Polynitroaniline as brightener for zinc–nickel alloy plating from non-cyanide sulphate bath

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Abstract. **Electro-polymerization of orthonitroaniline was carried out on graphite electrode in hydrochloric acid medium. Zinc–nickel alloy deposition was carried out in the presence of polynitroaniline in acid sulphate bath. The bath constituent and bath variables were optimized through Hull cell experiments. The current efficiency and throwing power were measured. High shift of potential towards more cathodic direction was observed in presence of addition agent. Corrosion resistance test revealed good protection of base metal by zinc–nickel coating obtained from the developed electrolyte. SEM photomicrograph shows fine-grained deposit in the presence of addition agent. The consumption of brightener in the lab-scale was 0.01 gL^{-1} for 1000 amp-h.**

Keywords. **Electrodeposition; electropolymerization; polynitroaniline; SEM studies; Zn–Ni alloy.**

1. Introduction

Electroplated zinc coatings are considered as one of the many ways of corrosion protection of steel. Recently, interest in Zn–Ni alloy coating has increased owing to its better mechanical and corrosion properties compared with pure zinc coatings (Shears 1989; Angelopoulos 2001; Brooks and Erb 2001; Muller *et al* 2002). The use of zinc and its alloys for improving the corrosion resistance of coated steel has been growing world wide (Sharples 1990; Alfantazi *et al* 1996; Vishalakshi Ravindran *et al* 2004) and as a substitute for toxic and high cost cadmium coating. In the automotive industry, for example, its use has been growing in search of increasing the corrosion resistance of chassis. The Zn–Ni alloy obtained by electrodeposition process with nickel varying between 8% and 14% by weight, give corrosion protection five to six times superior to that obtained with pure zinc deposits (Anicai *et al* 1992). The electrodeposition of Zn–Ni alloy is classified by Brenner (1963) as an anomalous co-deposition where zinc, the less noble metal, is preferentially deposited. There are some propositions to explain the anomalous co-deposition of Zn–Ni alloys. The first attributes the anomalous co-deposition to a local pH increase, which could induce zinc hydroxide precipitation and would inhibit nickel deposition (Higashi *et al* 1981; Fukushima *et al* 1988). It was, however, later that anomalous co-deposition occurred even at low current densities (Horans 1981), where hydrogen formation was unable to cause large alkalinization effects. Another proposition is based on the electrode potential deposition of zinc on nickel-rich zinc alloys or on nickel nuclei (Nicol and Philip 1976; Swathirajan 1986).

To get good bright deposit certain organic compounds are being used in the bath solution. Development of these brighteners for non-cyanide acid sulphate solution is continuously taking place even though few efficient commercial brighteners are available (Arthoba Naik *et al* 2001; Kariyanna *et al* 2003, 2004a, b; Abou-Krisha *et al* 2005; Kariyanna and Venkatesha 2005). It is evident from the available literature that the single addition agent generally does not produce good deposit over a wide current density range. In order to get good deposit, two or more addition agents are required (Abou-Krisha *et al* 2005). The presence of many addition agents poses problems in determining their consumption during plating. Also some of the addition agents cause pollution problem and health hazard (Arthoba Naik *et al* 2000; Arthoba Naik and Venkatesha 2003, 2005).

In the present work, efforts have been made to develop non-cyanide acid sulphate bath containing single brightener. Here, electrooxidative polymerization of orthonitroaniline was carried out on graphite electrode in 4M hydrochloric acid in a single compartment cell (Sachin *et al* 2005). Thus obtained polymer polynitroaniline (PNA) was subjected to Hull cell experiment. The polymer acts as a very good brightener and it is easily soluble in the bath solution.

2. Experimental

All the chemicals used were of LR grade and easily soluble in water. In the preparation of solutions, distilled water was used. The standard Hull cell of 267 mL capacity was used

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to optimize the bath constituents. The Hull cell experiments with the bath solution (table 1) were carried out without agitation. The pH of the solution was adjusted with 10% H_2SO_4 or sodium bicarbonate 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 and degreased by dipping in boiling trichloroethylene. The scales and dust on the steel plates were removed by dipping in 10% HCl solution and were subjected to electro-cleaning process. After this the steel plate was washed with water and used for the experiment as such. After the Hull cell experiment the plate was removed from the solution and subjected to bright dip in 1% nitric acid for 5–10 s followed by water wash. The nature and appearance of zinc plating was carefully studied and recorded through the Hull cell codes (figure 1).

