

ADDITIVE CHARACTERISTICS IN MIXED CHLORIDE ZINC ELECTROLYTES

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Considering the pollution hazards and high industrial effluent treatment costs, non-cyanide zinc plating baths have been developed. Acid type plating baths have been successfully used in electrogalvanising of steel wires and strips due to high plating rates and low operating cost. Chloride baths have come into use recently because of the ease of control and higher rate of deposition. In the present study, an attempt was made to explore the characteristics of few additives in mixed chloride electrolytes. Presented in this paper are the results of investigations on cathode current efficiency, throwing power and brightness of zinc deposits obtained from mixed chloride zinc electrolytes in presence of piperonal, sodium ligno sulphonate, p-toluene sulphonamide, phenol sulphonic acid and dihydroxynaphthalene additives. Among the various organic additives studied, piperonal and dihydroxy naphthalene gave bright deposits with a better throwing power.

Keywords: Non cyanide zinc, effect of additives and brighteners.

INTRODUCTION

Zinc has long been used as a coating material for steel because of its good corrosion protection either alone or in combination. The expanded demand for galvanised steel has caused extensive studies to be made on zinc plating. Electrodeposited zinc coatings have some special characteristics which are beyond any other metal at such a low cost. Considering the pollution hazards and high industrial effluent treatment costs, non-cyanide zinc plating baths have been developed [1,2]. Acid type plating baths have been successfully used in electrogalvanising of steel wires and strips due to high plating rates with low operating cost. Chloride baths have come into use recently because of the ease of control and higher rate of deposition. Weak acidic baths are often used for bright zinc plating and these are capable of producing decorative and functional deposits in rack and barrel applications [3]. In the light of the known improvement of deposit characteristics by introduction of certain additive compounds [4-6], it was thought that a study on the effects of organic additives in zinc deposition would be useful. Presented in this paper are the results of

investigations on cathode current efficiency, throwing power and brightness of zinc deposits obtained from mixed chloride zinc electrolytes in presence of piperonal, sodium ligno sulphonate, p-toluene sulphonamide, phenol sulphonic acid and dihydroxy naphthalene additives.

EXPERIMENTAL

Laboratory grade chemicals were used to prepare the plating solution consisting of 65 g/l zinc chloride, 135 g/l potassium chloride, 25 g/l ammonium chloride and 2 g/l glue. The electrolyte was prepared using de-ionised water and treated with activated carbon and zinc dust for 8 hours at 333 K to remove the impurities. The electrolyte was then subjected to dummy electrolysis at low voltage for 24 hours, filtered through a G-4 crucible and used for plating. The pH was maintained at 6.3.

Hull cell studies

To examine the nature of zinc deposits over a wide current density range in presence of various organic compounds, Hull cell (267 ml capacity) experiments were carried out in the above bath composition at different additive concentrations at 2 Amp cell current for a duration of 5

minutes each at 323 K. From the recorded Hull cell pattern, concentration of the additive was optimized.

Current efficiency studies

Experiments were carried out on stainless steel specimens of 2.5 cm x 2.5 cm size in presence of various additives on zinc solutions at 323 K and at current densities ranged from 3 to 8 A.dm⁻² for a duration of 600 coulombs. From the weight of the deposits obtained, current efficiency (C.E) was determined.

Throwing power studies

Experiments were carried out on mild steel specimens of 3.5 cm x 4.0 cm using Haring and Blum cell at 323 K and at 5 A.dm⁻². The throwing power (T.P) of the solution was calculated using the formula

$$T.P (%) = \frac{P-M}{(P+M-2)} \times 100$$

where P is the primary current distribution and M is the metal distribution ratio (i.e., the ratio of the weight of the deposit from the nearest cathode, W_n to the weight of the deposit on the farther cathode, (w_f).

Cathodic polarization studies

Cathodic potential under galvanostatic conditions was measured using a three electrode cell assembly. The deposits were made on 2.5 cm x 2.5 cm mild steel sheets. The specimen which was masked with a lacquer to expose 1 cm² area served as working electrode. A platinum foil of 2.5 cm x 2.5 cm served as counter electrode and a saturated calomel electrode (SCE) served as reference electrode. The cathodic potential (E) was recorded at various current densities (i) ranging from 1 to 10 A.dm⁻² and the polarisation curve was obtained by plotting E vs log i.

