

## EFFECTS OF NUMBER OF SUBSTITUENTS AND MOLECULAR WEIGHT OF POLYAMINES ON THE NON-CYANIDE ALKALINE ZINC PLATING PROCESS<sup>#</sup>

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**Abstract.** The effects of the number of substituents and molecular weight of polyamines in the non-cyanide alkaline plating bath on cathodic polarization, cyclic voltammogram, morphology, brightness and bright ranges of zinc electrodeposited coating were investigated. Cathode polarization measurements showed that the polyamines all increased cathode polarization of the plating process. In addition, cyclic polarization curves of the 5 cycles also showed that adsorption and desorption of these polyamines were stable in the plating process. The Hull method pointed out that these polyamines created semi-bright ranges in the low current density. Moreover, the polyamine Bt-700 had the strongest effects on the brightness of the deposits at almost whole range of current density if its concentrations was sufficient. Surface morphology also showed that adding these polyamines made the crystals of deposits fine, smooth and uniform which agreed with increasing cathodic polarization.

**Keywords:** Polyquaternium-7, Polyethyleneimine, non-cyanide alkaline zinc plating, zinc deposit.

**Classification numbers:** 2.5.3.

### 1. INTRODUCTION

On the world, the non-cyanide alkaline zinc plating solution which was commercialized very early in the 1960s [1] has recently become a commonly used plating bath. In Viet Nam, the bath is used more widely due to some outstanding advantages such as: low zinc content, low toxicity, good quality of deposits, easy passivation, and good throwing power. Especially, because of simple waste treatment, the non-cyanide alkaline bath is environmentally friendly, which is a matter of great concern at present. However, the non-cyanide alkaline bath without additives will provide poor quality coatings that cannot be used in industry [2 - 5]. So, the use of additives in the non-cyanide alkaline bath may solve this problem.

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In 1979, Zehnder *et al.* [6] used polyamine sulfone in a range of 0.1 to 100 g/L, in combination with a few g/L of pyridine or nicotine to improve the quality of the zinc coating. Some polyamines were used as additives for non-cyanide alkaline bath by Ortiz-Aparicio *et al.* [2] and Shanmugasigamani *et al.* [3]. In Viet Nam, nowadays, additive systems for the non-cyanide alkaline bath used in the industries are all imported, and no published documents of the additives have been found. In our previous research, we have investigated the effects of molecular weight of polyamines on the non-cyanide alkaline zinc plating process [7]. The results showed that molecular weight of polyamines had strong effects on the non-cyanide alkaline zinc plating process in which the heavier molecular weight, the stronger effects. However, not only the molecular weight of polyamines but also the molecular structure of polyamines has effects on the plating process, especially the number of substituents on nitrogen. In this paper we present the effects of the number of substituents and molecular weight of polyamines on the non-cyanide alkaline zinc plating process, in order to improve some properties of the plating process.

## 2. MATERIALS AND METHODS

### 2.1. Materials

The non-cyanide alkaline zinc plating solution contains major constituents: 140 g/L NaOH, 15 g/L ZnO (base solution) and polyamines with various content. All of chemicals were used at pure grade and dissolved by deionized water. The polyamines added in the plating bath include polyethyleneimines with a molecular weight of 1800 u (Bt18) and 70.000 u (Bt700) and polyquaterniums-7 with the molecular weight of 2000 u (Q7-20) and 70.000 u (Q7-700). The molecular structures of the polyamines are showed in Fig. 1 and Fig. 2.

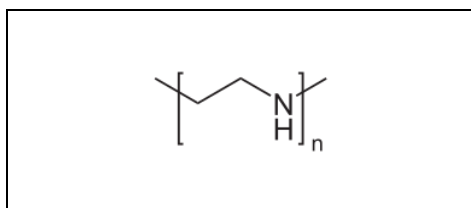


Figure 1. Polyethyleneimine.

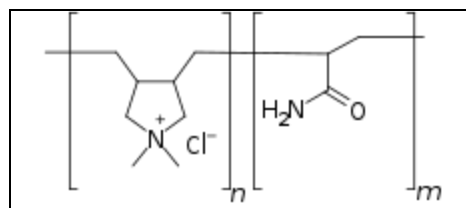


Figure 2. Polyquaternium-7.

