

## Effect of condensation product on electrodeposition of zinc on mild steel

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**Abstract.** Electrodeposition of zinc on steel was obtained from acid chloride bath containing condensation products (CP) of 3,4,5-trimethoxy benzaldehyde (TMB) and chitosan (CTN). The effect of bath constituents, pH, current density and temperature on the nature of deposit was studied by Hull cell experiments. The bath composition and operating parameters were optimized. The adhesion, ductility and corrosion resistance of the deposits were discussed. Throwing power and current efficiency values under different plating conditions were measured. SEM photomicrographs of the deposit were taken to study the surface morphology. The inclusion of addition agent in the deposit was investigated from IR spectrum of the scrapped deposit. The consumption of brightener in the lab scale is  $10 \text{ mL}^{-1}$  for 1000 amp-h.

**Keywords.** Acid chloride bath; brightener; condensation product; electrodeposition.

### 1. Introduction

Electrodeposited zinc has been used extensively in automotive and other industrial sectors as a protective coating for large quantities of steel wires, strips, sheets, tubes and other fabricated ferrous metal parts. Zinc deposits offer good protection and decorative appeal at low cost. Since zinc is anodic to steel, it protects the base metal even if the deposit is porous. An acid zinc bath is used where it is desirable to have a high plating rate with maximum current efficiency (Schneider 1977). However, the critical pre-treatment requirements and the poor throwing power of these solutions restrict their use to plate only on regular shaped articles. Considering pollution hazards and high industrial effluent treatment costs, non-cyanide zinc baths have been introduced in place of cyanide solutions (Ostrow and Kessler 1970). Zinc coatings are obtained either from cyanide, non-cyanide alkaline or acid solutions (Venkatesha *et al* 1985; Wang 1992; Degorre 1993; Budman 1995; Zeng 1996; Bapu *et al* 1998; Arthoba Naik *et al* 2000, 2001; Arthoba Naik and Venkatesha 2005). Because of the pollution and high cost associated with cyanide, deposition from other baths such as sulphate, chloride, and mixed sulphate–chloride baths are gaining importance. Good deposition depends mainly on the nature of bath constituents. Generally, a plating bath contains conducting salts, buffering agents, complexing agents and metal ions. Among these the complexing agents effectively influence the deposition

process, solution properties and structure of the deposit. The action of these complexing agents is specific and depends on pH, nature of anion, temperature and other ingredients of the medium. The effectiveness and ease of operation of these baths are totally dependent on the brightener additive systems used in the bath (Ramachandran and Mayanna 1992). Few developed addition agents are surface active (Venkatesha *et al* 1985; Arthoba Naik *et al* 2000, 2001; Arthoba Naik and Venkatesha 2005) and change the characteristics of metal solution interface properties, form complex with metal ions (Venkatesha *et al* 1988) and are adsorbed on a cathode surface. Most of the addition agents possess electroactive functional groups (Geduld 1974; Arcilless 1979; Venkatesha 1987; Parthasarathy 1989). Usually, the electroplating baths are associated with two or more addition agents and are essential to obtain a quality deposit. Too many ingredients cause difficulties in maintaining the operating parameters of the bath solution during the plating process. Therefore, it is essential to develop the bath with a single additive that could produce a quality deposit.

In the present study, the bath solution was prepared using zinc chloride, ammonium chloride, boric acid and CP. For the preparation of CP, various primary amines and aldehydes are subjected to condensation reaction (Morrison and Boyd 1973). Among these, the CP formed between TMB and CTN produced bright deposit. The Hull cell experiment was employed to optimize the current density, pH and temperature, over which good quality deposit was obtained. The throwing power and current efficiency of the solution were also determined at various current densities.

