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# The Effect of Polyvinyl Alcohol 16000 on the Alkaline Non-Cyanide Zinc Plating Process

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## ABSTRACT

The effect of polyvinyl alcohol (PVA) having molecular weight 16,000u in alkaline non-cyanide zinc plating bath on the characteristics of zinc plating process has been investigated. The SEM images indicated that zinc particles produced in plating bath were either in block form if plating bath without PVA or in slice form if plating bath with PVA. The size of zinc particles depended on PVA concentrations in plating bath. If the content of PVA in plating bath increased, the zinc grain size reduced. Hull Cell tests also illustrated that surface of zinc deposition improved for plating bath with PVA. Semi-bright scope of zinc plated coating expanded if the PVA concentration in plating bath grew. However, bright scope did not appear in all samples from plating bath with various concentrations of PVA. It was reasonable due to PVA playing a role as primary additive for zinc plating as other authors confirmed. Interestingly, cathodic polarizations were increased in presence of PVA. Throwing power increases significantly with increasing PVA concentration.

## 1. Introduction

A large quantity of fabricated ferrous metal parts coated with electrodeposited zinc deposits have been used generally in automotive and other industrial fields. The good protection, decorative appearance and low cost are advantages of zinc electro platings. The zinc coatings protects steel substrates in two mechanism: barrier and sacrificial protections. Because of environmental concerns, alkaline free-cyanide zinc electrolytes have been introducted as alternative solution for cyanide zinc baths [1]. In the early 1960s, alkaline free-cyanide zinc electrolytes had been known but they were not used widely because of bad coatings and unsuitable additives. Recently with development of organic additives, alkaline non-cyanide zinc electroplating systems have been used widely. This process have advantage as low toxicity, simple waste treatment, low make-up costs, good throwing power etc. [1].

Organic additives are playing a very important role in producing bright and uniform layers during zinc deposition. One or more additives can be used in the same process. The first one is called the carrier or the primary additive and its main function is to refine and to generate semi- brightness. The second one is called secondary additive or brightener which used to produce full bright layers of the deposit [2-7]. Polyvinyl alcohol (PVA) played a role as a primary additive due to PVA owing to the polarity of the carbon-oxygen bond. Adsorption of PVA on surface of metals inhibits discharge of Zn ions [8,9]. Shanmugasigamani et al. studied the role of several additives in bright zinc deposition from alkaline non-cyanide baths [8] and confirmed that PVA was as the best studied additive with a range of concentrations from 0 to 2 g/L. Moreover, PVA was also used as bath additives for nickel-zinc alloy bath [5]. However, PVA yielded partial grain refinement, but the deposits were only semi-bright. In published articles, molecular weight of PVA is not mentioned and so the effect of PVA with molecular weight of 16000u (PVA 16000) on alkaline free-cyanide plating process is studies in this work

## 2. Materials and methods

### 2.1. Materials

Zinc plating solution contains major constitutes: NaOH 140 g/L, ZnO 15 g/L (base solution = BS) with PVA 16000 in various concentrations. Hydrochloric solution at 10% volume was used for pickling the surface of steel. All chemicals were used at P grade and dissolved by deionized water.

### 2.2. Sample preparation

Mild steel panels (100x70x1.2 mm) were degreased by immersion in UDYPREP-110EC (Enthone) with concentration of 60 g/L at temperature from 50 to 60 $^{o}$C for 5÷10 min. After that the samples were immersed in a solution containing HCl (10% volume), urotropine (3.5g/L) at ambient temperature for 2÷5 min.

Zinc electroplating process: all samples were electro deposited by using rectifier.

### 2.3. Analysis

The standard Hull cell of 267 mL capacity was used to optimize the bath constituents and bath parameters. The zinc electroplated steel plates were rinsed in water and given bright by dipping in 0.3% volume nitric acid for 2-3 s. Based on these plates, effects of PVA on properties of zinc plating at various current densities were carefully studied.

The cathodic polarization plots were examined by potentio dynamic polarization method carried out on an Autolab PGSTAT 30 (at Institute for Tropical Technology) with three electrode cell using Ag/AgCl as reference electrode, platinum (Pt) with surface area of 1.5cm$^2$ as

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auxiliary electrode and steel with diameter of 1 cm as working electrode at scan rate of 2mV/s. Cathodic polarization was expressed i-E relations.