All the experiments were conducted at 303 ± 1 K. The addition agent, PNA, was prepared by the electrochemical oxidation of orthonitroaniline. Graphite electrodes were used as anode and cathode. The electrolyte was 4 M HCl containing 0·04 M orthonitroaniline. The electrolysis was carried out at a current density of 1 A cm^{-2}. After the completion of the electrolysis, the formed polymer was separated from the reaction medium, recrystallized from acetone and used for electrodeposition study. The addition agent, PNA, was dissolved in 100 mL ethyl alcohol (0·2 g w/v), prior to experiments and a known amount of this solution was added to the electroplating bath solution. The bath solution was stirred for 30 min and then subjected to Hull cell experiments.

The deposits were obtained at a constant current density from the optimized solutions in a rectangular methacrylate cell of capacity 2·5 l. Polished, degreased and electrocleaned cathodes of 3×4 cm^2 were used. These plated steel cathodes were used to test the different properties and corrosion resistance of the deposit. Experiments were done in triplicate. Standard experimental procedures were adopted for the measurement of adherence, ductility, hardness etc. In all the above studies the average thickness of the deposit was 10 μm.

For corrosion resistance test, the coating with an average thickness was obtained on 3×4 cm^2 steel panels. Steel plates after deposition were given bright dip followed by passivation in a solution containing 200 gL^{-1} of sodium dichromate and 2 mLL^{-1} of sulphuric acid at 303 K for

Table 1. Basic bath composition and operating conditions.

Constituents	Conc. (gL^{-1})	Operating conditions
ZnSO$_4$·7H$_2$O	140	Anode: zinc metal (99·99%)
NiSO$_4$	2	Cathode: mild steel
H$_3$BO$_3$	10	Temperature: 298 K
Na$_2$SO$_4$	80	Cell current: 1 A

10 s. The chromated samples were dried for 24 h in a clean atmosphere before testing in a salt spray chamber in accordance with ASTM standard method B-117 using 5% neutral NaCl solution (308 K).

