Effect of Urea Derivatives on Alkaline Zinc Plating Solutions

B.Mayelerinathan* and G.N.K.Ramesh Bapu**

Central Electrochemical Research Institute Karaikudi-630 006.
*Department of Industrial Chemistry, Alagappa University, Karaikudi- 630 003.

In the present investigation, an attempt was made to electrodeposit zinc using an eco-friendly zincate electrolyte as a total substitute for cyanide solutions. Without additives the deposits are powdery and grey in appearance. Hence a systematic Hull cell study was made to obtain a smooth, fine-grained semi-bright deposit over a wide current density range in presence of urea, thiourea, acetyl thiourea and N-ethyl thiourea. Current efficiency and throwing power of the solution were determined. The deposits were characterised for adhesion, porosity and hardness. Corrosion characteristics of the deposits were studied in 3.5% sodium chloride solution and the results were discussed.

Key words: Zinc deposition, alkaline non-cyanide, additives, current efficiency and throwing power-corrosion behaviour

Introduction

Electrogalvanising is the process of electrodeposition of zinc. It is much more economical than any other zinc coating method and imparts long life to components compared with paint coatings of equal thickness. The electrode potential of zinc is more negative than iron and provides excellent electrochemical protection against corrosion to steel parts under ordinary atmospheric conditions. Moreover zinc deposits exhibit sacrificial protection to iron and steel and hence ferrous materials are protected even if the deposit contains pores or discontinuities [1-3]..

In electrogalvanising acid baths are employed where it is desirable to have a high plating rate at low cost and high current densities are to be employed. The throwing power of these solutions restricts their use to plating on any plain shaped articles. Alkaline cyanide and presently evolving eco friendly non-cyanide baths posses good throwing power and are therefore quite suitable for plating on irregularly shaped articles.

The effectiveness and ease of operation of the later electrolyte is totally dependent on the proprietary additive system used in the bath [4-10]. Most of the details are patented and the commercial solutions are proprietary which has a number of merits and demerits [11].

In the present investigation, an attempt was made to electrodeposit zinc using an eco-friendly zincate electrolyte as a total substitute for cyanide solutions. Without additives the deposits are powdery and grey in appearance. Hence a systematic Hull cell study was made to obtain a smooth, fine-grained semi-bright deposit over a wide current density range in presence of urea, thiourea, acetyl thiourea and N-ethyl thiourea. Current efficiency and throwing power of the solution were determined. The deposits were characterised for adhesion, porosity and hardness. Corrosion characteristics of the deposits were studied in 3.5% sodium chloride solution and the results were discussed.

Experimental

The alkaline non-cyanide zinc plating bath contained 10 g/l zinc oxide, 100 g/l sodiun hydroxide, 1 g/l glue and 1 g/l gelatine. Laboratory grade chemicals were used and the plating solution was prepared in distilled water. The solution was pre-electrolysed at 0.3 A/dm^2 and filtered through a G-4 crucible. The pH of the filtrate was made adjusted to 11.5 and made up to 1 litre. All experiments were carried out on mild steel substrates at 30 °C.

Hull cell experiments

To judge the quality and nature of the zinc deposits in presence of urea (U), thiourea (TU) acetyl thiourea (ATU) and ethylthio urea (ETU) at various current density, plating was carried out on polished mild steel sheets (10 X 7 cm) at 1 amp cell current for 5 minutes using a standard 267 ml Hull cell. From the resulting deposit pattern, the optimum concentrations of the above additives for a wide semi-bright deposit range was determined.

* Author for correspondence
Email: **bapu2657@yahoo.com

Current efficiency (CE%)

The cathode current efficiency of the zinc deposit in presence of the optimum concentration of the additives was found at 1 to 4 A/dm² for duration of 1000 coulombs. From the weight of the deposits obtained, the current efficiency was determined using the relation,

$$CE\% = \frac{\text{Experimental weight}}{\text{Theoretical weight}} \times 100 \qquad …(1)$$

Throwing power (TP%)

The effect of the additives on throwing power of the zinc plating solution at various current densities was determined using Haring –Blum cell. The deposit was made at 1 to 4 A/ dm² for 30 minutes on polished steel cathodes positioned at a distance ratio of 1:5 from the perforated zinc anode. From the weight of the deposit obtained at the near cathode (W_n) and far cathode (W_f), the TP was calculated using the relation [12],

$$TP\% = \frac{L\text{-}M}{L+M\text{-}2} \times 100 \qquad …(2)$$

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

Characterisation of the deposit

The zinc deposits plated on mild steel specimens were characterised for adhesion, porosity and hardness using bend test, ferroxyl test and vickers indentation method respectively. The corrosion resistance of the deposits were studied in 3.5% sodium chloride solution using a three electrode cell assembly employing galvanostatic and potentiodynamic-polarisation techniques[13, 14].

