Electrochemical Studies of Zn-Mn Alloy Plating from Acid Sulphate Bath using Condensation Product 4-Chloro-2-Nitro-N-Phenyl Methylidene Aniline using as a Brightener

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ABSTRACT

Zn-Mn alloy coatings were deposited on mild steel substrate using acidic sulphate bath at room temperature. Electrodeposition of Zn-Mn alloys of different composition, morphology and structure depending on the cathodic potential was found. The alloy electrodeposition from sulphate bath was carriedout in presence of condensation product formed between 4-chloro-2-nitro aniline and salicylaldehyde. The bath constituents were optimized through Hull-cell experiments. Operating parameters such as pH, temperature and current density were also optimized. Current efficiency and throwing power were measured. Polarisation study is carriedout under galvostatic condition. SEM photomicrographs showed fine-grained deposit in the presence of condensation product. IR spectrum of the deposit showed inclusion of condensation product in the deposit during plating. Their structure and morphology were characterized by X-ray diffraction (XRD).

Keywords: Condensation product; Hull-cell studies; Manganese sulphate; Sulphate bath; Zinc sulphate

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INTRODUCTION

Electroplated zinc coatings are considered as one of the main methods used for the corrosion protection of steel. Recently the interest Zn-Mn alloy coating has increased owing to its better mechanical and corrosion properties compared with pure zinc coatings [1-3]. There is a growing interest on the electrodeposited Zn-Mn alloys because of their superior protective properties [4]. Zn-Mn alloys are mainly obtained from sulphate-citrate baths [5,6]. The electrodeposition conditions permit to obtain high manganese content in the coatings at high applied current densities. Gabe et al. have reported that a Zn-Mn alloy with a manganese content of approximately 30% shows the highest corrosion resistance. This highest corrosion resistance is associated with the monophasic structure of the coating [7]. Studied the influence of bath composition on the corrosion behaviour of Zn-Mn coatings and reported that alloys with manganese contents around 11% had a high corrosion resistance due to their monophasic structure. The other electroplating solutions that have been considered were an alkaline sulphate pyrophosphate bath [8,9] and an acidic chloride bath without complexing agents [10]. These alloys present a double protective mechanism combining a sacrificial protection and the formation of a practically insoluble protective surface layer. In the present work, an attempt has been made to develop a bright zinc-manganese alloy deposition on mild steel. It is known that the condensation product of aldehydes and amines are good brightners than single aldehydes or amines in the bath solution [11]. This may be due to the presence of electroactive $>C = N$ group in the molecule. Various amines and aldehydes were subjected to condensation reaction [12-14] and studied in a basic zinc sulphate bath. Among these, the condensation product formed between 4-chloro-2-nitro aniline and salicylaldehyde is effective in getting good

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deposit [15]. The deposits were synthesized with specific commercial additives designed for zinc electrodeposition in acidic media. Composition structure and morphology of the Zn-Mn films were studied by SEM and XRD.

