Study of HCD Electroplating By Phenolsulfonic Acid Baths

By S. Hirano, Y. Oyagi & T. Izaki

In recent years, new tin-plating baths, such as methanesulfonic acid and alkanolsulfonic acids, have been widely tested. High-current-density (HCD) tin-plating by phenolsulfonic acid-based baths has been studied at Nippon Steel Corporation for developing a high productivity tinning process. The relationship between the properties of tinplate and plating conditions (current density, stannous ion concentration, flow rate) was investigated, using laboratory circulation cells. As a result, it was elucidated that the increase of stannous ion concentration in baths enabled HCD plating at a high flow rate of electrolytes and that the quality of HCD electrodeposited tinplate was excellent. Highly corrosion-resistant tinplate could be obtained by electroplating at a current density of 220 A/dm², a tin concentration of 50 g/L and a flow rate of 5.5 m/sec.

Phenolsulfonic acid baths, halogen baths and alkaline baths have been used as plating solutions for tinplate production. The production of tinplate¹⁻³ has recently become a matter of worldwide concern, and tin-plating by methanesulfonic acidbased baths, for instance, has been reported.⁴⁻⁵ Nippon Steel studied HCD electroplating by conventional phenolsulfonic acid baths, and this paper reports on the effects of current density, stannous ion concentration and flow rate on tinplate quality characteristics.

Experimental Procedure

Cold-rolled steel sheets 0.20 mm in thickness were used for this experiment. The sheets were alkaline-cleaned, pickled and set in circulation cells (shown in Fig. 1) to make samples at a stannous ion concentration of 20-80 g/L, a cathode current density of 5-300 A/dm² and a flow rate of 2-9.5 m/sec. The samples made were of two kinds, one with a tin coating weight of 2.8 g/m², the other with a tin coating weight of 11.8 g/m². Samples of the latter were subjected to melting at a heating rate of 40 °C/sec and a quenching temperature of 80 °C.

Observations of appearance, secondary electronic image,





measurement of gloss, and current efficiency were made. Gloss was measured at a reflection angle of 60° and, in the case of the 2.8 g/m² tinplate, if the gloss measured more than 250, the product was regarded as bright tinplate. For the 11.2 g/m^2 tinplate, if the gloss was greater than 700, the product was regarded also as bright tinplate. The tin coating weight was measured by X-ray fluorescence. For the 2.8 g/m² tinplate, the iron exposure value⁶ (IEV) was measured to evaluate the coating. For the IEV measurement, a solution of 20 g/L Na₂CO₃, 20 g/L NaHCO₃ and 0.3 g/L NaCl was adjusted to pH 10, the sample was polarized to 1.2 V vs. SCE at room temperature, and the current value was measured 3 min later for use as the IEV. Because tin is passivated and iron is dissolved anodically in the IEV measuring environment, the iron exposure is smaller as the IEV decreases. For the 11.2 g/m² tinplate, the iron solution value (ISV), alloy tin couple (ATC) value and tin crystal (TC) were evaluated by ASTM methods.

Results and Discussion

Current Efficiency

Figure 2 shows the current efficiency of the plating bath at a stannous ion concentration of 20 g/L. The limiting current density was 30 A/dm² at a flow rate of 2 m/sec. The limiting current density increased as the flow rate increased, however, and reached 75 A/dm² at a flow rate of 9.5 m/sec. In the plating bath at a stannous ion concentration of 50 g/L (shown in Fig. 3), it was clear that the limiting current density reached 75 A/dm² at a flow rate of 2.0 m/sec, 200 A/dm² at 5.5 m/sec and 300 A/dm² at 9.5 m/sec. Moreover, in the plating bath at a stannous ion concentration of 80 g/L (shown in Fig. 4), the limiting current density reached 150 A/dm² at a flow rate of 2 m/sec and 300 A/dm² when more than 5.5 m/sec.

The limiting current density is considered to increase as a result of thinning of the steel sheet/plating bath boundary layer, caused by the increase in flow rate and the increase in mass transfer quantity resulting from the increase in stannous ion concentration. It was clear that increasing the limiting current density was more effective in increasing the stannous ion concentration than in increasing the flow rate.



Fig. 2—Current efficiency of plating bath at stannous ion conc. of 20 g/L.



Fig. 3-Current efficiency of plating bath at stannous ion conc. of 50 g/L.



Current density, A/dm²

Fig. 5—Bright current density range of non-reflowed tinplate.

Appearance of Non-reflowed Tinplate (Tin Coating Weight: 2.8 g/m²)

Figure 5 shows the silvery bright current-density-range of non-reflowed tinplate. If this range is exceeded, the appearance of the tinplate becomes gray or powdery, but if this range is not reached, the current is in the so-called low-currentrange, and the appearance of the tinplate becomes dull white. The bright current-density-range showed a tendency to become wider with increasing flow rate or stannous ion concentration. The upper limit value of the bright current-densityrange is near the value of the limiting-current-density for specified plating conditions. It is considered, therefore, that the upper limit value of the bright current-density-range increased because the limiting-current-density increased as a result of the increased stannous ion concentration and increased flow rate.

