Technical Article

Electrodeposition of Zinc From an Alkaline Non-cyanide Bath: Influence of a Quaternary Aliphatic Polyamine

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The effect of a guaternary aliphatic polyamine (QAA) on zinc electrodeposition in an alkaline non-cyanide medium was investigated using voltammetry and chronoamperometry. Addition of QAA to the zinc solution led to a decrease in the exchange current density (i₀), suggesting that QAA inhibits the zinc reduction process. This was confirmed through a study of the initial stages of crystal growth using atomic force microscopy (AFM), which revealed that the crystals grew with a multilayer structure. Such a structure is characteristic of crystals grown in the presence of an organic compound that acts as an inhibitor. X-ray diffraction analysis of the zinc coatings showed that the presence of QAA in the solution favored the growth of crystals with a (101) orientation. Coatings grown in solutions containing QAA had a smaller grain size than crystals grown in QAA-free solutions. As a result, coatings were compact and shiny. Zinc coatings grown in the presence of QAA displayed



Fig. 1—Typical voltammograms obtained from a base solution of 0.25M ZnO + 4.0M NaOH, with QAA concentrations of a) 0.0, b) 5.0 and c) 10 mL/L. AISI 1018 steel electrode, v = 30 mV/sec. Inset: Variation of the current density of the cathodic peak (i_{e}) with varying scan velocity for the electrodeposition of zinc from base solutions with different additive concentrations. (•) 0.0, (\blacktriangle) 5.0, (\bigstar) 10 mL/L.

Nuts & Bolts: What This Paper Means to You

No plating process can work unless there is adequate cleaning and rinsing. At the same time, these operations generate wastewater, spent solutions and sludge, and as a result, use too much water, energy and chemicals (\$\$\$). This paper covers a mathematical means of providing the most effective cleaning and rinsing with the least production of waste and consumption of resources. While the math may be daunting to some, there is likely an engineer in many organizations who could put this information to good use. lower corrosion rates compared to those grown in the absence of QAA. This effect was attributed to a change in overall crystal morphology (i.e., multilayer growth, change of crystal orientation and decrease in grain size) due to the presence of QAA in solution.

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 basis 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.1 However, the critical pretreatment 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, noncyanide zinc baths have been introduced in place of cyanide solutions since the 1960s.² Low toxicity, simple waste treatment, low make-up costs, good plate distribution and use of steel tanks have been a few practical advantages in choosing an alkaline non-cyanide zinc baths for plating.

In general, zinc is electrodeposited from electrolytic baths containing conducting salts, buffers and additives. Of these components, the additives are of fundamental importance because they enable the production of coatings with particular physical characteristics (e.g., corrosion resistance and adhesion) and chemical characteristics (e.g., composition). The effects of the additives are complex and variable. Generally, additives modify the deposition overpotential and may also modify the nucleation kinetics and the growth of the crystal.³⁻⁵ Mirckova, et al.⁶ have shown that the use of anisaldehyde bisulfite and Na-N-benzylnicotinate as brighteners during zinc electrodeposition in alkaline media affects the evolution of hydrogen and the distribution of this gas in the coating. In addition, diverse organic compounds, including gelatin, sodium citrate, triethanolamine and fluorosurfactants, have been used as additives to obtain fine-grained zinc deposits from zinc alkaline baths.7-8 Other additives such as caffeine, vanillin and glycerol increase the electrochemical efficiency and the throwing power of the bath.9-13 In studies of the effect of aminated additives on the electrodeposition of Zn-Ni alloys in alkaline media, Müller,

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Table 1

Cathodic Peak (E_{cp}), Cross-over Potential (E_{co}), & Overpotential (η) Values, Associated with Zinc Electroreduction on AISI 1018 Steel from a Base Solution with Different Additive Concentrations

Additive (mL/L)	$E_{_{CP}}(V_{_{Hg/HgO}})$	$E_{CO}^{}\left(V_{_{Hg/HgO}}^{}\right)$	(V)
0.0	-1.460	-1.402	-0.058
0.1	-1.462	-1.403	-0.059
5.0	-1.510	-1.410	-0.100
10.0	-1.520	-1.408	-0.112

*et al.*¹⁴ observed that the presence of amines in the bath enabled the production of alloy coatings with constant nickel composition.

