

## Electrodeposition and compositional behaviour of Zn-Ni alloy

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This paper discusses the optimization of an electroplating bath for smooth and uniform deposition of zinc-nickel alloy on mild steel. Electroplating has been carried out in a chloride bath using glycine and gelatin as additives. The effect of bath conditions and operating parameters on chemical composition, micro-hardness and appearance of the deposit have been studied and discussed. The experimental results reveal that a bright Zn-Ni alloy having about 13.6 %Ni is showing good performance against corrosion. The corrosion resistance of the deposit is found to be characteristic of its %Ni content, and is improved drastically after chrome passivation. The bath follows anomalous codeposition with preferential deposition of Zn over the entire current density range used for the study. The increase of %Ni in the deposit with current density is due to the depletion of more readily depositable  $Zn^{2+}$  ions at the cathode. No transition current density, at which the codeposition behaviour changed from the anomalous to normal type, was observed during the study. The increase of %Ni in the deposit at high current density (c.d.) is attributed to high ratio of  $Ni^{2+}/Zn^{2+}$  in the bath. The effect of temperature on the plating process showed that codeposition of metals on the cathode is diffusion controlled.

**Keywords:** Zn-Ni alloy, Chloride bath, Glycine, Gelatin

**IPC Code (s):** C25D3/56

Zinc-nickel alloys show better corrosion resistance than pure zinc. The deposit with 12-15% Ni content ensures improved protection against red rust corrosion even when heat treated and meets automotive industry specifications. In order to enhance the corrosion resistance of zinc coating, it is alloyed with metals of the iron group (such as nickel, iron and cobalt)<sup>1,2</sup>. Amongst the zinc alloys, zinc-nickel alloys with different nickel content have been most successful<sup>3,4</sup>. Chromate conversion coating of Zn-Ni electrodeposit enhances its corrosion resistance<sup>5-8</sup>. Although, the zinc-nickel alloy electrodeposits are mainly used as coating to improve the corrosion resistance of automobile steel bodies<sup>9</sup>, these coatings have been considered for several other applications such as electrocatalytic water electrolysis<sup>10</sup> and in the electronic industries<sup>11,12</sup>. This alloy is also considered as a viable alternate to cadmium for plating aircraft and commercial steel parts<sup>13</sup>.

The corrosion resistance of Zn-Ni alloy depends particularly on the percentage of nickel in the deposit. Gomez *et al.*<sup>14</sup> found that the presence of particular additives in the electrodeposition bath improved the surface homogeneity, which leads to better corrosion resistance, even for an alloy with low Ni content.

Generally, Zn-Ni alloys are less active than pure zinc, have a lower corrosion velocity and offer less galvanic protection to the steel. The preferential dissolution of zinc at the start of corrosion offers good galvanic protection. However, this leads to Ni enrichment of the alloy, which rises corrosion potential towards nobler values offering less cathodic protection to the steel<sup>15</sup>. The composite coating on Zn-Ni alloy gives improved corrosion resistance by forming a passive film which acts as a protective barrier<sup>16,17</sup>. The aim of this work is to optimize a stable electroplating bath for smooth and uniform Zn-Ni alloy over steel and study its compositional behavior towards corrosion. It also envisages the effect operating parameters like current density, temperature and pH of the bath on the composition of the deposit.

### Experimental Procedure

The composition and operating parameters of the bath has been optimized using standard Hull cell using 1 amp cell current<sup>18</sup>. Polished mild steel cathode panels of standard size and pure zinc anode were used for Hull cell study. The solutions were prepared in distilled water using laboratory grade chemicals. A

PVC cell of 500 mL in capacity was used for electroplating with cathode-anode space of about 5 cm. The steel panels having an exposed area of 4 cm<sup>2</sup> were used as cathodes for regular study of deposits. The bath temperature was kept at 298 K, except while to investigate the influence of temperature. Electrodeposition was carried out galvanostatically for required thickness.