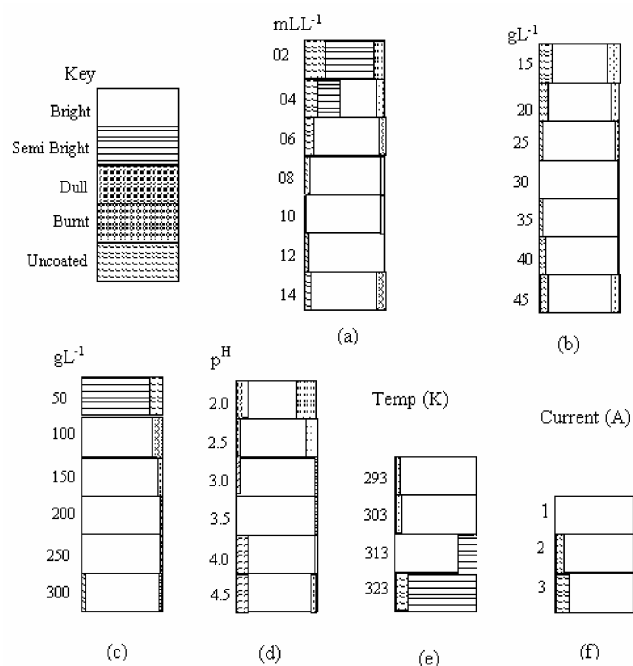
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## 2. Experimental

The chemicals used were of AR grade and easily soluble in water. For the preparation of solutions, distilled water was used. The standard Hull cell of 267 mL capacity was used to optimize the bath constituents. The Hull cell experiments with bath solution (table 1) were carried out without agitation. The pH of the bath solution was adjusted with 10% hydrochloric acid or sodium carbonate solution. Zinc plate of 99.99% purity was used as anode. The anode was activated each time by immersing in 10% HCl followed by water wash. Mild steel plates (AISI-1079) of standard Hull cell size were mechanically polished to obtain a smooth surface. The scales and dust on the steel plates were removed by dipping in 10% HCl and were subjected to electrocleaning process. These steel plates were washed with water and used for the experiments as such. After plating experiment, the plates were subjected to bright dip in 1% nitric acid for 2 s followed by water wash. The nature and appearance of zinc plating was carefully studied and recorded through Hull cell codes as shown in figure 1(a).

**Table 1.** Basic bath composition and operating conditions.

Bath composition	Conc. (gL <sup>-1</sup> )	Operating conditions
ZnCl <sub>2</sub>	35	Anode: zinc metal (99.99% pure)
NH <sub>4</sub> Cl	150	Cathode: mild steel
pH	2.5	Temperature: 298 K



**Figure 1.** Hull cell figures: (a) effect of condensation product, (b) effect of ZnCl<sub>2</sub>, (c) effect of NH<sub>4</sub>Cl, (d) effect of pH, (e) effect of temperature and (f) effect of cell current.

All the experiments were conducted at  $298 \pm 1$  K. The CP was prepared as follows. 1 g TMB was dissolved in 10 ml acetic acid, the solution heated to activate the aldehyde and 1.3 g CTN in 10 ml 5% acetic acid was added drop wise to the solution and refluxed for about 3 h at 70°C, then the yellow coloured solution was obtained. The solution as such was used for the Hull cell studies. A known amount of condensation product in mL was added to the bath solution. The bath solution was stirred for 30 min and then used for the Hull cell experiments.

The deposits were obtained at a constant current density from the optimized solution taken in a rectangular methacrylate cell of 2.5 L capacity. Polished, degreased and electrocleaned cathodes of  $3 \times 4$  cm<sup>2</sup> were used for plating. Experiments were done in triplicate. Standard experimental procedures (Parthasarathy 1989) were adopted for measurement of properties of the deposit such as ductility, adherence etc. In all the above studies the average thickness of the deposit was 20  $\mu$ m.

For corrosion resistance test, coated steel plates of  $3 \times 4$  cm<sup>2</sup> area were given bright dip followed by passivation in a solution containing 200 gL<sup>-1</sup> of sodium dichromate and 2 mL<sup>-1</sup> of sulphuric acid at 303 K for 5 s. These passivated samples were dried for 24 h in a clean atmosphere and subjected to neutral salt spray test in accordance with ASTM standard method B-117 using 5% neutral sodium chloride solution at 303 K.

Polarization studies were carried out by using a three-compartment cell. The area of zinc anode was 2 cm<sup>2</sup>. Mild steel was used as cathode with an exposed area of 2 cm<sup>2</sup>. The cathode potential was recorded galvanostatically with respect to standard calomel electrode at different current densities. Haring and Blum cell was used to measure throwing power and the current distribution ratio between anode and cathodes was 1 : 5. For determining consumption of brightener, a rectangular cell of 2.5 L capacity was used.

IR spectra of the condensation product and the scrapped deposit were taken to know the inclusion of addition agent. SEM photomicrographs were taken to know the nature of deposit in the presence of addition agents.