Surface morphologies of zinc electrodeposits were evaluated by scanning electron microscopy (SEM) using Jeol-JSM-6510LV (Japan) at Institute for Tropical Technology.

Effect of PVA on the throwing power was evaluated by Haring-Blum method with a metal distribution ratio of 5 applying Field’s formula.

Cathodic current efficiencies were calculated by comparing the amount of metal deposition between in fact and in theory according to Faraday's laws.

## 3. Results and Discussion

### 3.1. Cathodic polarization plots

Polarization measurements are an important research tool in investigations of a variety of electrochemical phenomena. Such measurements permit studies of the reaction mechanism and the kinetics of corrosion phenomena and metal deposition [11]. Hence, the study of the cathodic polarization curves is very necessary because polarization affects the electro deposition processes and helps us in understanding the nature of electro deposition. For these reasons, the cathodic polarization curves of zinc deposition on steel cathodes were recorded potentio dynamically.

The cathodic polarization plots during zinc electro deposition from the alkaline non-cyanide bath containing PVA in various concentrations were recorded and shown in Fig. 1.

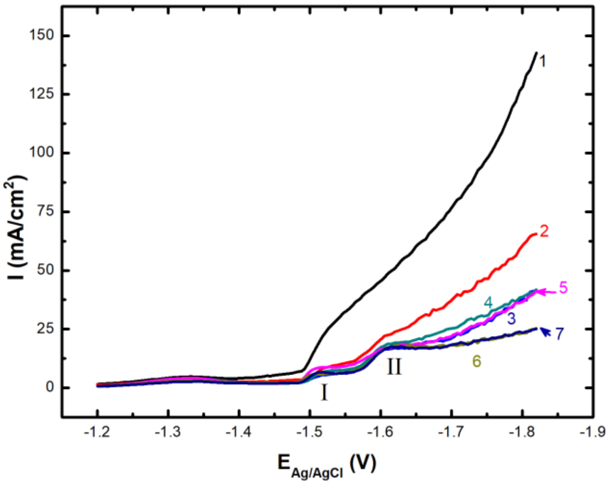

**Figure 1. Polarization behavior of zinc deposition from BS bath with PVA: 0.00 g/L (1), 0.05 g/L (2), 0.10 g/L (3), 0.25 g/L (4), 0.50 g/L (5), 1.00 g/L (6), 1.50 g/L (7) at scan rate of 2 mV/s.**

These plots were swept from the open current potential towards the negative direction at a scan rate of 2mV/s. In all cases, the polarization curves were characterized by appearance of the first cathodic peak (I) followed by either rapid rise in current density for plating bath without PVA or the second cathodic peak (II) for plating baths containing PVA. There was little difference between PVA plating baths at concentrations of 1.0 and 1.5g/L.

For the plating bath without PVA, the cathodic polarization plot had a peak I followed by rapid growth in current density. It was assigned to the reduction of $Zn^{2+}$ to Zn that is corresponding to the reaction below [12]:

$$Zn(OH)_4^{2-} + 2e^- \leftrightarrow Zn + 4OH^- \quad \text{(i)}$$

The following four step reaction path has been proposed for the deposition of zinc from zincate solution where reaction (iii) as the rate determining step [13]:

$$Zn(OH)_4^{2-} \leftrightarrow Zn(OH)_3^- + OH^- \quad \text{(ii)}$$

$$Zn(OH)_3^- + e^- \rightarrow Zn(OH)_2^- + OH^- \quad \text{(iii)}$$

$$Zn(OH)_2^- \leftrightarrow ZnOH + OH^- \quad \text{(iv)}$$

$$ZnOH + e^- \rightarrow Zn + OH^- \quad \text{(v)}$$

Since $Zn^{2+}$ preferred to exist as a tetra or hexa-coordinate species, the coordinated $Zn(OH)_3^-$ is more likely to exist as $Zn(OH)_3(H_2O)^-$, thus step (iii) became as (vi) below:

$$Zn(OH)_3(H_2O)^- + e^- \rightarrow Zn(OH)_2^- + OH^- + H_2O \quad \text{(vi)}$$

It was also possible that PVA replaced the presence of $H_2O$ in the complex $Zn(OH)_3(H_2O)^-$ as step (vii).

$$Zn(OH)_3(H_2O)^- + PVA \leftrightarrow Zn(OH)_3(PVA)^- + H_2O \quad \text{(vii)}$$

Hence, energy is needed to break the PVA complex to deposit zinc on steel surface. It might be the reason of appearance of the peak II.