EXPERIMENTAL SECTION

The plating bath solutions were prepared using distilled water with AR grade chemicals. All the electrochemical experiments were carried out at room temperature with air agitation. The pH of the solution was adjusted by 10% dil. sulphuric acid and sodium corbonate solution. Zinc metal plate of 99.99% purity was used as anode and polished steel specimen was used as cathode The Hull-cell experiments with the bath solutions were carried out at 2 A cell current for 10 min, given in Table 1. The total volume of Hull-cell was 267 mL with an anode dimension 6 cm × 6.5 cm (zinc metal). The anode was activated each time by immersing in 10% HCl followed by water wash. The cathode dimension 10 cm × 7.5 cm (mild steel) of standard Hull-cell size were mechanically polished to obtained smooth surface and degreased by dipping in boiling trichloroethylene. The scales and dust on steel plates were removed by dipping in 10% HCl solution and were subjected to electrocleaning process. Then these steel plates were washed with water and used for experiments as such. After the plating experiments, the plates were subjected to dip in 1% nitric acid for 2 s followed by water wash [16]. The nature and appearance of zinc plating was carefully studied and recorded through the Hull-cell codes. All the experiments were conducted at 303 K. A known amount of condensation product was added to the plating bath. The bath solution was stirred for 30 min and a Hull-cell was employed to assess and optimized the condition for the production of good deposits. A cell current of 1 A was used for 10 min. Condensation product was synthesized from equimolar amounts of 4-chloro-2-nitroaniline (0.70 mL) with chemical formula, $C_6H_5NC_2O_2Cl$ (AR grade, Sisco-chem industries, Mumbai, India), and Salicylaldehyde (1 g) with chemical formula, $C_7H_6O_2$ (AR grade sd Fine chemicals, Mumbai, India), in ethanol and acetic acid media (20 + 20 mL), under reflux conditions for 3 h at 343 K. The completion of the reaction was confirmed through TLC and the resultant solution was diluted to 100 mL with distilled water and a known amount of this solution was added to the electroplating bath solution. Hull-cell studies were carried out using a 267 ml cell at current I=1 A and duration t=10 min [17-20]. Polarization studies were carried out by using a three compartment cell. The area of zinc anode was 2 cm^2. Mild steel was used as cathode with an exposed area of 2 cm^2. The cathode potential was recorded galvanostatically with respect to saturated calomel electrode, at different current densities. Throwing power is the ability of the plating solution to deposit uniformly over the cathode surface and is measured as the ratio of the weight of the deposit obtained on the cathode surface placed near the far end from the anode. For determining the throwing power a Haring and Blum cell was used to measure throwing power. The bath solution was taken in the cell. Two mild steel cathodes (each 7.5 × 4.8 cm^2) were kept at distance of 1:5 ratios on either side of zinc anode (7.5 × 4.8 cm^2). The DC current passed through the cell for 10 min. After the experiment, cathodes were rinsed with water, alcohol and finally dried. The weights of the deposit on nearer cathode (W1) and on the further cathode (W2) were determined [21]. Throwing power (TP) of the bath solution was calculated using the equation:

$$\% TP = \frac{5 - R}{R \times 100}$$

Or by the equation where R=W1/W2

$$\% TP = \frac{K - M}{K + M - 2} \times 100$$

Where, K is the ratio of the distance from the anode the farther and nearer cathode respectively, and M is the ratio of the metal obtained on the nearer and farther cathodes IR spectrum of the scrapped deposit was taken to ascertain the inclusion of addition agents. SEM photomicrographs were taken to ascertain the nature of deposit in the presence of addition agents (Figure 1).
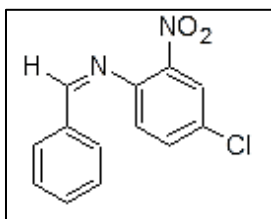

Figure 1: 4-chloro-2-nitro-N-phenylmethylidene aniline

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Table 1: Basic bath composition and operating conditions

Bath composition	Quantity (gL^{-1})	Operating condition
$ZnSO_4 \times 7H_2O$	200	Anode: zinc metal (99.99%)
$MnSO_4 \times H_2O$	4	Cathode : mild steel
Na_2SO_4	60	Plating time: 10 min
H_3BO_3	16	pH: 3.0
CTAB	2	Temperature: 293 -303 K
		Cell current: 1 A

RESULTS AND DISCUSSION

Hull-Cell Studies
Influence of condensation product:
Basic bath solution gave coarse dull deposit between the current density ranges of 1-3.5 A dm^{-2} at 1 A cell current. To improve the nature of the deposit, CP$_2$ formed between 4-chloro-2-nitro aniline and salicylaldehyde was used as brightener. A known amount of CP$_2$ was added to the bath solution. At lower concentration of the condensation product, the deposit was semi-bright between the current density range of 1-3.5 A dm^{-2} at lower current density, dull and at higher current density burnt deposit was obtained. With increase in the concentration, the nature of the deposit was improved. At a concentration of 4 ml.L^{-1} of the condensation product as shown in Table 2, the Hull-cell panels were bright between the current density ranges of 1-4 Adm^{-2}. With further increase in the concentration of condensation product gave dull deposit in the low current density region. So based on the above observations, the concentration of condensation product was kept at 4 mL.L^{-1} as optimum (Figures 2a and 2b).

Influence of zinc sulphate:
To find out the effect of zinc metal ion concentration, zinc sulphate concentration was varied from 40-320 g/l. A low concentration bright deposit was observed in the current density region 0.5 and 3 A dm^{-2}. At low current density region, uncoated and at high current density region, burnt deposits were obtained. With increase in the concentration of zinc sulphate the brightness was extended to lower and higher current density regions. At concentration of 200 g/l satisfactory bright deposit was obtained in the current density range 1-4 A dm^{-2} at 1 A cell current. With further increase in the concentration of zinc sulphate no improvement in the nature of the deposit was observed. The concentration of zinc sulphate was fixed at 200 g/l as optimum (Figure 2c).

