Novel Technique for Replenishing Tin & Controlling Tin Baths

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This paper deals with a new patented process for maintaining the tin concentration in tin electroplating baths that use insoluble anodes, particularly in methane sulfonic acid systems. It is also applicable to soluble anode processes that use currents in excess of 500 amps. This paper will provide: A description of the technology; a summary of the advantages of the technology; an overview of the cost benefits; and some examples of operation in the field with cost reductions and reduction of F006 sludge. When using insoluble anodes in a MSA system, all of the tin plated out comes from the tin MSA in solution, which results in paying a significant premium for the tin you plate; build-up of MSA in the solution, necessitating periodic bailouts; adding back expensive tin MSA and additives; and waste treating the bailed-out solution. This technology replaces the tin plated out with tin metal, at a significantly reduced cost compared to tin from tin MSA; eliminates bail-outs and additions of costly brighteners and additives; reduces waste treatment costs and sludge produced; and operates with constant tin and acid concentrations.

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The Challenge:

Precious Plate Inc. in Niagara Falls New York had obtained a new contract to plate a narrow tin stripe on continuous reel-to-reel parts. The plating solution of choice was based on methane sulfonic acid. The equipment chosen included stripe plating cells using insoluble anodes. The line was to run at 70 feet per minute on a 24 hour seven day a week schedule. Each of the two stripe cells would require approximately 19 amperes to deposit the required thickness.

Extrapolating from past history with insoluble anodes in methane sulfonic acid systems running at much lower annual ampere-hours, showed that chemical replacement costs would be high and the load on the waste treatment system would increase. This was due to the fact that all of the tin plated would come from the tin methane sulfonic acid. No tin is dissolved at the insoluble anode – oxygen is liberated from the dissociation of water per equation 1. As the tin plates out at the cathode, the free methane sulfonic acid rises as per equation 2.

Eq. 1 $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$
Eq. 2 $(CH_3SO_2O)_2Sn + 2H^+ + 2e^- \rightarrow Sn^0 + 2CH_3SO_2OH$

To replenish the tin and keep the free acid in control, periodic bath bailouts are required. These bailouts must be waste treated, producing F006 sludge. After bailout the tin metal in the bath must be replaced with tin methane sulfonic acid at a significant cost premium over metallic tin; and brighteners and grain refiners must be added to bring their concentration back to the level maintained before the bailout.

The Solution:

Precious Plate Inc. enlisted the help of a local chemical equipment manufacturer to solve the problems highlighted above. Novel technology was developed. Essentially, this process employs a tin replenishment cell hydraulically connected to the plating cell. A description of the various elements of the process follows (Refer to the numbers shown in the process diagram, Fig. 1 below):

10	plating cell
12	tin replenishment cell
14	insoluble anode in the plating cell
16	cathode in the plating cell (product to be plated such as continuous strip)
18	rectifier connected across the plating cell
20	electrolyte in the plating cell
22	soluble tin anode in the tin replenishment cell
24	cathode in the tin replenishment cell
26	rectifier connected across the tin replenishment cell
28	proton exchange membrane

30	anolyte in the tin replenishment cell
32	catholyte in the tin replenishment cell
34	return line from tin replenishment cell to plating cell
36	pump to return solution from the tin replenishment cell to the plating cell
38	gravity overflow to the tin replenishment cell
40	controller to proportion the current in the tin replenishment cell to the current in the plating cell

