

# Conversion from Halogen Bath to Environment-Friendly Methane Sulfonic Acid (MSA) Bath in Electrolytic Tinning Line (ETL) at East Japan Works (Chiba), JFE Steel<sup>†</sup>

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## Abstract:

*In response to stricter regulations on the concentration of fluoride (F) dissolved into water from wastes enforced in the year 2000, JFE Steel's East Japan Works (Chiba) performed a costly detoxification treatment for F-containing halogen sludge discharged from the electrolytic tinning line (ETL), and at the same time, JFE Steel began study of a project to convert this line from a halogen bath process to a low environmental load methane sulfonic acid (MSA) bath. In this changeover, first, the literature on the MSA process was reviewed and MSA tinplate was evaluated experimentally in the laboratory. Tin mill black plate (TMBP) produced by JFE Steel at East Japan Works (Chiba) was then sent to U.S. makers who had already converted to the MSA-ETL process in order to evaluate MSA tinplate produced under industrial conditions, and operational data were collected using JFE Steel's No. 1 ETL at East Japan Works (Chiba). Quality and operational differences between the halogen and MSA baths were identified through these tests, and remodeling of the existing equipment and introduction of new equipment were carried out to overcome these problems. Operation of the modified line producing tinplate with a MSA bath began in January 2005. As a result, none of the feared quality or operational problems have been encountered, and the electrolyte cost, including tin, has been greatly reduced from the initial plan.*

## 1. Introduction

JFE Steel's East Japan Works (Chiba) No. 2 electrolytic tinning line (2ETL) is the main ETL at this works. A halogen bath, with SnCl<sub>2</sub> and NaHF<sub>2</sub> as its main components, had been used as the plating bath. In the past, the halogen sludge which formed in the plating bath had been sold as a tin source, but with the enforcement of stricter regulations on the concentration of fluoride (F) eluted from waste in the year 2000 (regulatory value for land areas, including rivers: 8 ppm or less, and marine areas: 15 ppm or less), disposal by sale become difficult. As a countermeasure, the company began using a costly detoxification treatment process for the generated halogen sludge, and at the same time, launched a study of a project to convert the halogen bath process to a methane sulfonic acid (MSA) bath process which does not produce waste.

As part of this study, the authors reviewed the literature<sup>1-5)</sup>, carried out a bench-scale experimental evaluation of MSA tinplate in the laboratory, submitted tin mill black plate produced by JFE Steel to makers in the U.S. for industrial-scale tests, and performed operational tests using 1ETL at East Japan Works (Chiba). The results showed that the quality of tinplate produced by the MSA process is substantially the same as that produced with a halogen bath, and it was concluded that conversion of

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the bath was feasible. The main problems for operation with an MSA bath at 2ETL were operational stability and the electrolyte cost. This paper describes the equipment improvements carried out to overcome these problems and the results achieved.

## 2. Features and Problems of MSA Bath

The MSA bath is a plating bath which is composed mainly of methane sulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ) and  $\text{Sn}^{2+}$ , and has the following features:

- (1) The proper electrolysis current density ( $10\text{--}55\text{A}/\text{dm}^2$ ) is wide, being similar to that with the halogen bath. This means that it is possible to apply the same cell structure as with the halogen bath.
- (2) Sludge generation is small (no more than 1 t/m; with halogen bath: 15 t/m).
- (3) Because the main components of the sludge are  $\text{Sn}(\text{OH})_4$  and  $\text{SnO}_2$ , recycling is easy.

On the other hand, the following points were a concern, and these were taken up as problems in this project.

- (1) The MSA bath is strongly corrosive ( $\text{pH} < 1$ ).
- (2) Lines in the U.S. which had previously converted to MSA reported problems with bare stain (soiling by cohering oil and tar components), which occurred because the bath temperature exceeded the cloud point of the surfactant in the initial stage of conversion, and rolled-in defects due to precipitation of tin on the conductor rolls.
- (3) The unit cost of the electrolyte is extremely high in comparison with the halogen bath.