Results and discussions
Hull cell studies

The current density at any point (Y) on the Hull cell cathode can be obtained using the equation,
c.d. at Y = Cell current (5.1-5.24 log Y) where, Y is the distance in cm from the high current density end.

The effect of adding urea, thiourea, acetyl thio urea, and ethyl thio urea in 0.1 to 0.4 g/l in to the zinc plating solution on the nature of the deposit was obtained using the Hull cell. In general, without additives the deposit was powdery. An optimum concentration was arrived for each additive where a fine-grained semi-bright deposit was obtained and the results were given in Table 1.

Table 1. Optimum concentration of additives and current density (c.d.).

Optimum additive concentration (g/l)	Optimum c.d for semi-bright deposit A/dm²
Urea 0.2	0.8
Thiourea 0.3	2.2
Acetyl thiourea 0.3	1.3
0.2	1.4

Current efficiency

The current efficiency of the zinc plating solutions in presence of the additives at their optimum concentrations was determined at different current density ranges between 1 and 4 A/dm² at 30 °C (Table 2). It could be seen that the current efficiency was decreased with current density in presence of additives under study.

Table-2. Effect of additives on current efficiency

Additives	Current efficiency (%)			
	Current density, (A/dm²)			
	1	2	3	4
No additive	89	88.2	82.5	77.9
Urea (0.2 g/l)	88	83.2	79.9	73.2
Thio urea (0.3 g/l)	83.3	79.9	77.5	71.1
Acetyl thio urea (0.3 g/l)	73.1	71	68.2	64.5
Ethy thio urea (0.3 g/l)	72.3	67.5	62.2	60.8

Compared to alkaline cyanide and pyro phosphate zinc solutions, the alkaline non-cyanide zinc solutions exhibited better current efficiency values and gave smooth deposits even at higher current densities.

Throwing power

In Table-3 was given the throwing power data of zinc baths in presence of additives at 1 and 2 A/dm² at 30 °C.

Table-3. Effect of additives on throwing power

Additives	Throwing power (%)	
	Current density, (A/dm²)	
	1	2
No additive	47.2	52.3
Urea (0.2g/l)	66.3	70.8
Thiourea (0.3 g/l)	58.2	60.2
Acetyl thiourea (0.3g/l)	41.2	46.9
Ethyl thiourea (0.3 g/l)	44.9	48.2

The TP increases with current density. Without additives, the zinc bath had a TP of 47% and 52% at 1 and 2 A/dm^2 respectively. Addition of urea and thiourea improved the TP whereas ATU and ETU had shown a decreased trend.

Characterisation of zinc deposit
Porosity

Ferroxyl test was employed to test the porosity of 3,6,9 and 12 micron thickness of the zinc deposit obtained in presence of various additives. Zinc specimens of 3 microns showed 6-8 pores per square inch area and the presence of additives decreased the number of pores by blocking the substrate. With samples of 6 microns thickness the deposit was pore free even without additives.

Corrosion resistance

The effect of additives under study on corrosion behaviour of the 6 microns zinc samples was studied in 3.5% sodium chloride solution both by galvanostatic and potentiodynamic polarisation method. Typical galvanostatic (Figs. 1 & 2) and potentio dynamic polarisation curves (Figs. 3 & 4) for 6 and 12 microns deposits were shown.
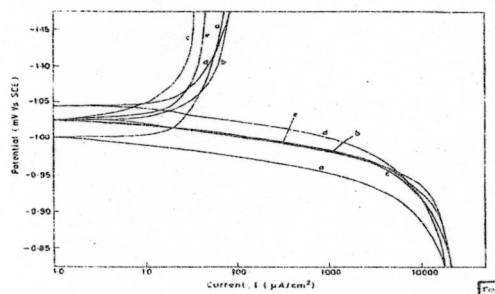

Fig.1. Effect of additives on galvanostatic polarisation behaviour of 6 microns thick zinc deposit in 3.5% NaCl solution.
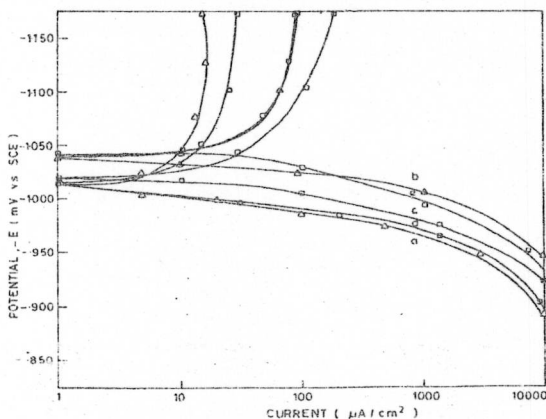

