Electrodeposition of Zinc from Chloride Solution

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The electroplating of zinc is carried out in the presence of 3,4,5-Trimethoxy benzaldehyde from a chloride bath. The bath constituents are optimized through Hull cell experiments. Operating parameters such as pH, temperature, and current density are also optimized. The current efficiency and throwing power are measured at different current densities. Polarization study is carried out under galvanostatic conditions. Corrosion resistance test indicated good protection of steel by the coating. The consumption of brightener is determined in the laboratory scale. SEM photomicrographs revealed fine-grained structure of the deposit from the optimum bath. IR spectrum of the scratched deposit showed inclusion of addition agent.

Introduction

The use of zinc-plated articles is increasing due to its sacrificial protection of steel from corrosion. This sacrificial protection is due to the fact that the zinc is a less noble metal and cathodically protects the steel even in places where the deposit is damaged. Zinc coatings are obtained either from cyanide, non-cyanide alkaline or acid solutions[1−6]. 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. Few developed addition agents[7−9] are surface active and changes the characteristics of metal solution interface properties, form complex with metal ions[10] and are adsorbed on a cathode surface. Most of the addition agents possess electroactive functional groups[11−13]. 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. Some of these agents smoothen the deposit over a wide current density range and the other addition agents influence the production of bright deposits. Therefore, it is essential to develop the bath with a single additive that could produce a quality deposit. In the present work, efforts have been made to develop a bath solution containing a single additive.

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Experimental

The chemicals used were of AR grade and the solutions were prepared with distilled water. The standard Hull cell of 267 mL capacity was used to optimize the bath constituents and operating parameters. The pH of the bath solution was adjusted with 10% HCl or sodium carbonate solution. Zinc plate of 99.9% purity was used as an anode. The mild steel plates of standard Hull cell size were mechanically polished, and degreased by dipping in boiling trichloroethylene followed by acid dip and water wash. After the Hull cell experiments, the plates were subjected to bright dip in 1% nitric acid for 3 to 5 seconds followed by water wash. The nature and appearance of the zinc plating were carefully observed and recorded through the Hull cell codes (Figure 1a).
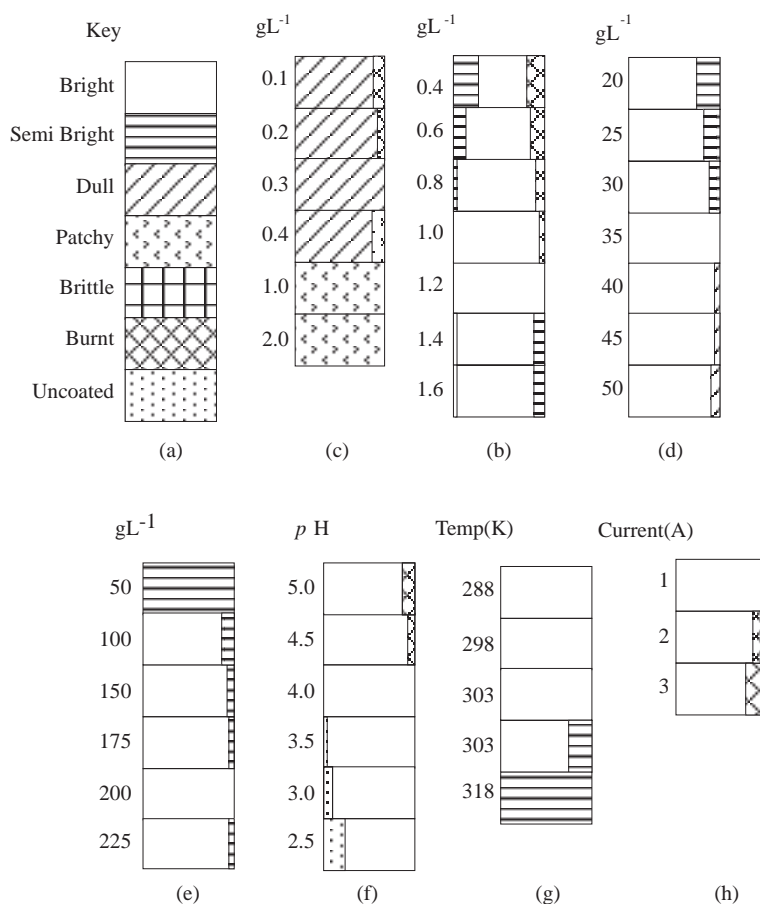

Figure 1. Effect of bath constituents and bath variables on Hull cell cathode b) 3,4,5-Trimethoxy benzaldehyde, c) EDTA, d) Zinc chloride, e) Ammonium chloride, f) pH, g) Temperature, h) Cell current.