The cathode was mechanically polished with progressively finer grade of emery paper and, prior to deposition, was washed by alkali cleaning. Before immersion the cathode was neutralized in a 10% HCl solution. After deposition, alloy films were washed with distilled water, dried with hot air and weighed. The composition of each alloy was determined by colorimetric method<sup>19</sup>. The micrographs of the deposits were examined by scanning electron microscope (SEM), (Model JEOL, JSM-6380 LA). The presence of Ni in the deposit was confirmed by EDAX. Micro-hardness of alloy deposits (25 μm) was measured by Vickers method using micro Hardness Meter (Wickers Model 3212). The cathode current efficiency of deposition was determined by knowing the mass and composition of the deposit<sup>20</sup>. The corrosion behavior of the electrodeposits was studied using Metrohm Electrochemical Workstation (Model PGSTAT 30). The corrosion rates were determined directly from corrosion current without the need for Tafel slope values or use of the Stearn-Geary equation. Polarization curves have been studied at a scan rate of 5 mV/s, in a potential ramp of ± 250 mV from open circuit potential (OCP). The corrosion behaviors of electrodeposited Zn-Ni alloys were studied under conditions of with and without passivation. The compositions of the basic bath for Zn-Ni alloy plating and chrome passivation are as given in Tables 1 and 2.

## Results and Discussion

The deposits with grayish white/bright/black powdery and semi-bright appearance are obtained over the wide c.d. of 1.0-5.0 amp/dm<sup>2</sup>. The effect of bath constituents on Hull cell patterns are shown in the Figs 2-6. Hull cell code is as given in Fig. 1.

### Effect of zinc chloride

Figure 2 presents the Hull cell patterns obtained at various concentration of zinc chloride. At lower concentration of ZnCl<sub>2</sub>, a bright deposit was observed only at small region of high c.d. Increase of ZnCl<sub>2</sub>

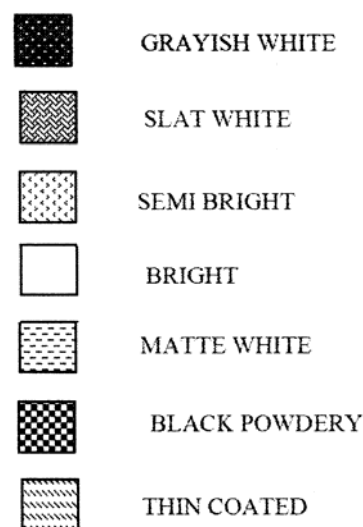


Fig. 1—Hull cell code

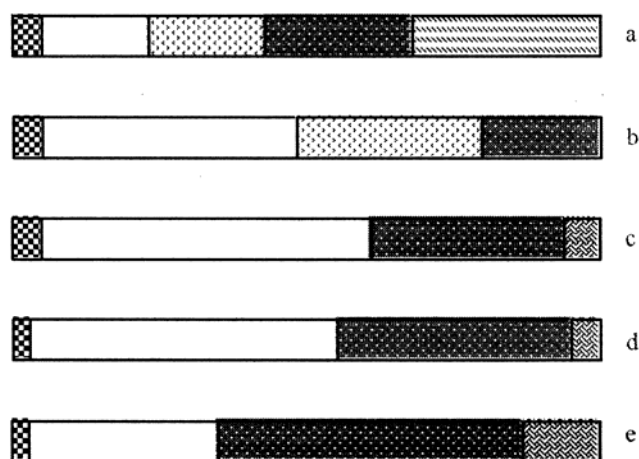


Fig. 2—Effect of zinc chloride on Zn-Ni alloy plating bath at 303 K, at 1A cell current for duration of 5 min (a) 20 g/L, (b) 40 g/L, (c) 60 g/L, (d) 80 g/L, (e) 100 g/L.

