

Characteristics of Non – Cyanide Acid Zinc Plating Baths and Coatings

M. Chandran,*⁺

R. Lekshmana Sarma* and

R. M. Krishnan

Central Electrochemical Research Institute,
Karaikudi 630 006

*Vivekananda College,
Agasteeswaram 629 701.

SUMMARY – Zinc coatings may be electrodeposited from cyanide, alkaline or acid baths. However, cyanide electrolytes are highly toxic and substantial investment is required for effluent treatment. Hence, they are being replaced by chloride and non-cyanide alkaline electrolytes.

Results from a study on the conductivity, cathode polarisation, throwing power, cathode current efficiency, and anode efficiency of a bromide bath are given. The nature of deposit, its microhardness, porosity and structure, characterised using the scanning electron microscope, are reported.

Keywords: non-cyanide electrolytes, zinc plating baths, bromide baths

INTRODUCTION

Zinc-coated iron and ferrous metal parts are of commercial importance because the zinc protects them sacrificially at low cost¹. Passivation processes further improve the protection, by enhancing the corrosion resistance as well as providing a colour finish². Zinc coatings can be obtained by various methods such as hot dipping, sherardizing, metal spraying and electroplating. Among these methods, electroplating is advantageous because it can be performed at room temperature and the coating thickness can easily be controlled. Various plating solutions based on chloride, sulphate, fluoroborate, cyanide, pyrophosphate, tartrate, sulphamate, acetate, chloride-sulphate, and citrate^{3–12} have been reported.

The authors have themselves reported data on the electrodeposition of zinc from bromide-based electrolytes^{13,14}. Results on the conductivity, cathode polarisation, throwing power, cathode current efficiency and anode efficiency of this bromide bath are now presented; the nature of the deposit, its microhardness, porosity and structure are reported.

EXPERIMENTAL PROCEDURE

Composition and Conductivity of Baths

The compositions of the plating baths are shown in Table I and the respective conductivities in Table II. Bath conductivity was measured using a digital conductivity meter.

Cathode Polarisation

Different cathode currents were passed through specimens of cold-rolled mild steel and soluble zinc anodes in 800 cm³ of the plating solutions. Cathode potentials were measured against a SCE at 30°C and subsequently related to the applied current density.

Throwing Power

The throwing power of the bath was measured using a Haring and Blum Cell at 1.0 and

2.0 A dm⁻² at pH 4 and 30°C. The assembly consisted of a rectangular cell with two sheet metal cathodes measuring 9 x 5 x 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. From the weight of deposit at the near cathode (C_n) and far cathode (C_f), throwing power was calculated using¹⁵,

$$\text{Throwing power (\%)} = \frac{(K-C)}{(K+C-2)} \times 100 \quad (1)$$

where *C* is the metal distribution ratio between the near and far cathode and *K* is the ratio of the respective distances of the far and near cathodes from the anode.

Current Efficiency

The electrodeposition assembly consisted of a pure soluble zinc anode and a cold rolled steel cathode of equal size of 5 x 2.5 x 0.1 cm immersed in 800 cm³ solution contained in a one litre wide mouthed glass vessel. Plating was carried out at different current densities and the current efficiency was calculated by weighing the specimens before and after plating.

Nature of Deposit and Porosity

The nature of each deposit was examined visually and microscopically. Deposits of different thickness were tested for their porosity by the ferroxyl test¹⁶. The electrodeposits were degreased, electrocleaned and dried. The ferroxyl solution was prepared by dissolving NaCl (50 g dm⁻³) and white gelatin (50 g dm⁻³) in distilled water at 45 °C. Filter paper strips of 1 x 1 cm size each were impregnated with the above solution and dried. Before placing a strip on the sample it was moistened with a few drops of NaCl (50 g dm⁻³) solution. After 10 minutes, the paper strips were removed and placed in a solution of potassium ferricyanide (10 g dm⁻³). The porosity of each deposit was evaluated on the basis of blue spots formed on the filter paper. The results were expressed as the percentage of the defective area.