All the experiments were conducted at 303 ± 1 K. The addition agents were dissolved in a small amount of alcohol and transferred to the bath solution (Table 1). The bath solution was stirred for 30 minutes and then subjected to Hull cell experiments.

The deposits were obtained at constant current density from the optimized solution in a rectangular cell. Polished, degreased and electrocleaned cathodes of 2.5×10 cm^2 were used. These steel cathodes were plated and used to test different properties such as porosity, ductility and adhesion[14]. For corrosion

resistance test, a coating with an average thickness of 15 μm was obtained on 5×5 cm^2 steel panels. Steel plates after deposition were given a bright dip in 1% nitric acid followed by chromate passivation. The chromated samples were subjected to the salt spray test according to the ASTM standard method B-117 using 5% neutral sodium chloride solution at 308 K[15].

Table 1. Basic bath composition and operating conditions

Bath composition	Concentration (gL^{-1})	Operating conditions
ZnCl$_2$	30	Anode: Zinc metal (99.99%)
NH$_4$Cl	150	Cathode: Mild steel
H$_3$BO$_3$	20	Cell current: 1 A
		Plating time: 10 min
		pH: 4.5
		Temperature: 298 K
		Agitation: Air

A three-compartment cell was used for polarization studies. The area of the electrodes (anode and cathode) exposed was 2 cm^2. The cathode potential was recorded, galvanostatically, with respect to the saturated calomel electrode, at different current densities in the presence and absence of addition agents. For current efficiency and throwing power measurement, the Haring and Blum cell was used. For throwing power measurement, the distance between the anode and cathodes was a 1:5 ratio. For determining the consumption of brightener a rectangular cell of 2.5 L capacity was used. SEM photomicrographs of the plated steel specimens from the bath with and without addition agents at a current density of 3.0 Adm^{-2} were taken. The IR spectrum of the scraped deposit from the optimum bath solution was used to determine the inclusion of addition agents in the deposit.

Results and Discussion

Hull cell studies

Deposits obtained from Hull cell experiments with the basic bath solution (Table 1) were coarse dull between the current density 1.0 to 3.0 Adm^{-2} at 1 A cell current. To improve the nature of the deposit various organic compounds were used as primary addition agents. Among these additions, gelatin gave a fine dull deposit over a wide current density region. The concentration of gelatin varied from 0.1 to 2.0 gL^{-1}. At lower concentration, the deposit was dull in the lower current density region (<1.0 Adm^{-2}) and fine dull in the current density of 1.0 to 3.5 Adm^{-2}. At and above 3.5 Adm^{-2} the deposit was burnt in appearance. With an increase in the concentration of gelatin, the fine dull area was extended towards the high and low current density regions. At a concentrations of 0.3 gL^{-1}, the nature of the deposit was fine-grained over the current density range of 0 to 4 Adm^{-2}. At still higher concentrations the nature of the deposit changed from fine dull to patchy dull. As a result, the concentration of gelatin was fixed at 0.3 gL^{-1} in the bath solution. The Hull cell patterns are shown in Figure 1b.

Further experiments were conducted by keeping the gelatin concentration at 0.3 gL^{-1}, with organic compounds having amine and aldehyde as functional groups. Among the additives tried, 3,4,5-Trimethoxy benzaldehyde (TMB) gave a mirror bright deposit. Further Hull cell experiments were conducted to fix the concentration of TMB for good brightness. The concentration of TMB varied from 0.1 to 2.0 gL^{-1}. At lower

concentrations (< 1.2 gL^{-1}) of TMB, the specimens suffered dull deposits at the lower current density region and were burnt at the higher current density region. At a concentration of 1.2 gL^{-1}, the deposit on the Hull cell cathode was mirror bright in appearance over the entire current density at 1 A cell current. Above 1.2 gL^{-1} a brittle deposit was obtained in the higher current density region. Based on the above results, the concentration of TMB was fixed at 1.2 gL^{-1} as optimum in the bath solution. The effect of TMB on Hull cell panels is shown in Figure 1(c).

