

## Zinc Electroplating-Hull Cell Studies

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**Abstract.** Influence of additives in acid zinc chloride plating bath was observed. Eight various types of additives were used and effect was studied using Hull cell test. The zinc plating was carried out using bath, zinc chloride 50-60 g/l, boric acid 20 g/l, potassium chloride 250-275 g/l, at pH 5.0-5.4, temperature 35-40 °C, cell voltage 1-1.1 V, cell current 1.5 A and plating duration five minutes. Appearance of the deposit was best at vanillin 2.5 g/l.

**Keywords:** zinc electroplating, Hull cell, appearance, additives

### Introduction

A bright zinc electroplating bath is described containing zinc and an additive containing >1 substituted or unsubstituted polyether, >1 aliphatic unsaturated acid containing aromatic or heteroaromatic groups and <1 aromatic or N-heteroaromatic aldehyde. Thus zinc electroplating was done in a bath containing zinc chloride 100, potassium chloride 200, boric acid 20, polyethylene glycol 10, *o*-methoxycinnamic acid 0.75, 2-hydroxy-3-methoxybenzaldehyde 0.2, and 4-methoxybenzaldehyde 0.1 g/l at 0-20 A/dm<sup>2</sup> and pH 5.5. Bright extremely ductile zinc electroplates were obtained with a moderate degree of leveling (Arcilesi and Alan, 1977).

A cyanide-free bath is described for the electroplating of bright zinc. A typical bath contains: zinc chloride 60, potassium chloride 195, boric acid 30 g/l, butylnicotinate dimethyl-sulfate aromatic quaternary compound 0.03 and 2,3,7,9-tetramethyl-5-decayne-4,7-diol, polyethylene glycol ether (1:2) 5 g/l. The plate after fifteen min at 40 A/ft<sup>2</sup> acquired a smooth, bright, and uniform finish. Butylnicotinate dimethyl-sulfate quaternary compound and 2,3,7,9-tetramethyl-5-decayne-4,7-diol, polyethylene glycol ether (1:2) 5 g/l. The pH of the bath was 5.8 and the steel test plate after fifteen min at 40 A/ft<sup>2</sup> acquired a smooth, bright, and uniform finish (Creutz *et al.*, 1979).

Bright zinc electrodeposition can be obtained by the addition of brighteners in the plating bath. Bright deposits improve the appearance of the article, besides offering good corrosion resistance. The effects of different additives in the zinc bromide plating baths using Hull cell technique are explained. Among the different additives studied, vanillin gives the bright deposits (Chandran *et al.*, 1999).

A new brightener was used for zinc plating. It was the reaction product of aromatic aldehyde/aliphatic alkanol- amine in polyoxyethylene glycol with addition of water/other polar solvents (Szczepaniak and Stainslaw, 1990). The effects of gelatin and *p*-tolualdehyde were explained in a chloride bath. Bright zinc coating was obtained, throwing power; current efficiency and polarization study were also carried out (Koji *et al.*, 1994).

Naphthalene sulfonic acid-formaldehyde condensation product, sodium benzoate, fatty alcohol, polyethylene glycol ether with ten ethylene glycol units and nonylphenol polyethylene glycol ether (sulfonated and sulfated) with ten ethylene glycol units in a bath containing zinc chloride, potassium chloride and boric acid were studied. It yields bright zinc deposits on brass steel (Ulrich *et al.*, 1994).

Thiourea, polyethylene glycol and nitrilotriacetic acid were used in a weak acid ammonium chloride bath followed by alkaline medium containing sodium hydroxide, zinc, vanillin and coumarin. The electroplated zinc was passivated with dilute chromic acid with good stability (Hao and Yunke, 1997).

The durability of passivation in zinc electroplating has been studied using weak acid zinc bath free from cyanide and ammonia for zinc plating, and yellow and colorless passivating solutions for passivation process (Haque *et al.*, 2003a). Recently, coloring of electroplated zinc was reviewed (Haque *et al.*, 2003b).

