

Characteristics of an Alkaline Tartrate Zinc Plating Bath

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Zinc electrodeposits offer protection to steel against atmospheric corrosion both by galvanic and envelop effects. The cyanide process for zinc electrodeposition is increasingly being replaced by chloride and many other noncyanide formulations.¹⁻³ Use of newer complexing agents such as nitrilotriacetates (NTA)⁴, gluconates,⁵ and borogluconates⁶ offer promising results. The present investigation is aimed at developing tartrate as a complexing agent in an alkaline medium for zinc plating. The studies of zinc deposition from tartrate baths are presented along with a comparison with existing zinc baths.

EXPERIMENTAL PROCEDURE

Cathode Polarization

Different cathode currents were passed through specimens of cold-rolled mild steel and soluble zinc anodes in 800 ml of the solution. Cathode potentials were measured vs SCE and subsequently plotted against the applied current densities for solution temperatures of 30 and 40°C. The slope of the polarization curve (dE/di) was calculated for each solution.

Conductivity of Solutions

Using a digital conductivity meter the conductivity of each of the solutions was measured. Generally, a plating bath having a good conductivity is associated with less energy consumption and greater throwing power.

Current Efficiency

For current efficiency experiments the electrodeposition assembly consisted of electrolytically pure soluble zinc anodes and a steel cathode of equal size (5 × 4 × 0.25 cm), immersed in a 800-ml solution in a 1-liter wide-mouthed glass vessel. The solution was normally agitated and, when necessary, heated using a heater with magnetic stirrer. For current efficiency determination, each specimen was

weighed before and after plating, and the weight of the deposits was determined from the difference.

Hull Cell Studies

Hull cell experiments were carried out with solutions containing 12 g/L zinc oxide, 120 g/L sodium hydroxide, and 75 g/L sodium potassium tartrate (Rochelle salt), and varying quantities of furfuraldehyde, for producing bright deposits of zinc. A cell current of 1 A was used for a duration of 10 min. A regulated DC power supply was used as the current source, and a calibrated ammeter along with the cell constituted the electrical circuit. Hull cell panels of mild steel were used. The temperature was maintained at ± 1°C. Electrolytic zinc was used as the anode material.

Throwing Power

Throwing power was measured in each case by using a Haring and Blum cell. The assembly consisted of a rectangular cell, with two sheet-metal cathodes measuring 9 × 5 × 0.1 cm, filling the entire cross-section at both ends and a perforated anode of the same size, kept in the cell such that the distance of it from one of the cathodes is 1/3 of that from the other. Throwing power was calculated using the following formula:⁷

$$\text{Throwing Power \%} = \frac{(K - C)}{(K + C - 2)} \times 100$$

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

Surface Morphology

The surface of zinc electrodeposits obtained from Rochelle alkaline bath with and without furfuraldehyde, and from conventional baths were examined using a metallurgical microscope, to the magnification of 400× and photographs were taken.

RESULTS AND DISCUSSION

Bath Development

Rochelle's salt is chosen as an alternate complexing agent to replace cyanide in alkaline conditions. Detailed investigations were carried out at different temperatures and with varying bath constituents. Table I presents the optimized bath composition. Increase of temperature and current density decreased the current efficiency, while the rate of buildup increased with increase in current. At all temperatures, above 2 A/dm² in general, a gray deposit was obtained, while at 40°C the surface was found to be matte white. The change of cathode efficiency and rate of buildup was also studied at a given current density with time. In general the rate of buildup was found to depend on the temperature and on the concentrations of zinc and hydroxyl ions (see Figs. 1-3).

If v is the rate of deposition, then

$$v = dW/dt \propto (Zn)^x (OH)^y (\text{tartrate})^z$$

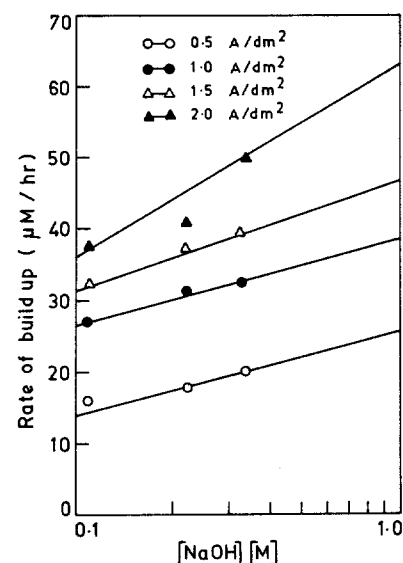


Figure 1. Variation of the rate of buildup with sodium hydroxide concentration at constant zinc and tartrate ion concentrations.