To overcome these problems, the cell structure was remodeling and measures were taken to minimize electrolyte loss. The following chapters describe the respective countermeasures and their effects.

## 3. Remodeling of Cell Structure

Based on an advance study, three types of quality problems were feared in the plating cells, bare stain, carbon contamination, and rolled-in defects due to tin deposits on the conductor rolls.

The first problem, bare stain, is a type of contamination that adheres to the steel strip when the oily component dispersed in the bath coheres. This problem occurs when the bath temperature exceeds the cloud point of the brightening agent (surfactant). The “cloud point” is the solubility limit of the brightening agent, i.e., the temperature at which the brightening agent becomes insoluble, resulting in white turbidity, and is approximately  $60^\circ\text{C}$  in the case of the brightening agent used here. With conventional halogen bath operation, bare stain does not occur even if the temperature in the cell exceeds

$65^\circ\text{C}$  due to electrolysis, but bare stain does occur when using an MSA bath if the cloud point is exceeded. As a countermeasure for bare stain, plating bath cooling was strengthened to prevent bath temperature rise. The equipment-related countermeasures for preventing bath temperature rise are described below.

- (1) The circulation pump capacity was increased (before remodeling:  $1.14\text{ m}^3/\text{min} \times 14$  pumps, after remodeling:  $1.5\text{ m}^3/\text{min} \times 14$  pumps) to alleviate heat stagnation in the plating cells.
- (2) Because electrolyte accumulation at the delivery side of cells increased due to the increased electrolyte circulation rate, outflow control holes were provided at the cell delivery side and side wall of the delivery side to prevent overflow of the electrolyte (**Fig. 1**).

These countermeasures made it possible to control the bath temperature in the cells to less than  $50^\circ\text{C}$  during high current operation ( $8\,000\text{ A}/\text{cell}$ ). To date, bare stain has not occurred.

Problem 2 was carbon contamination, in which carbon eluted from the carbon plate anode bed used in the halogen bath adheres to the steel strip. This problem was expected if the carbon plate anode bed is immersed in the strongly acidic MSA bath. As a countermeasure, the anode bed material was changed to Ti plate, which is stable in the MSA bath. As a result, carbon contamination has not occurred to date.

Problem 3 was deposition of tin on the conductor rolls, which is thought to occur because part of the plating current which should flow from the anodic electrode to the cathodic steel strip passes directly to the conductor roll. Therefore, a plate was provided to cut off the current between the anodic electrode and the conductor roll (Fig. 1). This measure reduced the frequency of tin deposits on the conductor rolls to approximately 1/5 of the former level.