Table 1—Composition and operating parameters for electrodeposition of Zn-Ni alloy

Bath composition	Molar conc.	Operating parameters
Zinc chloride	0.30	pH: 4
Nickel chloride	0.20	Temperature: 298 K
Ammonium chloride	1.50	Anode: Pure zinc
Potassium chloride	0.40	Current density: 1-5 Amp/dm <sup>2</sup>
Glycine	0.06	
Gelatin	2 g/L	

Table 2—Composition and conditions of yellow chromating bath

Variables	Amount
Sodium dichromate	160 g/L
Sodium sulphate	50 g/L
Sodium nitrate	50 g/L
Nitric acid	4 ml/L
Temperature	298K
Immersion time	25-50 s
pH	1-2

increased the bright region uniformly up to 60 g/L. But further increase of  $ZnCl_2$  decreased the bright region as shown in the Fig. 2d and 2e. Hence 60 g/L of  $ZnCl_2$  is fixed as its optimized concentration.

#### Effect of nickel chloride

Figure 3 shows the effect of nickel chloride on Hull cell panels. At 20 g/L of  $NiCl_2$ , black deposit of high %Ni was observed at low c.d. side. This is likely due to normal codeposition of alloy with preferential deposition of Ni. The increase of  $NiCl_2$  increased the brightness of the deposit uniformly up to 90 g/L with reduced black region as shown in Fig. 3b-3d. Hence, 90 g/L of  $NiCl_2$  is fixed as optimum concentration.

#### Effect of ammonium chloride and potassium chloride

To increase the conductivity of the bath, KCl and  $NH_4Cl$  were used in combination. Concentration of KCl was varied from 10 to 130 g/L. The appearance of deposit has improved only up to 70 g/L and further addition of KCl was found to show adverse effect. Hence, concentration of KCl is maintained at 70 g/L through out the study. But addition of  $NH_4Cl$  brought

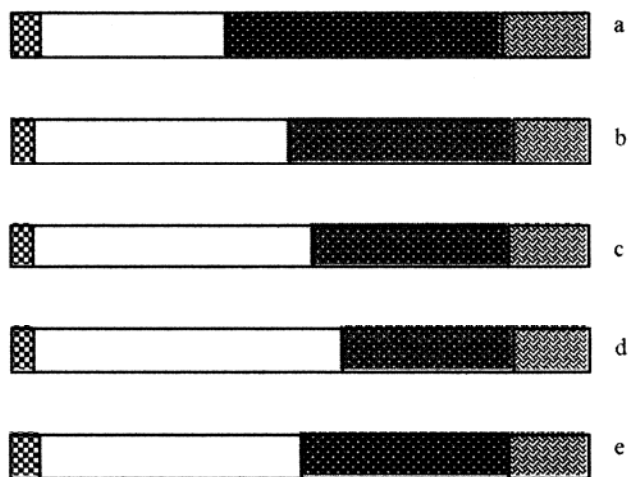


Fig. 3—Effect of nickel chloride on Zn-Ni alloy plating bath at 303 K, at 1A cell current for duration of 5 min (a) 20 g/L, (b) 50 g/L, (c) 70 g/L, (d) 90 g/L, (e) 110 g/L.

significant change in the appearance of the deposit more likely due to availability of metal ions in the complex form. A smooth deposit was found over a wide range at 110 g/L as shown in Fig. 4e. It was also observed that the operating Hull cell voltage has decreased with increase of salt concentrations in the bath.