Moreover, PVA was able to adsorb on the peaks of substrate surface, which inhibited zinc deposition at peaks and promoted discharge of zinc ions at valleys, because PVA owed to the polarity of the carbon-oxygen bond. Consequently, leveling effect was formed on surface.

However, these hypotheses should be investigated by further studies.

### 3.2. Hull cell test

Hull cell is often used by researchers to find out what is wrong when a plating station begins to produce rejects. Because a Hull cell produces a deposit that is a true reproduction of the electro plate obtained at various current densities within the operating range of a particular system, it allows experienced operators to determine multiple process parameters.

Hull cell patterns obtained from alkaline non-cyanide bath containing PVA with various concentrations were presented in Fig. 2.

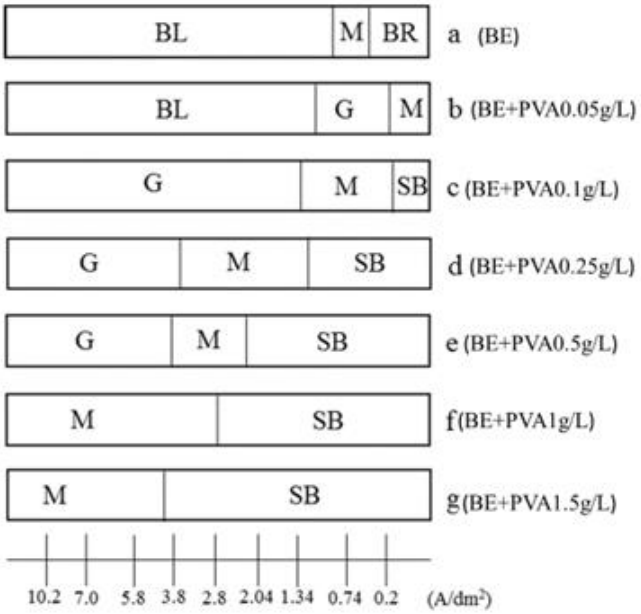

**Figure 2. Hull cell pattern obtained from BS containing PVA. Code for Hull Cell figures: BR-bright, M-matte, BL-black, G-grey, SB-semi-bright.**

For the Hull cell patterns obtained from alkaline non-cyanide bath without PVA, the surface of zinc was bright at low current density (≤ 0.2 A/dm$^2$). If the current density grew, the zinc electrodeposit became rougher and darker. At high current density (≥ 2.8 A/dm$^2$), the zinc electrodeposit was black and zinc deposited on steel surface in the form of large grains leading to rough surface. Some authors also confirmed that the grain size of zinc deposition depended on the current density [13]. The grain size of zinc deposition was large if the current density was high. It might be explained that the deposition of zinc occurred through four steps as mentioned above from reaction (ii) to reaction (v) among them the reaction (iii) as a rate determining step. In plating solution without PVA, reaction (iii) became (vi). If the rate of reaction (vi) occurred faster than the rate of transport of ions to the site of discharge, powdery non-adherent deposits was formed. Thus, in order to achieve bright and useful deposits the rate of reaction (vi) must be reduced [12, 13]. This could be only achieved thanks to using organic additives.

The results showed that the samples from alkaline non-cyanide bath with PVA became smoother and brighter in comparison with that from alkaline non-cyanide bath without PVA. If the PVA concentration increased, the zinc deposition surfaces became smoother. It can be explained that in presence of PVA, the reaction (vi) was modified. It was possible that PVA replaced the presence of $H_2O$ in $Zn(OH)_3(H_2O)^-$ and became $Zn(OH)_3(PVA)^-$ as reaction (vii) above. As a result, the reaction (vi) became (viii) below:

$$Zn(OH)_3(PVA)^- + e \rightarrow Zn(OH)_2^- + OH^- + PVA \qquad \text{(viii)}$$

Assuming reaction (viii) was much slower than (vi) because of the energy needed to break the PVA complex, would explain the grain refining properties of PVA [12].