In spite of the fact that aminated compounds have been widely used as additives for years, it is known that small changes in their structure produce considerably different results. The reasons are not yet well understood. The objective of the present work was to study the influence of an additive containing a quaternary aliphatic polyamine on the mechanism of zinc electrodeposition and on the morphology of zinc coatings from an alkaline non-cyanide bath, using AISI 1018 steel as the substrate. The electrochemical study was carried out using voltammetry and chronoamperometry. Deposit morphologies were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Experimental Procedure

The additive used in the present work contained a quaternary aliphatic polyamine (QAA) of the form $[-CH_2-CHOH-CH_2-N^+(CH^3)^{-2}]_n$. prepared by condensing diethanolamine with epichorohydrin. Zinc was electrolytically deposited from a base solution containing 0.25M ZnCl₂ and 4.0M NaOH. Different concentrations of QAA additive: 0.0, 1.0, 5.0 and 10.0 mL/L, were utilized. All reagents were of analytic grade and the corresponding solutions were prepared in deionized water (18 MΩ/cm).

The electrochemical study was performed in a conventional three-electrode cell with a water jacket. The working electrode was a disc of AISI 1018 steel of geometrical area 0.07 cm² (0.011 in²) enclosed in Teflon. A Hg/HgO electrode was used as the reference electrode and platinum mesh was used as the counter electrode. Prior to each experiment, the working electrode was polished to a mirror finish with 0.05- μ m alumina. All experiments were carried out under an ultrapure nitrogen atmosphere. The electrochemical experiments were carried out using a potentiostat/galvanostat^{**} coupled to a personal computer, equipped with software for data acquisition and experimental control. The AFM analysis was performed using an atomic force microscope^{***} in contact mode. Deposit morphology was evaluated using a scanning electron microscope ^{****}. The crystallographic orientation was determined using an x-ray diffractometer[†].

Results & Discussion

Voltammetric study

According to the Pourbaix diagram,¹⁵ two reactions are possible when a steel electrode is cathodically polarized in alkaline zinc solutions. The first reaction is the evolution of hydrogen as shown below:



Fig. 2—Typical voltammograms obtained from a base solution (0.25M ZnO + 4.0M NaOH), showing the switching potential (E_{λ}) and the cross-over potential (E_{co}). $E_{\lambda 1} = -1.422$, $E_{\lambda 2} = -1.418$, $E_{\lambda 3} = -1.412$, $E_{\lambda 4} = -1.403 V_{He/HeO}$.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$

$$(E' = -0.95 V_{H_{0}/H_{0}O}; pOH^{-} = -0.6).$$

The second reaction is the electrolytic deposition of zinc, mainly due to zincate ions $Zn(OH)_4^{-2.16}$ Although the reaction mechanism of zinc deposition is still a matter of discussion,^{17.18} it now seems accepted that the overall reaction is:

$$Zn(OH)_{4}^{-2} + 2e^{-} \rightarrow Zn(0) + 4OH^{-}$$
⁽²⁾

The conditional potential associated with this reaction depends on the concentrations of Zn and OH^{-} in the solution and is given by the following equation:

$$E'Zn(OH)_{4}^{-2}/Zn(0) = 0.34 - 0.03pZn' - 0.12*(14 - pOH') V_{Hg/HgO}$$
(3)

where pZn' = -log [Zn']_{total} and pOH' = -log[OH']_{total}. For the working conditions (pZn' = 0.6, pOH' = -0.6), E'Zn(OH)₄⁻²/Zn(0) = -1.43 V_{Hg/HgO}. The conditional electrode potential indicates that, thermodynamically speaking, hydrogen discharge should appear in preference to zinc.

In order to investigate the effect of the QAA additive on zinc electrodeposition in alkaline media, an electrochemical study was carried out at each of the additive concentrations considered: 0.0, 1.0, 5.0 and 10.0 mL/L. The voltammetric study was carried out the potential range 0.0 to $-1.6 V_{Hg/HgO}$. The potential scan was started in the cathodic direction from the rest potential. Figure 1 shows typical voltammograms obtained in the absence and presence of QAA. In the absence of QAA, during the cathodic scan, only a peak (I) associated with the reduction of Zn(II) to Zn(0) was observed. This peak appears at $E_{cp} = -1.460 V_{Hg/HgO}$. At more cathodic potentials, hydrogen evolution occurred. In the presence of QAA, the cathodic peak potential (E_{CP}) was displaced toward more negative potentials as the additive concentration was increased. Furthermore, the cathodic peak current density (ic) was practically independent of the additive concentration. The linear relation observed between i_{cp} and the square root of the scan rate $(v^{1/2})$ indicated that the reduction process was controlled by mass transfer at all of the additive concentrations considered (Inset Fig.1). The experimental behavior observed on the cathodic potential scan, is not in agreement with thermodynamic predictions. It may be explained if it is considered that in alkaline media, underpotential deposition of zinc on steel was present.¹⁹ For that reason, the overpotential required for hydrogen evolution on zinc was higher (about -0.7 V) compared to that for steel.