#### Effect of glycine

The effect of glycine on the Hull cell panels are given in the Fig. 5. With 1 g/L glycine, the deposit is bright only at the region about 4 Amp/dm<sup>2</sup>. The addition of 11g/L glycine showed very bright deposition over wide range of 1-5 A/dm<sup>2</sup> as shown in

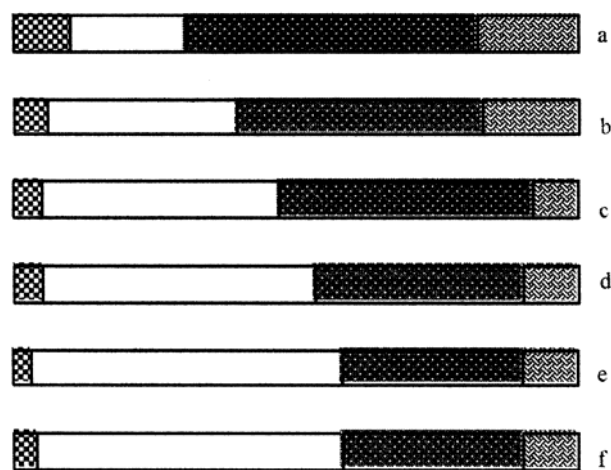


Fig. 4—Effect of ammonium chloride on Zn-Ni alloy plating bath at 303 K, at 1A cell current for duration of 5 min (a) no ammonium chloride, (b) 20 g/L, (c) 50 g/L, (d) 80 g/L, (e) 110 g/L, (f) 140 g/L.

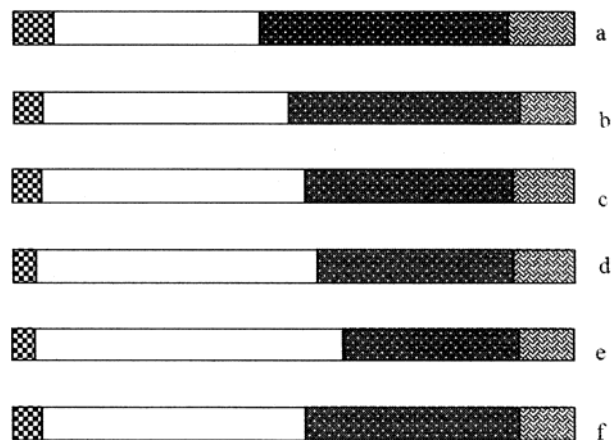


Fig. 5—Effect of glycine on Zn-Ni alloy plating bath at 303 K, at 1A cell current for duration of 5 min (a) without glycine, (b) 2 g/L, (c) 5 g/L, (d) 8 g/L, (e) 11 g/L, (f) 14 g/L.

Fig. 5e. Further increase of glycine has not altered the deposition characters considerably as shown in Fig. 5f.

#### Effect of gelatin

The effect of gelatin on Hull cell patterns are shown in the Fig. 6. In absence of gelatin a grayish white zinc rich alloy was obtained at high c.d. side (Fig. 6a). The effect of gelatin was tested at 1.0, 2.0, 5.0, 8.0 and 10.0 g/L. At 2.0 g/L of gelatin a bright deposit was observed at high c.d. side. Further addition of gelatin increased the bright region and reached the maximum between 1-5 Amp/dm<sup>2</sup> at 5.0 g/L. The concentration of 8.0 and 10.0 g/L was found to show no much improvement on the brightness (Fig. 6e and 6f).

#### Effect of current density

The c.d. has crucial role on the nature and composition of the Zn-Ni deposit as shown in Table 3 and Fig. 7. The bath produces a grayish white deposit with less %Ni at low c.d. side and produces a bright deposit at high c.d. At very high c.d. the deposit becomes brittle, flaky and porous with increased thickness. Figure 7 shows that the %Ni in the deposit increases with c.d. This increase of %Ni with c.d. unusual to anomalous codeposition (preferential deposition of less noble zinc) is due to depletion of more readily depositable zinc at cathode. In the present study, the ratio Ni<sup>+2</sup>/Zn<sup>+2</sup> in the bath being high, the %Ni in the deposit tends to be more with c.d. The cathode current efficiencies of the bath remain almost same over the entire current density as shown in Table 3. The hardness of the deposit is not appreciably changed though there is a slight increase with increase of %Ni content.

