### Characteristics of a Non-Cyanide Alkaline Zinc Plating Bath

By R.M. Krishnan, S. R. Natarajan, V.S. Muralidharan and Gurdeep Singh

Zinc coatings are widely applied for corrosion protection of iron and steel. The protection offered is not because of envelope effect alone, but is largely a result of zinc's anodic behavior in any electrochemical reaction. The authors describe experimental investigations of nitrilotriacetic acid (NTA) solutions and compare their deposition characteristics with others commonly used.

he cyanide process for electrodeposition of zinc is increasingly being replaced by chloride and noncvanide processes. The chloride baths have found practical applications over the past few years. With a proper combination of brightener additives, these baths produce bright, leveled deposits that readily accept a chromate finish.' These baths have certain disadvantages, however, such as high corrosivity, lower throwing power than cyanide, and susceptibility to iron contamination, which causes difficulty in chromating. Substitution of a complexing agent for the cyanide has been reported to widen the bright plating range.<sup>24</sup>Use of newer completing agents such as nitrilotriacetates for electrodeposition of zinc has been studied previously by the authors.<sup>5</sup>The present studies report results of investigations of the polarization and hydrogen permeation characteristics of cathodes, of conductivity and throwing power of the baths, and of the self-corrosion of anodes.

#### **Experimental Procedure**

#### Cathode Polarization

Different cathode currents were passed through specimens of cold-rolled mild steel and soluble zinc anodes in 800 mL of solution. Cathode potentials were measured against SCE and

## Table 1BathCompositions

Acid sulfate Zinc sulfate	Quantity, g/L
Sodium acetate	30
Aluminum sulfate	30
Cyanide bath	
Zinc cyanide	60
Sodium cyanide	23
Sodium hydroxide	53
Chloride electrolyte	
Zinc chloride	104
Potassium chloride	215
pH 5.0	
NTA-based electrolyte	
Zinc sulfate	75.0
Sodium hydroxide	60.0
Nitrilotriacetic acid	95.6

subsequently plotted vs. the applied current density for solution temperatures of 30 and 40 'C. The slope of the polarization curve (dE/dt) was calculated for each solution.

#### Conductivity of Solutions

The conductivity of each of the different solutions was determined by a digital conductivity meter.' Generally, a plating bath having high conductivity is associated with less energy consumption and greater throwing power.

#### Throwing Power

Throwing power was measured in each case by use of a Haring and Blum Cell. The assembly consisted of a rectangular cell with two sheet metal cathodes measuring  $9 \times 5 \times 0.1$  cm, filling the entire cross-section at both ends, and a perforated anode of the same size. The anode was placed between the cathodes so that its distance from one of the cathodes was one-fifth of its distance from the other. Throwing power was calculated by using the following formula?

Throwing power (percent) = 
$$\frac{K-C}{K+C-2} \times 100$$

where C is the metal distribution ratio between the nearer cathode and the farther, and K the ratio of the distances, respectively, of the farther and nearer cathodes from the anode.

#### Hydrogen Permeation Set-Up

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The glass cell used was similar to that used by earlier investigators,<sup>7</sup> and was fashioned so that water could be circulated. It had two compartments connected through Teflon bushings clamped between two stainless steel sheets. The bushings had a hole of one cm<sup>2</sup> cross-sectional area. Both compartments could accommodate a platinum auxiliary electrode and a Hg/ HgO/0.2N NaOH reference electrode.

A steel membrane plated on one side with palladium was fixed between the Teflon bushings. The compartment facing the palladium-plated side was filled with 0.1 N NaOH solution pre-electrolyzed by a current of 10  $\mu$ A. The cell was connected to a potentiostat and a constant potential of 300 mV vs. the Hg/



Fig. 1—Polarization curves for mild steel cathodes in different zinc plating baths at 30 °C.

