Zinc with about 40 percent manganese was deposited at a cathode current efficiency of 60 percent in a sulfate/citrate bath with a flow rate of 2 m/sec. A small amount (0.15 g/L) of sodium thiosulfate was added to maximize efficiency. Coatings with a consistent, desired composition were produced using a conventional, horizontal electrogalvanizing line equipped with nozzles for uniform solution flow.

Steel plated with zinc alloys provides good corrosion resistance, weldability, paintability, and mechanical properties. Zinc-iron and zinc-nickel are two of the alloys that have been used extensively by Japanese automakers demanding coatings with exceptional corrosion resistance.

Another alloy that has shown promise is zinc-manganese. The codeposition of manganese from a sulfate/citrate bath also affords the excellent corrosion protection, paintability, and other properties desired by automobile manufacturers. A viable process that produces a zinc alloy containing approximately 40 percent manganese has been developed.

Experimental Procedure
The sulfate/citrate bath contained zinc sulfate, manganese sulfate, and sodium citrate, which acts as a completing agent (Table 1). In some experiments, the bath composition and pH were varied; pH was adjusted using sodium hydroxide or sulfuric acid.

Electrodeposition was conducted under potentiostatic or galvanostatic conditions using a flow cell with a steel cathode and a parallel Pt-coated titanium anode (Fig. 1). During potentiostatic electrolysis, the potential was measured through a capillary, which was inserted from the back of the cathode to the cell. To avoid disturbing electrolyte flow, the top of the capillary was set at the level of the cathode surface. The reference electrode was Ag/AgCl.

Table 1

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Cone., mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄·7H₂O</td>
<td>0.24</td>
</tr>
<tr>
<td>MnSO₄·H₂O</td>
<td>0.18</td>
</tr>
<tr>
<td>Na₃C₆H₅O₇·2H₂O</td>
<td>0.612</td>
</tr>
</tbody>
</table>

*pH 5.6.

![Flow cell diagram](image1)

![Effect of current density and flow rate on Mn content of deposit](image2)

![Effect of temperature on Mn content of deposit](image3)
The deposit obtained was dissolved in dilute hydrochloric acid. The dissolved zinc and manganese were analyzed by atomic absorption spectrometry to determine the alloy composition and cathode current efficiency. To maintain the bath, the reduction of oxidized manganese ions was monitored. Bath stability was evaluated by measuring the precipitates that formed after storage for 20 days at 50°C. Trivalent manganese was reduced to Mn$^{2+}$ ions using pieces of zinc and manganese. The absorbance of the bath was measured to determine whether or not reduction had occurred.

Zinc-manganese alloys were electrodeposited on steel strip in a horizontal electrogalvanizing line using plating cells equipped with electrolyte-injecting, slit-type nozzles. The uniformity of the alloy deposits was determined by examining the distribution of zinc and manganese in the depth direction of the coatings by glow-discharge spectrometry.

**Alloy Composition**

The effect of current density and flow rate on the composition of Zn-Mn alloys deposited from the standard bath is shown in Fig. 2. Only zinc, which is electrochemically more noble than manganese, was deposited in the low-current-density range (<10 A/dm$^2$). The two metals were codeposited at a higher current density. The content of manganese, which is less noble than zinc, increased with increasing current density. Manganese peaked at 30 or 40 A/dm$^2$ and decreased with further increases in current density. In this current density range, the deposit was burned.

An increase in flow rate extended the current density range to a point at which only zinc was deposited, and decreased the Mn content when current density was fixed. Furthermore, an increase in flow rate shifted the current density at which the Mn content peaked.

The effect of temperature on the composition of alloys electrodeposited from the standard bath is shown in Fig. 3. Raising the temperature had about the same effect as increasing the flow rate.

Figure 4 shows the effect of pH on the Mn content of the coating deposited from the standard bath. The Mn content declined with a decrease in pH.

The relationship between the Mn content of the deposit and the metal percentage of Mn in the bath (Mn$^{2+}$/Zn$^{2+}$ + Mn$^{2+}$ by wt) is shown in Fig. 5. The total metal ion concentration was kept constant at 0.42 M. The percentage of Mn in the deposit increased directly with the metal percentage of Mn in the bath, but the increase depended on current density. The effect of the sodium citrate concentration is shown in Fig. 6. A decrease in sodium citrate reduced the Mn content of the deposit.

As mentioned earlier, the composition of electrodeposited Zn-Mn alloys varied considerably with a change in plating variables. The effects of these variables on partial cathodic polarization curves were investigated. Figure 7 shows partial cathodic polarization curves for Zn-Mn alloy.
electrodeposition from the standard bath at 50°C with a flow rate of 2 m/sec. Figure 8 represents the effect of flow rate and temperature on partial cathodic polarization curves.