#### Effect of pH

Generally, in zinc-Fe group metal (Ni, Co and Fe) alloy deposition the pH has little effect on deposition from the baths containing simple metallic ions<sup>20</sup>. The

change of Zn-Ni alloy composition with pH (Table 3) is due to complexing of zinc ions with additives. The preferential deposition of zinc in Zn-Fe group metal alloy is explained through adsorbed Zn(OH)<sub>2</sub> film at cathode (due to local decrease of pH by evolution of

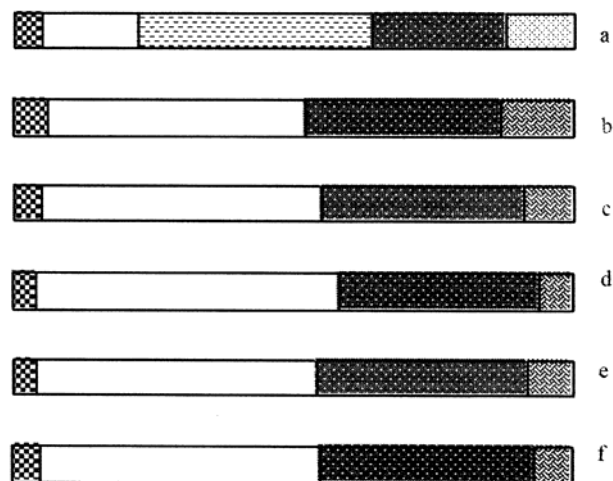


Fig. 6—Effect of gelatin on Zn-Ni alloy plating bath at 303 K, at 1A cell current for duration of 5 min (a) without gelatin, (b) 1 g/L, (c) 2 g/L, (d) 5 g/L, (e) 8 g/L, (f) 10 g/L.

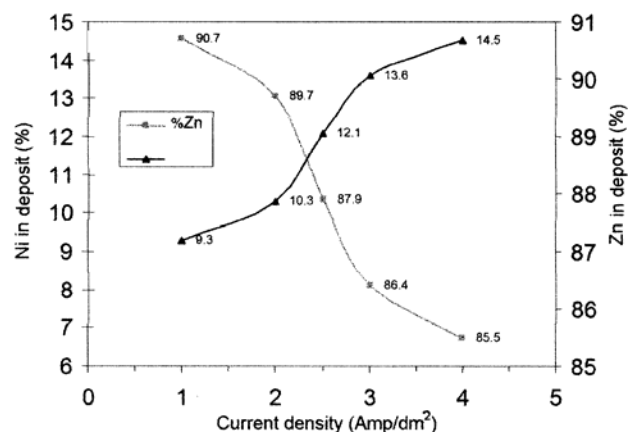


Fig. 7—Effect of current density on %Ni and %Zn content of the alloy deposits during deposition from optimized bath at 298 K and pH 4.

Table 3—Effect of c.d. and pH on deposition characteristics of Zn-Ni alloy deposit at 298 K

c. d.(A/dm <sup>2</sup> )	pH of bath	(%)Ni in deposit	Vickers hardness V <sub>200</sub>	cathode current efficiency (CCE)	Appearance of the deposit
1.0	4.0	9.3	85.6	92.4	Grayish white
2.0	4.0	10.3	80.8	91.8	Semi bright
2.5	4.0	12.1	103.6	90.8	Bright
3.0	4.0	13.6	107.6	90.3	Bright
4.0	4.0	14.5	108.8	89.4	Bright
3.0	3.0	12.5	-	84.0	Bright and brittle
3.0	5.0	14.2	-	88.0	Bright and flaky

hydrogen) which inhibit the deposition of more noble nickel<sup>14</sup>. However, in the present experimental conditions, the increase of %Ni in the deposit with pH indicates that the metal ions are in complex form, and it is not sufficient enough to inhibit the deposition of more noble nickel.