Fig.2. Effect of additives on galvanostatic polarisation behaviour of 12 microns thick zinc deposit in 3.5% NaCl solution.
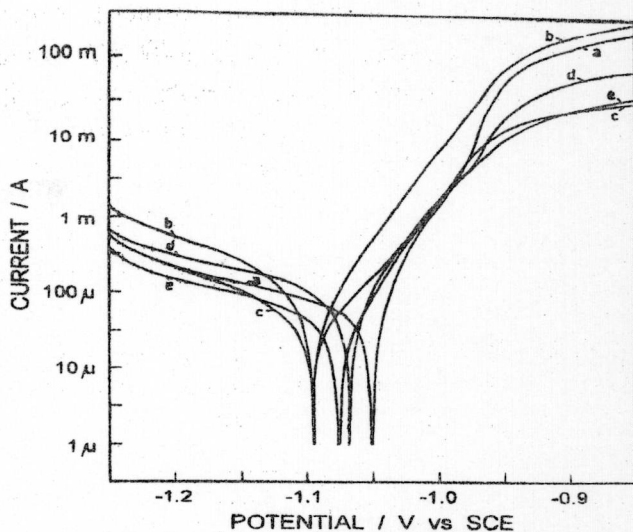

Fig.3. Effect of additives on potentiodynamic polarisation behaviour of 6 microns thick zinc deposit in 3.5% NaCl solution.
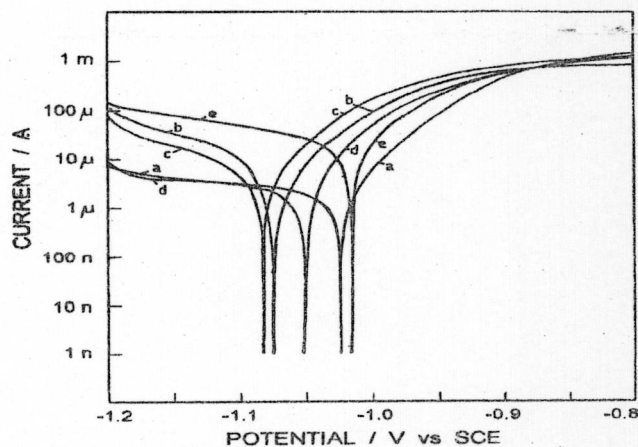

Fig.4. Effect of additives on potentiodynamic polarisation behaviour of 6 microns thick zinc deposit in 3.5% NaCl solution.

From the E-log I curves the corrosion current and corrosion potential was obtained by Tafel extrapolation method. The results are compared with steel and the corrosion data were given in Tables 4 and 5

Table 4. Effect of additives on corrosion behaviour in 3.5% NaCl solution by galvanostatic polarisation method. System Icorr (μa/cm^2) -Ecorr (mV vs SCE)

System	Icorr (μa/cm^2)	-Ecorr (mV vs SCE)	b$_a$ (mV/ decade)	b$_c$ (mV/ decade)
Steel	34	618	80	110
Zinc	15	1002	30	110
Zn+U	17	1025	30	100
Zn+TU	16	1025	55	110
Zn+ATU	18	1045	46	95
Zn+ETU	16	1027	31	85

Compared to mild steel, the corrosion potentials of all zinc deposits were shifted to about 400mV towards cathodic in NaCl solution. It suggested that zinc deposits in presence of additives also protect the steel cathodically more than two times.

Table-5. Effect of additives on corrosion behaviour in 3.5% NaCl solution by potentiodynamic polarisation method.

System	I_{corr} ($\mu a/cm^2$)	$-E_{corr}$ (mV Vs SCE)	b_a (mV/decade)	b_c (mV/decade)
Steel	34	560	70	110
Zinc	12	1050	35	95
Zn+U	13	1097	30	100
Zn+TU	14	1095	55	100
Zn+ATU	15	1075	56	95
Zn+ETU	13	1070	61	88

The data obtained using potentiodynamic method was in very good agreement with above method. Thus zinc deposits protect the steel substrate sacrificially and increases the life of the components. The organic additives adsorb on the deposit and provide a barrier protection to the substrate thereby enhancing the corrosion resistance of the components in service.

Conclusion

A smooth, fine grained and semi-bright zinc deposit was obtained in presence of urea, thio urea, acetyl thio urea and ethyl thio urea and the optimum concentrations were arrived at. Among the additives under study, urea and thio urea gave a better throwing power and current efficiency. Presence of additives decreased the extent of porosity and enhanced the corrosion resistance to about two folds.

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