## 3. Results and discussion

### 3.1 Hull cell studies

**3.1a Effect of condensation product:** Basic bath solution gave coarse dull deposit between the current density range of 1 and 7 Adm<sup>-2</sup> at 2 A cell current. To improve the nature of deposit, CP was added to the bath solution. With increase in the concentration, the nature of deposition improved and at a concentration of 10 mL<sup>-1</sup> of CP, the Hull cell panels were bright between the current density range of 0.5 and 8 Adm<sup>-2</sup>. With further increase in the concentration of CP, the nature of the deposit became burnt at higher current density region. Therefore, on the

basis of the above observations, the concentration of CP was kept at  $10 \text{ mL}^{-1}$  as optimum. The Hull cell patterns are shown in figure 1a.

**3.1b Effect of zinc chloride:** To find out the effect of zinc ion, the zinc chloride concentration was varied from  $15\text{--}45 \text{ gL}^{-1}$  keeping CP at  $10 \text{ mL}^{-1}$ . At low current density region, dull deposits and at high current density region, burnt deposits were obtained (figure 1b). With increase in the concentration of zinc chloride, the brightness range was extended to higher and lower current density regions. At a concentration of  $30 \text{ gL}^{-1}$ , a satisfactory bright deposit was obtained. Above this concentration of zinc sulphate, no improvement in the nature of deposit was observed. The concentration of zinc sulphate was fixed at  $30 \text{ gL}^{-1}$  as optimum.

**3.1c Effect of ammonium chloride:** Ammonium chloride was added to increase the conductance of the bath solution. The concentration of ammonium chloride was varied from  $50\text{--}300 \text{ gL}^{-1}$ . At lower concentrations, the Hull cell panels showed semibright deposit at low current density region and dull at higher current density region. The semibright and dull regions were found to be reduced with increase in the concentration of ammonium chloride and at  $200 \text{ gL}^{-1}$ , the deposit was bright over a current density range of  $0\text{--}8 \text{ Adm}^{-2}$ . Further increase in the concentration ( $>200 \text{ gL}^{-1}$ ) did not introduce any effect on the nature of deposit and on the conductance also. So, the concentration of ammonium chloride was fixed at  $200 \text{ gL}^{-1}$  in the bath solution. The Hull cell patterns showing the effect of ammonium chloride are given in figure 1c.

**3.1d Effect of pH and temperature:** To know the effect of pH, the pH of the bath solution was varied from  $2\text{--}5$ . At higher pH, the Hull cell panels showed burnt deposit at high current density region. At pH  $3\text{--}5$ , satisfactory deposit was obtained. At lower pH ( $<3\text{--}5$ ), the specimens had dull deposit at low current density region. From the above observations, the pH of the bath solution was kept at  $3\text{--}5$  as optimum. The Hull cell patterns are as shown in figure 1d.

To study the effect of temperature on Hull cell experiments, the plating experiments were carried out in a thermostat. The temperature of the thermostat was varied from  $293\text{--}323 \text{ K}$ . At lower temperatures ( $<303 \text{ K}$ ), the deposition was bright in the current density range  $1\text{--}8 \text{ Adm}^{-2}$  at  $2 \text{ A}$  cell current. Above  $313 \text{ K}$ , the deposit was dull in the low current density region. Therefore, the optimum operating temperature range was  $293\text{--}298 \text{ K}$ . The Hull cell panels showing the effect of temperature are shown in figure 1e.

**3.1e Effect of cell current:** The Hull cell experiments were carried out at different cell currents ( $1\text{--}3 \text{ A}$ ) for  $10 \text{ min}$  using optimum bath solution. It was found that at a cell

current of  $1 \text{ A}$  the deposit was bright in the current density range  $0\text{--}1\text{--}5\text{--}6 \text{ Adm}^{-2}$ . At a cell current of  $2 \text{ A}$ , the deposit was bright in the current density range of  $1\text{--}8 \text{ Adm}^{-2}$ . At a cell current of  $3 \text{ A}$  the deposit was bright over the current density range between  $2$  and  $8 \text{ Adm}^{-2}$ . The Hull cell patterns are as shown in figure 1f.