The amount of Zn and Mn in the deposits was determined by atomic absorption spectrometry. Once these data were collected, the partial current densities \( i \) of Zn and Mn were calculated:

\[
\begin{align*}
\text{Zn:} & \quad i_{\text{Zn}} = \frac{W_{\text{Zn}}}{m_{\text{Zn}}/2} \frac{96,500}{t} \\
\text{Mn:} & \quad i_{\text{Mn}} = \frac{W_{\text{Mn}}}{m_{\text{Mn}}/2} \frac{96,500}{t}
\end{align*}
\]

where \( W_{\text{Zn}} \) is the weight of Zn in the deposit in g/dm\(^2\), \( W_{\text{Mn}} \) is the weight of Mn in the deposit in g/dm\(^2\), \( m_{\text{Zn}} \) is the atomic weight of Zn (65.37), \( m_{\text{Mn}} \) is the atomic weight of Mn (54.94), \( Q \) is the quantity of electricity (c) applied (\( Q = 270 \text{c} \) at -1400 mV or less and 40 or 135 c at -1300 mV or a more noble potential), \( t \) is the electrolysis time in sec, and \( A \) is the area of deposition in dm\(^2\) (\( A = 0.17 \text{dm}^2 \)).

Even at a potential range less noble than that in which the limiting current density was reached, the partial current density of zinc varied with the potential. However, the partial current density was relatively high at a high flow rate and temperature. This indicates that the partial current density of zinc is controlled by diffusion. Elevating the temperature increases the diffusion constant of zinc and zinc-citrate complex ions and the zinc ion concentration due to a decrease in the formation constant of zinc-citrate complex ions.

The slight increase in the partial current density of zinc at -1700 to -1900 mV maybe the result of agitation caused by an increase in hydrogen evolution. The decrease in the partial current density of zinc in the less-noble potential range may be related to an increase in pH in the vicinity of the cathode due to abundant hydrogen evolution, which promotes the formation of zinc-citrate complex ions, thus suppressing zinc deposition.

Manganese began to be deposited at -1500 to -1600 mV. The partial current density of Mn approached the limiting current density with high polarization and decreased at a potential range less than that of the limiting current density, where the deposit was burned. An increase in the flow rate raised the limiting current density. However, the partial polarization curve of Mn was only slightly changed by flow-rate changes except in the range producing burnt deposits. Temperature increases also had only a slight effect on the partial cathodic polarization curve of Mn. These results indicate that the deposition rate of Mn is not diffusion controlled in the region in which useful Zn-Mn alloys are deposited.
The partial current density of hydrogen was affected by diffusion at a potential more noble than -1700 mV, but only slightly so at a less noble range. The slope of the partial polarization curve for hydrogen changed sharply at -1700 to -2100 mV (Fig. 8c), demonstrating that hydrogen evolution was promoted.

Only zinc was deposited at -1100 to -1500 mV (Figs. 7 and 8). When manganese began to be codeposited with zinc, the partial current density of Mn increased sharply toward the less noble direction, whereas the partial current density of Zn decreased somewhat, resulting in an increase in the Mn content of the alloy. An increase in flow rate and temperature increased the partial current density of zinc (due to the promotion of diffusion) but did not affect that of Mn. The Mn content of the deposit decreased with increasing flow rate and/or temperature.

The deposition potential of Zn shifted to the noble direction and its partial current density increased when the solution pH was reduced from 5.6 to 5.0 (Fig. 9). On the other hand, the deposition potential of Mn became less noble. These observations indicate that: (1) the zinc-citrate ion formation was reduced by the pH decrease, which increased the uncompleted Zn ion concentration and thereby increased the limiting current density of Zn, and (2) the formation of manganese-citrate complex ions was increased by the decrease in pH. The net result was promotion of Zn and suppression of Mn deposition. A decrease in the concentration of sodium citrate may decrease the formation of zinc-citrate complex ions, thus increasing the partial current density of zinc and its deposition rate.

Cathode Current Efficiency

The cathode current efficiency decreased as the manganese content of the deposit increased (Fig. 10). Cathode current efficiency is expressed as follows:

\[
η = \frac{(i_{\text{Zn}} + i_{\text{Mn}})}{(i_{\text{H}_2} + i_{\text{Mn}} + i_{\text{Zn}})} = \frac{1 + i_{\text{H}_2}/i_{\text{Zn}}}{(1 + i_{\text{H}_2}/i_{\text{Mn}} + i_{\text{H}_2}/i_{\text{Zn}})} = \frac{1 + i_{\text{H}_2}/i_{\text{Mn}}}{(1 + i_{\text{H}_2}/i_{\text{Zn}} + i_{\text{H}_2}/i_{\text{Mn}})}
\]

