

## EFFECT OF ADDITIVES ON ELECTRODEPOSITION OF ZINC

A SENTHIL KUMAR\*, C SENTHIL RAJA PANDIAN\*, J AYYAPPARAJU AND G N K RAMESH BAPU

*Central Electrochemical Research Institute, Karaikudi 630 006. INDIA*

*\* Centre For Education, Central Electrochemical Research Institute, Karaikudi 630 006. INDIA*

[Received: 23 March 2001

Accepted: 15 May 2001]

*The effect of thiourea, sulphosalicylic acid and  $\beta$ -alanin are studied in acid zinc sulphate solution. Hull cell studies are made to optimize concentration of the above additives. Current efficiency, throwing power, cathodic polarisation and corrosion behaviour in 3.5% NaCl are studied under optimum concentration of additives and their effects are reported. Structure of deposits are characterized using scanning electron microscope.*

*Keywords: Electrodeposition, zinc sulphate bath, additives, current efficiency, throwing power, corrosion resistance, structure.*

### INTRODUCTION

Electrodeposition of zinc on steel is one of the highest volume process in plating. Zinc finds its widest application in industry to protect large quantities of iron and steel wire, sheet steel and other fabricated ferrous metal parts sacrificially against corrosion [1]. The protection is further enhanced by passivation processes, which improve the corrosion resistant and permit colour finishes [2]. Weakly acidic zinc sulphate baths were found suitable for use on plating of steel castings and steel wires or strip in high speed continuous lines due to high electrical conductivity, high plating rate and low operating cost. Because the bath has poor throwing power and produces matte white deposits, it necessitates to improve the nature of deposits, corrosion resistance and throwing power using some organic additives. The major purpose of adding the organic additives being (a) to improve the appearance and properties of deposits and/or (b) to improve the operating performance of the plating bath. Many organic additives were reported [3-9] and used satisfactory in the weak acidic bath [10-16]. It was observed that the additives gave bright deposit but poor throwing power and corrosion resistance. In order to obtain smooth deposits with improved throwing power and satisfactory silver gray appearance, in the present study the authors have studied the influence of three additives thiourea, sulphosalicylic acid and  $\beta$ -alanin on zinc plating from acid sulphate bath. Results on current efficiency,

throwing power, cathode polarisation and corrosion resistance have been reported.

### EXPERIMENTAL

Laboratory reagent grade chemicals were used to prepare the zinc sulphate electrolyte consisting of 300 g.l<sup>-1</sup> ZnSO<sub>4</sub> and 30 g.l<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The electrolyte was prepared using de-ionized water and digested with activated carbon at 333 K to remove the organic impurities. The electrolyte was then subjected to dummy electrolysis at low voltage, filtered through a G-4 crucible and used for plating. The pH was maintained at 3.

#### Hull cell studies

To judge the quality and nature of the zinc deposits from the sulphate electrolyte over a wide current density range, plating was carried out on polished mild steel sheets using a standard 267 ml Hull cell for 5 minutes at 3 ampere cell current and at pH 3. The optimum concentration of thiourea, sulphosalicylic acid and  $\beta$ -alanin additives were arrived at using the Hull cell at various concentrations.

#### Current efficiency

The cathode current efficiency of the zinc sulphate electrolyte in presence of various additives was found at 303 K for a duration of 600 coulombs at current density ranged between 3 and 10 A.dm<sup>-2</sup>. From the weight of deposit obtained, current efficiency was determined.



### Throwing power

A Haring-Blum cell was employed to determine the throwing power of the solution at 4 A.dm<sup>-2</sup> at pH 3 and 303 K. Plating was carried out for 30 minutes on steel cathodes, positioned at a distance ratio of 1:5 from the perforated zinc anode. From the weight of deposit obtained at the near cathode ( $W_n$ ) and far cathode ( $W_f$ ) the throwing power (TP) was calculated using the Field's formula [17].

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

where L is the linear ratio and M is the metal distribution ratio,  $W_n / W_f$ .

### Cathode polarisation

Steel cathode of 1 cm<sup>2</sup> area was polarised under galvanostatic conditions in the presence of zinc solution with and without additives. Steel sheet was used as working electrode (cathode), a platinum foil and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. The cathodic potential (E) was recorded at various current densities (i) ranging from 10 A.dm<sup>-2</sup> and the polarisation curve was obtained by plotting E vs log i.