#### Effect of temperature

Bath temperature also has prominent role on the composition and appearance of the Zn-Ni deposit as exhibited by other Zn-Fe group metal alloys. The %Ni in the deposit increases with temperature (Table. 4). This is due to the fact that an increase in temperature favors the deposition of that metal which was preferentially deposited, because it speeded up the diffusion and thus relieved the depletion of metal at the cathode<sup>20</sup>. As the system follows anomalous codeposition, the zinc (less noble) being deposits preferentially, an elevation of temperature has increased the content of the zinc as depicted in the Fig. 8.

#### Corrosion studies

The corrosion behavior of electroplated specimens was studied in aerated 5% NaCl solution and Tafel plots are shown in Fig. 9. The value of  $E_{\text{corr}}$  and  $I_{\text{corr}}$  for Zn-Ni alloys obtained under different conditions are given in Table 5. A linear relationship was observed between the %Ni in the deposit and its corrosion resistance till 3 Amp/dm<sup>2</sup>. The results show

Table 4—Effect of temperature on %Ni content of the deposit of Zn-Ni alloy deposit at 3 Amp/dm<sup>2</sup> and pH 4

Temp. (K)	(%)Ni in deposit	Appearance of deposit
288	2.98	308
318	3.23	14.8
13.6	11.8	10.4
9.8	Silver white	Bright
Bright	Grayish white	Grayish white

Table 5— $I_{\text{corr}}$  value of Zn-Ni alloy electroplates on mild steel in aerated 5% NaCl obtained at pH 4 and temperature 298 K

Plating c.d. (A. dm <sup>-2</sup> )	(%) Ni	pH of bath	without passivation		with passivation	
			$E_{\text{corr}}$ (-mV)	$I_{\text{corr}}$ ( $\mu\text{A.cm}^{-2}$ )	$E_{\text{corr}}$ (-mV)	$I_{\text{corr}}$ ( $\mu\text{A.cm}^{-2}$ )
1	9.3	4.0	1044	35.35	1118	18.36
2	10.3	4.0	1075	32.08	1110	15.86
2.5	12.1	4.0	1077	26.95	1130	12.53
3	13.6	4.0	1052	20.20	1094	10.45
4	14.5	4.0	1076	22.39	1124	12.30

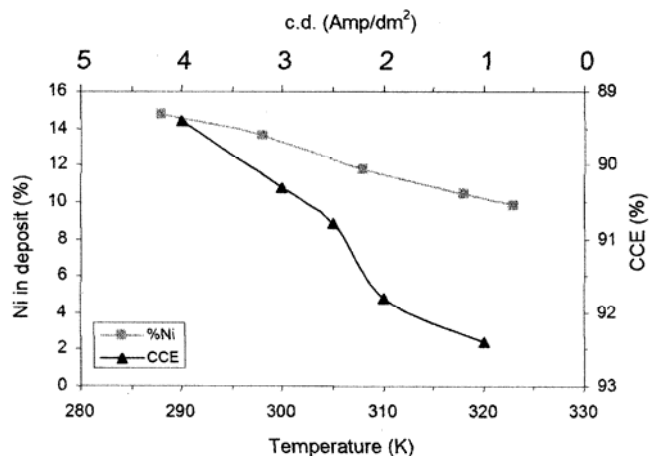


Fig. 8—Effect of temperature on %Ni content of the alloy (at 3 Amp/dm<sup>2</sup> and pH 4) and current density on cathode current efficiency (CCE) during deposition from optimized bath at 298 K and pH 4.