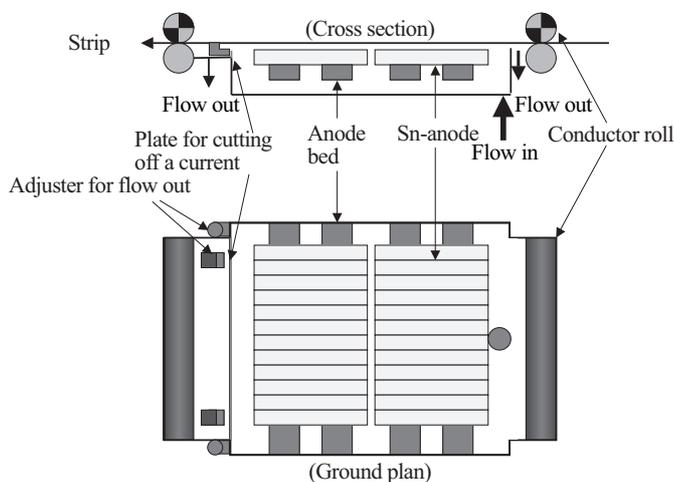


Fig. 1 The schematic illustration of cell structure after remodeling

## 4. Minimization of Electrolyte Loss

### 4.1 Introduction of Countercurrent Rinse

Figure 2 shows a schematic illustration of the present plater section of 2ETL. The plating cells in 2ETL are horizontal-type cells. Bottom side plating is performed on the 1st floor, and top side plating is performed on the 2nd floor. Before conversion, the electrolyte was recovered by a reclamation tank at the entry side of the 3rd floor, but the recovery rate was only approximately 50%. Because the unit cost of the electrolyte used in the MSA bath is about 4 times higher than that in halogen bath, the monetary loss with this recovery rate would be prohibitive. The authors therefore studied introduction of a multi-stage countercurrent rinse to improve the recovery rate. In order to design equipment which would achieve a target recovery rate of 95% or higher, the number of countercurrent rinse stages and makeup water supply rate were studied by simulation.

Figure 3 shows a diagram of the simulation model. As preconditions, electrolyte drag-in and drag-out by the steel strip were assumed to be constant, and the simulation was performed using the following mass balance equation ((drag-in) = (drag-out)) in a steady state:

$$Q \times K_{n-1} + q \times K_{n+1} = Q \times K_n + q \times K_n \dots (1)$$

Here,  $Q$  is the amount of drag-in and drag-out of solution by the steel strip,  $q$  is the amount of rinse makeup water, and  $K_n$  is the concentration in the  $n$ th stage (per-

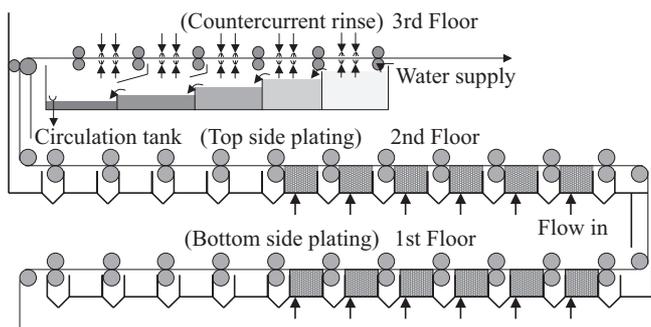


Fig.2 The schematic illustration of plater section structure after remodeling

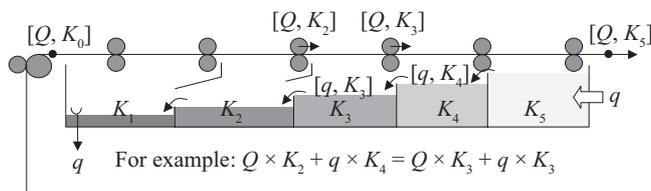


Fig.3 The schematic illustration of countercurrent rinse simulation model in case of  $n = 5$

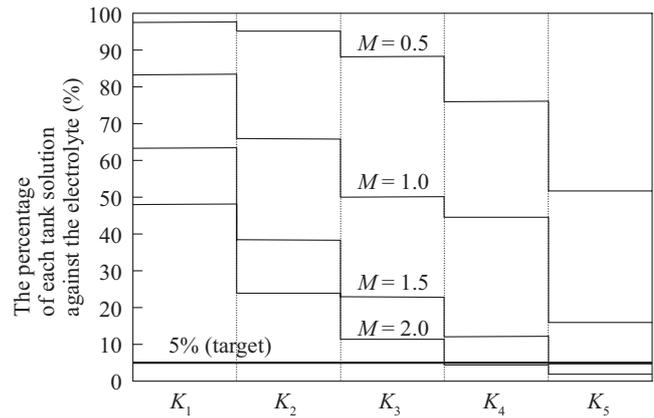


Fig.4 The Result of countercurrent rinse simulation in case of  $n = 5$

centage of solution concentration in respective tanks when the electrolyte concentration is assumed to be 100%).