A three-compartment cell was used for the polarization studies. The area of zinc anode was 2 cm^2. The cathode was mild steel and the area exposed was 2 cm^2. The cathode potential was recorded, galvanostatically, with respect to saturated calomel electrode at different current densities. For current efficiency and throwing power measurement, the Haring and Blum cell was used. For throwing power measurement the current distribution ratio between anode and cathode was 1 : 5. For determining consumption of brightener, a rectangular cell of 2·5 l capacity was used. In all these experiments, pH of the solution before and after the experiments and the cell voltage at various operating conditions were recorded. SEM photomicrographs were taken to ascertain the nature of the deposit in presence of addition agent.
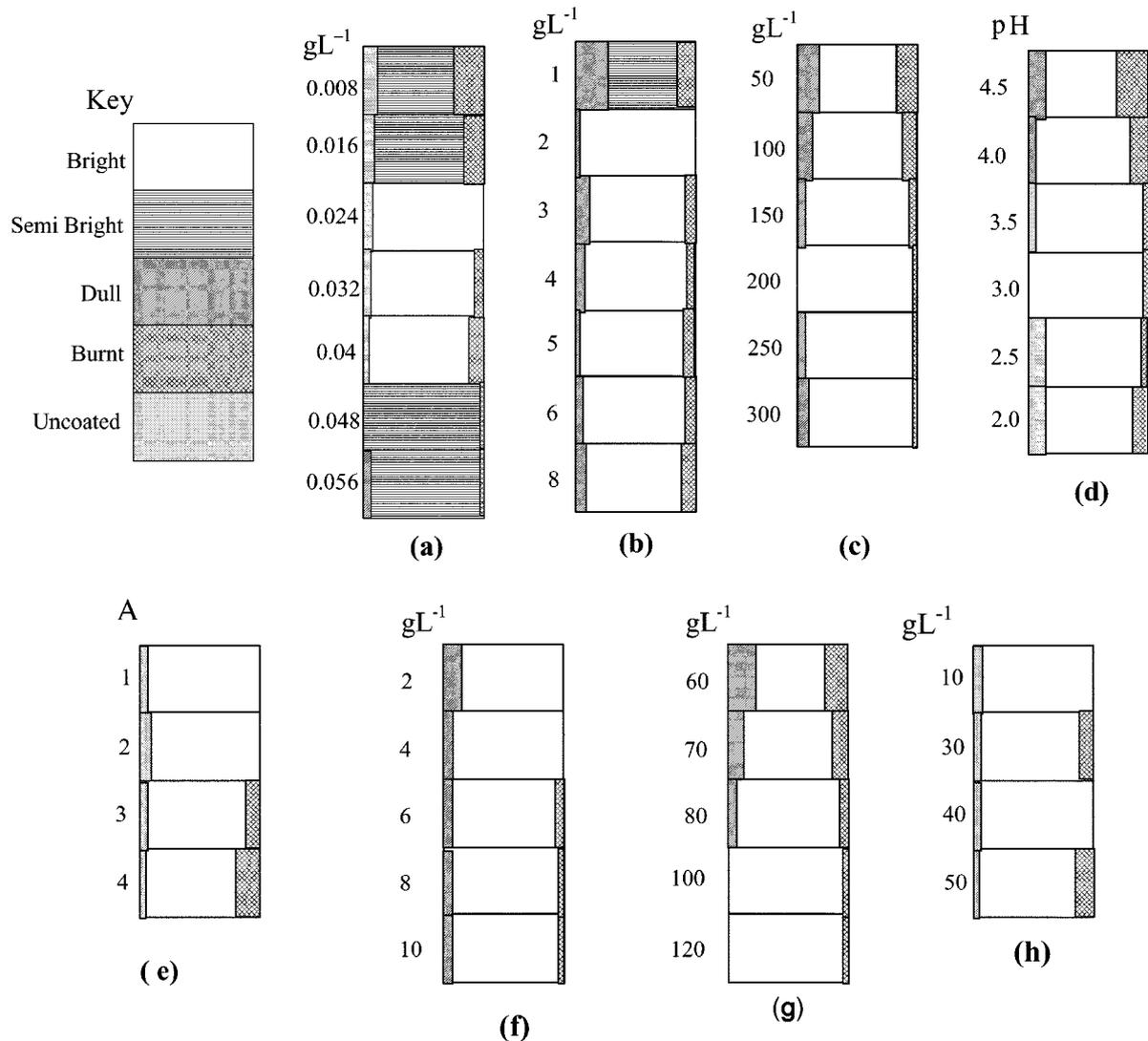
3. Results and discussion

3.1 *Hull cell studies*

3.1a *Effect of polynitroaniline*: Deposits obtained from Hull cell experiments with the basic bath solution containing zinc sulphate, sodium sulphate, CTAB and boric acid gave coarse dull deposit between the current density range of 0·5 and 3·5 Adm^{-2} at 1 A cell current. To improve the nature of the deposit, polynitroaniline (0·2 g w/v) was dissolved in 100 mL ethyl alcohol and a known volume of this solution was added to the bath. At low concentration of polynitroaniline the deposit was semibright between the current density range of 1 and 3 Adm^{-2}. At low current density, dull and at high current density, burnt deposits were obtained. With increase in the concentration of poly-nitroaniline, nature of deposit improved and at a concentration of 0·024 gL^{-1} the Hull cell panels were bright between the current density range of 0·5 and 3·5 Adm^{-2}. Further increase in the concentration of polynitroaniline up to 0·04 gL^{-1} does not affect the nature of the deposit, but above 0·04 gL^{-1} gave dull deposit in the high current density region. Based on the above observation, the concentration of the polynitroaniline was kept at 0·024 gL^{-1} as optimum. The Hull cell patterns are shown in figure 1a.