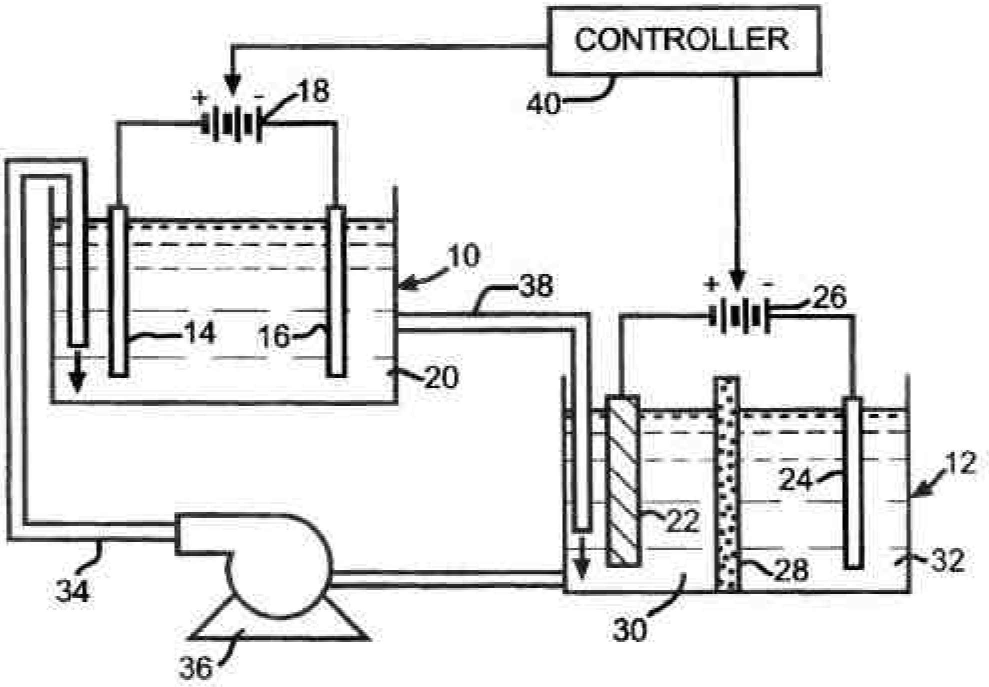


Figure 1

In an actual continuous reel-to-reel plating line, solution is pumped from a lower sump tank to the upper plating cell and allowed to return by gravity to the lower sump. Heaters or cooling coils are installed in the lower sump and continuous filtration is usually performed. The tin replenishment cell is hydraulically connected to this sump. The lower sump and the associated pumping circuits are not depicted in the process diagram (Fig. 1).

With the tin replenishment cell installed, tin metal plated out at the cathode of the plating cell is replaced by tin from a soluble anode in the replenishment cell, not from the addition of tin methane sulfonic acid, as is the case when using insoluble anodes in the plating cell with no tin replenishment cell. The free acid does not rise because hydrogen is liberated at the cathode of the tin replenishment cell in proportion to the tin dissolved at the anode of the replenishment cell.

Referring to the equations below, the process with the tin replenishment cell installed is as follows:

In the plating cell, oxygen is liberated at the insoluble anode as per equation 3. Tin is plated on the cathode as per equation 4, resulting in the lowering of the tin concentration in solution and an increase in the free acid concentration. The solution is continuously re-circulated from the plating cell to the anolyte chamber of the tin replenishment cell via the lower plating sump (not shown). In the tin replenishment cell, tin is electrochemically dissolved into the anolyte at the soluble tin anode and combines with the free acid produced in the plating cell liberating hydrogen ions per equation 5. The hydrogen ions pass through the proton exchange membrane into the catholyte chamber, which is filled with methane sulfonic acid of approximately the same concentration as the plating bath. They replace those lost to the evolution of hydrogen gas at the tin replacement cell cathode as per equation 6. Some tin ions pass through the membrane (approximately 5%) and are deposited at the tin replacement cell cathode as per equation 7.

Several membranes both anionic and cationic were investigated during the development of the process. Some of the membranes investigated allowed no tin ions to pass through the membrane but had poor strength and/or chemical resistance. While the preferred membrane allows a small percentage of tin to pass into the catholyte chamber, it is mechanically sound and relatively unaffected by the methane sulfonic acid solution and the organic wetting agents and brighteners commonly employed in tin plating solutions. An electronic control circuit was designed and added to the rectifier connected across the tin replacement cell. This sensed the current drawn by the plating rectifier and continuously varied the current on the tin replacement cell rectifier, keeping it at a settable percentage of the plating current.