The lower limit value of the bright current density range showed a tendency to increase as a result of increased ion concentration. This is presumably because the increase in stannous ion concentration accelerated mass transfer and increased the low-current-range, in which dendritic crystals may grow.

The bright current-density-range became wider as a result of the increased stannous ion concentration and increased flow rate. It became clear that this is because the increase in upper limit value of the bright current-density-range is very large compared with lower limit value of the range.

Appearance of Reflowed Tinplate

(Tin Coating Weight: 11.2 g/m²

Figure 6 shows the mirror-like appearance of the bright current-density-range of reflow tinplate. As in the case of 2.8 g/m² tinplate, the bright current-density-range of this tinplate showed a tendency to become wider with increasing flow rate or stannous ion concentration. The change in low-current-range was not so large as that of 2.8 g/m² tinplate. This is



Fig. 4—Current efficiency of plating bath at stannous ion conc. of 80 g/L.



Fig. 6—Bright current density range of reflowed tinplate.



Fig. 7—Relation of current density and IEV at stannous ion conc. of 20 g/L.



Fig. 8—Relation of current density and IEV at stannous ion conc. of 50 g/L.



Current density, A/dm²

Fig. 9—Relation of current density and IEV at stannous ion conc. of 80 g/L.

presumably because the tin was melted and leveled at that time.

IEV

Figures 7-9 show the result of measurement of the IEV of non-reflowed tinplate. The IEV showed a tendency to decrease at first with increasing current density in the bath at any stannous ion concentration, remain at $0.1-0.3 \text{ mA/dm}^2$, then increase to 30 A/cm^2 at the flow rate of 2.0 m/sec; $50 \text{ A/} \text{dm}^2$ at a flow rate of 9.5 m/sec, and stannous ion concentration of 20 g/L; and 125 A/dm^2 at a flow rate of 2.0 m/sec; and in excess of 200 A/dm^2 at a flow rate of 5.5 m/sec and stannous ion concentration of 50 g/L. These current densities at which the IEV began to increase nearly correspond with the limiting current densities. It is considered, therefore, that if the limiting current densities are exceeded, the uniform electrodeposition of tinplate is interrupted by hydrogen gen-



Fig. 10—ATC value of 11.2 g/m² tinplate produced at current density of 20 A/dm².



Fig. 11—ATC value of 11.2 g/m² tinplate produced at current density of 100 A/dm².



Fig. 12—ATC value of 11.2 g/m² tinplate produced at current density of 200 A/dm².

eration. On the other hand, in the low-current-density-zone, which is the low-current-range, the measured IEV is high, presumably because the uniform tin coating was deteriorated.

The IEV of tinplate produced at a stannous ion concentration of 80 g/L was somewhat lower than that of tinplate produced at 50 g/L. From this fact, it may be said that the tin coating is more uniform for tinplate produced at 80 g/L.

ATC Testing

Figures 10-12 show the results of measurement of the ATC value of reflowed tinplate produced at a flow rate of 5.5 m/ sec. When the current density was 20 A/dm² (Fig. 10), the ATC value showed a tendency to decrease with increasing alloy tin coating weight in the plating bath at any stannous ion concentration. When the current density reached 100 A/dm² (Fig. 11), however, the ATC value of tinplate produced at a



Fig. 13—Relation of current density and ISV at stannous ion conc. of 20 g/L.



Current density, A/dm²

Fig. 15—Relation of current density and ISV at stannous ion conc. of 80 g/L.



Fig. 17—Relation of current density and TC at stannous ion conc. of 50 g/L.

stannous ion concentration of 20 g/L, the lowest tin concentration in this test, did not decrease with increasing alloy tin coating weight. Because the current density of 100 A/dm² is far above the cathodic limiting current density of the plating bath at a stannous ion concentration of 20 g/L, the tin coating is not uniform. The measured ATC value is high, presumably because the alloy layer coating was insufficient when the tinplate was subjected to reflow treatment.

When the current density was 200 A/dm² (Fig. 12), the tendency of the ATC value was the same as at 100 A/dm², but the ATC value for tinplate produced at a stannous ion concentration of 80 g/L, at which the tin concentration was high, showed a tendency to become somewhat lower than that of tinplate produced at 50 g/L. As described earlier, when the current density was as high as 200 A/dm², tinplate produced at a stannous ion concentration of 80 g/L is superior in coating uniformity to tinplate produced at 50 g/L. The reason is



Current density, A/dm²

Fig. 14—Relation of current density and ISV at stannous ion conc. of 50 g/L.



Fig. 16—Relation of current density and TC at stannous ion conc. of 20 g/L.