Effect of ammonium chloride

To increase the conductivity of bath solution certain conducting salts having chlorides and sulphates are added. Some of these salts not only act as conducting salts but also influence the nature of the deposition and dissolution of the anode. In the present bath, sodium chloride, potassium chloride and ammonium chloride were added to the bath solution. The presence of sodium chloride and potassium chloride showed a bright deposit only in the narrow current density range (1.5 to 3 Adm^{-2}). Ammonium chloride produced mirror bright deposits in the wide current density range. The concentration of ammonium chloride was varied from 50 to 250 gL^{-1} in the bath solution. At lower concentrations (< 200 gL^{-1}), the Hull cell cathodes suffer dull and semibright deposit in the higher current density region. At a concentration of 200 gL^{-1} the deposit which was mirror shining bright in the entire current density range at 1 A cell current. Higher concentration (> 200 gL^{-1}) gave a dull deposit which was observed in the high current density region. Hull cell panels showing the effect of ammonium chloride are given in Figure 1(c). The amount of ammonium chloride was fixed at 200 gL^{-1} in the bath solution.

Effect of zinc chloride

Zinc chloride concentration was varied from 10 to 45 gL^{-1} by keeping gelatin at 0.3 gL^{-1}, TMB at 1.2 gL^{-1} and ammonium chloride at 200 gL^{-1} in the bath solution. At lower concentrations of zinc chloride, a bright deposit was observed in the low current density range between 0 to 3 Adm^{-2} at 1 A cell current. At the higher current density region (> 3 Adm^{-2}) a semibright deposit was noticed. It was further noticed that the Hull cell patterns were almost free from semibright deposits when the amount of zinc chloride reached 35 gL^{-1}. At still higher concentration (> 35 gL^{-1}) the deposits suffered from a dull deposit at the the higher current density region. The concentrations of zinc chloride, a based on the above observations, was fixed at 35 gL^{-1} as optimum. Hull cell panels are shown in Figure 1(d).

Effect of pH and temperature

The pH of the bath solution was varied from 2.5 and 5.0. At low pH between 2.5 and 3.5, the Hull cell patterns showed an uncoated area in the low current density region. At a pH of 4.0 a satisfactory mirror deposit was obtained on the steel specimen in the entire current density range (0 to 4 Adm^{-2}). With an increase in pH, above 4.5, the deposit becomes dull and at a higher current density region a burnt deposit was obtained. By these observations the pH of the bath solution was fixed at 4.0. The effect of pH on deposit nature is shown in Figure 1(f).

To see the effect of temperature on Hull cell experiments, bath solution of optimum concentration was prepared. The Hull cell was placed in a thermostat and filled with bath solution. The experiments were

conducted when the solution in the bath attained the required temperature. The studied temperature range was 288 to 318 K. At lower temperatures the deposition was mirror bright in the current density range of 0 to 4 Adm^{-2}. With an increase in the temperature above 303 K the bright range was decreased and finally the dull deposit was obtained at and above 318 K. The influence of temperature on deposit nature is shown in Figure 1(g).

Effect of cell current

The bright current density range of the deposit was observed by conducting the Hull cell experiments for 5 min at different cell currents (1 to 3 A) using the bath solution containing zinc chloride (35 gL^{-1}), TMB (1.2 gL^{-1}), gelatin (0.3 gL^{-1}), ammonium chloride (200 gL^{-1}), boric acid (30 gL^{-1}) and at pH 4.0. It was noticed that at a cell current of 1 A, the deposit was bright in the current density range of 0.5-4 Adm^{-2}. At a cell current of 2 A, the deposit was bright in the current density range 0.5-7.5 Adm^{-2}. At a cell current of 3 A the deposition was bright over the current density range 0.5-8.0 Adm^{-2}. Above 8.0 Adm^{-2}, a burnt deposit was observed. Through the above observations it was found that the optimized bath produced a bright deposit in the current density range of 1-8.0 Adm^{-2}. Hull cell patterns are shown in Figure 1(h).