### 2.2. Sample preparation

Low carbon steel plates with different dimensions (100 × 60 × 1.2 mm for Hull cell test, 50 × 50 × 1.2 mm for SEM characterization, and Ø10 mm for polarization test) were grinded by abrasive paper of 600 grit SiC, and then degreased by immersion in a solution of 60 g/L UDYPREP-110EC (Enthone) at 50 - 60 °C for 5 - 10 min. After that the samples were immersed in solution containing HCl (10 % v/v) and urotropine (3.5 g/L) at ambient temperature for 2 - 5 min. In the zinc plating process, all samples were electrodeposited by using a rectifier.

### 2.3. Methods of analysis

Effects of polyamines on the bright and semi-bright range of the zinc deposits were determined by Hull cell test method. The brightness of the zinc deposits was determined by Progloss 3, model 503 (Germany) according the ISO 2813 standard. The cathodic polarization and cyclic voltammogram curves were examined by using Autolab PGSTAT 30 connected with

3 electrodes including: reference electrode Ag/AgCl, counter electrode platinum, and working electrode as steel with area of 0.785 cm<sup>2</sup>, with scan rate of 2 mV/s in plating solutions. SEM images were taken by scanning electron microscope JEOL-JSM-6510LV.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effects of the number of substituents and molecular weight of polyamines on cathodic polarization

In theory of electroplating, all the factors that increase the cathodic polarization result in fine crystals. The cathodic polarization curves show the effect of additives on the reduction of metal ions. The results presented in Fig. 3 and Fig. 4 are polarization curves at a scan rate of 2 mV/s in the solutions containing additives with various molecular weights and number of substituents and the base solution. In Fig. 3, adding Q7-20 or Bt18 with concentration of 0.5 g/L to non-cyanide alkaline zinc plating solution increases cathodic polarization compared to polarization measurements in base solution. Bt18, a secondary polyamine, has effects on cathodic polarization stronger than Q7-20, a quaternary polyamine. Similarly, in Fig. 4, adding Bt18 or Bt700 with concentration of 0.5 g/L to base solution also increases cathodic polarization compared to that in base solution. Bt18 with light molecular weight has effects on cathodic polarization stronger than Bt700 with heavy molecular weight. In all cases, the polarization curves are characterized by the appearance of the cathodic peak (I) in the potential range of -1.5 to -1.55 V, when scanning towards the more negative potential.

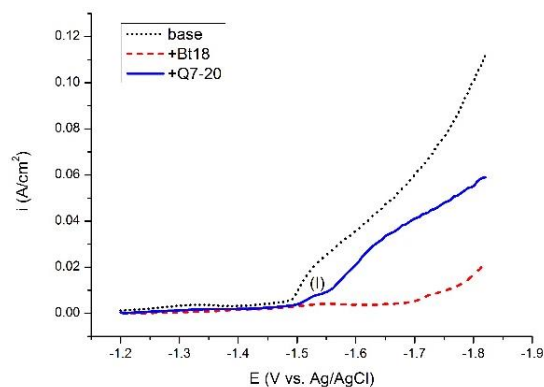


Figure 3. Influence of the number of substituents on cathodic polarization.

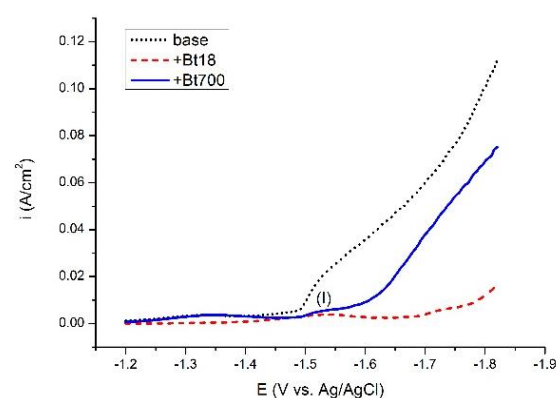


Figure 4. Influence of molecular weight on cathodic polarization.

For further study of the effects of number of substituents and molecular weight of polyamines on cathode polarization and the overpotential of plating processes, cyclic voltammogram curve of the steel electrode was measured in base solutions alone and in combination with different additives, with a scan rate of 2 mV/s, at 25 °C. The results are shown from Fig. 5 to Fig. 7.