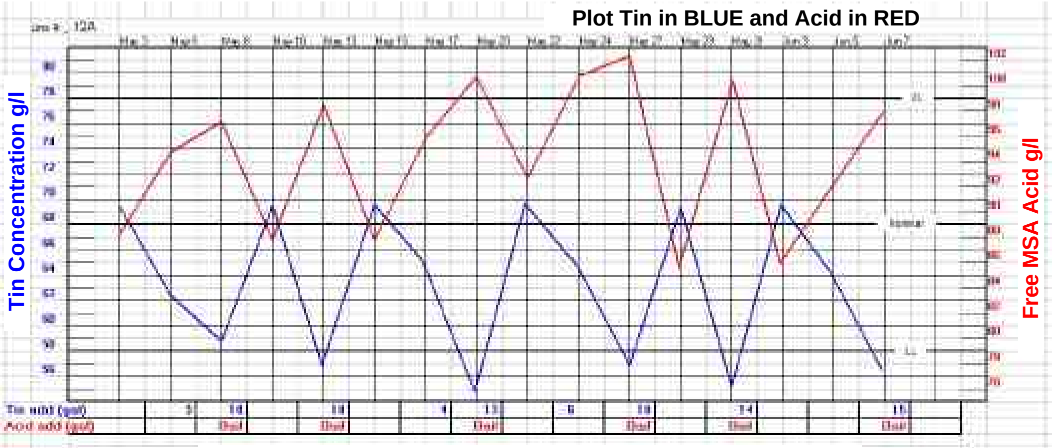
Eq. 3 $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$
Eq. 4 $(CH_3SO_2O)_2Sn + 2H^+ + 2e^- \rightarrow Sn^0 + 2CH_3SO_2OH$
Eq. 5 $Sn^0 + 2CH_3SO_2OH \rightarrow (CH_3SO_2O)_2Sn + 2H^+ + 2e^-$
Eq. 6 $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ [~95%]
Eq. 7 $(CH_3SO_2O)_2Sn + 2H^+ + 2e^- \rightarrow Sn^0 + 2CH_3SO_2OH$ [~5%]

The Results:

At the end of the development phase a tin replacement cell was built and installed on the new line. The cell size was approximately 24 inches wide by 36 inches long by 30 inches deep, which fit easily under the rails of the selective plating line. The cell had a single membrane and was sized for a maximum of 50 amps based on experimental data gathered during investigation of the proton exchange membrane. The average current used on the cell was about 37 amps. The average current used on the two stripe plating cells was about 38 amps and the calculated cathode current efficiency was 92% for an effective current used to plate tin of 35 amperes. Thus the current used by the tin replacement cell was about 5.7% more than the 35 amps required by the plating cell. This excess current was required to plate the tin that passed through the membrane onto the tin replacement cell cathode.

Bath bailouts were eliminated and the process control of the solution was simplified. Only small adds of tin methane sulfonic acid were required to make up for drag out losses. Waste treatment and sludge disposal costs were reduced due to elimination of bailouts. The net annual savings after energy and membrane replacement costs was in excess of $40,000. The capital cost of the equipment was less than $30,000. A summary of the cost savings is shown in Figure 3.

Based on the success of the program, two double membrane cells designed for a maximum of 100 amps each were built. (A view of the cell is shown in figure 4) These were installed on a strip plating line that plated 0.000240 inches average matte tin thickness on 1.6 inch wide strip. The line ran at approximately 70 feet per minute at about 2,500 amps. Significant additions of tin methane sulfonic acid were required on this line to counter the effects of tin losses due to anode/cathode efficiency imbalance and drag out. These additions resulted in the free acid increasing, which necessitated periodic bailouts. After installation of the tin replacement cells, bailouts were eliminated, and tin methane sulfonic acid additions were markedly reduced. The savings on this line exceeded those of the stripe plating line and resulted in a faster payback of the equipment. Tin and acid concentrations on this line had varied widely historically, but were very much easier to control after installation of the tin replacement cells. Control charts before and after the installation of the tin replacement cell are shown in Figure 2.