Current efficiency and throwing power

Current efficiency and throwing power were measured at different current densities by using optimized bath solution. Current efficiency was measured by taking the solution in a rectangular methacrylate cell of 1 L capacity. At lower current density (1 Adm^{-2}), the current efficiency was 88%. At a current density of 2 Adm^{-2} the efficiency was increased to 92%. This trend continued up to 3 Adm^{-2} and after 3.0 Adm^{-2} the current efficiency was decreased and at 6.0 Adm^{-2} it was found to be 78%.

Throwing power was measured by using Haring and Blum cell at different current densities. At lower current densities the throwing power was 38%. With an increase in current density it was increased and attained a maximum value of 40% at 4 Adm^{-2} (Table 2). The variation of current efficiency and throwing power with bath constituents and bath variables at 4 Adm^{-2} are given in Table 3.

**Table 2.** Current efficiency and throwing power at different current densities

Current density (Adm^{-2})	Current efficiency (%)	Throwing power (%)
1	88	37
2	92	38
3	93	39
4	90	40
5	86	40
6	78	39

Operating Voltage

The variation of operating Hull cell voltage with ammonium chloride at different Hull cell currents is shown in Figure 2. The voltage of the bath solution decreases with increase in the concentration of ammonium chloride up to 70 gL^{-1}. Above this concentration there is no appreciable change in the voltage.

Table 3. Influence of bath components and parameters on current efficiency and throwing power at 4 Adm^{-2}

Bath constituents	Range	Current efficiency (%)	Throwing power (%)
ZnCl$_2$, gL^{-1}	20-40	80-92	38-40
NH$_4$Cl, gL^{-1}	50-250	84-92	28-40
Gelatin, gL^{-1}	0.1-0.5	85-92	24-40
3,4,5-Trimethoxy benzaldehyde, gL^{-1},	0.5-2.0	87-92	36-40
pH	3.0-5.5	82-92	26-40
Temperature, K	293-323	80-92	28-40
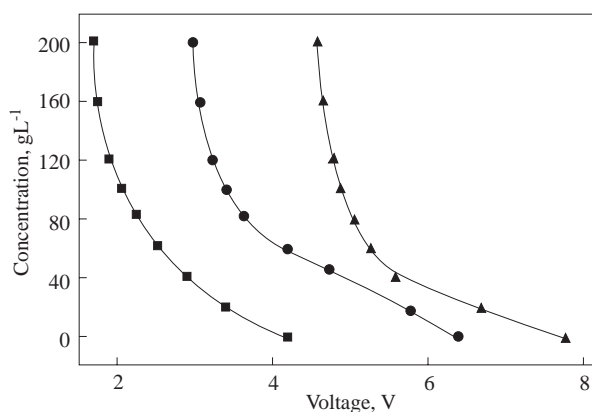
Figure 2. Effect of ammonium chloride on operating Hull cell voltage at different cell currents.
▲ : 3 A,   ●: 2 A,   ■ : 1 A

Polarization study

The potential of the steel cathode was measured galvanostatically with respect to a saturated calomel electrode at different current densities. The variation of potential in the presence of different bath constituents is shown in Figure 3. The shift in the potential was at maximum in the presence of both TMB and gelatin and was least in the absence of addition agents. This property of addition agents is responsible for a fine-grained deposition and hence for the bright deposit.

SEM and IR studies

The nature of crystal growth in the presence and absence of addition agents is explained with the help of SEM photomicrographs. SEM photomicrographs are shown in Figure 4.

In Figure 4A crystal growth is not uniform since the basic bath produced the deposit having different and slightly larger crystal size. In Figure 4B the crystal size of the deposit obtained from the bath containing gelatin is uniform when compared with the deposit obtained from the basic bath. In Figure 4C perfect crystal growth and uniform arrangement of the crystals was observed. The solution containing both gelatin and 3,4,5-trimethoxy benzaldehyde produced further refinement in crystal size and hence the deposit was bright (Figure 4D).