Cyclic voltammogram curves of the steel electrodes measured in base solutions alone and with additive Bt18 0.5 g/L are presented in Fig. 5. The CV curves have shown the peaks more clearly than the cathodic polarization curves in the above Fig. 3 and Fig. 4. In the CV curves, it could be seen that peaks I<sub>c</sub> and I<sub>a</sub> are corresponding to the zinc reduction process and the dissolution process of deposits, respectively. Specially, there are two peaks I' <sub>c1</sub> and I' <sub>c2</sub> on the cathodic branch of the CV curve measured in the solution with additive Bt18. Adding the

additive Bt18 suppressed the reduction of zinc at peak  $I_{c1}$  and caused an appearance of a larger peak  $I_{c2}$  at more negative potential.

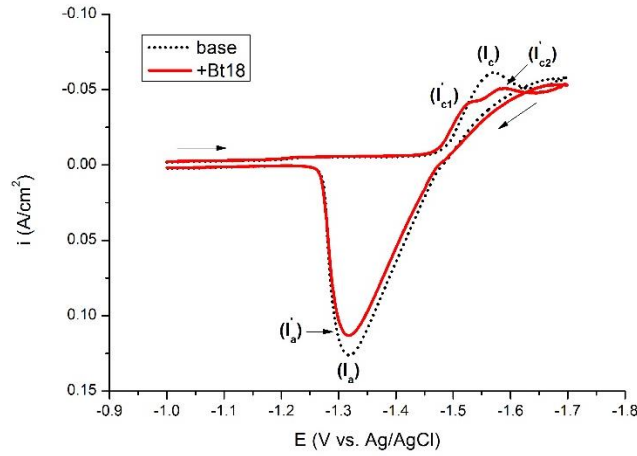


Figure 5. Cyclic voltammogram curves of the steel electrodes measured in base solutions alone and with additive Bt18.

For base bath, the cathodic voltammogram curve with peak  $(I_c)$  is followed by a rapid growth in current density, which is attached to the plating process. The reduction process of  $Zn^{2+}$  to Zn which forms deposit occurs according to the following reactions [3, 8]:



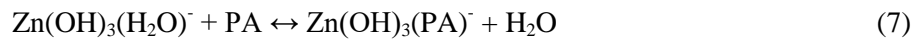
The reactions take place in 4 steps, of which the 3rd step has the slowest speed by the charge transfer process. Reaction (3) plays a decisive role in the reaction rate [3, 8]:



$Zn^{2+}$  usually exists in the complex of 6-coordination or complex 4-coordination  $Zn(OH)_3^-$ , so  $Zn(OH)_3^-$  becomes  $Zn(OH)_3(H_2O)^-$ , and reaction (3) becomes reaction (6):



when additives such as polyamines (PAs) were added, PAs in solution replace water in the complex  $Zn(OH)_3(H_2O)^-$ , reaction (3) becomes reaction (7).



Therefore, the energy needed to break the PAs complex for zinc deposition on steel surfaces is reason for the peak  $(I_{c2})$ . Moreover, the PAs molecular structure has polarization of carbon-oxygen bond, which has the ability to adsorb on the top of the metal substrate surface resulting in surface levelling. When scanning to more negative potentials, desorption of additive PA occurs which is also a reason of the formation of peak  $(I_{c2})$ . This was also reported by Hsieh *et al.* [9].

The kinetic mechanism of zinc electrodeposition process has been shown by Lee [10]. Kardos [11] has studied and provided explanations for the mechanism of surface leveling process. The study of surface leveling in high current density areas was presented in an article of Bai *et al.* [12]. The studies showed that the adsorption of organic compounds, on the electrode surface, inhibits the metal depositing reaction by "preventing" the depositing process, which means that electrode reactions cannot occur on the areas occupied by organic molecules. If the adsorption kinetics of the inhibitor are controlled by molecular diffusion onto the electrode surface, then with the change of the diffuse layer thickness on the micro site, the adsorption of the inhibitor will be larger at micropeaks. At these points, the diffuse layer thickness is small and thus the inhibitor transport onto the electrode surface is faster. On the contrary, much less absorption will occur at microgrooves and therefore the metal tends to favor deposition at the microgrooves. Therefore, the molecular weight of polyamines greatly affects their impact on the leveling and brightening processes in the zinc plating. However, these assumptions need further investigation to clarify.