3.1b *Effect of CTAB*: The concentration of CTAB was varied from 2–8 gL^{-1}, keeping the concentration of zinc sulphate at 140 gL^{-1}, nickel sulphate at 4 gL^{-1}, sodium sulphate at 80 gL^{-1}, PNA at 0·024 gL^{-1} and boric acid at 10 gL^{-1}. At low concentration of CTAB, the nature of deposit was semibright in the current density range of 0·3–3·5 Adm^{-2}. Above 3·5 Adm^{-2} burnt deposit was observed. With increase in the concentration of CTAB from 1–8 gL^{-1}, burnt area was reduced and at a concentration of 2 gL^{-1},

Figure 1. Hull cell figures: (**a**) PNA, (**b**) CTAB, (**c**) $ZnSO_4 \cdot 7H_2O$, (**d**) pH, (**e**) current (A), (**f**) $NiSO_4 \cdot 7H_2O$, (**g**) Na_2SO_4 and (**h**) H_3BO_3.

bright deposit was obtained in the current density range of 0·4–3·5 Adm^{-2} and above this concentration no change in the nature of deposit was observed. Therefore, the concentration of CTAB was fixed at 2 gL^{-1} as optimum in the bath solution. The Hull cell patterns are shown in figure 1b.

3.1c *Effect of zinc sulphate*: To know the effect of zinc metal ion concentration, the zinc sulphate concentration was varied from 50 gL^{-1}–300 gL^{-1}, keeping the concentration of sodium sulphate at 80 gL^{-1}, boric acid at 10 gL^{-1} and CTAB at 2 gL^{-1}. At lower concentration of zinc sulphate, bright deposit was observed in the current density range between 1 and 3 Adm^{-2}. At low current density range (<1 Adm^{-2}), a thin deposit and above 3 Adm^{-2} burnt deposit was observed. It was noticed that the Hull cell patterns were almost free from burnt deposit when the concentration of

zinc sulphate reached 200 gL^{-1}. At still higher concentrations (>200 gL^{-1}), there was no change in the nature of deposit. Influence of the concentration of zinc sulphate on Hull cell patterns is shown in figure 1c. The concentration of zinc sulphate was fixed at 200 gL^{-1} as optimum.

3.1d *Effect of pH*: In order to study the effect of pH on nature of deposit, the pH of the bath solution was varied from 2–5. At low pH between 2 and 2·5, the Hull cell pattern showed burnt deposit at high current density region and uncoated area on low current density region. At pH 3, satisfactory results were obtained and the specimens were completely free from burnt and uncoated regions. With increase in pH above 4 the deposit became dull and cloudy. By these observations the pH of the solution was fixed at 3 in the bath solution. The effect of pH on the nature of deposit is shown in figure 1d.

3.1e *Effect of cell current:* The Hull cell experiments were carried out at different cell currents (1–3 A) for 5 min using optimized bath solution. It was found that at a cell current of 1A, the deposit was bright in the current density range 0·3–4 Adm^{-2}. At a cell current of 2A and 3A the bright current density area was reduced and the high current density region was covered with burnt deposit. From these observations it was found that the optimized bath produces bright deposition in the current density range of 0·3–4 Adm^{-2}. The Hull cell patterns are shown in figure 1e.

3.1f *Effect of nickel sulphate:* To find out the effect of nickel metal ion concentration, nickel sulphate was varied from 2–10 gL^{-1} by keeping the concentration of PNA at 0·024 gL^{-1}, zinc sulphate at 200 gL^{-1}, sodium sulphate at 100 gL^{-1}, boric acid at 40 gL^{-1} and CTAB at 2 gL^{-1}. At lower concentration of nickel sulphate (< 1 gL^{-1}), bright deposit was observed in the current density range between 1 and 3·5 Adm^{-2}. With increase in the concentration of nickel sulphate (up to 4 gL^{-1}), bright deposit was extended in the current density range of 0·5–4 Adm^{-2}, with further increase in the nickel sulphate concentration in the bath solution, a reduction in the bright current density range and increase in the uncoated and burnt area was observed. Based on the observation the concentration of nickel sulphate in the bath solution was fixed at 4 gL^{-1} as optimum. The effect of nickel sulphate concentration on nature of deposit is shown in figure 1f.