Without Tin Replenishment Cell

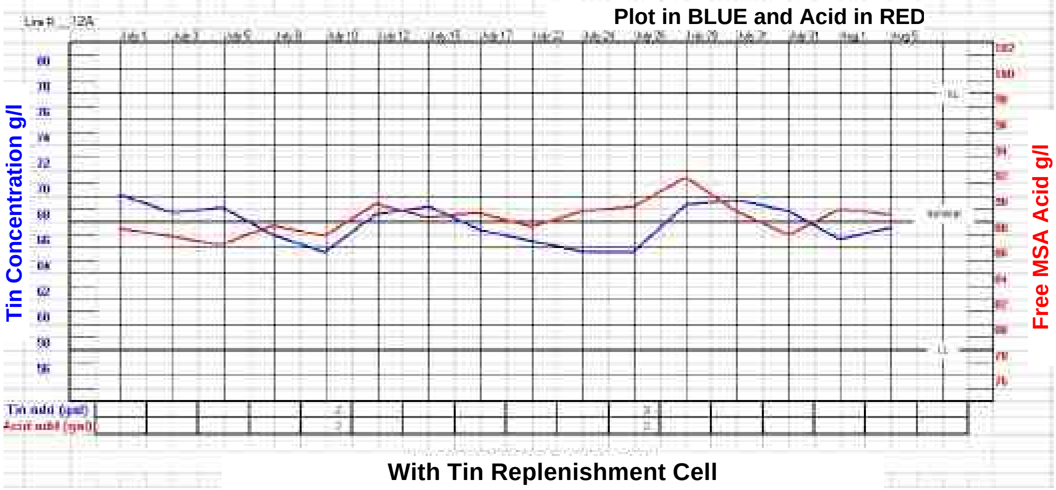


Figure 2

Conclusion:

This technology[*] was proven successful in tin methane sulfonic acid applications using insoluble anodes, as well as applications using higher currents with soluble anodes. Reduction in costs, and waste produced, and improved process control were demonstrated. The control of tin and acid concentration in the plating bath was achieved by varying the current on the tin replacement cell in relation to the current on the plating cell – raising the current to increase tin and decrease free acid concentration, or lowering the current to increase free acid and decrease tin concentration. The units used were compact and easy to install on existing plating lines.