### Corrosion behaviour

The effect of additives on corrosion resistance of the zinc deposits was studied in 3.5% NaCl solution by galvanostatic polarisation method. The electrolyte was prepared from Analar reagent grade chemicals. A three electrode cell assembly was used. The working electrode (WE) was masked with lacquer to expose 1 cm<sup>2</sup> area. A platinum foil of 2.5 x 2.5 cm was used as the counter electrode (CE) with saturated calomel as reference electrode (RE). The WE was cleaned and kept in the 5% NaCl electrolyte for 20 minutes to establish a stable rest potential. The WE was polarised from -200 mV to +200 mV to the rest potential (OCP) against SCE. The current was increased in steps from zero and the potential between the WE and the SCE was measured at a steady state. From the E vs log i curves the corrosion potential ( $E_{\text{corr}}$ ) and corrosion current ( $i_{\text{corr}}$ ) was obtained using Tafel extrapolation method [18]. A duplicate test was

made in each case and at every time the test solution was changed.

### Structure of the deposits

The effect of additives on the structure of zinc deposits were examined using scanning electron microscope at 1000 x magnification.

## RESULTS AND DISCUSSION

### Hull cell studies -- Effect of thiourea

The legends for recording the deposit pattern obtained using Hull cell studies are shown in Fig. 1. The effect of thiourea additions to the zinc plating solution on the nature and quality of deposit is shown in Fig. 2. In the absence of additive (Fig. 2a), a matte white deposit was found between 1.5 to 12 A.dm<sup>-2</sup>. With 2.5 g.l<sup>-1</sup> thiourea addition, the entire range had shown a matte white pattern. A fine semi bright deposit was found from 1.5 to 12 A.dm<sup>-2</sup> at 5 g.l<sup>-1</sup> thiourea addition. With further additions, a similar pattern as with 5 g.l<sup>-1</sup> was found and no significant improvement was seen on the nature of the deposit at 7.5 g.l<sup>-1</sup>. Hence, the concentration of thiourea was optimised at 5 g.l<sup>-1</sup>.

### Effect of sulphosalicylic acid

Fig. 3 shows the deposit pattern obtained with sulphosalicylic acid. With 0.5 g.l<sup>-1</sup> addition, (Fig. 3b) a semi bright range was observed between 2.5 and 12 A.dm<sup>-2</sup> which upon further addition narrowed to 6.5 to 12 A.dm<sup>-2</sup>. A matte white deposit was obtained below 6.5 A.dm<sup>-2</sup> at 1 g.l<sup>-1</sup> addition (Fig. 3c). Increasing the

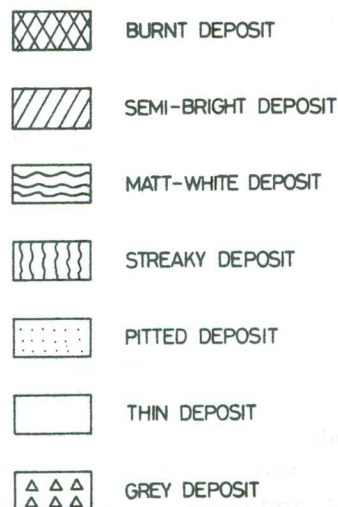


Fig. 1: Legends for Hull cell patterns



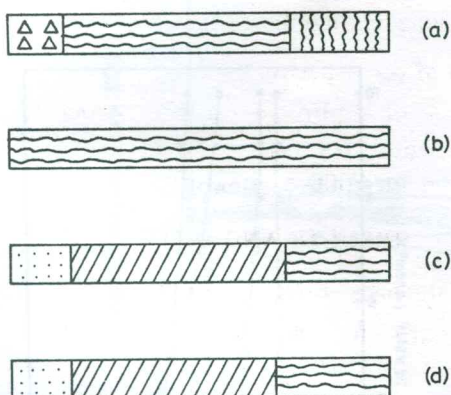


Fig. 2: Effect of thiourea in zinc sulphate bath  
 pH = 3, cell current = 3 ampere  
 (a) No addition (b) 2.5 g.l<sup>-1</sup> thiourea  
 (c) 5.0 g.l<sup>-1</sup> thiourea (d) 7.5 g.l<sup>-1</sup> thiourea