On inverting the direction of the potential scan toward anodic

^{**} Model 273A Potentiostat/Galvanostat, Ametek - Princeton Applied Research, Oak Ridge, TN.

^{***} Model Nanoscope E, Veeco Instruments (Digital Instruments), Woodbury NY. **** Model DSM-5400 LV, JEOL USA, Inc., Peabody, MA.

[†] Model X'PERT PRO, Royal Philips Electronics N.V., Eindhoven, the Netherlands. [‡] System XUVM, Fischer Technology, Windsor, CT.

Table 2

Variation of the Charge Transfer Coefficient (α_c) & Exchange Current Density (i_d) During the Reduction of Zinc in a Base Solution with Different Concentrations of the Additive QAA

Additive (mL/L)	с	i_0 (mA/cm ²)
0.0	0.43	45.70
0.1	0.38	13.50
5.0	0.38	8.15
10.0	0.38	6.78

potentials, an oxidation peak (I_a), that corresponds to the oxidation of the reduced species formed during the cathodic scan, was observed. In addition, a cross-over between the cathodic and anodic scans was also observed. Such behavior is characteristic of processes that involve the formation of a new phase.²⁰ The potential at which the cross-over occurs, which is known as the cross-over potential (E_{co}), can be used to identify the mechanism of the metal reduction process.^{20,21} At all additive concentrations, the shape of the voltammograms and location of E_{co} were similar.

The behavior of the crossover potential (E_{co}) was studied by fixing the switching potential (E) at the foot of the reduction peak. From the data obtained, it was found that the crossover potential (E_{co}) was independent of E , as can be seen in Fig. 2. In these cases, E_{co} values should correspond to the conditional potential (E') of the redox couple.²⁰

Table 1 shows the E_{∞} average values obtained from solutions containing QAA. In this work a value of -1.403 V_{Hg/HgO} was obtained for E_{∞} in the absence and presence of QAA, which agrees well with the



Fig. 4—Tafel lines for base solutions containing different additive concentrations. (\triangle) 0.0, (\bigcirc) 1.0, (\square) 5.0, (\times) 10 mL/L QAA.

Parameters for Corrosion in a Solution of 3.5 wt% NaCl of Zinc Coatings Obtained from Solutions with Different Additive Concentrations

Coating	i_{corr} (μ A/cm ²)	$E_{\rm corr}^{}(V_{\rm Hg/HgO}^{})$	CR (mm/yr)
1	89.00	-1.01	2.67
2	85.11	-1.05	2.56
3	79.43	-1.03	2.39
4	56.23	-1.05	1.69

one calculated from the equation (1) for the couple $Zn(OH)_{4}^{-2}/Zn(0)$ [E'Zn(OH)₄⁻²/Zn(0) = -1.43 V_{Hg/Hg0}] within experimental error. It is possible to conclude that the reduction reaction involved the majority Zn(OH)₄⁻² species, indicating that the zinc reduction proceeded via reaction 2, as has been suggested by Cain, *et al.*¹⁶ From this, it can be concluded that the additive QAA did not form complexes with Zn(II) under the working conditions and that its effect was mainly at the electrode surface. This fact shows the usefulness of this technique in order to calculate the conditional potential of the couple metallic ion/deposited metal.

Table 1 also shows the values of the zinc reduction overpotential ($E_{CP}-E_{CO}$) observed at different additive concentrations. The magnitude of the overpotential increased with increasing additive concentration. This suggests that the additive acted at the interface, creating a barrier in the proximity of the electrode surface that had a blocking effect on electrodeposition. Therefore, additional energy was required to discharge the zinc ions.

Rotating Disc Electrode (RDE) Studies

Rotating disc electrode (RDE) linear voltammetry was used to characterize the effect of the QAA additive on the kinetics parameters of the zinc electrodeposition process. Before commencing the RDE study, the AISI 1018 steel electrode was covered with a layer of zinc deposited at $-1.50 \text{ V}_{\text{Hg/HgO}}$ for 20 sec, and an electrode rotation rate of 2000 rpm.

Figure 3 shows a typical family of current-potential curves obtained at different additive concentrations. At anodic potentials, before the reduction wave, the curves show a region that corresponds to charge transfer. At more cathodic potentials, a region of mixed current was observed in which both charge transfer and mass transfer contributed to the total current density. At even more cathodic potentials, a plateau was observed, indicating that in this potential range the reduction process was limited by mass transfer. Finally, the potential region in which the hydrogen evolution reaction occurred was observed. In addition, as the QAA concentration in the solution was increased, the current-potential curves were displaced to more negative potentials.