Table I. Influence of Current Density and Temperature on the Current Efficiency, Rate of Buildup, and Nature of the Deposits Obtained from Tartrate Bath

Temperature (°C)	Current Density (A/dm ²)	Cathode Efficiency (%)	Rate of Buildup (µm/hr)	Nature of the Deposit
30	0.5	98.5	16.8	Slightly gray
	1.0	80.2	20.6	Uniform matte white
	1.5	75.1	37.4	Slightly gray
	2.0	71.3	57.74	Uniform matte white
	2.5	80.6	68.9	Uniform matte white
40	3.0	78.9	80.7	Slightly gray
	0.5	92.7	15.8	Slightly black
	1.0	86.8	29.19	Slightly black
	1.5	77.9	42.73	Slightly black
	2.0	92.5	63.4	Matte white
50	2.5	84.7	71.8	Matte white
	3.0	79.0	80.80	Matte white
	0.5	92.0	15.7	Slightly blackish
	1.0	87.1	29.7	Slightly blackish
	1.5	87.6	46.07	Slightly blackish
	2.0	95.0	64.8	Gray
	2.5	85.0	72.3	Gray
	3.0	81.2	83.09	Gray

Bath composition: ZnO, 9 g/L; NaOH, 120 g/L; Rochelle salt, 50 g/L.

Table II. Composition of Zinc Baths Used

Bath	Constituent	Concentration (g/L)
Acid sulfate	Zinc sulfate	240
	Ammonium chloride	30
	Aluminum sulfate	60
Cyanide	Zinc cyanide	60
	Sodium cyanide	23
	Sodium hydroxide	53
Chloride	Zinc chloride	104
	Potassium chloride	215
NTA bath	pH 5	
	Zinc sulfate	75
	Sodium hydroxide	60
	Nitritotriacetic acid	95.6
Rochelle bath A	pH 10.5	
	Zinc oxide	12
	Rochelle salt	75
Rochelle bath B	Sodium hydroxide	120
	Zinc oxide	9
	Rochelle Salt	50
	Sodium hydroxide	120

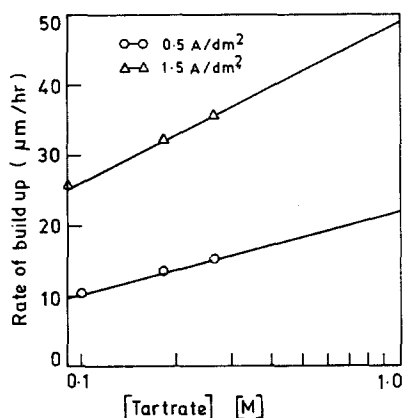


Figure 2. Variation of the rate of buildup with tartrate concentration at constant zinc and hydroxyl ion concentrations.

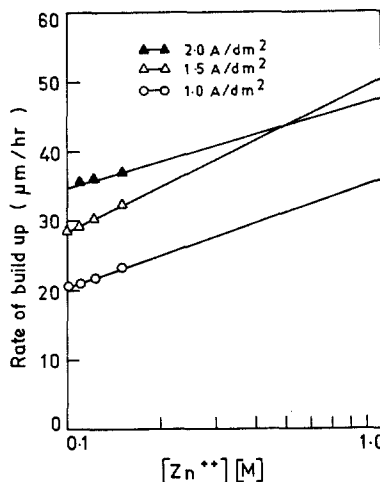


Figure 3. Variation of the rate of buildup with zinc concentration at constant hydroxyl and tartrate ion concentrations.