Measurement of reflectivity

The mild steel specimens deposited in presence of additives were evaluated for brightness using gloss meter. The instrument was calibrated to 100% reflectivity using a plane mirror and the reflectivity of the deposits were read directly on the gloss meter.

RESULTS AND DISCUSSIONS

Hull cell studies

Hull cell studies were carried out in the mixed chloride zinc electrolytes containing definite amount of piperonal (PNL), sodium ligno sulphonate (SLS), p-toluene sulphonamide (PTS), 1,5-dihydroxy haphthalene (DHN) and phenol-4-sulphonic acid (PSA). Among these additives PNL

and DHN produced a fine grained bright deposits over a wide current density range. But SLS, PTS and PSA gave powdery deposits at all concentration ranges under study and the bright range was observed only at a narrow region. The patterns recorded are shown in Figs. 1a to 1e.

PNL was varied from 1.0 to 4.0 g/l. At 1g/l, the deposit was smooth and bright in the current density range of 2 to

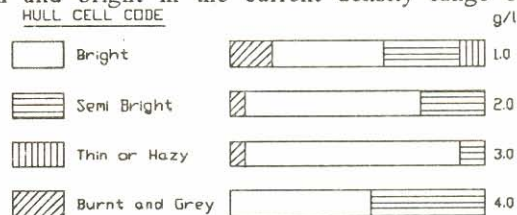


Fig. 1(a)

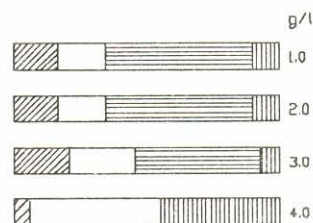


Fig. 1(b)

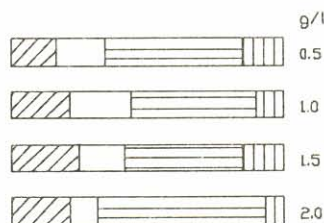


Fig. 1(c)

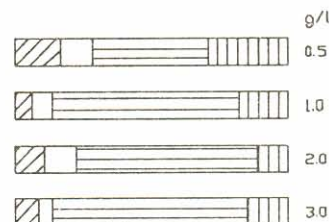


Fig. 1(d)

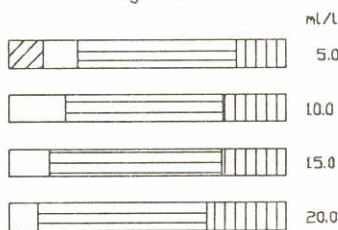


Fig. 1(e)

Fig. 1: Hull cell pattern obtained with various concentrations of piperonal (1a), 1,5-dihydroxy naphthalein (1b) sodium ligno sulphonate (1c), p-toluene sulphonamide (1d) and phenol sulphonic acid (1e)

Cell current = 2 Amp. Temp = 323 K. Time = 5 min. pH = 6.3

7 A.dm⁻². On increasing the concentration, the bright range widened and at 3 g/l, a smooth and fine grained deposit was observed between 1 to 8 A.dm⁻². Further additions (4 g/l) produced a dull deposit with an iridescent appearance. The optimum concentration was fixed as 3 g/l.

DHN was tried in the concentration range 1 to 4g/l. Up to 3 g/l additions the deposits were unsatisfactory and the bright range was observed over a narrow region. Increasing the concentration to 4 g/l, a bright deposit was obtained over 1 to 8 A.dm². The optimum concentration was fixed as 4 g/l. As other additives gave powdery deposits, they were not characterised further.

Studies on current efficiency

The current efficiencies of zinc deposits in presence of PNL and DHN additives at different current densities are shown in Fig. 2. Zinc bath without additive had a current efficiency of 95 to 98% whereas baths with additives possessed values slightly lesser than this. The current efficiency was seen to increase with current density up to 5 A.dm⁻². Further increase in current density, however, decreased the efficiency of the solution. The observed decreasing trend on current efficiency with organic additives was reported to be due to the role of the additive molecule in the stacking process of deposited metal atoms on the cathode. The organic compounds may physically impede the growth mechanism and thus influence the brightening of the coatings. This process will consume energy resulting in a decrease of the measured current efficiency [7].