⁺ For correspondence: retnamkr@rediffmail.com

M. Chandran, R. L. Sarma and R. M. Krishnan,
Trans Inst Met Fin. 2003, **81**(6), 207

TABLE 1 Bath compositions used in electrochemical experiments

Bath	Composition	/ g dm ⁻³
A	<u>Bromide baths</u>	
	ZnBr ₂	160
	H ₃ BO ₃	80
	KBr	50
	CH ₃ COONa	20
B	ZnBr ₂	160
	H ₃ BO ₃	80
	KBr	50
	CH ₃ COONa	20
	Polyethylene glycol	0.5
C	<u>Sulphate bath</u>	
	ZnSO ₄	240
	CH ₃ COONa	30
	Al ₂ (SO ₄) ₃	30
D	<u>Cyanide bath</u>	
	Zn (CN) ₂	60
	NaCN	23
	NaOH	53

TABLE II Conductivity of different plating baths

Bath	Conductance / x10 ⁻² S cm ⁻¹
A	11.52
B	11.35
C	5.74
D	21.00

Microhardness Measurements

A diamond pyramid was pressed into the deposit under a load of 25 g for 15 s with the indentation diagonal measured after the load was removed. The microhardness in kg mm⁻² was determined in each case by using,

H_v = 1854 x L/d² (2)

where L is the load applied in g and d is the diagonal of the indentation in μm.

Structure of deposits

The structure of zinc deposits were examined using a scanning electron microscope at 2000 x magnification

RESULTS AND DISCUSSION

Conductivity of the baths

Table II shows the conductivity of different baths. The values for the bromide based baths,

TABLE III Percentage throwing power for electrodeposition of zinc from various baths at 30°C

Bath	Current Density / A dm ²	Throwing Power / %
A	1.0	+6.22
	2.0	+8.13
B	1.0	+8.84
	2.0	+12.35
C	1.0	-7.70
	2.0	-2.80
D	1.0	+12.70
	2.0	+50.10

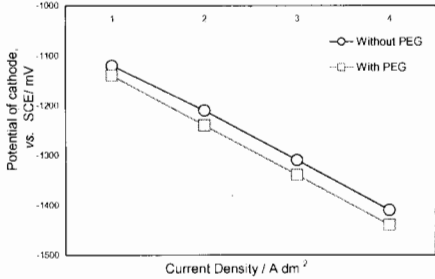


Figure 1: Polarisation curves for mild steel cathodes in bromide zinc baths at 30°C

A and B, were higher than those for the conventional sulphate baths. Generally, a plating bath having high conductivity is associated with lower energy consumption and greater throwing power.

Cathode polarisation

The potential of the steel cathodes at different current densities during deposition from the zinc bromide bath, with and without additive was measured and the polarisation curves shown in Figure 1. The presence of the additive, polyethylene glycol increased the cathode potential of the zinc solution considerably. This accounts for the observed increase in throwing power values in its presence (Table III).

Throwing power

Deposition from baths containing complexes usually takes place at higher cathode potentials and is therefore associated with enhanced throwing power. Non-complexing baths such as the acid sulphate bath are associated with poorer throwing power. Values for the throwing power for different baths are given in Table III; a value of 12.35 was observed for bath A at a current density of 2 A dm⁻².

Cathode Current Efficiency

Cathode current efficiency, rate of build-up and the nature of deposits are summarised in Table IV. The results show that the cathode current efficiency increases with increase of current density up to 2.0 A dm⁻² and then decreases with increase of current density. This is due to the evolution of hydrogen at high current density. In the presence of the additive, polyethylene glycol, the current efficiency was found to decrease in accordance with an earlier report¹⁷. The rate of the build-up of the deposit increased with the increase of current density (Table IV).