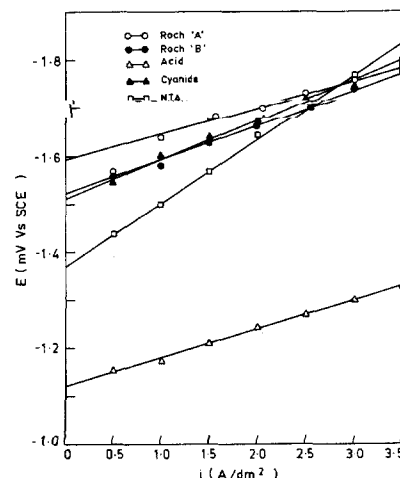


Figure 4. Polarization curves for mild steel cathodes in different zinc plating baths at 30°C.

It was found that the rate of zinc deposition was found to vary linearly with $\log (Zn^{++})$ concentration, with a slope of 1.6 ± 0.2 decade⁻¹, and with \log of hydroxyl ion concentration and \log tartrate concentration with slopes of 1.5 ± 0.1 decade⁻¹ respectively; hence, the rate of buildup of zinc deposit was:

$$K (Zn)^{1.6} (OH)^{1.5} (\text{tartrate})^{1.5}$$

where K is a constant.

Comparison With Conventional Baths

Table II presents the composition of various zinc baths used.

Cathode Polarization and Conductivity

The potential of steel cathodes at different current densities during zinc deposition from different baths was measured versus SCE (see Fig. 4). The potentials in Rochelle Bath A at all current densities are more negative as compared to other baths while the potentials in cyanide and Rochelle Bath B are comparable. The greater shifts in cathode potentials are a result of the discharge of tartrate complexed zinc ions. When zinc is not complexed, deposition is possible at moderately low negative potentials.

Higher cell voltages were exhibited (Table III) by all complexing baths with Rochelle baths exhibiting cell voltages in between those of cyanide and NTA. Because of the enhanced mobilities of the hydroxyl and tartrate

Table III. Conductivity and Other Data for Different Baths

Bath	Conductivity mho/cm × 10 ⁻²	Slope (dE/di)		Cell Voltage at 1 A/dm ² (V)
		30°C	40°C	
Sulfate	4.9	60	60	1.1
Cyanide	15	40	60	1.5
NTA bath at pH 10.5	5.9	120	130	1.6
Rochelle bath A	21.5	50	60	1.5
Rochelle bath B	23.81	50	60	1.5

Table IV. Comparison of Current Efficiencies (%) of Various Zinc Baths

Current (A/dm ²)	Cyanide (30°C)	Sulfate (30°C)	NTA (30°C)	Rochelle Bath B		
				(30°C)	(40°C)	(50°C)
0.5	93.0	95.7	90.2	98.5	92.7	91.8
1.0	96.7	98.0	88.2	80.2	85.8	87.1
1.5	98.6	99.3	80.4	75.1	77.9	87.6
2.0	—	—	75.9	91.3	92.5	94.7
2.5	—	—	78.3	80.6	86.7	84.8
3.0	—	—	80.4	78.9	79.0	82.0

Table V. Percentage Throwing Power of Each of the Different Zinc Baths at 30°C

Current Density (A/dm ²)	NTA Bath		Acid Sulfate Bath	Chloride Bath	Cyanide Bath	Rochelle Bath	
	pH 8.5	10.5				A	B
0.5	—	—	—	—	—	53.2	41.7
1.0	23.0	23.4	-7.7	8.8	12.7	24.4	40.4
2.0	24.6	21.1	-2.8	21.4	50.1	21.1	36.0

ions the conductivity of the Rochelle bath was found to be the highest.

The slope of the polarization curve and the polarization resistance (dE/di) increased with temperature, with greater current efficiency and rate of buildup in all the baths.

Because the discharge of zinc tartrate complex occurs at high negative potentials, the cell voltage is also higher.

Comparison of Current Efficiencies

The current efficiency decreased with current density up to 2 A/dm² and

was found to increase afterwards in Rochelle and NTA baths, at all temperatures. The sulfate bath exhibited higher current efficiencies, while the current efficiencies of complexed zinc baths are comparable (Table IV).

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, a noncomplexing bath such as acid sulfate is associated with poor throwing power (Table IV).