# Table 2 Conductivity and Other Data for Different Electrolytes

	Conductivity	Slope (dE/di) mΩ		Cell voltage at 1 A/dm <sup>2</sup>	
Electrolyte	mho cm <sup>-1</sup> x 10 <sup>-2</sup>	30 °C	40 °C	(v)	
1. Acid sulfate	4.9	60	60	1.1	
2. Cyanide	15	40	60	1.5	
3. NTA-based electrolyte	5.9	120	130	1.6	



Fig. 2—Polarization curves for mild steel cathodes in different zincplating baths at 40  $^\circ\text{C}.$ 

HgO/0.2N NaOH electrode was applied to the specimen. After the initial current reached steady state, the other compartment (facing the unplated side) was filled with the test solution, which was allowed to deposit zinc on the steel membrane. The permeation current was recorded simultaneously for 30 to 40 min. The measurements were made at 30 'C for different zinc baths and the permeation currents compared. The compositions of the various electrolytes studied are given in Table 1.

### **Results and Discussion**

Cathodic Polarization and Conductivity of Electrolytes

The potential of the steel cathodes at different current densities during deposition of zinc from different electrolytes was measured against SCE. Figures 1 and 2 show the polarization curves at 30 and 40 'C, respectively. The potentials in NTAbased electrolyte at all current densities were more negative when compared to other electrolytes. The greater shifts in



Fig. 3-Variation of permeation current with time in conventional baths. Fig.4—Variation of permeation current with time in NTA-based baths.

 Table 3

 Percentage Throwing Power of Each of Different Electrolytes Studied

No.	Temperature "C	Current density A/dm²	NTA-based pH 8.5	electrolyte pH 10.5	Acid sulfate electrolyte	Chloride electrolyte	Cyanide electrolyte
1.	30	1.0	23.0	23.4	-7.7	8.8	12.7
2.	30	2.0	24.6	21.1	-2.8	21.4	50.1
3.	40	1.0	17.3	17.7			
4.	40	2.0	12.6	11.2			
5.	50	1.0	21.2	19.6			
6.	50	2.0	19.7	6.5			

# Table 4 Data from Hydrogen Permeation Studies

Current (μΑ/cm²)					
Electrolyte		Maximum peak	Plateau ± 0.01	Q <sub>⊬</sub> millicoulombs (± 0.1)	
1. Acid sulfa 2. NTA-bas	ate ed electrolyte	100	45	49.0	
at pH 7		72	47	44.0	
at pH 8.5		92	66	61.5	
at pH 10.	5	100	67	68.0	
3. Cyanide		90	76	70.0	

cathode potentials are a result of the discharge of NTAcomplexed zinc ions. When zinc is not complexed, the potentials are less negative, though in the case of zincate and zinc cyanide solutions, zinc deposition at moderate potentials was possible. The potential values are closer in electrolytes of cyanide and NTA complexes.

Table 2 shows the data on cell voltage, conductivities and polarization resistance. The last was determined from polarization curves. The NTA-based bath exhibits a higher cell voltage, even though its conductivity is moderate. Because of the enhanced nobilities of hydroxyl and cyanide ions, cyanide baths exhibit medium cell voltage and the highest conductivity. The low cell voltage exhibited by the acid sulfate bath is a result of the discharge of noncomplexed zinc occurring at lower potentials, though its conductivity is poor.

The slope of the polarization curve and the polarization resistance (dE/di) increase with temperature for both the cyanide and NTA-based electrolytes, resulting in greater current efficiency and rate of build-up. Because the discharge of the zinc-NTA complex occurs at high negative potentials, the cell voltage is also higher.

#### Throwing Power

Deposition from solutions of complexes usually takes place at higher cathode potentials and is thereby associated with enhanced throwing power. On the other hand, non-completing electrolytes, such as acid sulfate, are associated with very poor throwing power. A throwing power of about 50 percent was found possible with the cyanide electrolyte at 2 A/dm<sup>2</sup>. For NTA-based electrolytes the throwing power was considerably higher than the acid sulfate or chloride and was very little influenced by pH variations at 30 °C, although at 40 °C somewhat lower values were observed. An increase in pH caused a decrease in throwing power at 50 "C (Table 3).

#### Hydrogen Permeation

Figures 3 and 4 illustrate the variation of permeation current with time in the case of cold rolled steel cathodes coated with palladium on one side and polarized at one A/dm<sup>2</sup>. The maximum current (i<sub>max</sub>) was high for an acid sulfate bath as deposition of zinc was taking place from the complex-free bath at lower cathode potentials and PH. The parameter Q<sub>4</sub>, which is the charge resulting from ionization of permeated hydrogen, assumes its least value because of the high efficiency of zinc deposition from the bath. The cyanide bath exhibits a high Q<sub>H</sub> value, indicating the possibility of hydrogen embrittlement. The higher plateau values for cyanide electrolytes suggest a high deposit porosity which may allow easier degassing by baking. The NTA-based electrolyte was found to be associated with an even smaller Q<sub>H</sub> value (44.0 mC) and because it would be easily amenable to deembrittlement from the viewpoint of commercial-scale operations (Table 4). Figure 5 shows how the variations of  $i_{max}$  and  $Q_{H}$  increase with pH, as well as with an increase in rate of build-up and current efficiency.



