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A review of organic additives in zinc electrodeposition process (performance and evaluation)

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ABSTRACT

This review provides an overview of some important studies and investigations performed on various organic additives in zinc electrodeposition process. Organic additives are widely used due to their special functions during the electrodeposition of zinc or its alloys. These additives are found to affect the growth and crystal building of deposits through their adsorption on the cathode surface. Most of these additives act as hydrogen inhibitors and crystal growth modifiers, so an appropriate addition is necessary for the formation of fine-grained, smooth, and compact deposits. The presence of metallic impurities in the industrial electrolytes cannot be neglected as well. Most of these impurities decrease the induction period associated with the zinc electrodeposition process resulting in deterioration of the zinc deposit quality and decrease of the cathodic current efficiency. Accordingly, some additives are used to reduce the detrimental effect of these impurities and to improve the operating performance. Although, glues and gelatins are the most known additives in industry but searching for better ones with good stability, high efficiency, low cost, and being environmentally acceptable is still continuing. Therefore, this review considers previous studies conducted on various organic additives from different groups such as: quaternary ammonium salts, polymers, surfactants, natural compounds, organic acids, and ionic liquids salts. This study emphasizes as well the employed electrochemical techniques in evaluating the performance of organic additives during the electrolytic extraction of zinc.

1. Introduction

The utilization of organic compounds as additives in zinc electrodeposition was initially reported in 1907, when the effect of the addition of formaldehyde in acidic electrolyte on reducing the grain size of the deposit was examined (Snowden, 1907). A large range of organic additives is used during zinc electrodeposition in order to improve the properties of deposits (brightness, smoothness, grain size, stress) (Boto, 1975). Also, they are used to enhance the operating performance such as: cathodic depolarization, increasing cathodic current efficiency (CE), and decreasing power consumption (PC) (Recendiz et al., 2007). The organic additives are found to affect both the zinc deposition and crystal-building processes, also to reduce the detrimental effect of the existing metallic impurities in the zinc electrolytes on the cathodic CE (Bain et al., 1964; Robinson and O'Keefe, 1976). Additionally, their role in controlling the acid mist over the electrolysis cell cannot be neglected (Moriyama and Yamamoto, 1970; Dhak et al., 2011; Dhak et al., 2010; Cheng et al., 2004). Although the traditional colloidal additives such as glue, gelatin, Arabic gums, and some other organic additives have been widely used in industry and achieved good effects, but they are readily decomposed and environmental unfriendly for their shortcomings, such as bad chemical and thermal stability and high toxicity (Afifi et al., 1992; Zhang and Hua, 2012). Therefore, the searching for better additives with good stability, high efficiency and being environmentally acceptable is still continuing (Zhang and Hua, 2012).

The presence of metallic impurities in the zinc electrolyte is a major problem for the zinc electrodeposition process. Decrease in CE, change in deposit morphology, and cathodic polarization occur for electrolyte containing small concentrations of impurities (Muresan et al., 1996; Karavasteva, 1994; Ault and Frazer, 1988). The presence of more electropositive ions than that of zinc, such as Sb^{3+}, Ni^{2+}, Co^{2+}, Ge^{4+}, etc. could initiate the zinc re-dissolution process leading to a decrease in the CE (Ivanov, 2004; Stefanov and Ivanov, 2002; Stefanov et al., 1991). Low concentration level as parts per million of nickel and cobalt, even parts per billion of antimony, arsenic, and germanium are reported to influence negatively the zinc electrodeposition due to the re-dissolution of zinc deposit during the electrolysis process (Stefanov and Ivanov, 1997; Fosnacht and O'keefe, 1980; Beshore et al., 1987;

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Mackinnon et al., 1987; Gonzalez-Dominguez and Lew, 1995). Also, the negative role of lead as impurity in reducing the purity and quality of deposited zinc cannot be neglected as far as lead-based anodes are still used in this process (Mackinnon et al., 1979; Ichino et al., 1995). Smooth, compact and pure deposits with high current efficiencies are always obtained from pure electrolytes. However, various electrolyte purifications steps are very costly and affect negatively the economy of zinc industry. Accordingly, an alternative low cost method to reduce the detrimental effect of metallic impurities is to use appropriate organic additives (Alfantazi and Dreisinger, 2001).

Many electrochemical techniques have been developed to study the performance of additives on the various parameters associated with the zinc electrodeposition process. Among these techniques: Galvanostatic polarization, potentiodynamic polarization (Tripathy et al., 1998), cyclic voltammetry (Kerby et al., 1977; Gomes and da Silva Pereira, 2006), and electrochemical impedance spectroscopy (Cachet and Wiart, 1994). These techniques are also useful to determine the behavior and mechanism of the additives alone or combined with the metallic impurities. Although the specific mechanism of additives during zinc electrodeposition is not fully determined, the following facts could be established: (a) most of additives carry a net positive charge and migrate to the cathode where they are adsorbed; (b) their actual concentration in the deposit is extremely small and it is difficult to be confirmed analytically; (c) the columnar deposit growth is eliminated by additives presence in the electrolyte; (d) the electrolyte composition usually changes the electrochemistry of organic additives (Mackinnon and Brannen, 1982). Other direct and complex mechanisms of the action of additives in electrodeposition process have been proposed as well (Franklin, 1987; Kardos and Foulke, 1962; Roth and Leidheiser, 1953; Beacom and Riley, 1959; Malathy and Shenoi, 1977). Generally, the used additives are organic compounds with high molecular weight which could be adsorbed on the cathode and act as hydrogen inhibitors and crystal growth modifiers (Muresan et al., 1996; Tripathy et al., 1998).