where \(i_{\text{Zn}}, i_{\text{Mn}}, \) and \(i_{\text{H}_2}\) represent the partial current densities of zinc, manganese, and hydrogen, respectively. This equation demonstrates that the cathode current efficiency is determined only by the Mn content if \(i_{\text{H}_2}/i_{\text{Zn}}\) or \(i_{\text{H}_2}/i_{\text{Mn}}\) is constant; \(i_{\text{H}_2}/i_{\text{Zn}}\) is not constant in the potential range in which zinc and manganese are codeposited (Fig. 7). By contrast, \(i_{\text{H}_2}/i_{\text{Mn}}\) is nearly constant, as shown in Fig. 11, where data for deposits containing more than 10 percent by wt Mn are plotted. Because \(i_{\text{H}_2}\) and \(i_{\text{Mn}}\) are nearly
independent of flow rate and temperature in the range of
codeposition (Fig. 8), it is understood that \( \frac{i_0}{i_1} \) is not
affected by flow rate and temperature.

The effect of pH on cathode current efficiency is shown
in Fig. 12. Using the standard bath, the cathode current
efficiency was not affected by pH 5.0 to 5.6. However, the
cathode current efficiency decreased at pH values lower
than 4.5.

Although the standard bath (Table 1) has a high cathode
efficiency, this value is reduced as the manganese
concentration is increased. Therefore, additives for in-
creasing efficiency were investigated. Adding small
amounts of sulfur compounds such as sodium thiosulfate,
telluric acid, and selenic acid markedly increased effi-
ciency. Sodium thiosulfate proved to be the best because it
did not adversely affect corrosion resistance or paint
adhesion as did the other additives.

Figure 13 shows the effect of sodium thiosulfate on
cathode efficiency, which was increased from about 40 to
60 percent for alloys containing approximately 40 percent
Mn. Although adding 0.1 or 0.15 percent sodium thiosulfate
improved efficiency, the reason for this improvement has
not been clarified.

Bath Stabilization

A previous report" indicated that precipitation occurred in
a sulfate/citrate bath. In the study reported here, no
precipitates formed when the bath was stored at 50° C for
20 days at pH 5.4 to 6.0. However, Fig. 14 shows that
precipitate formation did occur at pH 3.0 to 5.4.

Divalent manganese ions are oxidized by dissolved
oxygen or oxidation reactions on insoluble anodes. An
increase in the concentration of oxidized Mn ions reduced
the cathode current efficiency. To avoid this, metal pieces
were used to reduce oxidized manganese ions to Mn\(^{2+}\) ions.
Figure 15 shows absorbance of the bath before deposition,
after plating using a platinum-coated titanium anode, and
after reaction with metallic zinc.

![Fig. 12—Effect of sodium thiosulfate additions on cathode current efficiency.](image)

![Fig. 13—Effect of pH on cathode current efficiency.](image)

![Fig. 14—Relationship between pH and precipitates formed in bath after 20 days at 50°C.](image)

![Fig. 15—Absorbance of bath (a) before plating, (b) after plating using 1.7 Faraday/L, and (c) after reaction with metallic zinc.](image)
After plating, a strong absorbance peak appeared at approximately 430 nm. However, the peak disappeared after the bath reacted with metallic zinc. The peak at 430 nm was believed to be characteristic of Mn\(^{3+}\)-citrate complex ions. Accordingly, the results described previously show that Mn\(^{3+}\) ions were generated during plating but were reduced to Mn\(^{2+}\) ions on the surface of metallic zinc. Trivalent Mn ions were also reduced on the surface of metallic manganese. Thus, oxidized Mn ions can be reduced by reaction with either zinc or manganese.

Manufacturing Process
Steel plated with Zn-Mn alloys can be produced on a conventional electrogalvanizing line using zinc and insoluble anodes and simultaneously supplying Mn ions to the bath by dissolving metallic manganese. However, plating variables must be strictly controlled to produce uniform Zn-Mn deposits. Alloy composition is sensitive to operating variables, especially to electrolyte flow in the plating cell. The flow should be uniform but is often undermined by the apparatus used for agitation.

To determine whether or not uniform deposits could be produced on an industrial scale, Zn-Mn alloys were plated on steel strip on a horizontal electrogalvanizing line equipped with slit-type, electrolyte-injecting nozzles. A depth profile (Fig. 16) analyzed by glow-discharge spectrometry showed that uniform alloy coatings were indeed produced.

Summary
The deposition potentials of zinc and manganese deposited from a sulfate/citrate bath at a high solution flow rate differed considerably. Codeposition of Zn and Mn occurred only at relatively high current density. The manganese content increased with increasing current density. The deposition rate of zinc increased with increasing flow rate and/or temperature, both of which promote diffusion, while that of manganese was not diffusion controlled. The pH affects complex ion formation and deposit composition. A pH of 5.4 to 6.0 prevented the formation of precipitates. Adding 0.1 or 0.15 g/L sodium thiosulfate improved cathode current efficiency. A uniform deposit was obtained on steel strip in a horizontal plating line equipped with nozzles for uniform solution flow.

References
9. R. Noumi et al., ibid.

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