The Hull Cell results were suitable with cathodic polarization curves. If PVA concentration rose, the complex $Zn(OH)_3(PVA)^-$ produced more and thus the deposition of zinc needed more energy to break the complex leading to reduce of current density for sample having high PVA concentration.

### 3.3. Morphology of the deposits

If the zinc plating process occurs at low current density, it requires more time. However, if the plating process conducts at higher current density, zinc electrodeposited coatings do not meet requirement of product. Therefore, the current density of 2 A/dm$^2$ was selected to create zinc deposit for studying the morphology. The surface morphology of zinc electrodeposited coatings obtained from non-cyanide alkaline bath containing PVA with various concentrations are displayed in Fig. 3.

As can be seen from Fig. 3a, the zinc deposition produced from alkaline non-cyanide bath without PVA was in block form, having diameter of approximately 5-7μm. However, the zinc deposition was in slice form if it was produced from plating bath containing PVA (as seen in Fig. 3 (b-g)). The zinc particle became smaller in a range of between 0.3 and 0.5 μm if the PVA concentration in plating bath increased. There was little difference among zinc coatings from plating baths containing PVA of high concentrations (≥ 0.5 g/L).

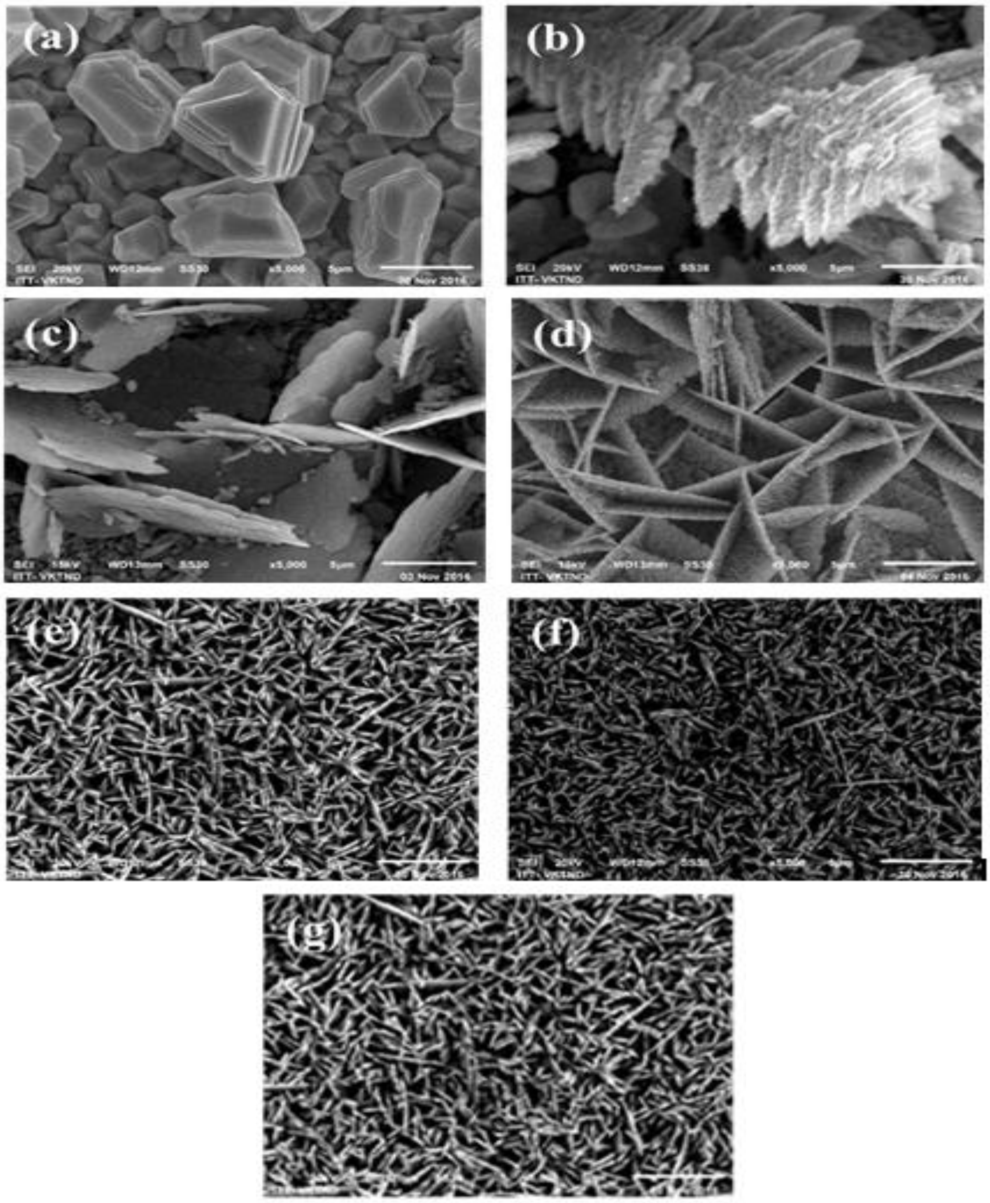