Charge transfer data can be used in the characterization of the kinetics of the zinc deposition reaction. Tafel plots showed a small charge transfer region, generally restricted to an overpotential range of -40 to -100 mV (Fig. 4). At more negative potentials the charge transfer region was followed by one of mixed control where components of both charge transfer and mass transport contributed to the overall current. However, a purely charge transfer controlled current density, i_{CT} , can be calculated from the total current density, i, via the expression.

$$\frac{1}{i} = \frac{1}{i_{CT}} + \frac{1}{i_{\lim}}$$
(4)

where i_{lim} is the mass transport controlled limiting current den-

sity, as measured from the plateau region of the current-potential curves. Having determined i_{CT} , the kinetics parameters - exchange current density (i_0) and mass transfer coefficient (α_c) - can be calculated using the Tafel equation:

$$\log|i_{CT}| = \log i_0 - \frac{\alpha_c nF}{2.3RT} \eta$$
(5)

where η is the overpotential [$\eta = \text{E-E'Zn}(\text{OH})_4^{-2}/\text{Zn}(0)$]. Figure 4 shows plots of log i_{CT} vs η , which were linear at all of the additive concentrations considered here. The values of i_0 and α_c obtained from these plots are listed in Table 2. The Tafel slope for the additive-free solution was 61.7 mV, which corresponds to a charge transfer coefficient of 0.43. As the additive concentration was increased, α_c decreased slightly. Given that, as shown above, the presence of the additive did not modify the electrochemical reaction involved in the reduction process, the decrease in α_c with increasing additive concentrations can be attributed to variations in the morphological characteristics of the deposits as a function of the deposition conditions. Furthermore, the value of i_0 decreased when the QAA concentration increased. The lower the exchange current density, the more sluggish were the kinetics.

Chronoamperometric Study

The chronoamperometric study of the zinc reduction process was carried out at each of the additive concentrations considered. Figure 5 shows a family of transients obtained under potentiostatic conditions (E = -1.53 V_{Hg/HgO}) in solutions with different additive concentrations. The transients have the form characteristic of diffusion-controlled nucleation processes in three dimensions (3D).²² In the first region of the transients, the current density increased until it reached a maximum (i_{max}). This behavior corresponds to an increase in the electroactive area and to the stabilization and growth of new nuclei. Subsequently, a drop in current density was observed, characteristic of processes controlled by mass transfer. The value of i_{max} decreased with increasing additive concentration. This result is associated with an increase in the discharge overpotential of the Zn ions caused by the adsorption of QAA on the electrode surface.

In order to analyze the initial stages of the zinc electrodeposition process in greater detail, AFM was used in the contact mode. AFM images of the deposits formed under potentiostatic conditions (-1.53 $V_{Hg/HgO}$) at t = 0.3 sec were recorded.

When the deposits were obtained from an additive-free solution, the deposit comprised hexagonal crystals of diverse size (Fig. 6a). The crystals were irregularly distributed over the electrode surface, and had a certain degree of perpendicular orientation with respect to the surface.



The deposits at time t = 0.3 sec formed from a solution containing QAA were characterized by oriented growth of crystals of different sizes (Fig. 6b). In addition, the formation of multilayered structures was observed in the initial stages of growth (inset of Fig. 6b), an effect characteristic of organic compounds that act as inhibitors of crystal growth.²³

Characterization of the Coatings

A scanning electron microscopy (SEM) study was carried out to further characterize the effect of QAA on the morphologies of the zinc deposits, obtained potentiostatically (E = -1.53 V_{Hg/Hg0}) in solutions containing different concentrations of QAA (0.0, 1.0, 5.0 and 10.0 mL/L). In all cases, the deposit thickness was 5 μ m (197 μ -in) measured by x-ray fluorescence. The SEM images of the deposits formed in the absence of QAA show hexagonal crystals (typical of pure zinc coatings) of similar size and different orientations (Fig. 7a), with uncoated zones between the crystals. XRD analysis (Fig. 7b) of this deposit showed that the crystals grew in two crystallographic orientations, (002) and (101), predominating the first one. These characteristics caused the zinc deposit to be of dark appearance, non-sticky and porous.