In this work, various additives for zinc electroplating from acid chloride zinc bath were studied using Hull cell on brass panels. The aim was to find out the optimum concentration of the additive at which the maximum brightness is obtained.

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## Materials and Methods

Zinc chloride, Qingdao Suchemint, China (technical grade); sulfuric acid, BDH, England (analytical grade) were used. Other chemicals, ethanol, vanillin, lysine, thiourea, dextrin, gelatin, butyl alcohol, triethanol amine, glucose, were of laboratory grade and were used as received.

In all experiments, the electrolytes for zinc plating were prepared using zinc chloride 50-60 g/l, boric acid 20 g/l, potassium chloride 250-275 g/l. The specific gravity of the bath was set to 26 Baume (Haque *et al.*, 2003a).

**Hull cell test.** The nature of the zinc deposit over a wide range of current density was examined by Hull cell test on twenty gauge brass sheet, locally purchased. The brass sheet was polished, mechanically buffed, degreased with ethanol, rinsed, pickled and thoroughly rinsed before plating.

**Cathode.** Brass panels, 2.5x4.0625 in<sup>2</sup>, were employed as cathode for Hull cell experiments.

**Anode.** Zinc metal of electrolytic grade 99.9% pure, having dimensions 2.5x2.5 in<sup>2</sup>, was used as anode.

The pH of the bath was 5.0-5.4, temperature 35-40 °C, cell voltage 1-1.1 V, cell current 1.5 A, and plating time five minutes.

## Results and Discussion

Results obtained from Hull cell experiments of zinc plating were summarized in Figs. 2-9. Eight sets of Hull cell experiments were carried out. Legend used for Hull cell studies is shown in Fig. 1.

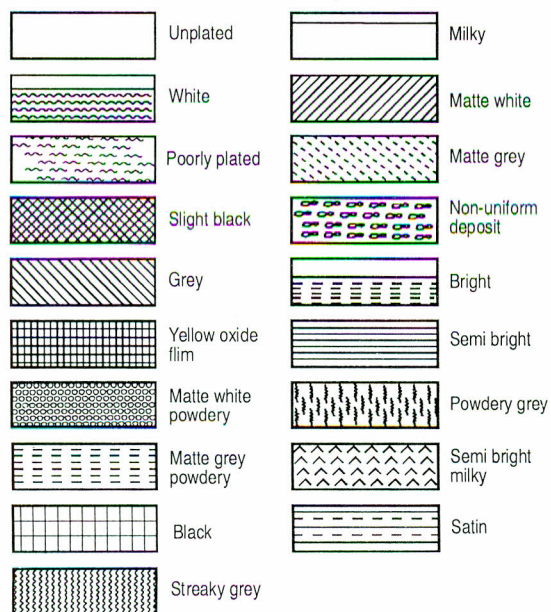


Fig. 1. Legend used for Hull cell studies.

In first run, the concentration of dextrin was varied from 0.5-5.0 g/l and results obtained were shown in Fig. 2. At dextrin, 0.5-1.0 g/l, satin plating was obtained in the range 0.2-2.3 cm. The nature of the deposit was good at dextrin 3.0 g/l, from 2.0-4.0 cm satin plating was obtained. Further increase in dextrin concentration, 4.0-5.0 g/l, gave mostly streaky grey deposits.