Fig. 5-Variation of  $I_{max}$  and  $Q_s$  with pH in NTA-based bath.

 Table 5

 Variation of Self-Corrosion Rate of Anodes with Time of Exposure (hr) at 30 °C

Corrosion rate (mold)					
Electrolyte	1	3	6	9	24
1. Acid sulfate	1.33	4.25	14.50	31.90	123.00
2. Cyanide	1.25	4.63	19,25	32.20	118.00
3. NTA-based electrolyte	0.25	1.25	6.25	10.50	43.00

The deposition of zinc from its NTA complex takes place at **References** very negative potentials above the reversible hydrogen evolution potential in this pH range. Discharge of hydrogen ions would take place with those of zinc while the recombination of atomic hydrogen to form molecular hydrogen is prevented in the presence of zinc. The increase in i<sub>max</sub> with pH should be attributed to the increase in reversible potentials for the hydrogen evolution reaction. A pH of 8.5 was found to be suitable for practical electrodeposition.

#### Self-Corrosion of Anodes

The zinc anode can undergo self-corrosion in electrolytes when not in use. One-cm-diameter zinc anodes were immersed in various baths and, after a specific period, loss of zinc in each case was determined by weighing, after cleaning and drying the specimens. Self-corrosion in NTA based-electrolytes was found to be the least while in acid sulfate it was, of course, the maximum. Prolonged exposure increased the corrosion in all baths. The observation of least corrosion in the NTA-based electrolyte could be because of passivation of the surface with oxides and hydroxides. In cyanide electrolytes, the formation of zincate and the zinc cyanide complexes would be favored at pH 11 (Table 5).

#### Conclusions

The experimental studies of the NTA-based electrolyte developed showed that the bath has some specific advantages with respect to electrolyte throwing power and self-corrosion of zinc anodes over conventional electrolytes for zinc plating.

- 1. H.S. Schneider, Plat. and Surf. Fin., 64,52 (June, 1977).
- 2. D.E. Weiner, Prod. finish. (London) 29, 10 (Oct., 1976).
- 3. J.A. Weber, P. Tomassi, and S. Sczcepaniak, Powloki ochronne, 23(1),33 (1977).
- 4. W. Francis, J.A. Weber and T. Zuk. *ibid.*, 6(3), 15 (1978).
- 5. R.M. Krishnan, V.S. Muralidharan, S.R. Natarajan and Gurdeep Singh, Metal Fin., 89(2), 15 (Feb., 1991).
- 6. H. Silmen, G. Isserlis and A.F. Averill, Protective and Decorative Coatings for Metals. Finishing Publications Ltd., Teddington, England, 1978; p. 6.
- 7. M.A.V. Devanathan and Z. Stachurski, Proc. Royal Soc., London, A270,88(1962).







Krishnan

Muralidharan

#### About the Authors

Dr. R.M. Krishnan is a senior member of the Plating Laboratory Team at the Central Electrochemical Research Institute, Karaikudi 623 006, India. He holds a PhD in chemistry.

S.R. Natarajan is head of the Industrial Metal Finishing Division of the Central Electrochemical Research Institute, as well as group leader in the Plating Laboratory. He holds an MA from Annamalai University and has worked on plating from aqueous and organic electrolytes for more than 30 years.

Dr. V.S. Muralidharan is a scientist at the Central Electrochemical Research Institute. He holds MS and PhD degrees from Banaras Hindu University. His technical interests include metal finishing, corrosion and passivation of metals and alloys, development of secondary batteries and solid electrolytes. Dr. Muralidharan has published more than 100 research papers.

Dr. Gurdeep Singh is an assistant professor at the Indian School of Mines, Dhanbad. He holds a PhD in chemistry from the same institution. His technical interests include metal finishing, corrosion, and pollution control.