**Figure 3. SEM images of zinc platings obtained from BE containing PVA with various concentrations: BE (a); BE+PVA 0.05 g/L (b); BE+PVA 0.10 g/L (c); BE+PVA 0.25 g/L (d); BE+PVA 0.50 g/L (e); BE+PVA 1.00 g/L (f).**

It could say that PVA affects the zinc deposition producing in the alkaline non-cyanide zinc plating process. PVA makes zinc deposition more homogeneous and smaller.

### 3.4. Throwing power and cathodic current efficiencies

Throwing power increases significantly with increasing PVA concentration from 0 up 0.5 g/L, then increases slowly and remains almost constant with higher PVA concentration. Fig. 4 shows that throwing power appears to be strongly dependent on PVA concentration but weaky dependent on current density.

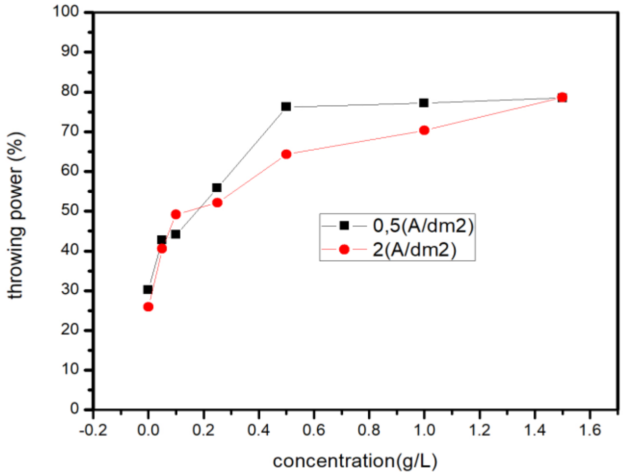

**Figure 4. Influence of PVA concentration on throwing power.**

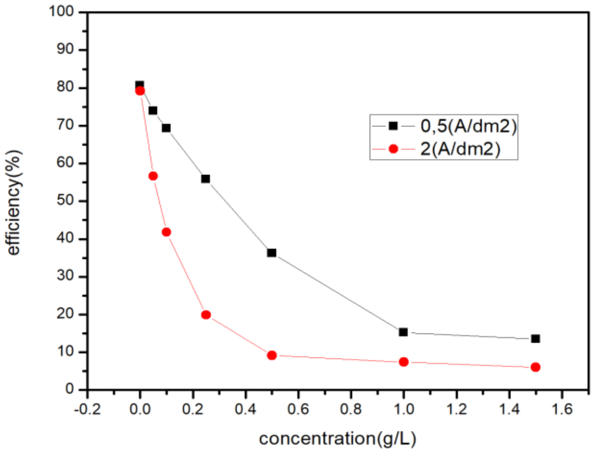

**Figure 5. Influence of PVA concentration on current efficiency.**

Fig.5 presents dependency of current efficiency on concentration of PVA 16000 in solution and on current density. The results show that current efficiency decreases sharply with increasing PVA concentration from 0 up 0.5g/L (at current density 0.5A/dm$^2$) and up 1g/L (at current density 2A/dm$^2$). On the other hand, at the same PVA concentration, current efficiency decreases with increasing current density. Reason of current efficiency decrease is more difficult discharge of Zn ions from complex $Zn(OH)3(PVA)^-$ because rate of reaction viii is significant slower than that of reaction vi.