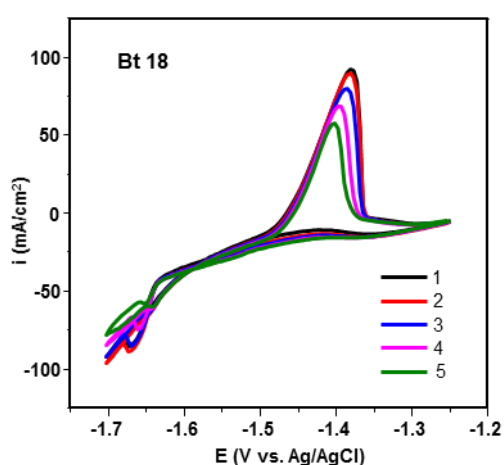


Figure 6. Cyclic voltammogram curve of the steel electrode was measured in base solution with additives Bt18.

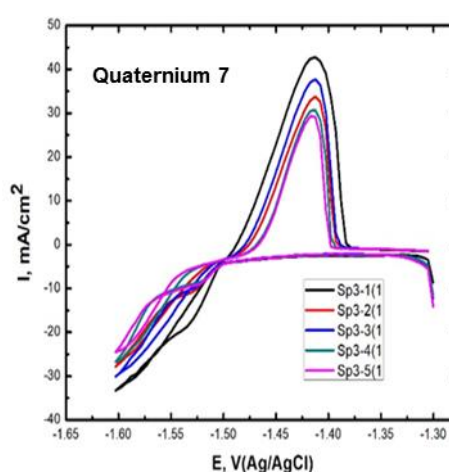


Figure 7. Cyclic voltammogram curve of the steel electrode was measured in base solution with additives Q7-20.

Cyclic voltammogram curves of the steel electrodes measured for 5 continuous cycles in base solutions with additives Q7-20 and Bt18, with a scan rate of 2 mV/s, at 25 °C were shown in Fig. 6 and Fig. 7. The results showed that adsorption and desorption of these polyamines are stable in the plating process.

### 3.2. Effect of the number of substituents and molecular weight of polyamines on the brightness and semi-bright ranges of zinc coatings

The Hull cell design helps to form a continuous range of small to large current densities on the same cathode. Therefore, only with one experiment, it could also identify the optimal current density region that the polyamines affect and the intensity of these effects can be determined through surface observation and bright measurement.

After experimenting in the Hull cell with other plating solutions with and without polyamines, which containing various concentrations of polyamines with various number of substituents and molecular weight, zinc deposits with various brightness and semi-bright ranges have been obtained respectively.

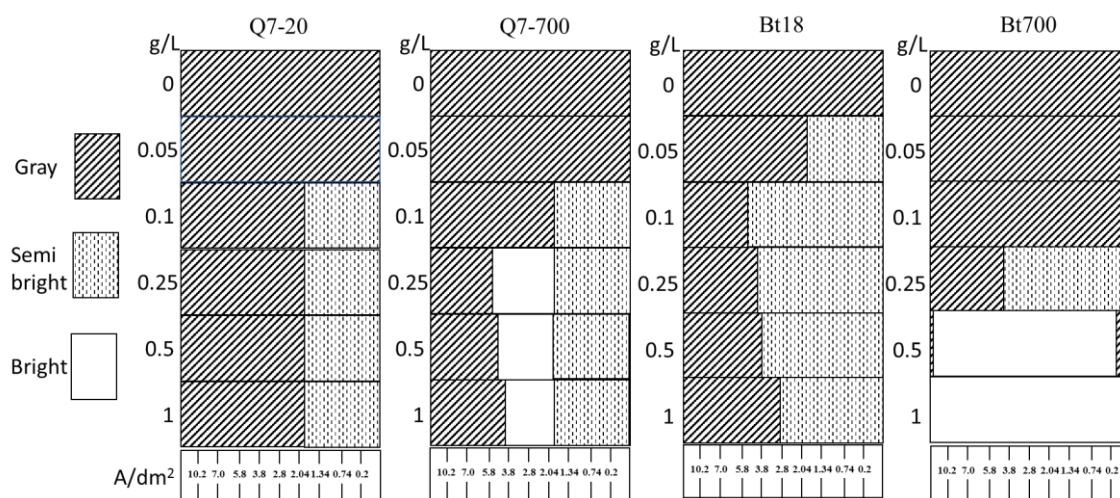


Figure 8. Hull cell patterns obtained from plating solutions containing polyamines.