The IR spectrum of the scraped deposit obtained from the optimum bath was used to determine the inclusion of addition agent in the deposit. The absorption peak at 1670 cm^{-1} in the IR spectrum (Figure 5) corresponds to the absorption frequency of –C=O group of 3,4,5-trimethoxy benzaldehyde, which confirms the inclusion of brightener in the deposit during plating.
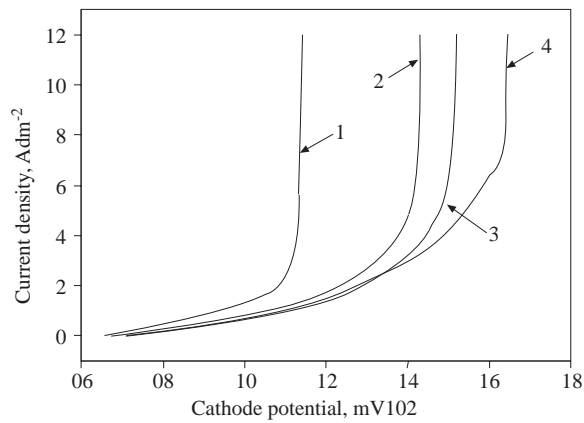
Figure 3. Effect of addition agents on cathode potential

    1) Basic bath (BB),
    2) BB + Gelatin
    3) BB + 3,4,5-Trimethoxy benzaldehyde
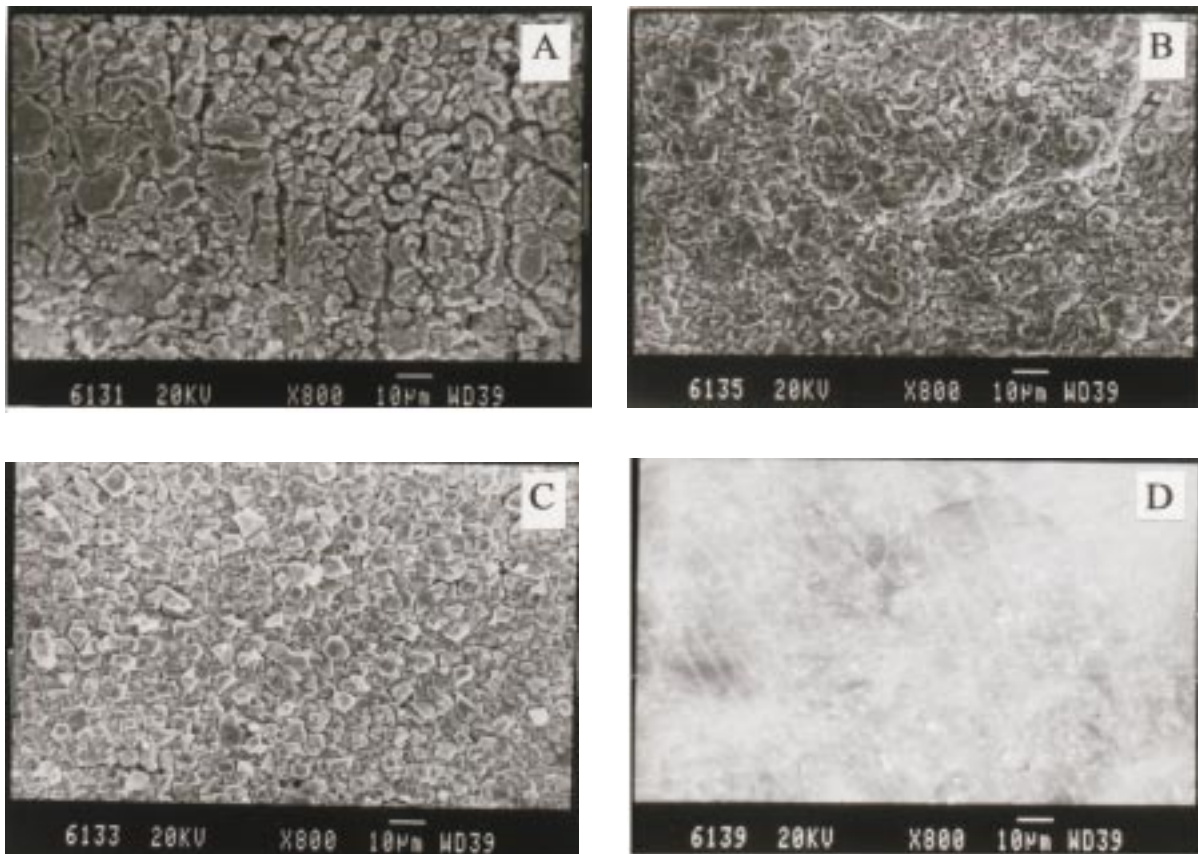   4) BB + EDTA + 3,4,5-Trimethoxy benzaldehyde