3.1g *Effect of sodium sulphate:* Sodium sulphate was added to increase the conductance of the bath solution. The concentration of sodium sulphate was varied from 80–100 gL^{-1} by keeping concentration of PNA at 0·024 gL^{-1}, zinc sulphate at 200 gL^{-1}, boric acid at 40 gL^{-1} and CTAB at 2 gL^{-1}. At lower concentration of sodium sulphate (< 80 gL^{-1}), the Hull cell panels showed burnt deposit at higher current density region and uncoated at low current density region. The burnt and uncoated regions were found to be reduced when the concentration of nickel sulphate was increased above 80 gL^{-1}, when the concentration of sodium sulphate reached 100 gL^{-1}, the deposit was bright over the current density region of 0·3–4 Adm^{-2}. Further increase of sodium sulphate concentration does not have any effect on the nature of the deposit. Based on the above observation the concentration of sodium sulphate was fixed at 100 gL^{-1} as optimum. The effect of sodium sulphate concentration on nature of deposit is shown in figure 1g.

3.1h *Effect of boric acid:* The aim of addition of boric acid to the electroplating bath was to control variation of H^{+} ion concentration in the bath solution. To see the optimum concentration of boric acid, the concentration was varied from 10–50 gL^{-1} by keeping the concentration of other addition agents at optimum concentrations. At lower concen-

tration of boric acid (< 10 gL^{-1}), the deposit was bright over the current density range between 0·5 and 3 Adm^{-2}. The bright area was extended between the current density range of 0·5 and 4 Adm^{-2} when the concentration of boric acid was 40 gL^{-1}. Higher concentration of boric acid will not cause any effect on the Hull cell pattern. So the concentration of boric acid was fixed at 40 gL^{-1}. The effect of boric acid on nature of deposit is shown in figure 1h.

3.2 Current efficiency and throwing power

Current efficiency and throwing power were measured at different current densities by using optimized bath solution. The current efficiency was measured by taking a rectangular methacrylate cell. At lower current density (1 Adm^{-2}), the current efficiency was found to be 93%. At a current density of 3 Adm^{-2}, the efficiency was increased to 94·6%. With increase in the current density above 4 Adm^{-2}, the current efficiency was found to be decreased and at 5 Adm^{-2} it was 87·2%.

Throwing power was measured by using Haring and Blum cell at different current densities. At lower current densities the throwing power was 21% and with increase in the current density it was increased to 22·4 (table 2).

3.3 Polarization study

The potential of steel cathode was measured galvanostatically with respect to saturated calomel electrode, at different current densities. Cathodic polarizations were measured using the bath solution with and without addition agents. The variation of cathode potential with current density is shown in figure 2. At any given current density, the cathode potential became more negative in presence of CTAB. This shift was still higher in presence of polynitroaniline. In many electroplating baths surfactants are being used as addition agents. These addition agents change the behaviour of cathode surfaces by adsorbing on the surface of the cathodes. The compound, CTAB, produces uniform deposit and thereby acts as a leveller.

PNA is a macromolecule, which contains the electroactive functional groups such as –C=N– and –NH groups. In the bath solution it forms complex with Zn and Ni metal ions and controls the rate of metal deposition. The deposition

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

Current density (Adm^{-2})	Current efficiency (%)	Throwing power (%)
1	93·0	21·0
2	93·8	21·6
3	94·6	22·4
4	92·0	22·0
5	87·2	21·6
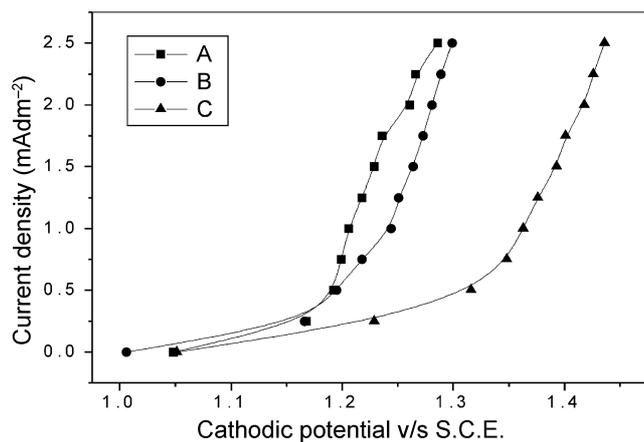
Figure 2. Effect of addition agents on cathodic potential (A = Basic bath (BB), B = BB + CTAB, C = BB + CTAB + PNA).

potential for metal ions in presence of PNA shifted to more (–) direction and leads to regular and uniform crystallization.