Current density, A/dm²

Fig. 18—*Relation of current density and TC at stannous ion conc. of* 20 *g/L.*

considered to be because dense alloy tin was produced by reflow treatment.

ISV

Figures 13-15 show the results of measurement of the ISV of reflowed tinplate. At a stannous ion concentration of 20 g/L, the ISV showed a tendency to increase at any flow rate when the limiting current density was exceeded. The cause of this tendency is considered to be the same as the cause of the increase in the IEV (*i.e.*, the uniformity of the tin coating was impaired). At a stannous ion concentration of 50 g/L, the ISV was high in the low-current-density zone. This is presumably because tin did not flow completely at the time of melting, as the low-current-density zone was the low-current range, and pinholes formed to cause iron solution. Also, the ISV showed a tendency to increase near the limiting current density. At a stannous ion concentration of 80 g/L also, high ISV was

observed in the low-current range.

Figures 16-18 show the results of measurement of the TC of reflowed tinplate. At a stannous ion concentration of 20 g/L, the TC of tinplate produced below the limiting current density was #7-9. At stannous ion concentrations of 50 and 80 g/L, TC did not noticeably change with the current density or flow rate and was stable at #6-9.

Conclusions

- 1. The limiting current density is increased by increasing the stannous ion concentration of the phenolsulfonic acid bath and the flow rate of the electrolyte.
- 2. It is possible to produce tinplate of excellent corrosion resistance at high current density (under optimum plating conditions).

Editor's note: Mr. Hirano presented this paper, for which he received an "Excellence in Presentation Award," at the AESF Continuous Steel Strip Symposium, Baltimore, MD, May 1996. This is an edited version of that presentation.

References

- 1. J. Lempereur et al., Proc. 4th Int'l. Tinplate Conf., 75 (1988).
- G.C. van Haastrecht et al., Proc. 4th Int'l. Tinplate Conf., 88 (1988).
- 3. D. Salm et al., Proc. 2nd Int'l. Tinplate Conf., 88 (1980).
- 4. J. van der Putten, *Proc. 2nd North American Tinplate Conf.*, Session 4 (1990).
- 5. G.A. Federman, Proc. 5th Int'l. Tinplate Conf., 88 (1992).

6. M. Tsurumaru et al., Proc. 2nd Int'l. Tinplate Conf., 348 (1980).







Hirano

Izaki

About the Authors

Shigeru Hirano is a senior researcher at the Yawata R&D Lab. of Nippon Steel Corp., 1-1 Tobihata-cho, Tobata-ku, Kitakyushu City 804, Japan. He is responsible for development of steel sheet for cans. He holds an MS from Kyushu Institute of Technology and has been involved with tinning process and tinplate since 1988.

Yashichi Oyagi is the chief researcher of the Yawata R&D Lab. of Nippon Steel Corp. and is responsible for development of surface-treated steel sheets. He holds a BS from Tokyo University and has worked in development of steel sheets for cans for 30 years.

Teruaki Izaki is a senior researcher at the Yawata R&D Lab. of Nippon Steel Corp. His responsibilities include development of electroplating process and leading the surface treatment group. He holds a BS from Kyushu University.



Material Sciences Corp. Appoints Thomas Moore & Edward Williams Material Sciences Corporation (MSC), Elk Grove Village, IL, has appointed **Thomas E. Moore** of AESF's Cleveland Branch to the position of executive vice president and chief operating officer. **Edward A. Williams**, AESF Toledo Branch member, has been named group vice president and general manager of MSC's Walbridge Coatings, Inc.

Moore began his career at MSC as general manager of its Walbridge Coatings subsidiary in 1984, was appointed vice president and general manager in 1987, and promoted to executive vice president and general manager in 1993. He holds a BSEE from Drexel University, and previously worked for Sharon Steel Corp.

Williams joined MSC Walbridge Coatings as plant manager in 1993. His previous business experience included engineering and management positions with Armco Steel Co. and National Steel Midwest Div. He received his BS in metallurgical engineering from the University of Cincinnati.

Anne Chasse

Joins Kinetico Sales Team

Santa Clara Valley Branch member **Anne Chasse** has been appointed as account representative with Kinetico Inc.'s Engineered Systems Division, Newbury, OH. In her new position, she will be responsible for increasing the sales of the company's high-purity water recycling systems in the western region of the U.S.

Chasse brings a strong sales background to the Kinetico team, and holds a bachelor's degree from the University of Connecticut. She will work out of the company's western regional sales office in California.

John Swanson

Promoted at LeaRonal Inc.

AESF Pittsburgh Branch member John Swanson has been promoted to technical manager, New Industrial Processes, at LeaRonal Inc., Freeport, NY. Previously technical service manager for the company's Ronastan TP division, he will still be involved with the technical service functions for the tinplate and wire industries, and will assume the additional responsibility of introducing new base metal processes to heavy industrial accounts. Specifically, he will be responsible for marketing and technical development of the company's new lead-free bearing process for the automotive industry. P&SF