The following equation can be obtained assuming  $q/Q = M$  in the above-mentioned equation.

$$K_{n-1} + M \times K_{n+1} = (1 + M) \times K_n \dots (2)$$

Using this equation, the concentration in each tank in a steady state was estimated using  $n$  (number of stages) and  $M$  (ratio of rinse makeup water and dragged-out electrolyte) as parameters. The electrolyte in the final stage is considered to be dragged out of the system. In other words, the concentration in the final stage is recovery loss as such. To achieve a recovery ratio of 95% or more, the concentration in the final stage must be reduced to less than 5%. Figure 4 shows the transition of the concentration in each tank in a 5-stage system ( $n = 5$ ) using  $M$  as a parameter. The concentration in the final stage can be reduced to  $<5\%$  by setting  $M$  at 1.5 or more. Here, it should be noted that the maximum number of stages was 5 due to equipment space restrictions. Accordingly, the evaporator capacity (capacity to evaporate increased water in the solution) was designed assuming  $n = 5$  and  $M = 1.5$ , and in addition, prevention of an increase in the electrolyte due to the amount of solution recovered.

### 4.2 Operation with Variable Number of Active Plating Cells

Conventionally, all of the cells at 2ETL were filled with electrolyte, including cells where electrolysis was not being performed. In these filled cells, electrolyte loss occurred due to slight splashing, and iron dissolved out of the steel strip. Furthermore, if electrolyte circulation is increased, a greater amount of sludge will be generated due to increased contact with the air and the resulting oxidation. Accordingly, in order to reduce electrolyte

loss, iron elution, and sludge generation, the equipment was remodeled to enable operation with a variable number of electrolyte-filled cells, so that only the cells where electrolysis is performed are filled. When producing tinfoil with a light coating weight, only about half of the cells are filled with electrolyte. A “keep wet spray” is used to prevent drying of the strip surface in cells which are not filled.

#### 4.3 Negative Effects of Electrolyte Loss Minimization

Electrolyte loss minimization in the plating section, which was implemented to reduce electrolyte loss, resulted in enrichment of Fe ions eluted from the steel strip and a rise in the Sn concentration due to Sn ions remaining in the bath, which was caused by the cathodic/anodic efficiency difference. In particular, an increased Fe concentration has the following negative effects.

- (1) Lowering of the brightener cloud point
- (2) Increase in sludge generation by promoting oxidation of Sn ions
- (3) Narrowing of the proper electrolysis current density range

An iron removal system was introduced to prevent these problems, and the Fe concentration is controlled to the limit value for these negative effects ( $<20$  g/l), as determined by an advance study.

If the residual Sn concentration in the bath increases, the amount of sludge generation will also increase and the proper electrolysis current density range will change. Furthermore, the free MSA concentration balance will be lost, with a negative influence on product quality, for example, plating uniformity. In order to prevent rises in Sn concentration, consumption of Sn by introducing insoluble anodes was investigated. In this study, it was judged that insoluble anodes corresponding to 2 cells are necessary, considering the balance of residual Sn in the bath due to the cathodic/anodic efficiency difference and Sn consumption when insoluble anodes are used. Accordingly, insoluble anodes were installed in one cell on each floor.

As a result of the various equipment-related measures described above, actual electrolyte recovery after conversion was approximately 98%, which exceeded the original target, and the Fe concentration and Sn concentration can be controlled to within the control target range.

## 5. Conclusion

An existing halogen process electrolytic tinning line was converted to the methane sulfonic acid (MSA) process. In order to prevent the anticipated problems, in this conversion project, the cell structure was remodeled, measures to minimize electrolyte loss were implemented, and an iron removal system was introduced. Commercial production with the remodeled MSA line began in Jan. 2005. Although various product quality-related problems such as bare stain had been a concern, none of these problems has occurred. An electrolyte recovery rate of 98% has been achieved, and the Fe concentration is being controlled to the standard value ( $<20$  g/l). The establishment of this technology made it possible to complete an electrolytic tinning process which is environment-friendly while also securing economy and product quality.

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