headings of the various chapters of this excellent book tell their own story:

- Surface Mining Land Use and Methods
- Land Reclamation Methods
- Sediment and Erosion Control
- Revegetative Studies
- Spoil Amendment Studies
- Acid Mine Drainage
- Mine Spoil Potentials for Work Quality and Erosion
- Studies of Effects of Mine Drainage
- Recovery of Acid Mine Lakes
- Area Reclamation Projects
- Surface Mined Land Reclamation in Germany
- Reclamation Costs
- AMD Control for a Small Company — Costs and Effects.

The theoretical text of this volume is amply supplemented by case studies, statistics, and observations drawn from a wide coverage of actual situations in the U.S.A. and Germany. Methodology and control techniques are clearly explained and illustrated. Anyone carrying the responsibility for disturbing the surface of the land by mining should welcome the wealth of information and guidance presented in this volume.

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