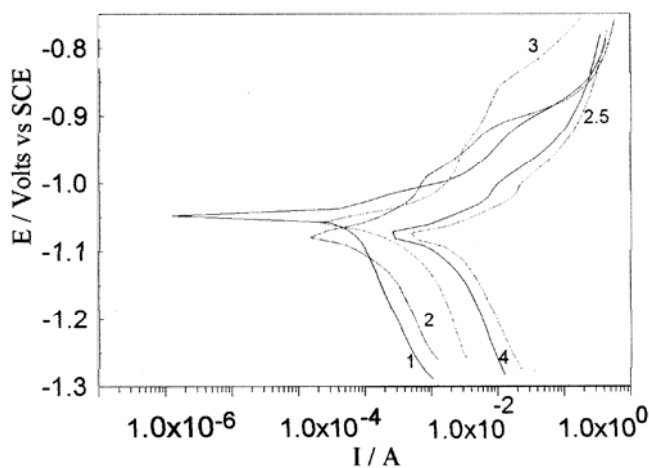


Fig. 9—Tafel plots for Zn-Ni alloy deposits obtained at different current densities as specified on the curves from the optimized bath 298 K and pH without passivation (at scan rate of 5 mV/s in a potential ramp of  $\pm 250$  mV from OCP).

that Zn-Ni alloy with about 13.6% Ni at about 3 Amp/dm<sup>2</sup> is highest corrosion resistant with least  $I_{\text{corr}}$  value. The superior corrosion resistance of Zn-Ni alloy coatings could be explained by the barrier protection mechanism theory. During corrosion, zinc dissolves preferentially, leaving a top layer enriched with nickel. This layer acts as a barrier to further attack.

The corrosion behavior of Zn-Ni alloy electroplates after chrome passivation is shown in Fig. 10. It was observed that chrome passivation has decreased  $I_{\text{corr}}$  considerably and has brought the  $E_{\text{corr}}$  value of all deposits almost together indicating that chromatinization has improved corrosion resistance of all deposits irrespective of c.d. at which they are plated. However, chromate treatment brought the  $I_{\text{corr}}$  of Zn-Ni alloy having 13.6% Ni to the minimum as shown in Table 5. The presence of Ni in the lattice structure of Zn-Ni alloy deposit was confirmed by the EDAX as shown in Fig. 11.

#### Surface study

SEM micrograph of the deposit revealed that c.d. plays a significant role in the phase structure of the deposit. The variation in the surface morphology of Zn-Ni alloy with c.d. is depicted in Fig. 12. A dull deposit was found at 1 Amp/dm<sup>2</sup> and it has become brittle and porous towards high c.d. Zn-Ni alloy deposit obtained at 3 Amp/dm<sup>2</sup> and pH 4 was found to be very smooth and uniform and shows peak performance against corrosion. The deposit was very dull and grayish white at low pH, bright at pH 4 and at very high pH, %Ni in the deposit increased along with increased roughness and porosity (Table 3).

On the basis of investigations made, the electroplating bath of Table 6 has been proposed for smooth and uniform Zn-Ni alloy electroplates having about 13.6% nickel showing good corrosion resistance.

Table 6—Composition of the optimized bath for smooth and uniform deposition of Zn-Ni alloy over mild steel

Bath composition	Amount (g/L)	Operating parameters
Zinc chloride	60	pH: 4
Nickel chloride	90	Temperature: 298 K
NH <sub>4</sub> Cl	110	Anode: Pure zinc
KCl	70	Current density: 3.0 Amp/dm <sup>2</sup>
Glycine	11	Agitation: Air
Gelatin	5	

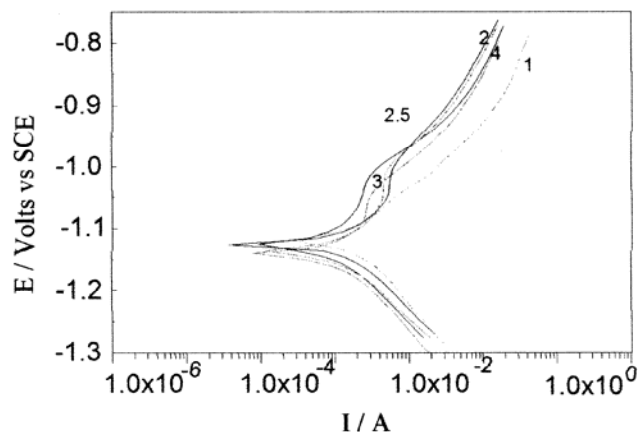


Fig. 10—Tafel plots for Zn-Ni alloy deposits obtained at different current densities as specified on the curves from the optimized bath 298 K and pH after chrome passivation (at scan rate of 5 mV/s in a potential ramp of  $\pm 250$  mV from OCP).