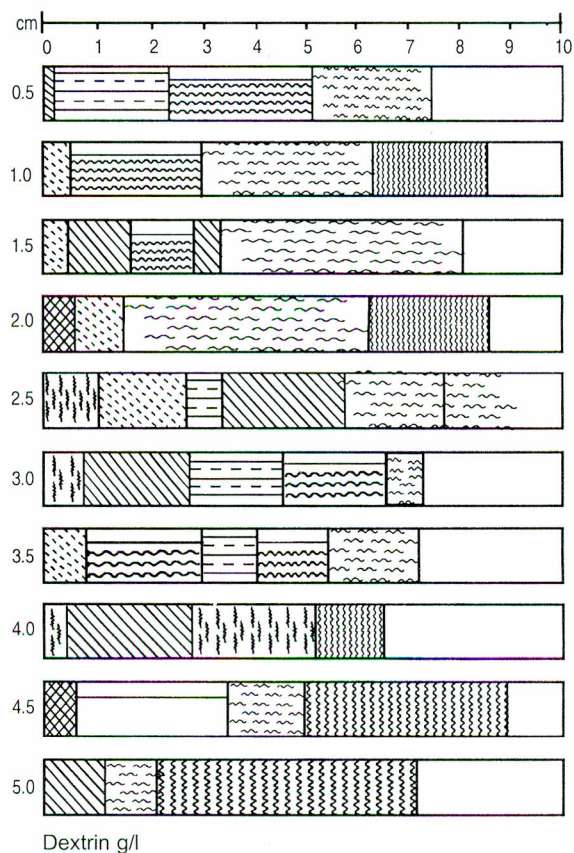


Fig. 2. Effect of dextrin on appearance of zinc plating.

In second set of experiments, the influence of thiourea on zinc deposit was studied, Fig. 3. The concentration of thiourea varied from 0.5-2.5 g/l. From Hull cell test panels it may be seen that matte grey deposits can be obtained to a greater extent from thiourea, 0.5 g/l. Above thiourea 1.0 g/l, the appearance of the deposit became worse and worse.

The effect of glucose, 0.5-5.0 g/l, was examined in third run, Fig. 4. Glucose, 0.5-2.0 g/l, gave matte grey powdery deposits in the range 0-2.0 cm. Milky deposits, 4.8-7.0 cm, was obtained at glucose 2.5 g/l. At glucose 3.0 g/l, matte white powdery deposits were obtained. Glucose, 3.5-5.0 g/l, gave matte grey deposits.

Results obtained from triethanol amine (TEA), 0.5-5.0 ml/l, were summarized in Fig. 5. White deposit was obtained, 0-1.4 cm, at triethanol amine 0.5 ml/l. From 1.4-5.8 cm, zinc was poorly

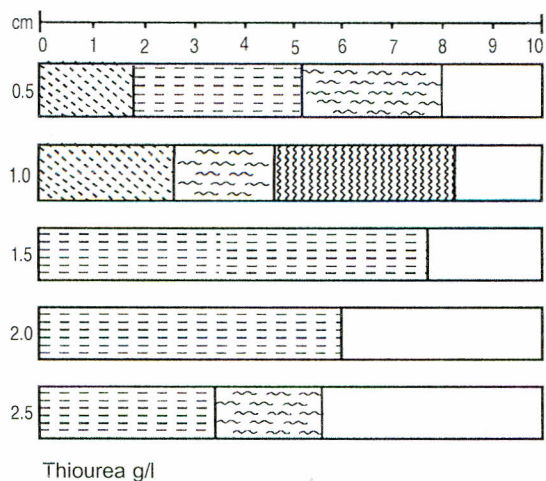


Fig. 3. Effect of thiourea on appearance of zinc plating.