The results in Fig. 8 and Tab. 1 are Hull cell patterns obtained from the alkaline zinc plating solutions including Bt700 from reference [7]. In the case of same number of substituents of polyamines, the brightness (BN) and semi-bright ranges (SBR) of the deposits using polyamines with low molecular weight Bt18 (BN = 14 and SBR < 3 A/dm<sup>2</sup>) and Q7-20 (BN = 4.6 and SBR < 2 A/dm<sup>2</sup>) were poorer than those of the deposits using polyamines with high molecular weight Bt700 (BN = 56.7 and SBR < 10 A/dm<sup>2</sup>) and Q7-700 (BN = 15.3 and SBR < 4.5 A/dm<sup>2</sup>), respectively.

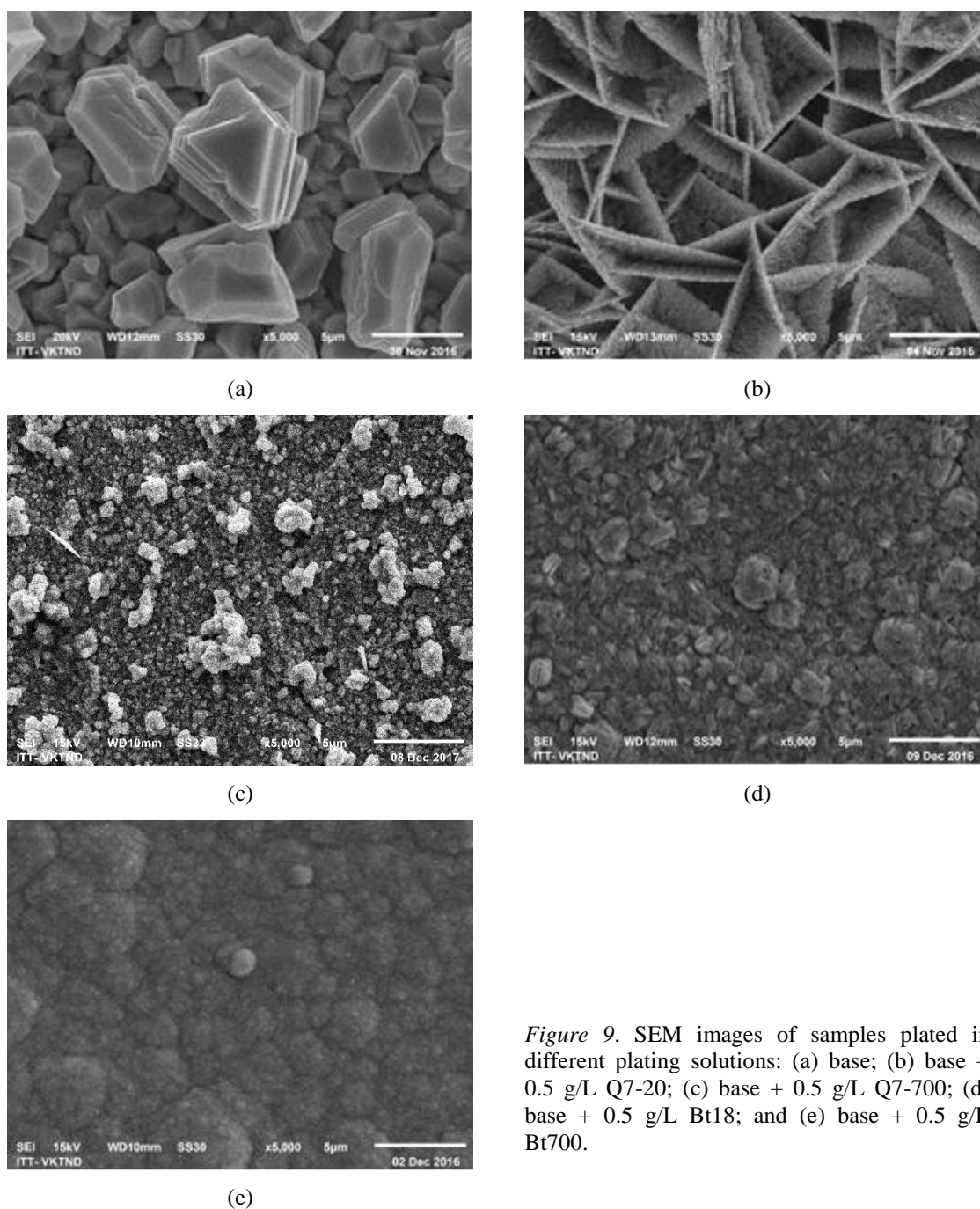
From these data, it could be easy to see that the brightness and semi-bright ranges of the deposits using secondary polyamines Bt700 and Bt18 were better than those of the deposits using quaternary polyamines Q7-700 and Q7-20, respectively in the case of same molecular weight of polyamines. It could be concluded that effects of polyamine with lower number of substituents and higher molecular weight on the brightness and semi-bright ranges of the deposits are stronger than those of other investigated polyamines. Therefore, Bt700 is the best.