3.4 *Corrosion resistance*

Mild steel panels of 2×2 cm^2 area were polished, degreased and treated with 10% hydrochloric acid followed by water wash. These plates were plated with zinc–nickel alloy from optimum plating bath at different current densities. In presence of addition agents, the deposits were pore-free in nature above a thickness of 5 μm as indicated by ferroxyl test. In absence of addition agents, the coating was highly porous even at a thickness of 10 μm.

The corrosion resistance of zinc–nickel alloy plated steel plates were tested by salt spray method (ASTM B-117). Mild steel plates (5×5 cm^2) were coated with zinc–nickel alloy from the optimum bath solution. These plates were given bright dip in 1% nitric acid followed by chromate passivation. Before subjecting to the salt spray test, the plates were kept in a clean and dry atmosphere for 24 h. Even after 120 h of salt spray test no white rust was observed on the specimens. This indicated good corrosion resistance of the deposit.

3.5 *Metallurgical properties*

An important property of an electrodeposit is its adhesion to the base metal. Usually, zinc–nickel deposits on mild steel have very good adhesion. To measure adherence, the zinc deposits of 10–20 μm thickness were obtained under optimum conditions of plating bath on mild steel plates (1×10 cm^2). These plated specimens were subjected to bend test through 90° and finally through 180°. Even after 180° bending no

crack or peel off was observed in the deposit. This reveals good adhesion of zinc deposit to the substrate. The more useful method for measuring microhardness involves making an indentation with an indenter of specified geometry under a specified load. The length of indentation is expressed in Vickers hardness number (VHN). Zinc–nickel alloy was electroplated on mild steel panels up to a thickness of 20 μm and a load of 50 g was employed. The microhardness of zinc–nickel alloy was found to be 130.

3.6 *SEM studies*

SEM photomicrographs of zinc–nickel alloy deposit obtained from basic bath solution with and without addition agents are shown in figure 3. These indicate that the basic bath produced only coarse-grained deposits. The grain size was refined further in presence of addition agents. Fine-grained smooth deposit was obtained from the bath solution containing an optimum concentration of all the addition agents.

3.7 *Consumption of brightener*

To know the amount of addition agents consumed in the 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 a time when the bath just started to give semibright deposit. The bath solution after use was subjected to Hull cell test by adding different amounts of polynitroaniline. The concentration of polymer, at which once again bright deposit was obtained, was determined. The amount of polynitroaniline consumed for 1000 amps-h was 0·01 gL^{-1}.