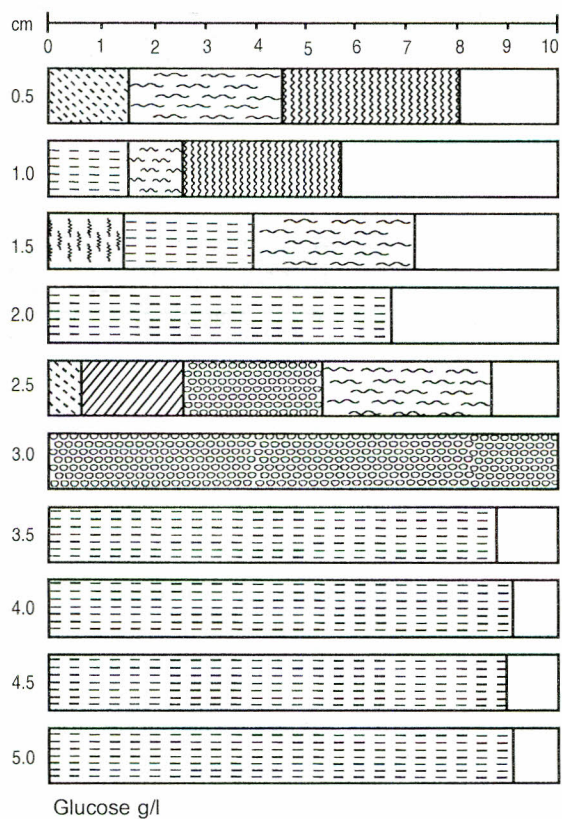


Fig. 4. Effect of glucose on appearance of zinc plating.

deposited. At triethanol amine 1.5-2.0 ml/l, matte grey powdery deposits were obtained, 0.6-5.6 cm. White deposit was obtained at triethanol amine 3.0 ml/l, 2.4-5.1 cm. Matte grey powdery plating was obtained, 0-5.5 cm, for triethanol amine 3.5 ml/l. Triethanol amine 4.0-4.5 ml/l gave milky deposit in the range 0.5-8.5 and 0.5-7.0 cm, respectively. Deposit was matte grey at triethanol amine 5.0 ml/l, as shown in Fig. 5.

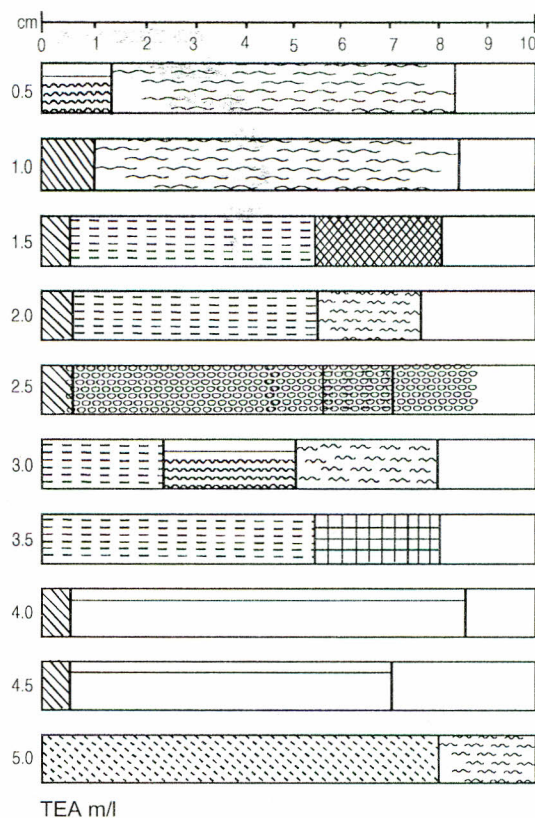


Fig. 5. Effect of TEA on appearance of zinc plating.

Influence of gelatin on zinc plating was reported in Fig. 6. The concentration of gelatin was varied from 0.5-2.5 g/l. At gelatin 0.5 g/l, matte grey powdery deposit, 0-0.2 cm; milky, 0.2-2.2 cm, grey, 2.2-4.7 cm and 6.5-8.0; semi-bright milky, 4.7-6.5 cm was obtained. Gelatin, 1.0 g/l, gave grey deposit, 0-7.5 cm. Semi-bright milky deposit was obtained over a wide range (0.7-8.0 cm) from gelatin 1.5-2.0 g/l. Gelatin 2.5 g/l, gave satin, 0-2.5 cm, and grey deposit, 2.5-8.8 cm.