Influence of manganese sulphate:
The concentration of MnSO4 was varied from 2-24 g/l by keeping zinc sulphate 200 g/l, sodium sulphate at 60 g/l, Boric acid at 16 g/l, and CTAB 2 g/l , respectively. At lower concentration of manganese sulphate, bright deposit was observed in the current density range 1-3.5 A dm^{-2}. At low current density region uncoated and at high current density region burnt deposits were obtained. The burnt and uncoated areas were found to be reduced with increase in the concentration of MnSO$_4$ and at 4 g/l, the deposit was bright over the current density range of 0.5-4 A dm^{-2} at 1 A cell current. With further increase in the concentration of MnSO$_4$ no improvement in the nature of deposit was observed. The concentration of MnSO$_4$ was fixed at 4 g/l as optimum (Figure 2d).

Influence of sodium sulphate:
Sodium sulphate was added to increase the conductivity of the bath solution. The concentration sodium sulphate was varied from 30-80 g/l. At low concentrations, the Hull-cell panels suffered uncoated area at low current density region was found to be reduced with increase in sodium sulphate concentration and at 60 g/l of sodium sulphate in the bath solution, the deposit was bright in the current density 1-4 A dm^{-2} ranges. Further increase in the concentration of sodium sulphate had no effect on the nature of the deposit. Therefore the concentration of sodium sulphate was fixed at 60 g/l in the bath solution (Figure 2e).

Influence of boric acid:
The concentration of boric acid was varied from 4-24 g/l, keeping the concentration of zinc sulphate and sodium sulphate. At 200 g/l and 60 g/l respectively. The Hull-cell panels suffered from dull at lower current density region and burnt at high current density region. The area of the burnt deposit was reduced with increase in concentration of boric acid. At 16 g/l of boric acid mirror bright deposit was observed in the current density range 0.5-4 A dm^{-2} at 1 A cell current. The concentration of boric acid was fixed at 16 g/l as optimum bath solution (Figure 2f).

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Influence of CTAB:

The concentration of CTAB was varied from 1-6 g/l. At low concentration of CTAB the nature of the deposit was observed in the current density range between 1 and 6 A dm^{-2}. In the low current density region, dull and at high current density region burnt deposits were obtained. With increase in the concentration of CTAB from 1-2 g/l satisfactory bright deposit was obtained in the current density range of 1-4 A dm^{-2} at 1 A cell current. With increase in the concentration above 2 g/l, no change in the nature of the deposit was observed. Therefore the concentration of CTAB was fixed at 2 g/l, as optimum in the bath solution (Figure 2g).

Influence of pH:

The bath solution pH was varied from 2 to 5, at lower pH between 2-2.5. The Hull-cell patterns showed an uncoated area in the low current density region. At pH 3.0 satisfactory bright deposits was obtained in the current density range 1-4 Adm^{-2}. With an increase in pH above 3.0 no deposit was noticed in the low current density region. By these observations the pH of the bath solution was fixed at 3.0. The effect of pH on the deposit nature (Figure 2h).

Influence of temperature:

To see the effect of temperature on Hull-cell experiments, the plating experiments were carriedout in a thermostat. The temperature of thermostat was varied from 293-323 K. The deposition was bright in the current density range between 1-3.5 A dm^{-2} at 1 A cell current at a temperature less than 303 K. Above 303 K the deposition was dull in low current density range. So the optimum temperature range was 293-303 K (Figure 2i).

Influence of cell current:

The Hull-cell experiments were carried out at different cell currents (1-3A) for 10 min using optimum bath solution. The Hull-cell patterns (Figure 2j). It was found that at a cell current of 1 A the deposit was bright in the current range of 0.5-4 A dm^{-2}. At a cell current of 2A, the deposit was bright in the current density range of 1-8 A dm^{-2}. At cell current of 3 A, the Hull cell panels showed burnt deposit at higher current density regions. This observation revealed that the bath gave bright deposit in the current density range 1-3.5 A dm^{-2} at 1A cell current.