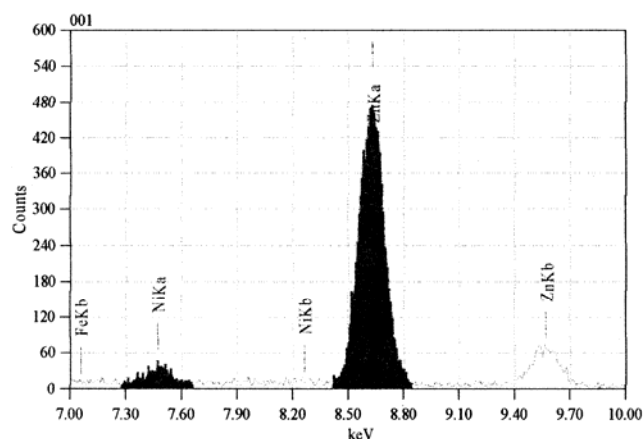


Fig. 11—EDAX of Zn-Ni alloy deposits obtained from optimized bath 298 K and pH 4.

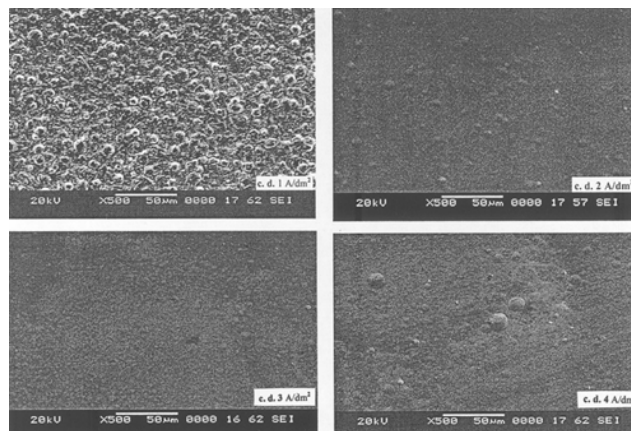


Fig. 12—SEM micrographs (500 magnification) of Zn-Ni alloy deposit obtained at current densities of 1.0 A/dm<sup>2</sup>, 2.0 A/dm<sup>2</sup>, 3.0 A/dm<sup>2</sup> and 4.0 A/dm<sup>2</sup> (all at pH 4).

### Conclusions

The electroplating of Zn-Ni alloys from the bath solutions under investigation, exhibits the phenomenon of anomalous codeposition. No transition current density, at which the codeposition behaviour changed from the anomalous to normal type, was observed during the study. The increase of %Ni in the deposit at high current density is attributed to high ratio of  $\text{Ni}^{+2}/\text{Zn}^{+2}$  in the bath. The effect of temperature on the plating process showed that the codeposition of metals is diffusion controlled. Electroplates having about 13.6%Ni was found to be very smooth and uniform showing good performance against corrosion. But they are dull and irregular at low %Ni in the deposit. The use of the additives has played a significant role in improving surface homogeneity and grain size. From the corrosion study, it may be concluded that not only does corrosion resistance depend on the %Ni in the deposits, but also it depends on their morphology. The hardness of the deposit is not appreciably improved though there is an increase with %Ni content of the alloy. Chromate conversion treatment of zinc-nickel electroplates improved the corrosion resistance of the coating up to about 2 times. Among the chromated specimens, chromated Zn-Ni alloy having about 13.6 wt.% of Ni has the highest corrosion resistance. On the basis of investigations made a stable chloride bath has been

proposed for smooth and uniform Zn-Ni alloy deposition over mild steel substrate.

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