Anode Efficiency

It is well known that during the electrodeposition of zinc, the anode efficiency will normally be higher than the cathode efficiency due to chemical attack of the solution on the zinc anode. The results of the study of anode efficiency experiments are presented in Table V. From these, it can be seen that the bromide bath also chemically attacks the zinc anode.

Nature of deposit

The nature of deposits at different current densities is presented in Table IV. A matt white deposit was obtained for all current densities studied.

Microhardness

The microhardness of zinc electrodeposits with thicknesses of 35 μm obtained from different baths at 1 and 2 A dm⁻² is given in Table VI. It can be seen that microhardness of 70.5 was observed for the deposit obtained from bath B at 1.0 A dm⁻².

POROSITY OF DEPOSITS

Table VII contains the results of porosity of zinc deposits from bromide baths for various thicknesses ranging from 8 to 24 μm. It may be seen from that the zinc deposit of thickness of 8 μm shows 5% porosity in the case of bromide bath without additive, whereas the zinc deposits obtained from the bromide bath with additive are pore-free.

Structure

Figure 2 shows micrographs of the zinc deposits obtained in the presence and absence of polyethylene glycol at magnifications of 2000 x. A fine-grained structure was observed in the presence of polyethylene glycol. In general, the presence of an additive in a bath, which increases cathode polarisation and shifts the deposition potential to more negative values compared to base zinc deposits, will yield a fine grained deposit.

TABLE IV Influence of Current Density on current efficiency, rate of build-up and nature of the deposit at 30 °C

Bath	Current Density / A dm ⁻²	Current Efficiency / %	Rate of Build up / μm hr ⁻¹	Nature of the Deposit
A	0.5	88.49	7.54	Matt white
	1.0	90.44	15.47	Matt white
	1.5	93.91	24.09	Matt white
	2.0	95.24	32.57	Matt white
	3.0	90.11	46.25	Matt white
	4.0	85.52	58.20	Matt white
B	0.5	85.14	7.26	Matt white
	1.0	88.45	15.13	Matt white
	1.5	91.12	23.37	Matt white
	2.0	94.05	32.17	Matt white
	3.0	89.16	45.74	Matt white
	4.0	84.75	57.97	Matt white

CONCLUSIONS

From the experiments carried out, the most effective bath composition and operating parameters to produce high quality electrodeposited zinc coatings is as follows: ZnBr₂ 160 g dm⁻³; H₃BO₃ 80 g dm⁻³; KBr 50 g dm⁻³; CH₃COONa 20 g dm⁻³; polyethylene glycol 0.5 g dm⁻³; Cathode Mild steel; Anode Pure zinc (99.99%); Temperature = 30 °C; Current Density 1 – 2 A dm⁻²; pH = 4.

ACKNOWLEDGEMENT

One of the authors (M.Chandran) expresses his sincere thanks to the Director, CECRI, Karaikudi, for having granted permission to make use of the facilities of the institute. He is also grateful to the Management, Vivekananda College, Agasteeswaram for the encouragement given in his research pursuits.

REFERENCES

1. H.Geduld, *Zinc Plating*, Finishing Publications Ltd., England, 1988.
2. N. M. Martyak, J. E. McCaskie and L. Harrison, *Met. Fin.*, 1996, **94**(2), 65.