Table 1. Effect of the number of substituents and molecular weight of polyamines on brightness and semi-bright ranges of zinc deposits in non-cyanide alkaline plating baths.

№	Additive content (g/L)	Semi-bright ranges* (A/dm <sup>2</sup> )				The highest brightness of samples at 60°			
		Bt700	Bt18	Q7-20	Q7-700	Bt700	Bt18	Q7-20	Q7-700
1	0	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2	0.05	n/a	< 2	n/a	n/a	n/a	2.1	n/a	n/a
3	0.1	n/a	< 5.5	< 2	< 2	n/a	4.0	0.6	18.8
4	0.25	< 5	< 5.5	< 2	< 5.5	11.6	8.3	0.9	26
5	0.5	0.7 to 10	< 4	< 2	< 5	51.4	15.7	1.5	19.1
6	1	< 10	< 3	< 2	< 4.5	56.7	14	4.6	15.3

\* Here, "semi-bright ranges" means current density ranges providing semi-bright deposits.

### 3.3. Effect of the number of substituents and molecular weight of polyamines to morphology of the sample plated in alkaline bath



*Figure 9.* SEM images of samples plated in different plating solutions: (a) base; (b) base + 0.5 g/L Q7-20; (c) base + 0.5 g/L Q7-700; (d) base + 0.5 g/L Bt18; and (e) base + 0.5 g/L Bt700.

SEM images of surface morphology of zinc deposits plated in different solutions were presented in Fig. 9. The SEM image of the surface plated in the base solution at a density of 2 A/dm<sup>2</sup> (Fig. 9a) shows that the particles are granular, rough, with particle size of 5 to 7 μm. Fig. 9(b) shows that the particles transform from granular to plate when polyquaternium 7 is added. The particle size decreases with increasing concentration of Q7-20. At concentration of 0.5 g/L Q7-20, the particles are similar to grain, with size about 0.5 to 1 μm, quite uniform, and the coating is smooth and semi-bright. Fig. 9(c) shows that when Q7-700 was added in the base

solutions, the particles transform to a slender form. The particle size decreases with increasing concentration of Q7. At concentration of 1 g/L Q7, the particle sizes are about 0.1 to 2  $\mu\text{m}$ , quite uniform, and the brightness of deposit increases. Fig. 9(d) and 9(e) show surface morphology of zinc deposits when Bt18, Bt700 was added in the base solutions. At concentration of 0.5 g/L, current density of 2 A/dm<sup>2</sup> the deposits are smooth and semi-bright.

#### 4. CONCLUSIONS

The results show that polyamines used have effects on zinc plating process in non-cyanide alkaline baths. Cathode polarization measurements indicated that the polyamines all increased cathode polarization of the plating process. In addition, cyclic polarization curves of the 5 cycles also revealed that adsorption and desorption of these polyamines were stable in the plating process. The Hull cell method pointed out that these polyamines created semi-bright ranges in the low current density. Moreover, the polyamine Bt-700 had the strongest effects on the brightness of the deposits at almost whole range of current density if its concentrations was sufficient. Surface morphology also showed that adding these polyamines made the crystals of deposits fine, smooth and uniform which agreed with increasing cathodic polarization.

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**Authors contributions:** Truong Thi Nam: methodology, investigation, manuscript. Le Ba Thang: methodology, supervision, formal analysis. Le Duc Bao: formal analysis, translation. Nguyen Van Khuong: formal analysis.

**Conflict declaration:** We have no conflict of interest to declare.

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