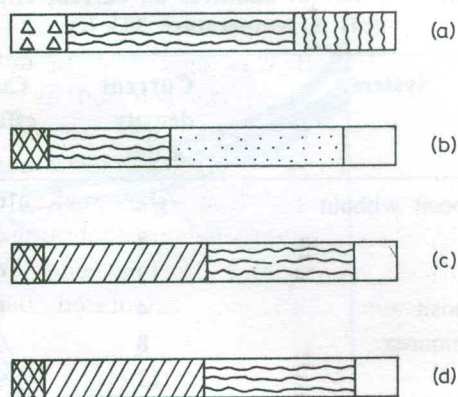


Fig. 4: Effect of  $\beta$ -alanine in zinc sulphate bath  
 pH = 3, cell current = 3 ampere  
 (a) No addition (b) 0.5 g.l<sup>-1</sup>  $\beta$ -alanine  
 (c) 1.0 g.l<sup>-1</sup>  $\beta$ -alanine (d) 1.5 g.l<sup>-1</sup>  $\beta$ -alanine

concentration of sulphosalicylic acid to 1.5 g.l<sup>-1</sup> (Fig. 3d) resulted a matte white region. Thus sulphosalicylic acid was optimised at 0.5 g.l<sup>-1</sup>.

#### Effect of $\beta$ -alanine

The effect of  $\beta$ -alanine in zinc sulphate bath was studied at 0.5 g.l<sup>-1</sup>, 1 g.l<sup>-1</sup> and 1.5 g.l<sup>-1</sup> and the deposit patterns are shown in Figs. 4(b-d). At low concentration (0.5 g.l<sup>-1</sup>), (Fig. 4b) the deposit was powdery in low current density region and matte white at high current density region. Further additions (Fig. 4c) improved the deposit nature and resulted a semi bright appearance between 5 to 12 A.dm<sup>-2</sup>. With higher concentration, 1.5 g.l<sup>-1</sup> of  $\beta$ -alanine (Fig. 4d) the pattern was the same as

for 1 g.l<sup>-1</sup> addition. Hence, 1 g.l<sup>-1</sup>  $\beta$ -alanine was optimised.

#### Effect of additives on current efficiency

The current efficiency of the zinc sulphate bath in presence of thiourea, sulphosalicylic acid and  $\beta$ -alanine are given in Table I. In the presence of additives the current efficiency was found to decrease slightly, but the effect is insignificant ( $\pm 2\%$ ). In general the additives hinder the deposition process and shows a lesser current efficiency [12]. The current efficiency was very slightly affected over a wide current density range. Thus the sulphate bath is suitable for operating at high current densities as required for strip and wire plating.

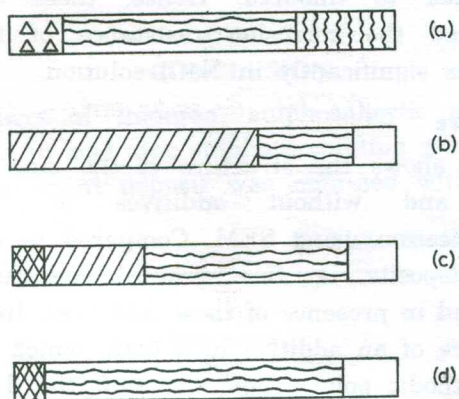


Fig. 3: Effect of sulphosalicylic acid in zinc sulphate bath  
 pH = 3, cell current = 3 ampere  
 (a) No addition (b) 0.5 g.l<sup>-1</sup> sulphosalicylic acid  
 (c) 1.0 g.l<sup>-1</sup> sulphosalicylic acid (d) 1.5 g.l<sup>-1</sup> sulphosalicylic acid

#### Throwing power

Among the various factors, the throwing power of a solution depends upon the design of the cathode and the presence of organic additives in the solution [19]. In the present system of study, the throwing power was determined in the presence of thiourea, sulphosalicylic acid and  $\beta$ -alanine each individually at 4 A.dm<sup>-2</sup> and the results are presented in Table II.

The throwing power of acid zinc sulphate bath was found to be 6.8% and in the presence of additives, a higher value was obtained. Thus the additives were found to improve significantly the throwing power at 4 A.dm<sup>-2</sup> and 303 K.