Polarization Studies

The potential of the steel cathode was measured galvanostatically with respect to saturated calomel electrode (SCE) at different current densities. The variation of potential in the presence of bath constituents is as shown in Figure 3. The shift in cathodic potential towards more negative direction was observed in presence of addition agents. This could be attributed to the formation of more stable electrical double layer by the condensation product.
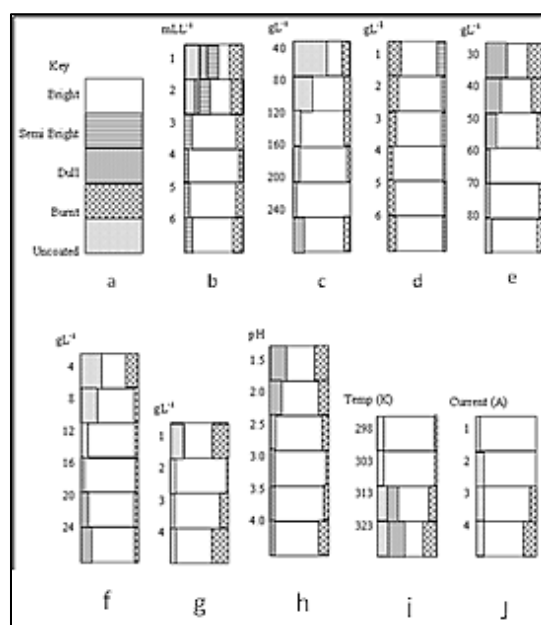

Figure 2: Hull-cell figures:(a) Key (b) CP$_2$ (c) ZnSO$_4$·7H$_2$O (d) MnSO$_4$·H$_2$O (e) Na$_2$SO$_4$ (f) H$_3$BO$_3$ (g) CTAB (h) pH (i) temperature (j) cell current

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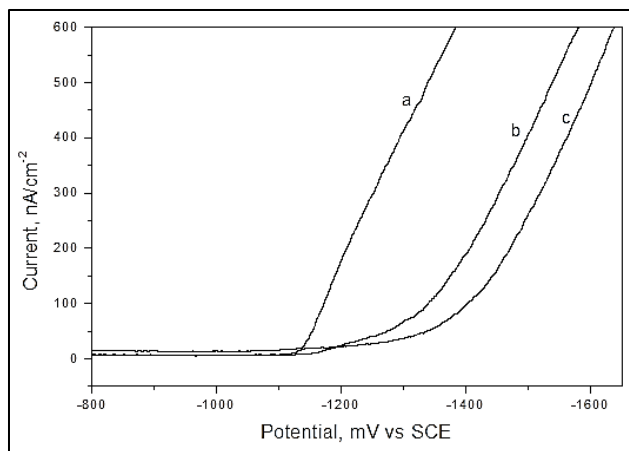
Figure 3: Effect of addition agents on cathodic potential (a) $ZnSO_4$ + $MnSO_4$ + $NaSO_4$ + H_3BO_3 (BB), (b) BB + CTAB (c) BB + CTAB + CP_2

Current Efficiency and Throwing Power

Current efficiency and throwing power were measured at different current densities by using optimum bath solution. At lower current densities (1 Adm^{-2}) the current efficiency was found to be 55%. At a current density of 2 Adm^{-2} the current efficiency was increased to 57%. The maximum current efficiency of 63% was found at 4 Adm^{-2}. With increase in current density above 4 Adm^{-2} the current efficiency was found to be decreased. Throwing power was measured by using Haring and Blum cell at different current densities. At low current densities the throwing power was 19% and with increase in the current density was increased to 27% is given (Table 2).

Table 2: Current density and throwing power at different current densities

Current density (Adm^{-2})	Current efficiency (%)	Throwing power (%)
1	55	19
2	57	21
3	61	24
4	63	27
5	53	25

