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### Plating Bath Parameters Affecting the Performance of Zinc-Nickel Alloys for Post-Plate Fabrication

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### ABSTRACT

In recent years, the demand for increased corrosion protection of ferrous substrates has significantly increased. Zinc-nickel alloy plating systems are being chosen to meet this need. Often these component parts are subjected to post-plate forming and fabrication processes. Ductility, hardness, and stress were thought to be important physical properties to maintain the integrity of the zinc-nickel deposit during these forming processes. To achieve these goals, the following operating parameters were found to be important: the donor type and denticity of the chelate, the chelate-to-total metal mole ratio and the secondary brightener concentration.

**Keywords:** zinc-nickel plating, post-plate fabrication, mechanical properties of electrodeposits, plating bath operating condition effects, plating bath chemical composition effects

#### Introduction

In recent years, automobile and industrial equipment manufacturers have been spearheading the need for increased corrosion protection of ferrous substrates. A number of Zn-alloy plating systems, as well chemical conversion coatings, have been developed to meet this need. From these various approaches, Zn-Ni alloy plating systems have been found to provide the best corrosion protection as well as welding and painting properties.

Zinc-nickel electroplating baths fall into two basic electrolyte categories: alkaline or slightly acidic. Alkaline systems require the use of strong chelates to solubilize nickel ions and keep them in solution. Weakly acidic systems typically have high concentrations of ammonium ions or mild chelates. These approaches make wastewater treatment more difficult. Several non-ammoniated and non-chelated acidic systems have been commercialized in recent years. However, they tend to be more troublesome to operate.

The alloy composition typically ranges from ~4-16% Ni in electrodeposited Zn-Ni alloy coatings. However, high alloy systems with 12-15% Ni have been found to provide optimum corrosion resistance in neutral salt spray and cyclic corrosion testing.

The automobile and industrial equipment manufacturers are demanding parts which have a more corrosion resistant finish, and which can undergo post-plate fabrication steps. Postplate fabrication processes can be bending, crimping and swaging, among others. Examples are shown in Fig. 1. Additionally, corrosion protection cannot be degraded during these post-plate forming processes. An alkaline high-Ni alloy plating system was chosen to meet these requirements.

This paper will discuss the operational parameters as well as deposit properties that will allow Zn-Ni deposits to undergo forming processes. The properties of the Zn-Ni deposits that were considered important to post-plate forming were alloy composition, stress, hardness and ductility. The process or plating bath parameters that were investigated were the type of chelate or mixed chelates, secondary brightener concentration and current density.

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Figure 1 - Examples of plated pre-formed parts.

#### **Coordination chemistry**

A coordination complex is the association of an ion or molecule, a ligand, with a metal ion. For an ion or molecule to function as a ligand, it must have at least one pair of electrons to donate to the metal ion. By sharing these lone pair electrons, a metalligand coordinate or chelate bond is formed. Common ligands are the halide ions, the anions of various oxo acids (such as nitrate, nitrite, carboxylate and sulfate), and neutral molecules with typical donor atoms being oxygen, nitrogen or sulfur. Examples of neutral ligands are ammonia, methylamine, water, methanol and dimethylsulfoxide.

Ligands such as fluoride, which can form one coordinate bond, are classified as unidentate. Compounds with more complex structures may have more than one donor atom. Compounds which can form two or more coordinate bonds are termed polydentate or multidentate chelates.

A ligand that binds through two sites is classified as bidentate, and three sites as tridentate.

Ethylenediamine, which has two amino groups, is bidentante. Citric acid has three carboxylic acid groups, and the anion is tridentate. One of the most commonly used chelating agents is

ethylenediamine tetraacetic acid or EDTA. The anion of EDTA can be hexadentate since it can form coordinate bonds through the two nitrogens and the four carboxylate oxygens. Multidentate chelates tend to form more stable metal ion complexes than unidentate ligands.