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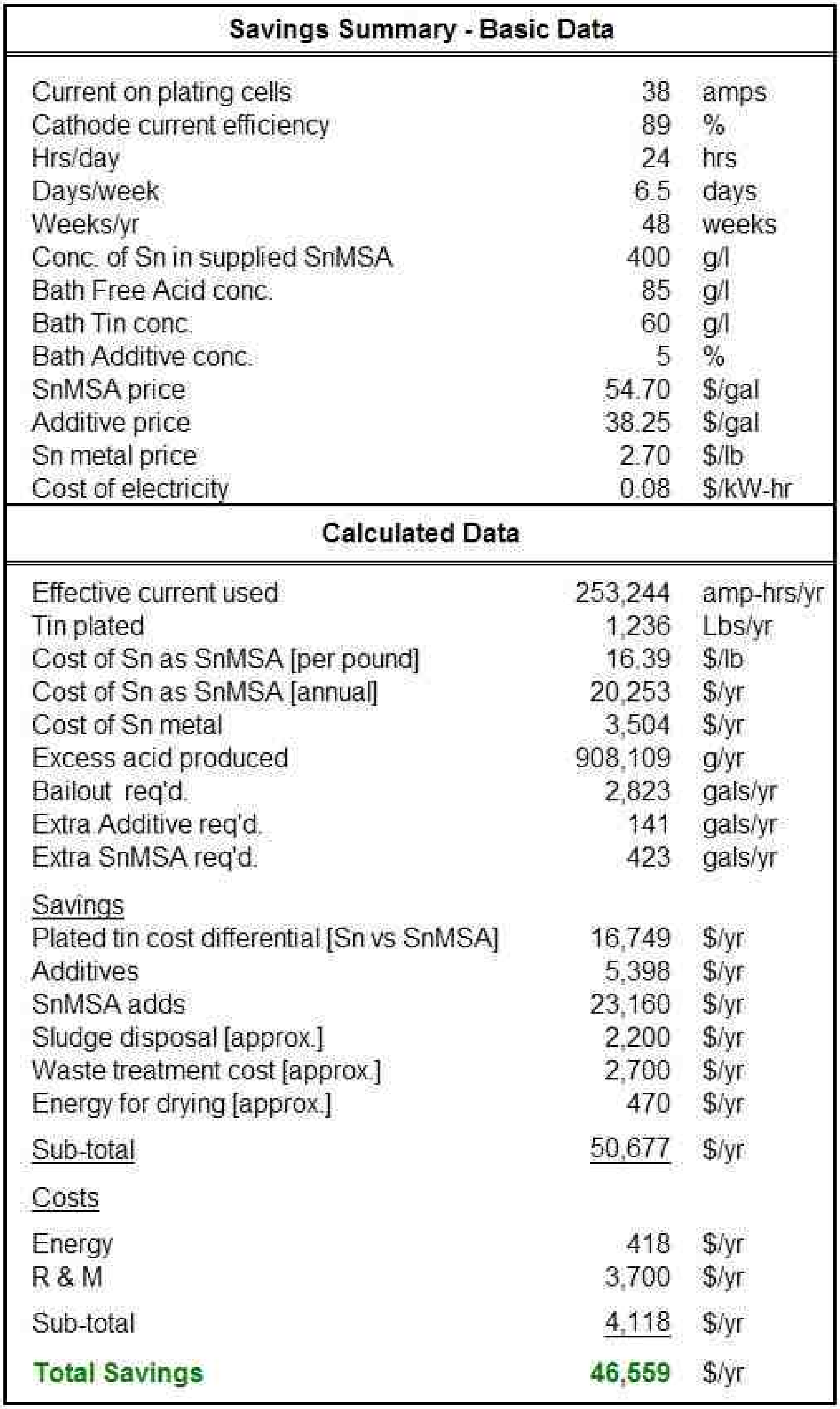
[*] TinSolve - a product of Precision Process Equipment Inc., Niagara Falls, NY



Savings Summary - Basic Data		
Current on plating cells	38	amps
Cathode current efficiency	89	%
Hrs/day	24	hrs
Days/week	6.5	days
Weeks/yr	48	weeks
Conc. of Sn in supplied SnMSA	400	g/l
Bath Free Acid conc.	85	g/l
Bath Tin conc.	60	g/l
Bath Additive conc.	5	%
SnMSA price	54.70	$/gal
Additive price	38.25	$/gal
Sn metal price	2.70	$/lb
Cost of electricity	0.08	$/kW-hr
Calculated Data		
Effective current used	253,244	amp-hrs/yr
Tin plated	1,236	Lbs/yr
Cost of Sn as SnMSA [per pound]	16.39	$/lb
Cost of Sn as SnMSA [annual]	20,253	$/yr
Cost of Sn metal	3,504	$/yr
Excess acid produced	908,109	g/yr
Bailout req'd.	2,823	gals/yr
Extra Additive req'd.	141	gals/yr
Extra SnMSA req'd.	423	gals/yr
Savings		
Plated tin cost differential [Sn vs SnMSA]	16,749	$/yr
Additives	5,398	$/yr
SnMSA adds	23,160	$/yr
Sludge disposal [approx.]	2,200	$/yr
Waste treatment cost [approx.]	2,700	$/yr
Energy for drying [approx.]	470	$/yr
Sub-total	50,677	$/yr
Costs		
Energy	418	$/yr
R & M	3,700	$/yr
Sub-total	4,118	$/yr
Total Savings	**46,559**	$/yr

Figure 3

Figure 4