**TABLE I: Effect of additives on current efficiency**  
(pH 3, temperature 303 K)

System	Current density $\text{A.dm}^{-2}$	Current efficiency %
Zinc deposit without additive	4	99.6
	8	99.4
	12	99.2
Zinc deposit + 5 g.l <sup>-1</sup> thiourea	4	99.2
	8	98.8
	12	98.3
Zinc deposit + 0.5 g.l <sup>-1</sup> sulphosalicylic acid	4	98.8
	8	98.2
	12	97.8
Zinc deposit + 1 g.l <sup>-1</sup> $\beta$ -alanin	4	99.3
	8	98.7
	12	97.8

### Cathode polarisation measurements

Cathode potential under galvanostatic conditions was measured in the zinc sulphate bath, with and without additives. The current density was varied from 1 to 10  $\text{A.dm}^{-2}$  and the potential was measured with reference to SCE. The polarisation curves are shown in Fig. 5. For a given current density, the presence of additives increased the cathode potential of the basic zinc solution considerably. This tendency was found to enhance more in the presence of thiourea and  $\beta$ -alanin. This accounts for the observed increase in throwing power values (Table II).

### Corrosion resistance

Figs. 6 and 7 present the effect of additives on zinc deposits for 5 and 10 microns thickness with respect to corrosion behaviour in 3.5% NaCl solution using galvanostatic polarisation technique and the values are given in Table III. From the

**TABLE II: Effect of additives on throwing power**  
(pH = 3, temperature 303 K, current density 4  $\text{A.dm}^{-2}$ )

System	Throwing power %
Zinc deposit without additive	6.8
Zinc deposit + 5 g.l <sup>-1</sup> thiourea	9.8
Zinc deposit + 0.5 g.l <sup>-1</sup> sulphosalicylic acid	8.0
Zinc deposit + 1 g.l <sup>-1</sup> $\beta$ -alanin	9.1

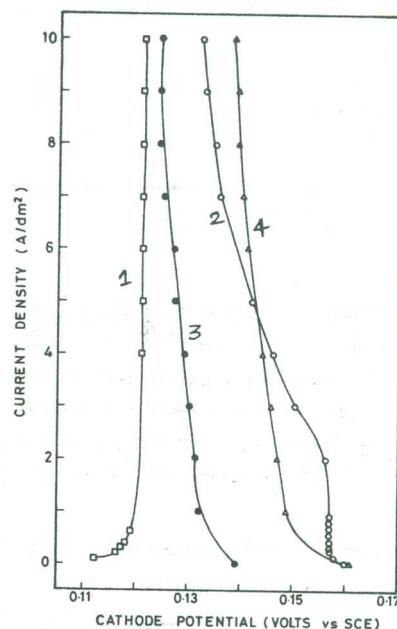


Fig. 5: Cathodic polarisation curves in zinc sulphate bath with various additives  
(1) Zinc sulphate bath (2) Zinc bath with 5 g.l<sup>-1</sup> thiourea  
(3) Zinc bath with 0.5 g.l<sup>-1</sup> sulphosalicylic acid  
(4) Zinc bath with 1 g.l<sup>-1</sup>  $\beta$ -alanin

figures it can be seen that the  $i_{\text{corr}}$  values for zinc deposits were considerably lowered when plated in presence of additives, irrespective of the deposit thickness. Among the additives  $i_{\text{corr}}$  values of zinc deposited from sulphosalicylic and  $\beta$ -alanin containing baths were considerably lower compared to thiourea. Hence, these additives improved the corrosion resistance of the zinc deposits significantly in NaCl solution.

### Structure

Fig. 8 shows the structure of the zinc deposits with and without additives at 1000 x magnification using SEM. Compared to the base zinc deposits, a fine grained structure was observed in presence of these additives. In general presence of an additive in a bath, which increase the cathodic polarisation and shift the deposition potential to move negative values compared to base zinc deposits, will yield to a fine grained deposit. This accounts for the observed fine grained deposits with these additives.