Alkaline Zn-Ni alloy plating systems require the use of one or more chelates to complex the nickel and prevent nickel hydroxide from precipitating. Chelates are not required to keep the zinc(II) cation soluble in highly alkaline media, since zinc(II) forms the soluble tetrahydroxyzincate ion. However, chelates are still able to complex zinc in alkaline solutions depending on the magnitude of the stability constant relative to hydroxide stability constants.

In this study, several effects of coordination chemistry on plating thickness, alloy composition, deposit stress, ductility and hardness were examined. The effect of chelate denticity was explored. Bi-, tri-, tetra- and penta-dentate chelates were utilized. Several donor atom classes also were utilized. Additionally, the mole ratio of chelate-to-total metal ion concentration was varied. For brevity of this paper, only data from selected chelate systems are presented.

#### Hull cell studies

Hull cell plating studies were used to determine which parameters affect plating thickness and alloy composition. In the following series of response surfaces, the effect of secondary brightener concentration and chelate-to-metal mole ratio on plating thickness can be seen.





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Obviously, current is the primary plating factor affecting plating thickness, but the secondary brightener concentration also is an important factor, as can be seen in Fig. 2. However, the chelate-to-metal mole ratio does not have a large effect.



Figure 2 - Thickness as a function of chelate ratio and secondary brightener concentration at (a) 7.0 A/ft<sup>2</sup>; (b) 20 A/ft<sup>2</sup>; (c) 40 A/ft<sup>2</sup> and (d) 70 A/ft<sup>2</sup>.

The effect of secondary brightener concentration and current density on alloy composition is shown in Fig. 3. The primary factor affecting alloy composition is secondary brightener composition. However, when the chelate-to-metal mole ratio is sufficiently large, the effect of secondary brightener concentration can be minimized.



Figure 3 - Alloy composition as a function of secondary brightener concentration and current density at (a) a 0.75 chelate-tometal ratio and (b) a 1.50 chelate-to-metal ratio.





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#### Deposit stress

Deposit stress of the various Zn-Ni alloy plating systems was measured using the bent strip technique. A Deposit Stress Analyzer (obtained from Specialty Testing & Development Co. of

York, PA) was used for all stress measurements. In the bent strip technique, a thin strip of metal is plated on one side. A protective lacquer coating prevents plating to the opposite side (Fig. 4a). Any stress in the plated deposit will cause curvature of the test strip (Fig. 4b). After plating, the spread in the legs of the test strip is measured (Fig. 4c). Stress is a function of the plating thickness and the deflection.



Figure 4 - The bent-strip method for measuring deposit stress: (a) stop-off lacquer application; (b) effect of compressive and tensile stresses; (c) deposit stress analyzer.

For a Zn-Ni plating system using a mix of two different chelates,  $C_1$  and  $C_2$ , the effect of current density and secondary brightener concentration on stress can be seen in Fig. 5. For this mixed chelate system, the stress decreased with current density and secondary brightener concentration. However, with this system, the Zn-Ni alloy underwent a dramatic change in stress as the deposit aged from compressive towards tensile. In some cases, the stress change was very rapid, and occurred within 15 to 30 minutes. For other conditions, the change was less rapid, but the stress change typically reached equilibrium within 24 hours after plating. For some conditions, the change resulted in a complete reversal of the stress from compressive to tensile. This radical change was unexpected.



Figure 5 - (a) Initial and (b) equilibrium deposit stress as function of current density and secondary brightener.

When a single chelate is used instead of the mixture of chelates, the net change in stress was much less. The following response surfaces in Figs. 6 and 7 show the effect of chelate-to-total metal mole ratio and secondary brightener concentration on the initial and equilibrium stress. Both the  $C_1$  and  $C_2$  chelate systems show that the stress change is minimized at a chelate-to-metal mole ratio of approximately 1.5:1.





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Figure 7 - (a) Initial and (b) equilibrium deposit stress for the C<sub>2</sub> system as a function of chelate-to-metal ratio and secondary brightener concentration.