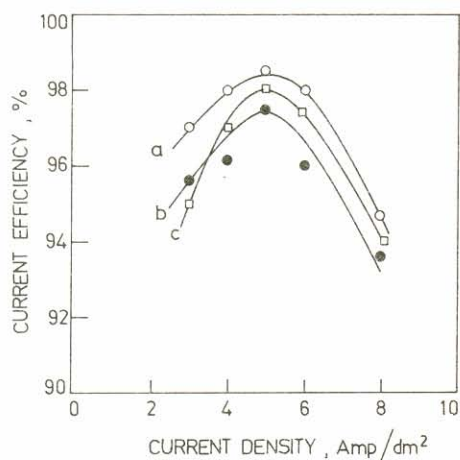


Fig. 2: Effect of additives on current efficiency at various current densities

(a) no additive (b) with 1,5-dihydroxy naphthalenein (4 g/l)
(c) with piperonal (3 g/l)

TABLE I: Effect of additives on throwing power

Chloride zinc electrolyte	Throwing power (%)
With no additive	13
With 1,5-dihydroxy naphthalenein	25
With piperonal (3 g/l)	16

Studies on throwing power

The throwing power values of the zinc plating solutions in presence of different additives are given in Table I. Basic zinc solution had a throwing power of +13% which increased to 25% with piperonal and to +16% with 1,5-dihydroxy naphthalene. In general chloride electrolytes are reported to improve the throwing power than sulphate baths and the organic additives preferentially act in the presence of potassium chloride [8,9]. This is in good accordance with the observed throwing power data.

Cathodic polarization studies

The variation of cathodic potential at different current densities in the range of 1 to 10 A.dm⁻² is shown in Fig. 3. For a given current density, the cathodic potential became more negative in the presence of additives and this tendency was found to enhance more in the presence of 1,5-dihydroxy naphthalenein. This shift of potential towards enhancing the cathode polarization. In most cases the additives are adsorbed on the surface to be plated and form a thin film that controls the deposition process by suppressing crystal growth resulting in smooth fine grained deposit (10). In general,

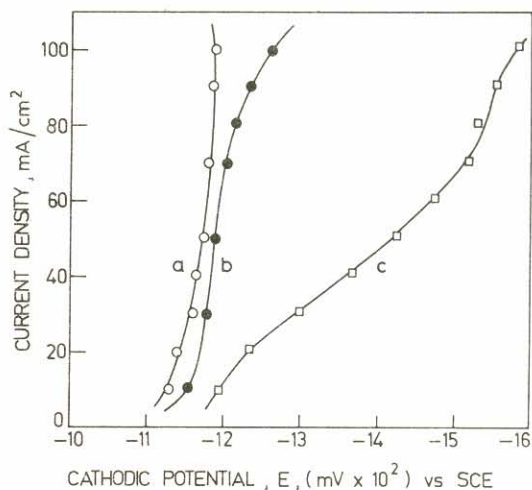


Fig. 3: Effect of additives on cathodic potential at various current densities

(a) no additive (b) with 1,5-dihydroxy naphthalenein (4 g/l)
(c) with piperonal (3 g/l)

TABLE II: Effect of additives on reflectivity

Chloride zinc electrolyte	Reflectivity (%)
With no additive	58
With 1,5-dihydroxy naphthalein	85
With piperonal (3 g/l)	80

additives which enhances the cathode polarization will result in fine grained deposit.

Reflectivity measurements

The reflectivity values of zinc deposits in presence of additives are shown in Table II. With piperonal and 1,5-dihydroxy naphthalene additives, a reflectivity value of 80% to 85% was obtained.

CONCLUSIONS

* Among the various organic additives studied, piperonal and 1,5-dihydroxy naphthalene gave a bright deposit over a broad current density range.

- * Presence of organic additives decreased the current efficiency of the plating solutions to a significant extent.
- * Presence of organic additives shifted the cathodic potential to more negative values and improved the throwing power.
- * A reflectivity of 85% to 90% was obtained with piperonal and 1,5- dihydroxy naphthalene.

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