## 4. Conclusions

PVA has effects on zinc deposited coatings' characterizations produced from alkaline non-cyanide zinc plating bath. The current density reduces in presence of PVA due to PVA replacing the present of $H_2O$ in complex $Zn(OH)_2(H_2O)^-$. With leveling effect, PVA helps the zinc plating surface to become smoother and to expand semi-bright scope. The surface morphology of zinc deposited coating shows that the zinc particles' size produced depends on PVA concentration. The zinc particles are in block form if plating bath without PVA, and in slice form if plating bath with PVA. If the concentration of PVA in plating bath increased, the zinc grains are more homogeneous and their size reduces sharply. Presence of PVA in base solution makes throwing power higher and current density lower.

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## References

1. Ramesh Bapu G.N.K., Devaraj G., Ayyapparaj J. - Studies on non-cyanide alkaline zinc electrolytes-J. Solid State Electrochem. **3** (1998) 48-51.

2.Ortiz-Aparicio J. L., Meas Y., Trejo G., Ortega R., Chapman T. W.- Eric Chainet. Effects of organic additives on zinc electro deposition from alkaline electrolytes, J. Applied Electro chemistry **43** (2013) 289-30.

3.Sciscenko I., Pedre I., Hunt A., Bogo H., González G. A. - Determination of a typical additive in zinc electroplating baths, Micro chemical Journal **127** (2016) 226-230.

4.Chandrasekar M. S., Shanmugasigamani S., Pushpavanam M.-Structural and textural study of electrodeposited zinc from alkaline non-cyanide electrolyte-Journal of Materials Science **45** (2010) 1160-1169.

5.Ortiz-Aparicio J. L., Meas Y., Chapman T. W., Trejo G., Ortega R.-Eric Chainet-Electro deposition of zinc in the presence of aternary ammonium compounds from alkaline chloride bath, J. Applied Electrochemistry, **45** (2015) pp. 67-78.

6.Shanmugasigamani S. and Push pavanam M.- Bright zinc-nickel alloy deposition from alkaline non-cyanide bath, Transactions of the Institute of Metal Finishing **86** (2008) 122-128.

7.Ramírez C., Calderón J. A. - Study of the effect of Triethanolamine as a chelating agent in the simultaneous electro deposition of copper and zinc from non-cyanide electrolytes, J. Electro analytical Chemistry **765** (2016) 132-139.

8.Ballesteros J. C., Torres-Martínez L. M., Juárez-Ramírez I., Trejo G., Meas Y. - Study of the electrochemical co-reduction of $Cu^{2+}$ and $Zn^{2+}$ ions from an alkaline non-cyanide solution containing glycine, J. Electro analytical Chemistry **727** (2014) 104-112.

9. Shanmugasigamani and Push pavanam M. - Role of additives in bright zinc deposition from cyanide free alkaline baths, J. Applied Electrochemistry **36** (2006) 315-322.

10.Arthoba Naik Y. and Venkatesha T. V.-A new condensation product for zinc plating from non-cyanide alkaline bath, Bulletin of Materials Science **28** (2005) 495-501.

11.Stern M. and Geary A. L.-Electrochemical Polarization. I. A Theoretical Analysis of the Shape of Polarization Curves, J. Electrochemical Society **104** (1957) 56-63.

12.Shanmugasigamani S., Pushpavanam M.- Voltammetric Studies on the Role of Additives in Bright Zinc Electrodeposition from an Alkaline Non-Cyanide Bath, Portugaliae Electro chimica Acta **27** (2009) 725-735.

13.Nakano H - Effects of plating factors on morphology and appearance of electrogalvanized steel sheets, Transactions of Nonferrous Metals Society of China **19** (2009) 835-841.