Surface Morphology and IR Studies

The natural crystal growth in the presence and absence of addition agents is explained with the help of SEM photomicrographs (JEOL-JSM-35LF) (Figure 4). SEM photomicrograph of the deposit obtained from the basic bath shows the crystal growth is not uniform, it produced deposit having different and slightly larger crystal size, But in presence of CTAB in the optimized bath showed uniform arrangement of crystals, refinement in crystal size and hence result in the bright deposit (Table 3). The IR spectrum of scraped deposit obtained from the optimum bath was used to test the inclusion of addition agents in the deposit. IR spectrum shows an absorption peak at 1630.51 cm^{-1} which corresponds to >C=N-group of condensation product. This confirmed the inclusion of condensation product in the deposit during electrodeposition. Figure 5 shows the IR spectrum of the scraped deposit.
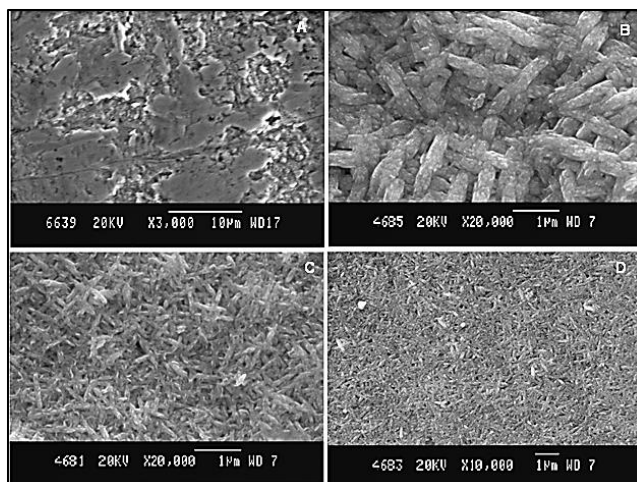
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Figure 4: SEM photomicrographs of the deposits obtained in the presence and absence of addition agents at 298 K; (a) basic bath (BB), (b) BB + CTAB, (c) BB +CTAB + CP₂, (d) optimized bath
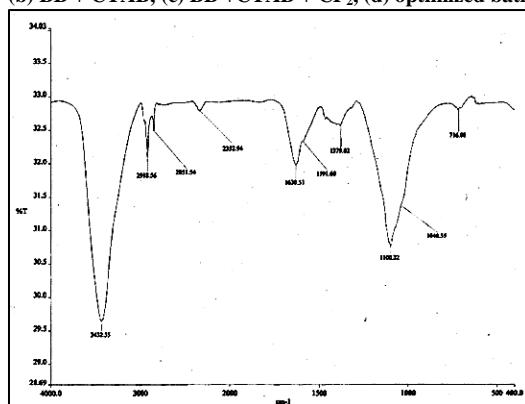

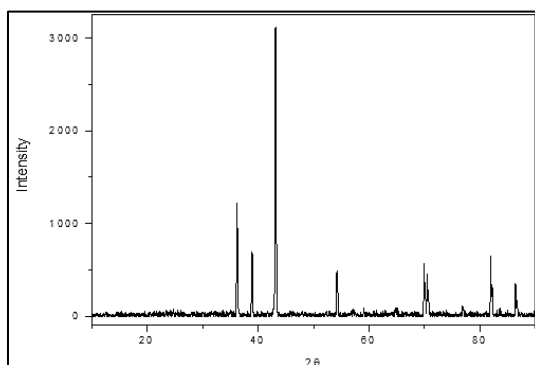**Figure 5: IR spectrum of the scraped Zn-Mn alloy deposit**

Figure 6: X-ray diffraction pattern of zinc obtained from basic bath

Figures 6 and 7 presents the X-ray diffraction pattern of the crystal structures of the zinc coating with and without additives. The 2θ values of the sample match with the standard JCPDS file. The crystalline size was determined from the full width at half maximum (FWHM) of the X-ray peaks present on the diffractogram and corresponding results are given in Tables 4 and 5.

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Table 3: Parameters derived from XRD data

Deposit	Basic bath			hkl
	2q	Average crystal size (nm)	'd' spacing	
Zn	36.3	32.26	2.4727	2
	39.01	31.26	2.3069	100
	43.24	30.29	2.0905	101
	54.34	29.17	1.6868	102
	70.05	39.26	1.3421	103
	82.07	49.65	1.1732	112
	86.53	51.44	1.1238	201
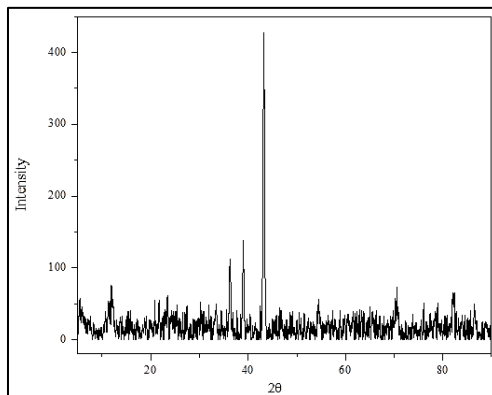
Figure 7: X-ray diffraction for Zn-Mn obtained from optimum bath

Table 4: Parameters derived from XRD data

Deposit	Optimized bath			hkl
	2q	Average crystal size (nm)	'd' spacing	
Zn-Mn	10.68	39.43	8.2765	2
	11.31	29.11	7.8168	100
	11.94	31.96	7.4057	101
	36.31	18.48	2.472	102
	39	30.74	2.3075	103
	43.23	25.67	2.091	112
	70.26	51.07	1.3386	201