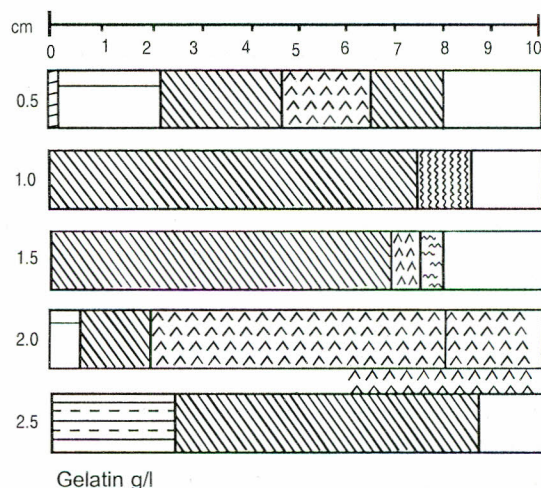
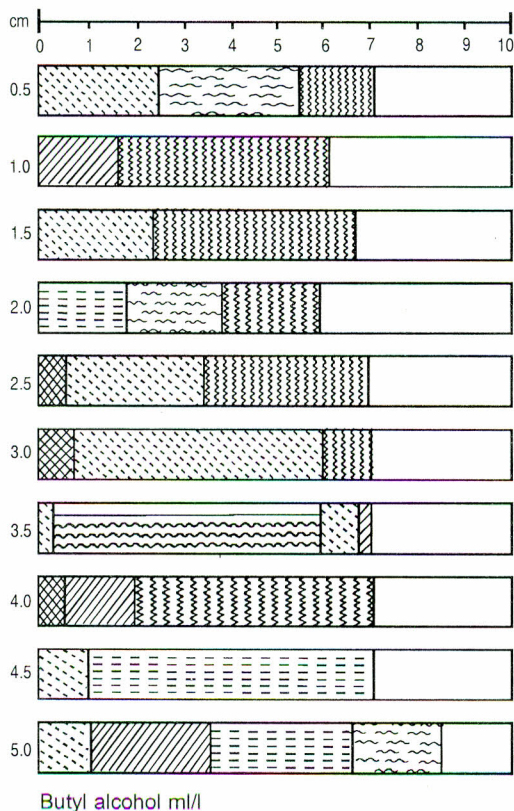


Fig. 6. Effect of gelatin on appearance of zinc plating.

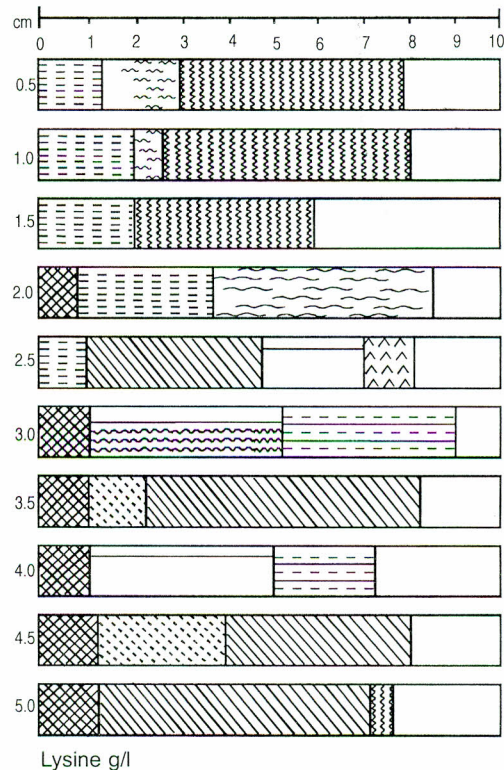
Concentration of butyl alcohol was varied from 0.5-5.0 ml/l and results obtained from Hull cell experiments were shown in Fig. 7. Butyl alcohol 0.5-1.5 ml/l gave matte grey deposit, 0-2.5 cm. The best results in case of butyl alcohol was obtained at 3.5 ml/l. Hull cell pattern showed, matte grey, 0-0.3 cm and 0.6-4.8 cm, white 0.3-0.6 cm, matte white deposit, 4.8-7.0 cm. Mostly matte grey deposits were obtained at butyl alcohol 4.5-5.0 ml/l.