For post-plate forming operations, keeping the stress in the deposit as close to neutral as possible is critical. Since the  $C_2$  chelate is more effective than the  $C_1$  system at reducing stress change, it is, therefore, the system of choice.

When the Zn-Ni alloy plating bath contains sufficient chelator relative to the amount of total metal, the [Ni]/[Ni+Zn] concentration ratio controls the alloy composition of the plated deposit.

Not unexpectedly, the nickel content in the alloy affects deposit stress. The effects of alloy composition and secondary brightener concentration can be seen in Fig. 8. Deposit stress is minimized when the deposit contains 12-15% Ni, preferably 13-14% Ni.



Figure 8 - (a) Initial and (b) equilibrium deposit stress for the C<sub>2</sub> system as a function of nickel-to-zinc ratio and secondary brightener concentration.





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#### Hardness

Hardness also was considered a deposit property that would affect post-plate forming processes. As can be seen in Fig. 9, the secondary brightener concentration does not affect hardness. As can be seen in Fig. 10, however, the chelate-to-total metal mole ratio significantly impacts the deposit hardness. From a deposit hardness standpoint, the chelate-to-metal mole ratio should be greater than 1.2:1 to minimize hardness.



Figure 9 - The effect of secondary brightener concentration on Vickers hardness.



Figure 10 - The effect of chelate-to-metal ratio and secondary brightener concentration on Vickers hardness.

#### Ductility

The ductility of the Zn-Ni alloy deposit was evaluated by a mandrel bend test. By bending a plated test panel over a defined radius, the elongation and adhesion of the plated layer can be measured. The use of a conical mandrel enables testing of a range of bending radii simultaneously.

The BYK Conical Mandrel Bending Tester (obtained from Paul N. Gardner Company, Inc.,

Pompano Beach, FL)(Fig. 11a) that was utilized in this test has an 8-inch (20-cm) long conical mandrel with a diameter decreasing from 1.5 inches (38 mm) to 0.125 inches (3.2 mm). Test panels were clamped into the mandrel bend tester. A drawbar was used to bend the test panels 180° around the mandrel (Fig. 11b). Test panels were marked at several specific mandrel diameters, and then were examined under 10× magnification for cracking or detachment from the substrate. Test panels were plated at a constant current density. Typical bent test samples are shown in Fig. 11c.

The results of bend testing can be seen in the Figs. 12 and 13. In Fig. 12, the minimum mandrel diameter, where no cracking was observed, is plotted versus various bath parameters. Thus, the smaller bend diameter value correlates to more ductility. For the  $C_1$  and the  $C_1+C_2$  chelate systems, the ductility is independent of current density, which only has a minor effect on ductility. The ductility is slightly higher at high current densities. This trend is similar to that found for deposit stress.

The type of chelate system, however, has a large effect on the ductility. In Fig. 13, the effect of the chelate-to-total metal mole ratio and secondary brightener concentration on bend diameter can be seen. Regions of this response surface show that the  $C_2$  chelate can achieve significantly better ductility as compared to the  $C_1$  and  $C_1+C_2$  chelate systems.

Both the chelate-to-metal mole ratio and the secondary brightener concentration are critical factors affecting ductility. Besides the type of chelate system, the secondary brightener concentration is the most important factor affecting ductility. The secondary brightener concentration must be keep below 15 g/L, preferably below 10 g/L. The chelate-to-metal mole ratio has a secondary effect on ductility. However, the ration must be keep above 1.2:1 for optimum results.





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Figure 11 - Bend test procedure: (a) conical mandrel bend tester; (b) test panels being bent over the conical mandrel; (c) examples of bent test panels.



Figure 12 - The effect of current density on ductility for the  $C_1$  and  $C_1+C_2$  systems.



Figure 13 - The effect of chelate-to-metal ratio and secondary brightener concentration on ductility.