3. J.Hajdu, AESF Sur/Fin'99 Proceedings, June 21–24, 1999 Cincinnati, Session 0, p 519.
4. J.R. Park and H.E. Kim, *Plat.Surf. Fin.*, 1999, **86**(6), 108.
5. J.Yu, *J. Electrochem. Soc.*, 1999, **146**(5), 1789.
6. R.M.Krishnan, S.R.Natarajan and V.S.Muralidharan, *Met. Fin.*, 1991, **89**(2), 15.
7. S. Jayakrishnan, E. Pushpa, R M Krishnan, S.Sriveeraraghavan and S.R. Natarajan, *Met. Fin.*, 1997, **95**(1), 20.
8. V.Ravindran, R.M.Krishnan and V S Muralidharan, *Met. Fin.*, 1998, **96**(10), 12.
9. R Sekar, S Sriveeraraghavan and R M Krishnan, *Bull. Electrochem.*, 1999, **15**(5–6), 219.
10. S.Sriveeraragavan, B.Srinivasan, R.M.Krishnan, S. Jayakrishnan and S. R. Natarajan, *Trans. Inst. Met. Fin.*, 2000, **78**(5), 201.
11. M.Wery, J.C.Catonne and J.Y.Hihn, *J Appl. Electrochem.*, 2000, **30**(2), 165.
12. Y.Arthoba Naik, T.V.Venkatesha and P.Vasutheva Naik, *Bull. Electrochem.*, 2000, **16**(11), 481.
13. M.Chandran, R.Lakshmana Sharma and R.M.Krishnan, *Bull. Electrochem.*, 1999, **15**(7–8), 242.
14. M.Chandran, R.Lakshmana Sharma and R.M.Krishnan, *Plat. Surf. Fin.*, 2001, **88**(4), 74.
15. E. Raub and K. Muller, *Fundamentals of Metal Deposition*, Elsevier, New York, 1967.
16. J. B. Kushner, *Electroplating Know How* H. Evansville, Indiana, 1974.
17. F.Hanna and H. Noguchi, *Met. Fin.*, 1988, **86**(11), 33.

TABLE V Anode efficiency at 30°C

Bath	Current Density / A dm ⁻²	Anode Efficiency / %
A	1.0	102.17
	2.0	100.26
B	1.0	100.20
	2.0	100.53

TABLE VI Microhardness of electrodeposits from various baths at 30 °C (35 μm)

Bath	Current Density / A dm ⁻²	Vicker's Microhardness / kg mm ⁻²
A	1.0	60.5
	2.0	52.8
B	1.0	70.5
	2.0	62.4
C	1.0	48.00
	2.0	46.80
D	1.0	54.31
	2.0	52.16

TABLE VII Porosity of electrodeposits of different thickness

Bath	Thickness / μm	Nature of the Deposit
A	8	5% porous
	16	Non-porous
	24	Non-porous
B	8	Non-porous
	16	Non-porous
	24	Non-porous

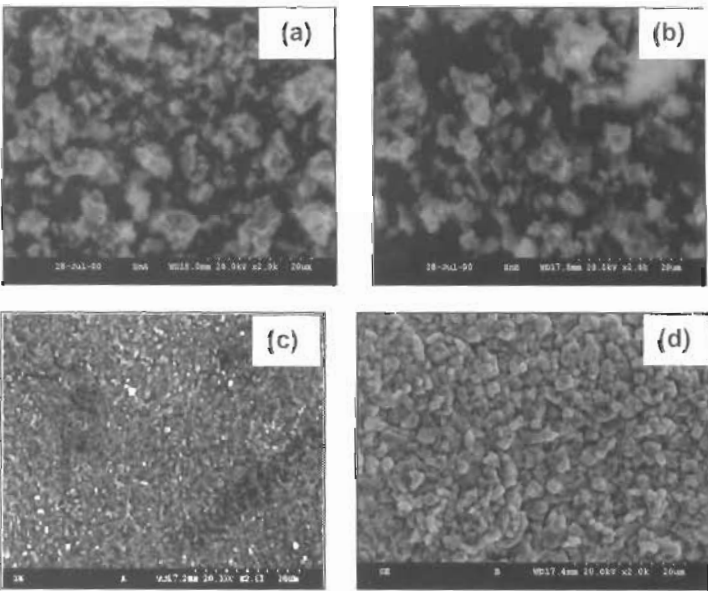


Figure 2: SEM micrographs showing structures of zinc deposits at 2000 x magnification.
(a) without PEG at 1.0 A dm⁻²
(b) without PEG at 2.0 A dm⁻²
(c) with PEG at 1.0 A dm⁻²
(d) with PEG at 2.0 A dm⁻²