Figure 4. Effect of addition agents on morphology of deposit (SEM)

    A: Basic bath (BB), B: BB + Gelatin,
    C: BB + 3,4,5-Trimethoxy benzaldehyde,
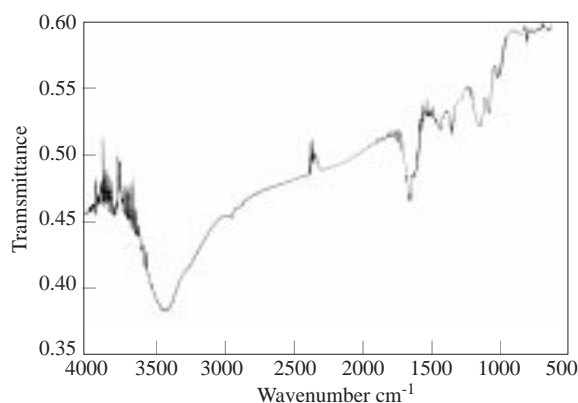   D: BB + Gelatin + 3,4,5-Trimethoxy benzaldehyde.

Figure 5. IR spectrum of the scratched deposit

Corrosion study

For a corrosion resistance study, the steel specimens were given a deposit of varying thickness (5 to 15 μm) from the optimum bath solution. After plating the specimens were subjected to a bright dip in 1% nitric acid followed by chromate passivation. The porosity of the deposit was tested with potassium ferricyanide paper. The paper soaked in 2% potassium ferricyanide paper was placed on the deposit for 5 min and no blue spots were observed. This test indicated a pore-free deposit. A further corrosion resistance test was carried out in a salt spray chamber. The deposited plates, after passivation, were subjected to a continuous spray of neutral 5% sodium chloride vapours. The deposit did not show any rust even after 96 hours of testing. This study indicated the good resistance of the deposit.

Adhesion and ductility

To test the ductility of the deposit, steel specimens of 10 cm length, 1 cm width and 1 mm thickness were plated separately at 1, 2, 3 and 4 Adm^{-2}. The total current was adjusted to get 10 μm thick deposit. All these specimens after bright dip and passivation were subjected to bending to 90^0 and finally through 180^0. No cracking or peel-off was observed even after 180^0 bending. This test revealed the good adhesion and ductility of the deposit.

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 determine 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 into the bath solution was recorded at the time when the bath started to give semibright deposit. The used bath solution was Hull cell tested by adding different amounts of TMB. The concentration of TMB was determined when a bright deposit was obtained. The amount of TMB consumed for 1000 Amps-hour was 0.4 g L^{-1}.

Conclusion

The available acid chloride baths which are in use in industries possess a narrow bright current density range[1-3], whereas the bath presented in this paper produces a bright deposit in the wide current density range of 0.5-8 Adm^{-2}. The bath contains only a single organic brightener and hence the operation and maintenance of the bath is easy. This is an advantage over other baths which contain many additives. The existing acid baths have poor throwing power whereas the developed bath possesses reasonably good throwing power (40%). In addition, the deposit is porous free and corrosion resistant as was indicated by corrosion tests of the deposit. The optimum bath composition and operating parameters are given in Table 4.

Table 4. Optimum bath composition and operating conditions

Bath composition	Range	Operating conditions
$ZnCl_2$, gL^{-1}	35	Anode: Zinc metal (99.9%)
NH_4Cl, gL^{-1}	200	Cathode: Mild steel
Gelatin, gL^{-1}	0.3	pH: 4.0
3,4,5-Trimethoxy		Temperature: 298-303 K
benzaldehyde, gL^{-1}	1.2	Bright current density
		Range: 0.5-8 Adm^{-2}
		Agitation: Air

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