Test panels from the various chelate systems were examined after bending under higher magnification using scanning electron microscopy (SEM). SEM micrographs of the  $C_1+C_2$  system at 500× and 5,000× can be seen Fig. 14, and the micrographs of the  $C_1$  system can be seen in Fig. 15. Both of these systems produce a somewhat amorphous deposit. This type of deposit is very fragile. Any type of post-plate manipulation will produce cracking and dusting. In Figs. 14a and 15a without any secondary brightener, cracks can be seen in the base layer below the amorphous top layer. The addition of secondary brightener helps to refine the grain structure, but the columnar grains are still quite large, not tightly packed and friable.





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Figure 14 - Electron micrographs of C<sub>1</sub>+C<sub>2</sub> chelate system plated at 10 A/ft<sup>2</sup> (0.93 A/dm<sup>2</sup>): with 0 g/L secondary brightener at (a) 500× and (b) 5,000×; with 10 g/L secondary brightener at (c) 500× and (d) 5,000×.

SEM micrographs of the  $C_2$  system at 500× and 10,000× can be seen Fig. 16. This system produced a much more refined grain structure. Comparing Figs. 14b and 15b to Fig. 16b, the finer grain structure of the  $C_2$  system can be seen in the 10,000× micrographs as compared to the 5,000× micrographs of the  $C_1$  and  $C_1+C_2$  systems. The addition of secondary brightener to the  $C_2$  system caused some small defects in the surface. These defects appear to be caused by folding of some the columns over the top of adjacent columns to relieve stress as the deposit is compressed during the bending process. In Fig. 15d, one of these defects was examined under high magnification, and the defect does not appear to expose the base substrate.

#### Conclusions

The objective of this study was to develop a Zn/Ni alloy plating system suitable for post-plate fabrication. To achieve this objective, the ductility of the system had to be increased while reducing stress, reducing hardness, and maintaining appearance. The following operating parameters were found to be important to meeting these goals: the donor type and denticity of the chelate, the chelate-to-total metal mole ratio and the secondary brightener concentration.

The type and denticity of the chelate was the most critical. The chelate was found to affect appearance, stress, and ductility significantly. Selecting the wrong chelate can cause the Zn-Ni deposit to appear dark-grey to black in color and amorphous in structure. This causes stress and ductility issues in the deposit.

In addition to the type of chelate used for Zn-Ni alloy plating, the chelate-to-total metal mole ratio, ([Chelate]/([Zn]+[Ni]), is critical to hardness and ductility. It also has an impact on minimizing stress. The [Chelate]/([Zn]+[Ni]) ratio should be maintained between 1:1 to 1.5:1 for best deposit properties.





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Besides the type of chelate employed, the secondary brightener concentration has the largest effect on ductility and plating thickness. The secondary brightener concentration must be optimized for stress reduction.

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Figure 15 - Electron micrographs of C<sub>1</sub> chelate system plated at 10 A/ft<sup>2</sup> (0.93 A/dm<sup>2</sup>): with 0 g/L secondary brightener at (a) 500× and (b) 5,000×; with 10 g/L secondary brightener at (c) 500× and (d) 5,000×.





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Figure 16 - Electron micrographs of C<sub>2</sub> chelate system plated at 10 A/ft<sup>2</sup> (0.93 A/dm<sup>2</sup>): with 0 g/L secondary brightener at (a) 500× and (b) 10,000×; with 5 g/L secondary brightener at (c) 500× and (d) 10,000×; with 10 g/L secondary brightener at (e) 500× and (f) 10,000×.





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#### About the author



**Dr. Len Diaddario** is a Senior Research Chemist in the Research & Development Laboratory at Pavco Inc. Len holds a B.S. in Chemistry from John Carroll University and a Ph.D. in Analytical Chemistry from Wayne State University. Len has over 30 years of industrial research experience in product and process development, including 15 years in metal finishing with Pavco Inc. Len's research interests include zinc, nickel, chromium and alloy plating along with various aspects of electrochemistry and chromatograph.