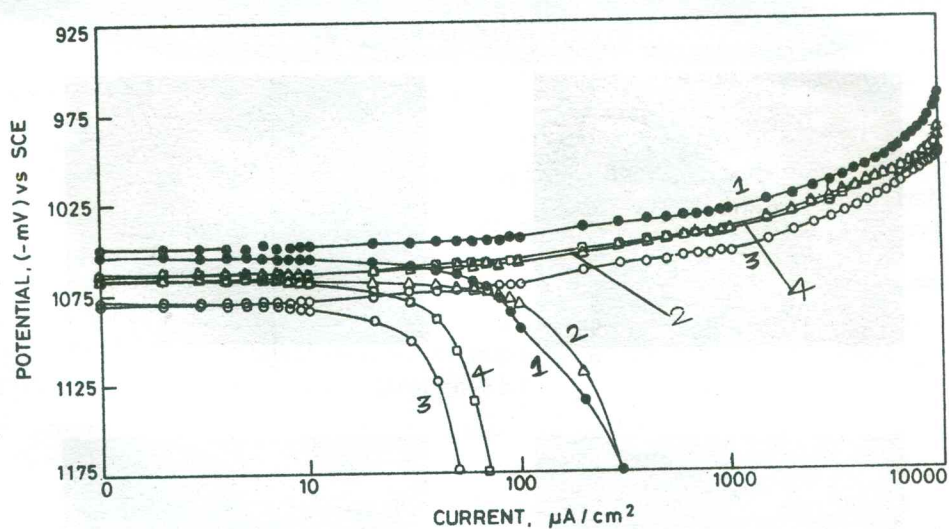


Fig. 6: Effect of additives on galvanostatic polarisation behaviour of zinc deposits (5  $\mu\text{m}$ ) in 3.5% NaCl solution  
(1) Zinc (2) Zinc-thiourea (3) Zinc-sulphosalicylic acid (4) Zinc- $\beta$ -alanin

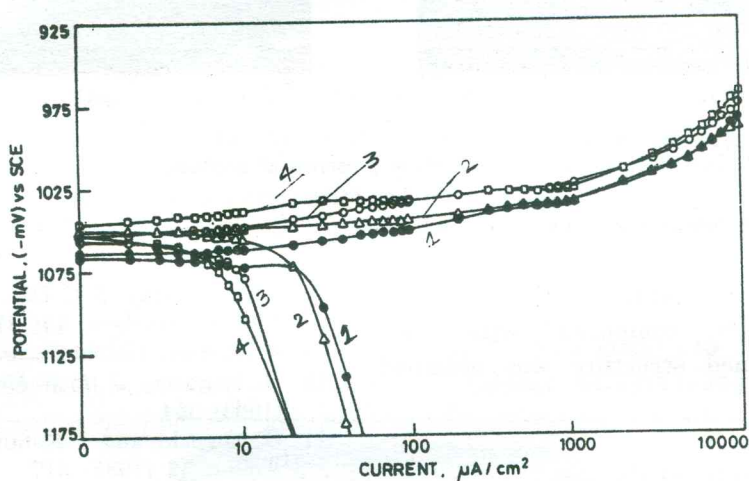


Fig. 7: Effect of additives on galvanostatic polarisation behaviour of zinc deposits (10  $\mu\text{m}$ ) in 3.5% NaCl solution  
(1) Zinc (2) Zinc-thiourea (3) Zinc-sulphosalicylic acid (4) Zinc- $\beta$ -alanin

### CONCLUSION

The effect of thiourea, sulphosalicylic acid and  $\beta$ -alanin in acid zinc sulphate solution were found. A semi bright deposit was obtained with 5  $\text{g.l}^{-1}$

thiourea or 0.5  $\text{g.l}^{-1}$  sulphosalicylic acid or 1  $\text{g.l}^{-1}$   $\beta$ -alanin. The additives improved the throwing power of the bath significantly without affecting the current efficiency. Irrespective of the deposit

TABLE III: Galvanostatic polarisation in 5% NaCl

Specimen	Deposit thickness = 5 microns		Deposit thickness = 10 microns	
	$E_{\text{corr}}$ (-mV vs SCE)	$i_{\text{corr}}$ ( $\mu\text{A.cm}^{-2}$ )	$E_{\text{corr}}$ (-mV vs SCE)	$i_{\text{corr}}$ ( $\mu\text{A.cm}^{-2}$ )
Electrodeposited zinc	1060	32	1065	28
Electrodeposited zinc + 5 $\text{g.l}^{-1}$ thiourea	1065	29	1065	29
Electrodeposited zinc + 0.5 $\text{g.l}^{-1}$ sulphosalicylic acid	1085	20	1050	20
Electrodeposited zinc + 1 $\text{g.l}^{-1}$ $\beta$ -alanin	1065	24	1055	18