### 3.2 Current efficiency and throwing power

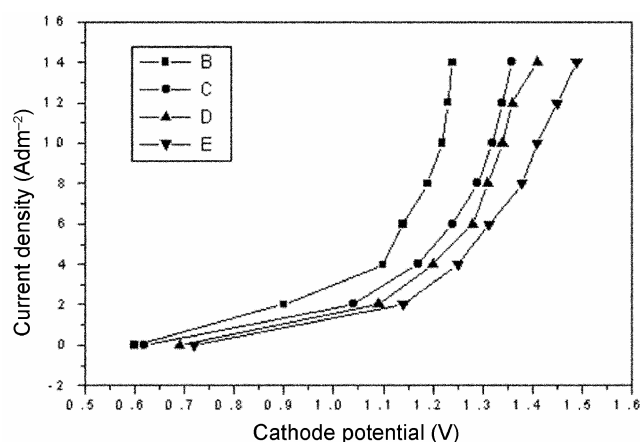
Current efficiency and throwing power were measured at different current densities by using optimized bath solution. At lower current density ( $1 \text{ Adm}^{-2}$ ), the current efficiency was found to be  $91\%$ . At a current density of  $4 \text{ Adm}^{-2}$ , the efficiency was increased to  $94\%$ . With increase in the current density above  $4 \text{ Adm}^{-2}$ , the current efficiency was found to be decreased and at  $5 \text{ Adm}^{-2}$  it was  $92\%$  (table 3).

**Table 2.** Optimum bath composition and operating conditions.

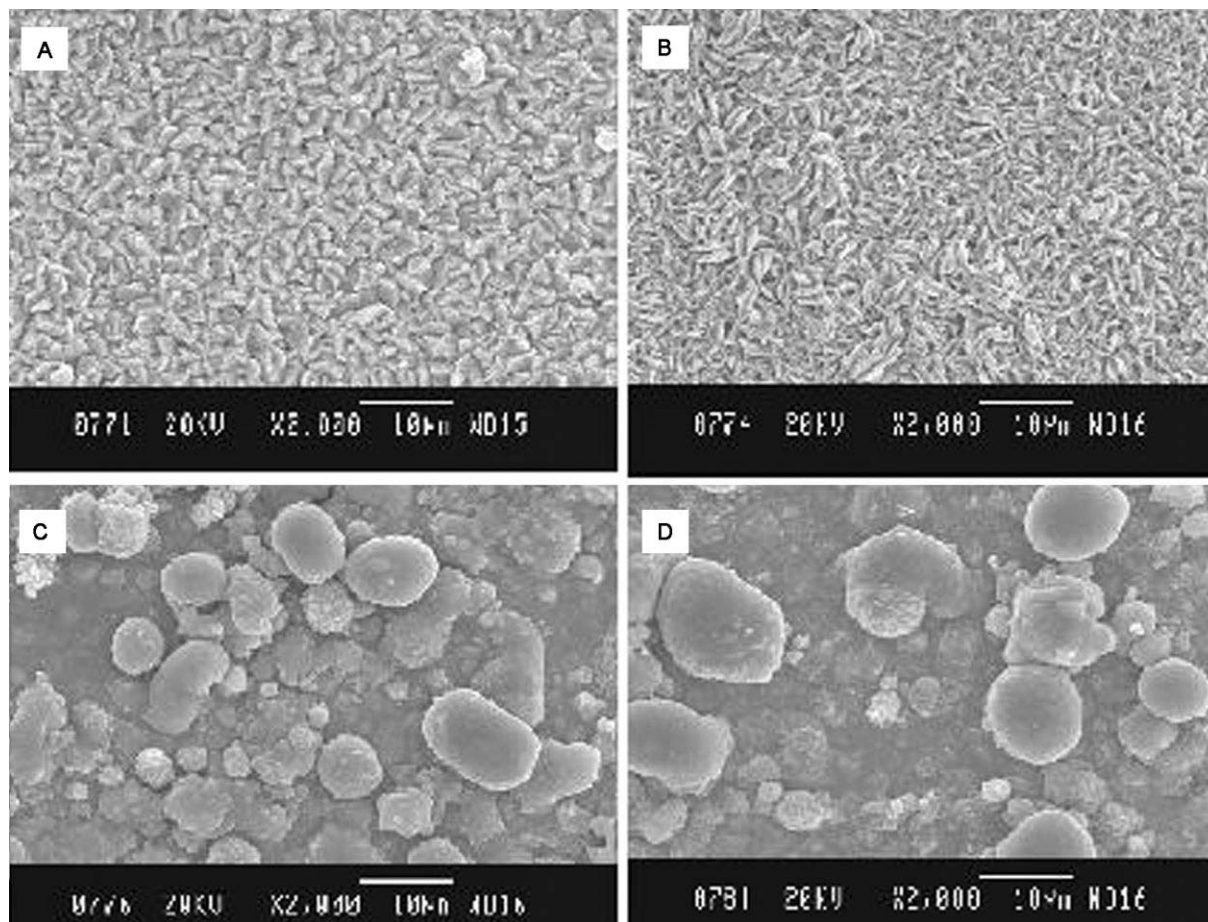
Bath composition	Conc. ( $\text{gL}^{-1}$ )	Operating conditions
ZnCl <sub>2</sub>	30	Anode: zinc metal (99.99% pure)
NH <sub>4</sub> Cl	200	Cathode: mild steel
CP ( $\text{mLL}^{-1}$ )	10	Temperature: $298 \text{ K}$
		pH: $3\text{--}5$
		Plating time: $10 \text{ min}$
		Bright current density range: $0\text{--}2\text{--}8 \text{ Adm}^{-2}$