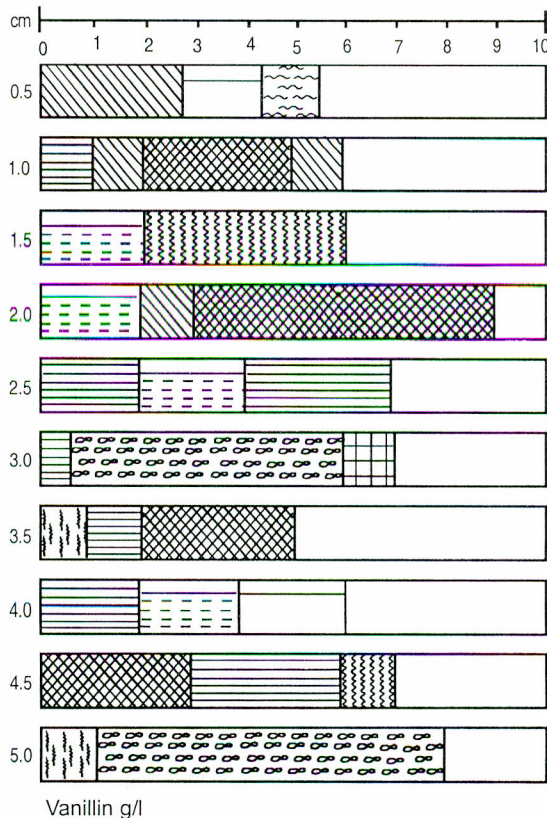
**Fig. 7.** Effect of butyl alcohol on appearance of zinc plating.

In the seventh set of experiments influence of lysine on zinc plating was studied. The concentration of lysine was varied from 0.5-5.0 g/l. Mostly matte grey powdery deposits were obtained from lysine 0.5-2.5 g/l. Lysine 2.5 g/l, gave matte grey powdery, 0-1.0 cm; grey 1.0-4.8 cm; milky, 4.8-7.0 cm; semi-bright milky deposit, 7.0-8.0 cm. At lysine 3.0 g/l, white deposit, 1.0-5.2 cm and satin, 5.2-9.0 cm, were obtained. Lysine 4.0 g/l, gave milky and satin deposits in the range, 1.0-5.0 cm and 5.0-7.2 cm, respectively. Further increase in lysine concentration gave matte grey and grey deposits, Fig. 8.

In the eighth run, vanillin, 0.5-5.0 g/l, was used. Results obtained from Hull cell experiments were summarized in Fig. 9. At vanillin, 0.5 g/l, milky grey deposit was obtained in the range 2.8-4.4 cm. Deposit was bright, 0-1.0 cm, at



**Fig. 8.** Effect of lysine on appearance of zinc plating.



**Fig. 9.** Effect of vanillin on appearance of zinc plating.

vanillin 1.0 g/l. Bright deposit, 0-2.0 cm, was obtained from vanillin 1.5-2.0 g/l. At vanillin 2.5 g/l, 2.0-4.0 cm, bright deposit; 0-2.0 cm and 4.0-7.0 cm, semi-bright deposits were obtained. At vanillin 3.0-3.5 g/l nature of the deposit was not good. Again bright deposit, 2.0-4.0 cm, was obtained at vanillin concentration 4.0 g/l. Semi-bright deposit, 3.0-6.0 cm, at vanillin 4.5 g/l was obtained. Further increase in concentration of vanillin, deposit was non-uniform. Best results in terms of brightness were obtained for vanillin 2.5 g/l (Chandran *et al.*, 1999).

### Conclusion

Effects of various additives on zinc plating from acid chloride zinc bath by performing Hull cell tests were studied. Results showed that only vanillin gave the bright deposit. It was concluded that bath comprising zinc chloride 50-60 g/l, boric acid 20 g/l, potassium chloride 250-275 g/l, vanillin 2.5 g/l at pH 5.0-5.4, temperature 35-40 °C and cell current 1.5 A produced bright deposit.

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