In this review, the influence of different categories of organic additives such as: glues, gelatins, quaternary ammonium salts, synthetic polymers, surfactants, natural compounds, organic acids, and ionic liquid salts on zinc electrodeposition process has been reported. Also, the effect of combination of some additives with certain metallic impurities has been discussed based on various studies. One of the goals of this review also is to highlight the evaluation methods of the efficiency of organic additives employing different electrochemical techniques as well as surface characterization techniques.

2. Kinetics studies and mechanism of zinc electrodeposition

In order to understand the kinetics of zinc electrodeposition, it is necessary to determine the occurred electrochemical reactions (cathodic & anodic) in this electrolysis process (Biegler and Swift, 1981). Based on the overall stoichiometric relationship, the electrodeposition of zinc in acidic electrolyte is accompanied frequently by hydrogen reduction and generally described as:

$$Zn^{2+} + 2e^- \rightarrow Zn_{(s)} \qquad E^\circ = -0.763V \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \qquad E^\circ = 0.00V \tag{2}$$

Oxygen is always evolved on the anode according to the following reaction:

$$H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_{2(g)} \qquad E^\circ = -1.229V \tag{3}$$

However, due to the high overpotential of hydrogen on zinc, hydrogen evolution shifts to a potential behind that for zinc deposition (Scott et al., 1987; Zhang and Houlachi, 2010). Nevertheless, hydrogen evolution is observed during the zinc electrodeposition from acidic electrolytes. Accordingly, the evolution of H_2 gas is often included in the reaction mechanism of zinc deposition (Kim and Jorné, 1980). A complicated model of reactions mechanism of hydrogen evolution and zinc reduction with great interest was proposed by Epelboin et al. (1975) then modified by Lee and Jorné (1992) as following:

$$H^+ + e^- \xrightarrow{K_1} H_{ads} \tag{4}$$

$$H^+ + H_{ads} + e^- \xrightarrow{K_2} H_2 \tag{5}$$

$$Zn^{2+} + Zn^+_{ads} + e^- \xleftrightarrow{K_3/K'_3} 2Zn^+_{ads} \tag{6}$$

$$Zn^+_{ads} + H_{ads} \xrightarrow{K_4} H^+ + Zn \tag{7}$$

$$Zn^+_{ads} + e^- \xrightarrow{K_5} Zn \tag{8}$$

$$Zn^{2+} + H_{ads} \xrightarrow{K_6} Zn^+_{ads} + H^+ \tag{9}$$

H^+ reacts directly with the active sites as reaction (4), while reaction (5) corresponds to the evolution of hydrogen in the form of gas, reaction (6) is an intermediate process of adsorption of Zn^{2+} ions on the cathode surface, and finally the formation of zinc deposit is presented by reactions (7) & (8). The adsorption of adions on the electrode surface follows Langmuir isotherm, and the reaction rates of electrochemical reactions are supposed in compliance with Tafel's law (Lee and Jorné, 1992). The mass action law can be described as:

$$\Gamma_1\frac{d\theta_1}{dt} = A_1(1 - \theta_1 - \theta_2) - A_2\theta_1 - A_4\theta_1\theta_2 - A_6\theta_1 \tag{10}$$

$$\Gamma_2\frac{d\theta_2}{dt} = A_3\theta_2(1 - \theta_1 - \theta_2) - A'_3\theta_2^2 - A_4\theta_1\theta_2 - A_5\theta_2 + A_6\theta_1 \tag{11}$$

where, Γ_1, Γ_2 are the maximum surface concentrations of H_{ads} and $Zn^+{}_{ads}$, respectively. θ_1 and θ_2 represent the surface coverage of H_{ads} and $Zn^+{}_{ads}$, respectively. $A_1 = K_1[H^+]$, $A_2 = K_2\Gamma_1[H^+]$, $A_3 = K_3[Zn^{2+}]$, $A'_3 = K'_3\,\Gamma_2{}^2$, $A_4 = K_4\,\Gamma_1\Gamma_2$, $A_5 = K_5\,\Gamma_2$, and $A_6 = K_6\,\Gamma_1[Zn^{2+}]$.

It is obvious that the main processes that occur during zinc electrodeposition are those of zinc reduction and hydrogen evolution. Their shares depend on the zinc equilibrium potential and the overpotential associated with the cathodic reactions. Depending on the electrolyte concentration, pH, temperature, and the discharged zinc ions (Sitnikova and Sitnikov, 2005).

3. Electrochemical evaluation methods for additives

Certain useful electrochemical techniques can be conducted during the electrodeposition to give better understanding of the kinetics in this process and to study the effect of additives in changing the electrochemistry of this system. Test methods such as: (1) galvanostatic polarization, (2) cyclic voltammetry (3) galvanodynamic scanning technique, (4) potentiodynamic polarization, and (5) electrochemical impedance spectroscopy are employed to determine the oxidation and reduction reactions on each metal at a potential polarized from its equilibrium value. Gonzalez-Dominguez (1994) published a review showing that a number of electrochemical techniques have been directed in the industrial environment. This review highlighted the beneficial usage of such polarization techniques during Zn and Pb electrodeposition at Cominco plant (B.C., Canada). A general definition of polarization is "the deviation in potential of an electrode as a result of the passage of current" the amount of polarization is referred to overpotential and generally is assigned by the symbol (η) (Beavers et al., 1993).

3.1. Galvanostatic polarization

The galvanostatic polarization technique determines the polarization behavior of an electrode by applying a constant current density