**Table 3.** Current efficiency and throwing power at different current densities.

Current density ( $\text{Adm}^{-2}$ )	Current efficiency (%)	Throwing power (%)
1	91	27.5
2	92	29.0
3	93	33.6
4	94	37.2
5	92	30.8



**Figure 2.** Effect of addition agents on cathodic potential. [B = basic bath (BB), C = BB + CTN, D = BB + TMB, E = BB + CP].



**Figure 3.** SEM photomicrographs of the deposits obtained at  $4 \text{ Adm}^{-2}$  in the presence and absence of addition agents at 298 K: **A.** basic bath (BB), **B.** BB + CTN, **C.** BB + TMB and **D.** optimized bath.

**Table 4.** Salt spray test conducted at different time intervals.

Plating bath composition	Treatment (h)	Observation
Basic bath (BB)	24	No white rust
	48	White rust
Optimized bath	24	No white rust
	48	No white rust
	72	No white rust
	96	White rust
Passivated deposit	24	No white rust
	48	No white rust
	72	No white rust
	96	No white rust
	480	No white rust

Throwing power was measured by using Haring and Blum cell at different current densities. At lower current densities the throwing power was 27.5% and with increase in the current density it increased to 37.2% at  $4 \text{ Adm}^{-2}$  (table 3).

### 3.3 Polarization studies

The potential of the steel cathode was measured galvanostatically with respect to saturated calomel electrode

at different current densities. The variation of potential in the presence of different bath constituents is as shown in figure 2. The shift in cathodic potential towards negative direction was observed in presence of addition agents.

### 3.4 Corrosion resistance

For corrosion resistance study, the steel cathodes having varying thicknesses, from 5–15  $\mu\text{m}$  were given. The specimens after plating were subjected to bright dip in 1% nitric acid followed by passivation. The corrosion resistance test was carried out in a salt spray chamber. The deposited plates, after passivation, were subjected to continuous spray of neutral 5% sodium chloride solution. The specimen did not show any rust even after 96 h of testing. This study shows good resistance of the deposit. The results of salt spray test is given in table 4.

### 3.5 Adhesion properties

Standard bend test was used to measure both adherence and ductility of zinc deposits. Mild steel panels of 1 mm