Table 5: Optimum bath composition and operating conditions

Bath composition	Quantity (gL^{-1})	Operating condition
$ZnSO_4 \times 7H_2O$	200	Anode: zinc metal (99.99%)
$MnSO_4 \times H_2O$	4	pH: 3.0 Plating time: 10 min
Na_2SO_4	60	Cathode: mild steel
H_3BO_3	16	Temperature: 293-303K
CTAB	2	Cell current: 1A
CP2	4	

CONCLUSION

In the present work the experiments produced good Zn-Mn alloy electrodeposition on the mild steel surface in the acid sulphate bath at different current densities. The addition agent of CTAB and the condensation product of 4-chloro-2-nitroaniline and salicylaldehyde. This improved the hardness of the deposit throwing power and current efficiency of the bath and hence gave a bright deposit. IR spectrum revealed the inclusion of additive in the deposit. At this optimum concentration, the deposit was found to be crystalline and fine grained as evidenced from SEM and XRD-studies. The particle size is reduced in the presence additives. Hence the alloy coating can be used for industrial application where high corrosion resistance. The additives are non-toxic, easily soluble in water, environment friendly and hence require no treatment the effluent, be easily commercialized. The optimized bath

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produces good deposit over wide current density range. The deposit is pore free and corrosion resistant. The throwing power is reasonably good. The brighter can be easily synthesized. The addition agents are non-toxic, easily soluble in water and hence require no treatment of the effluent. The bath could be easily commercialized.

REFERENCES

[1] JB Bajat; MD Maksimoic; VB Miskovic-Stankovic, S Zec. *J Appl Electrochem*. **2001**, 31, 355.
[2] E Beltowska-Lehman; P Ozga; Z Swiatec; C Lupi. *Surf Coat Technol*. **2002**, 444, 151.
[3] C Muller; M Sarret; T Andreu. *Electrochem Act*. **2003**, 48, 2397.
[4] GD Wilcox; B Peterson. *Trans Inst Met Finish*. **1996**, 74, 115.
[5] FI Danilov; VV Gerasinov; DA Sukhomlim; *Russ Electrochem*. **2001**, 37, 308.
[6] B Bozzini; E Griskonics; A Fanigluilo; A Sulcius. *Surf Coat Technol*. **2002**, 154, 294.
[7] N Boshokov; K Petrov; S Vitkova. *Met Finish*. **2002**, 100, 98.
[8] D Sylla; C Rebere; M Gadouleau; C Savall; J Creus. *J Appl Electrochem*. **2005**, 35, 1133.
[9] D Sylla; J Creus; C Savall; O Roggy; M Gadouleau. *Thin Solid Films*. **2003**, 424, 171.
[10] C Karwas; T Hepel. *J Electrochem Soc*. **1988**, 135, 839.
[11] KG Kariyanna; Y Arthoba Naik; TV Venkatesh; *J Ind Council Chem*. **2003**, 20, 43.
[12] Y Arthoba Naik; TV Venkatesha. *Bull Mater Sci*. **2005**, 28, 495.
[13] Y Arthoba Naik; TV Venkatesha; P Vasudeva Nayak. *Bull Mater Sci*. **2000**, 16, 481.
[14] Y Arthoba Naik; TV Venkatesha; P Vasudeva Nayak. *Indian J Chem Technol*. **2001**, 390.
[15] H B Muralidhara Y Arthoba Naik;TV Venkatesha. *Bull Mater Sci*. **2006**, 29, 497.
[16] B Bozzini; F Pavan; G Bollini; PL Cavallotti. *Trans Inst Met Finish*. **1997**, 75, 175.
[17] TE Ohtsuka; A Kuwamura; KT Uchida. *ISIJ Int*. **1995**, 35, 892.
[18] M Abou-Krisha. *J Appl Surf Sci*. **2005**, 252, 1035.
[19] Ramachandran; SM Mayanna. *Met Finish*. **1992**, 90, 61.
[20] DR Gabe; GD Wilcox; A Jamani; BR Pearson. *Met Finish*. **1993,** 91, 34.
[21] Y Arthoba Naik. Development and optimization of brightners for industrial zinc electroplating acid and non-cyanide alkaline baths, Kuvempu University, Shankaraghatta, **2002**.