In contrast to the bi-orientational crystal structure formed in the absence of QAA, the zinc crystals formed in the presence of QAA grew in a multilayer form following a single preferred orientation (Fig. 8a). XRD analysis (Fig. 8b) of this coating shows that the deposits formed in the presence of QAA grew mainly in a (101) orientation, with considerably less growth of crystals in a (002) orientation compared to the additive-free system. The deposits formed in the presence of QAA were compact, soft and shiny. The observed behavior was associated with the inhibiting effect of the additive during the initial stages of crystal growth, which was established in the AFM analysis, discussed previously.



Fig. 6—AFM images recorded at t = 0.3 sec, during the reduction of zinc from a base solution containing different concentrations of the additive: a) 0.0, b) 5.0 mL/L.



Fig. 7–a) SEM micrograph and b) X-ray diffraction (XRD) pattern of a zinc coating electrodeposited under potentiostatic conditions ($E = -1.5 V_{Hg/HgO}$) from an additive-free base solution. Thickness, 5.0 µm (~0.2 mil).



Fig. 8–a) SEM micrograph and b) X-ray diffraction (XRD) pattern of a zinc coating electrodeposited under potentiostatic conditions ($E = -1.53 V_{Hg/HgO}$) from a base solution containing 5.0 mL/L QAA. Thickness 5.0 μ m (~0.2 mil).

Corrosion Tests

In order to determine the influence of QAA on the corrosion resistance of the zinc coatings, corrosions tests were carried out using the technique of electrochemical polarization. For this test, coatings were potentiostatically (E = -1.55 V_{Hg/HgO}) grown on AISI 1018 steel. Additive concentrations were: 0.0 mL/L (coating 1), 1.0 mL/L (coating 2), 5.0 mL/ L (coating 3) and 10.0 mL/L (coating 4). All coatings were 5 μ m (197 μ -in) in thickness, as measured by x-ray fluorescence.

The corrosion resistance was evaluated by immersing the coating in a corrosive environment, specifically, a 3.5 wt% solution of NaCl. Prior to each experiment the solution was saturated with oxygen by bubbling the solution with ultrapure oxygen for 1 hr. The corrosion rate was determined according to ASTM G5 and G109 standards²⁴ for the electrochemical corrosion evaluation. The potential scan (v = 0.166 mV/sec) commenced at a potential 300 mV more cathodic than the corrosion potential (E_{corr}) and was scanned in an anodic direction until a current of 5 mA was



Fig. 9–Tafel polarization curves for zinc electrodeposited onto AISI 1018 steel at different concentrations of the additive QAA: a) 0.0, b) 5.0 and c) 10 mL/L.

observed. Figure 9 shows the typical behavior of the resulting Tafel curves. An anodic peak in the potential range -1.00 to -0.80 V_{Hg/HgO} was observed. This peak was associated with the formation of a passive film of zinc oxide. At more anodic potentials, between -0.80 and -0.45 V_{Hg/HgO}, a passive region was observed, originating from the passivating effect of the oxide film. Dissolution of the steel was subsequently observed at E = -0.45 V_{Hg/HgO}.

Table 3 shows the results of the evaluation of the corrosion parameters of the coatings. The corrosion rate decreased with increasing concentration of QAA in the solution from which the deposit was grown. The corrosion resistances observed at different additive concentrations were attributed to differences in structure and grain size of the zinc deposits formed at each additive concentration.

Conclusions

The mechanism of zinc electrodeposition in the studied medium was shown to occur via the reduction of zincate ions $(Zn(OH)_4^{-2})$. This mechanism was not modified upon the addition of QAA additive to the solution because it did not form complexes with the zinc ion under the conditions studied. The QAA additive mainly acted at the electrode surface, causing an increase in the overpotential of zinc reduction. Increasing the QAA concentration in the solution led to a decrease in the exchange current density (i_0) , suggesting that QAA acted as an inhibitor of the reduction process.

Atomic force microscopy (AFM) analysis of the crystals during the initial stages of growth showed that the QAA additive promoted the growth of crystals with a multilayered structure, which was characteristic of crystals grown in the presence of additives known as inhibitors. In addition, a change in crystallographic orientation was observed during crystal growth. In the absence of the additive, the zinc crystals grew in two preferred orientations, (002) and (101). Under those conditions, the coatings obtained were of dark appearance, dendritic and non-sticky. When the coatings were grown in solutions containing QAA additive, however, the crystals grew mainly in a (101) orientation and the coatings were compact and shiny. Coatings grown in the presence of QAA displayed lower corrosion rates than those grown in the absence of the additive. This behavior was attributed to the change in morphology and reduction in grain size with increasing additive concentration.

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