3.8 *Pilot plant study*

The commercial applicability of the developed bath was explored by performing the plating experiments in a vat bath of 25 L capacity. The bath solution with optimum concentration of bath constituents was prepared. Steel components of different sizes and shapes (plates, rods, nuts, bolts, small pipes, clamps, etc) were degreased, electrocleaned and given acid dip followed by water wash. These treated components were rigged by copper wire and connected to the negative terminal of d.c. source. Electroplating was carried out at different current densities with and without agitation of the bath solution. The components after deposition were removed from the plating vat and subjected to bright dip and passivation. The passivated articles were subjected to corrosion resistance test in a salt spray chamber. Adhesion of the deposit to the substrate was good as it was confirmed by bend test and hear test methods. The components of irregular shapes plated under stirred and unstirred conditions showed no rust at the recesses
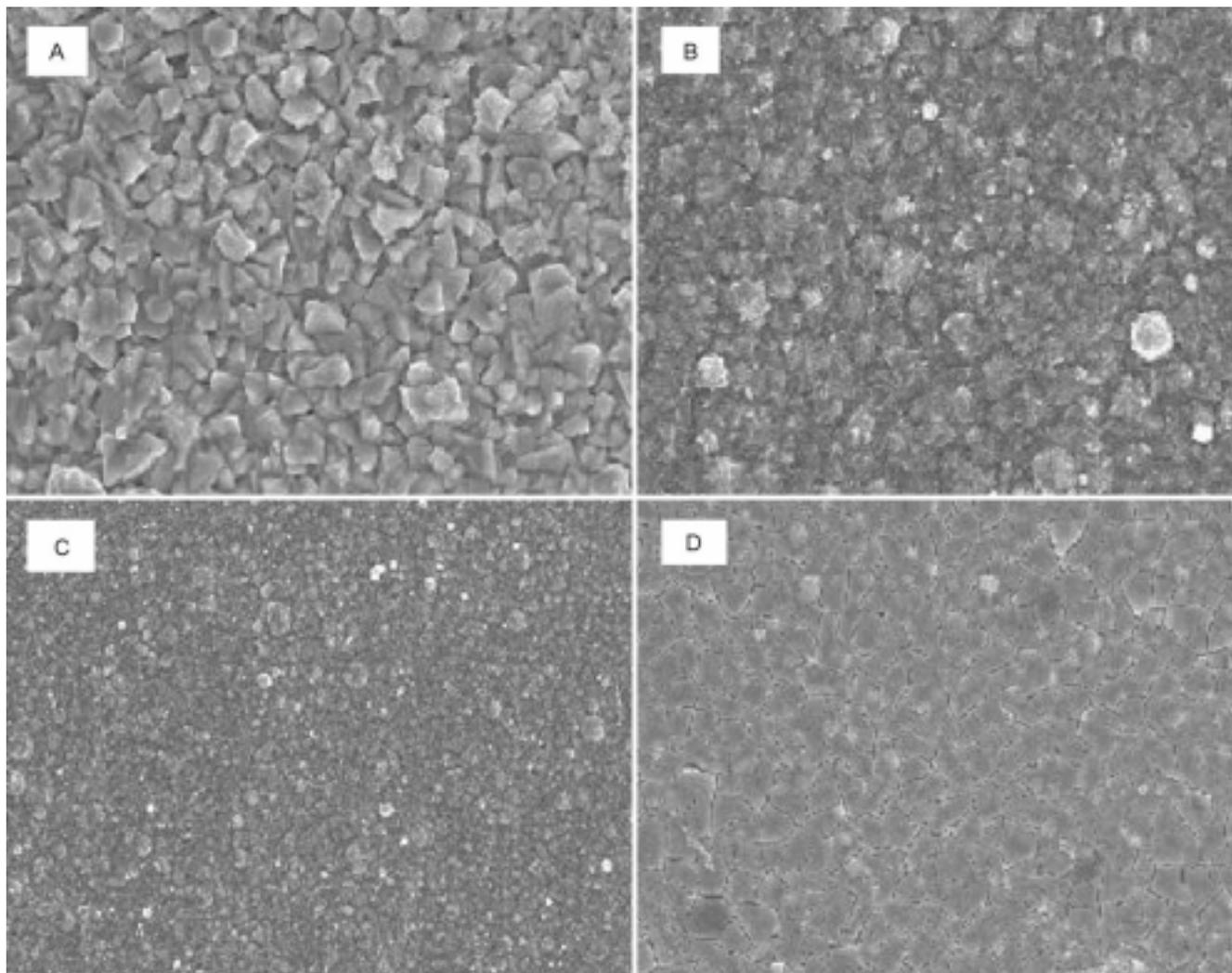
Figure 3. SEM photomicrographs obtained at a current density of 3·5 Adm^{-2}: **A**. Basic bath (BB), **B**. BB + CTAB, **C**. BB + CTAB + PNA and **D**. passivated deposit.

Table 3. Optimum bath composition and conditions.

Bath constituents	Range	Operating conditions
ZnSO$_4$·7H$_2$O (gL^{-1})	200	Anode: zinc metal (99·99%)
NiSO$_4$·7H$_2$O (gL^{-1})	4	Cathode: mild steel
PNA (gL^{-1})	0·024	Temperature: 293–303 K
Na$_2$SO$_4$ (gL^{-1})	100	Bright current density range: 0·5–4 Adm^{-2}
H$_3$BO$_3$ (gL^{-1})	40	Agitation: air
CTAB (gL^{-1})	2	

even after 98 h of salt spray test. This indicated the ability of the bath to produce uniform deposit on the components of irregular shape.

4. Conclusions

The developed bath produces good deposit over the current density range of 0·4–3·5 A dm^{-2}. The optimized bath composition is shown in table 3. The throwing power is reasonably good. The brightener can be easily synthe-sized. The addition agents are non-toxic, easily soluble in water and hence require no treatment of the effluent. The deposit is pore-free and corrosion resistant. The bath could be easily commercialized.

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