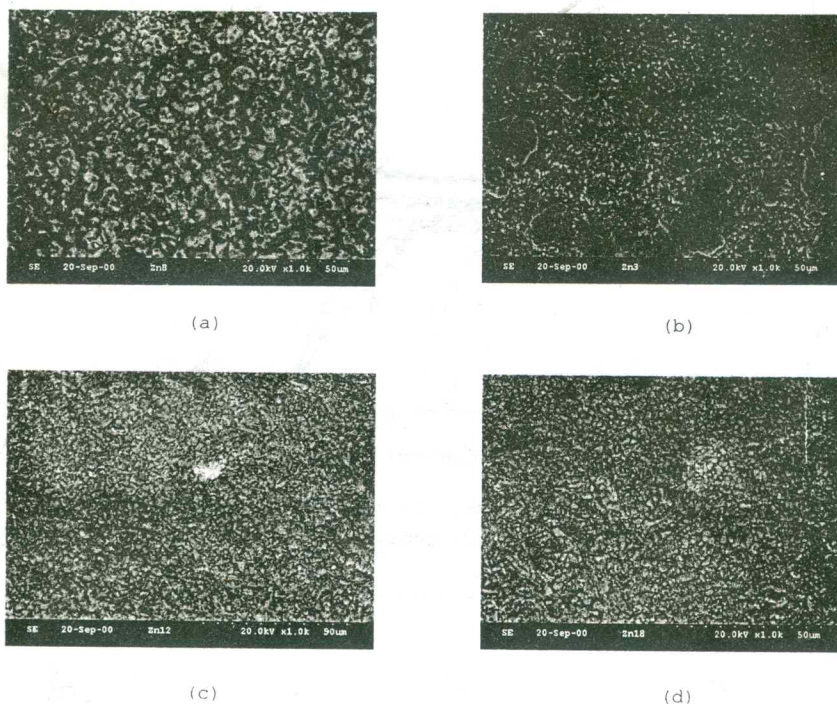


Fig. 8: SEM structure of zinc deposits in presence of additives at 1000 x magnification  
 (a) Zinc deposit (b) Zinc deposit with thiourea additive  
 (c) Zinc deposit with sulphosalicylic acid additive (d) Zinc deposit with  $\beta$ -alanine additive

thickness the additives improved the corrosion resistance significantly compared with zinc deposits. A fine grained structure was obtained with these additives.

## REFERENCES

1. H Geduld (Ed), *Zinc Plating*, ASM International, Metals Park, Ohio (1988)
2. N M Martyak, J E Mccaskie and Lew Harrison, *Metal Finishing*, **94(2)** (1996) 65
3. M Pushpavanam and B A Shenoi, *Metal Finishing*, **75(1)** (1977) 29
4. T V Venkatesha, J Balachandra, S M Mayanna and R P Dampal, *Metal Finishing*, **83(8)** (1985) 33
5. T V Venkatesha, J Balachandra, S M Mayanna and R P Dampal, *Metal Finishing*, **84(12)** (1986) 29
6. T V Venkatesha and S M Mayanna, *Metal Finishing*, **87(4)** (1989) 28
7. T V Venkatesha, *Bull Electrochem*, **12(7/8)** (1996) 472
8. B C Tripathy, S C Das, P Singh and G T Hefler, *Bull Electrochem*, **14(11)** (1998) 436
9. P Huelser, *Galvanotechnic*, **91(9)** (2000) 2440
10. H Noguchi, *J Inst Metal Finishing Japan*, **34** (1983) 554
11. H Noguchi and I Kotani, *J Inst Metal Finishing Japan*, **36** (1985) 317
12. F Hanna and H Noguchi, *Metal Finishing*, **86(11)** (1988) 33
13. F Galvani and I A Carlos, *Metal Finishing*, **95(2)** (1997) 70
14. RM Krishnan, C J Kennedy and S Jayakrishnan, *Metal Finishing*, **94(10)** (1996) 43
15. J Yu, Y Chen, H Yang and Q Huang, *J Electrochemical Soc*, **146(5)** (1999) 1789
16. M Chandran, R L Sharma and RM Krishnan, *Bull Electrochem*, **15(7/8)** (1999) 242
17. E Raub and K Muller (Eds), *Fundamentals of Metal Deposition*, Elsevier, New York (1967)
18. M G Fontanna and N D Greene (Eds), *Corrosion Engineering*, McGraw Hill Book Company, New York (1967)
19. H G Todt, *Trans Inst Met Finishing*, **51** (1973) 91