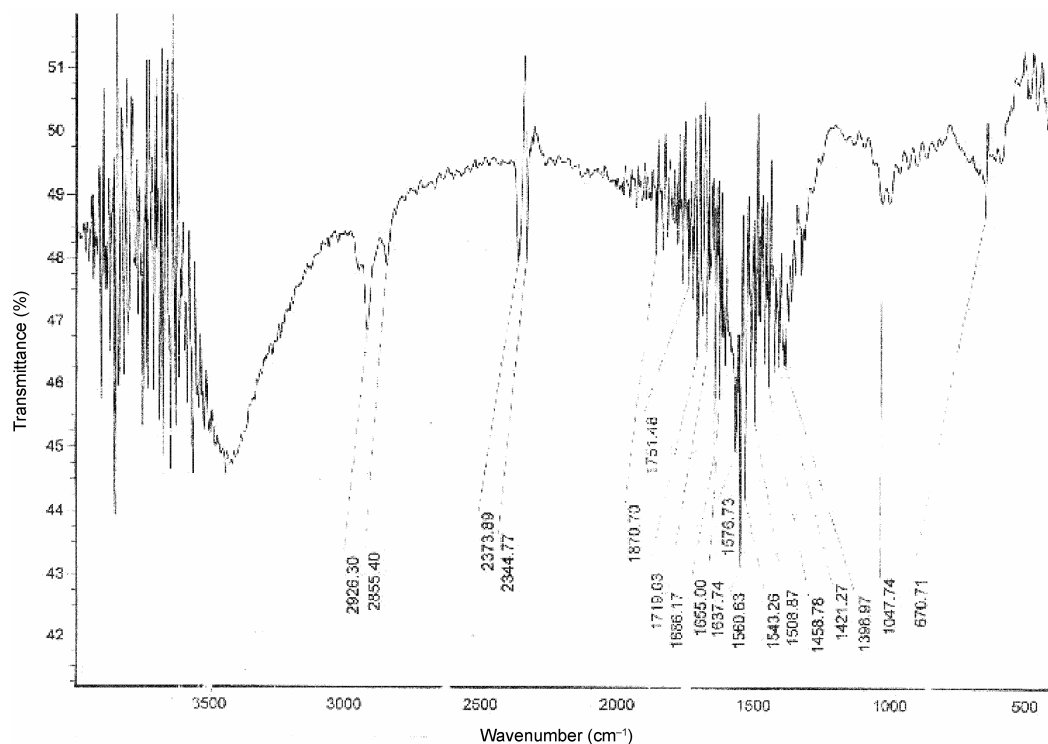


Figure 4. IR spectrum of the scrapped zinc deposit.

thick ( $1 \times 10 \text{ cm}^2$  area) were electroplated with zinc to different thicknesses ( $5\text{--}20 \mu\text{m}$ ). The samples were subjected to bending test through  $180^\circ$ . No crack or peel off in the deposit was noticed even after  $180^\circ$  bending of the specimen. This indicates the good adherence and ductility of zinc deposit on steel.

### 3.6 Surface morphology and IR studies

The nature of crystal growth in the presence and absence of addition agent is explained with the help of SEM photomicrographs and are shown in figure 3. SEM photomicrograph (figure 3a) of the deposit obtained from the basic bath shows coarse-grained deposit having irregular crystal size ( $\sim 3 \mu\text{m}$ ). Figure 3b shows the SEM photomicrograph obtained in presence of CTN having comparatively smaller grain size ( $\sim 2 \mu\text{m}$ ). In presence of TMB the porous free nature of deposit was observed due to still smaller grain size (figure 3c). The change in morphology can be associated to a strong blocking effect of CP, which causes an increased nuclei renewal rates leading to an increase in nucleation number and hence smaller grain size. The SEM photomicrograph (figure 3d) of the deposit obtained from the optimum bath shows perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence bright deposit.

The IR spectrum of the scrapped deposit obtained from the optimum bath was used to test the inclusion of the addition agent in the deposit. IR spectrum of the scrapped

deposit (figure 4) shows the inclusion of the condensation product in the deposit which was observed at  $1655 \text{ cm}^{-1}$ . This indicates the presence of C=N group in the condensation product. Also the position of the peaks indicated the changes in the structure of the addition agent during electrodeposition.

### 3.7 Consumption of brightener

In electroplating, the addition agents play an important role in producing lustrous deposits. The addition agents are consumed during plating and thus their concentration decreases. When this concentration goes below the optimum value, the deposit becomes dull in appearance. To know the amount of addition agents consumed in the present bath, 2.5 L of bath solution was taken and plating was carried out at different current densities. The total number of coulombs passed to the bath solution was recorded at the time when the bath just started to give semi-bright deposit. The used bath solution was Hull cell tested by adding different amounts of condensation product. The concentration of condensation product, at which once again bright deposit was obtained, was determined. The amount of condensation product consumed for 1000 amps-h was  $10 \text{ mL}^{-1}$ .

## 4. Conclusions

The optimized bath produces good deposit over a wide current density range. The optimized bath composition is

shown in table 2. The constituents of the bath are only condensation product and conducting salts. This is an advantage over other baths with too many constituents. The throwing power is reasonably good. The addition agents are non-toxic. The deposit has good adhesion property and is corrosion resistant.

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