Relatively, the deposits from a tartrate-based electrolyte exhibited bigger crystallites with uniform coverage, while the deposit from cyanide bath exhibited a fine-grained structure, with complete coverage of the surface. At 0.5 A/dm², 53% throwing power was observed from a tartrate-based electrolyte while the increase of current density decreased it. The throwing power of the Rochelle baths are comparable with both NTA and cyanide baths.

The surface of the electrodeposit from the acid bath was found to exhibit larger crystallites with less coverage.

Effect of Furfuraldehyde

Furfuraldehyde was reported as a brightener for the electrodeposition of zinc from NTA baths.⁸ The organic substances, when added in small quantities, may either adsorb on the electrode surface and hinder the formation of the deposit,⁹ or enhance or reduce the rate of the hydrogen evolution reaction.¹⁰ In order to verify whether zinc electrodeposition is affected by the presence of furfuraldehyde, current efficiency studies were carried out with increase in furfuraldehyde concentrations. The rate of hydrogen evolution was found to increase, while that of zinc deposition decreased (Table IV). The inhibition of zinc deposition was found to be more at lower than at higher current densities. Furfuraldehyde might have adsorbed on the growth sites of zinc nuclei and thereby prevented its growth.

The surface morphology of the zinc electrodeposit exhibited interesting features. In the presence of furfuraldehyde in the bath, complete coverage of the surface with microcrystals was observed. An increase of current density helped in the formation of growth, while at the same time retaining the

Table VI. Influence of Furfuraldehyde (28 g/L) on the Rate of Buildup, Current Efficiency, and Nature of the Deposit

Current Density (A/dm ²)	Without Furfuraldehyde			With Furfuraldehyde		
	Rate of Buildup (µm/hr)	Current Efficiency (%)	Nature	Rate of Buildup (µm/hr)	Current Efficiency (%)	Nature
0.5	16.8	90.3	Slight gray	6.6	77.3	Satin gray smooth
1.0	20.2	99.0	Uniform matte white	11.0	64.4	Satin gray with streaks
1.5	28.2	90.3	Slight gray	16.7	65.4	Light gray
2.0	27.4	81.9	Uniform matte white	16.5	48.2	Slate gray
2.5	23.0	78.2	Uniform matte white	17.8	41.2	Dark gray
3.0	20.2	70.4	Slightly gray	18.0	35.1	Dark gray

Bath composition: ZnO 12 g/L; NaOH 120 g/L; Rochelle salt: 75 g/L.

surface coverage. In the absence of furfuraldehyde the Hull cell patterns exhibited matte while up to 1.4 A/dm², while dark gray powdery deposits were noted at higher current densities. Increase of furfuraldehyde concentration up to 0.42 g/L decreased the current density for white deposit formation, while higher concentration helped in the formation of a matte white deposit up to 6.13 A/dm².

CONCLUSIONS

The alkaline tartrate bath is found to exhibit higher cell voltage, throwing power, and current efficiency com-

pared to cyanide and NTA baths. The rate of deposition of zinc was found to be influenced by both hydroxyl and tartrate ion concentrations. Furfuraldehyde adsorbs on the growth sites of the zinc nucleus and controls its growth. The hydrogen evolution reaction is enhanced in the presence of furfuraldehyde.

References

1. Classen, A., U.S. Patent 809,492, Jan. 9, 1906
2. Serota, L., *Metal Finishing*, 63(10): 105; 1965
3. Wild, A.M., *Electroplating and Metal Finishing*, 10:376; 1960
4. Krishnan, R.M. et al., *Metal Finishing*, 89(2):15; 1991
5. R. Takahashi, Japanese Patent, 8765/65, 1967
6. Kyowa Hakko Kogyo & Co. Ltd. and Hitachi Ltd., U.S. Patent 8,682,789, 1969
7. Silman, H. et al., "Protective and Decorative Coatings for Metals," Finishing Publications Ltd., Teddington, England, p. 6, 1978
8. Krishnan, R.M. et al., "Hull cell studies on bright zinc plating from noncyanide baths," communicated to Metal Finishing, U.K.
9. Fischer, H., *Electrochimica Acta*, 2:50; 1960
10. Fischer, H., *Electrodeposition and Surface Treatment*, 1:239; 1973 **MF**

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