# Zinc-Nickel Alloy Plating Utilizing Boxed Anode Technology

Rob Frischauf, Taskem, Inc., Brooklyn Heights, OH

Conventional alkaline zinc/nickel alloy plating processes typically contain complexors such as polyamines, which upon electrolysis form an undesirable side product, cyanide. The use of membrane technology has been investigated to eliminate its formation. By eliminating the anode from the solution with a box-membrane apparatus, the effective formation of the cyanide is halted. This exhibits improvement in several aspects of the plating performance as well as deposit appearance.

For more information, contact: Rob Frischauf Taskem, Inc. 4639 Van Epps Road Brooklyn Heights, OH 44131

Zinc-nickel alloy plating processes have long been utilized for the protection of automotive components in Europe, Japan, and more recently, the United States<sup>1</sup>. Valued as a replacement for cadmium<sup>2</sup>, the interest in zinc-nickel has increased tremendously in recent years. Conventional processes plate alloys ranging from 5-14% nickel from both alkaline solutions and acid-chloride based electrolytes. The corrosion resistance of higher alloys (12-14% nickel) has been shown to be five times greater than that of unalloyed zinc deposits<sup>3</sup>. The advantages of alkaline electrolytes are several fold: inherent non-corrosivity and non-activation of non-plated recesses and low current-density areas, single rectification can be used as opposed to separate zinc and nickel rectifiers, and the alloy composition is more consistent than that of acidchloride electrolytes<sup>1,4,5</sup>. Conversely, alkaline baths have lower efficiency and require much stronger complexors to solublize nickel salts, which can make waste treatment considerably more involved.

In order to complex nickel at high pH, alkaline electrolytes generally contain complex mixtures of polyamines. For several years, it has been suggested that during electrolysis, polyamines can form breakdown products at the anode, among which is cyanide<sup>6</sup>. Not only does this raise an environmental issue, but it has a negative effect on bath performance, alloy composition, and deposit appearance. This paper will examine the mechanism of the formation of cyanide, discuss its isolation and characterization, and outline steps to prevent the formation by using a box-membrane apparatus.

### **Experimental Procedure**

Plating tests with direct anodes were performed on the electrolyte using 2-liter cells. A steel Q-panel<sup>\*</sup> was used for a cathode complimented by 2 nickel and 2 zinc anodes. Figure 1 shows the configuration for experiments using the boxmembrane apparatus. A 4-liter cell was used, with a nickel-plated Q-Panel used as an anode, submerged in an alkaline anolyte. Both experiments were performed on the bath composition shown in Table 1. The bath was electrolyzed at 5 amps for

\*Q-Panel, 26200 First Street, Cleveland, OH 44145 Stock No. QD-35, 0.5x76x127 mm (0.02x3x5") 6 hours (30 AH) per day, maintaining zinc, nickel, caustic soda, and complexor levels.

In a separate test a reaction to prepare nickel

cyanide was carried out using 100 mls. of the bath formula from Table 1, to which 10 g/lsodium cyanide (NaCN) was added. After 24 hours. a precipitate was collected on Whatman #1 filter paper, washed with de-ionized water, and dried. Spectral analysis of the precipitates was performed on a Mattson 4020 Galaxy Series FTIR with dried



Figure 1 – Configuration using box-membrane apparatus.

samples being ground, mulled with mineral oil, and applied to a zinc-selenide window. The scanning range was set between 400-4000 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution.

Table 1	
c-Nickel Electrolyte	
Concentration	
10 g/l	
3.2 g/l	
106 g/l	
60 g/l	

## **Results & Discussion**

After the solution containing zinc and nickel anodes had been electrolyzed for 240 AH, a red precipitate was observed in the cell. The bath was filtered through Whatman #1 filter paper and the precipitate washed with de-ionized water and dried. The IR spectrum is shown in Figure 2.

Similar analysis was performed on the precipitate prepared from the addition of sodium cyanide to a fresh solution, with the results shown in Figure 3. It can be observed that the spectral traits, particularly the peaks in the 2115-2120 cm<sup>-1</sup> range, indicate that the compounds are a nickel cyanide complex.

During electrolysis, a metal anode, used directly in solution, acts as a site for the oxidation of polyamines to nitriles. As shown in Figure 4, the conversion is not direct, but requires nickel ions to



Figure 2 – FTIR spectrum of precipitate after 240 AH electrolysis using direct anodes.



Figure 3 – FTIR spectrum of precipitate formed through addition of sodium cyanide to plating solution.

be present. Nickel then cyanide is precipitated through the alkaline hydrolysis of the nitrile complex. Further experiments indicate the formation of nickel cvanide to be on the order of 10 mg/AH. \* The consumption rate for the polyamine was calculated to be 30-40 mg/AH. As the



*Figure 4 – Mechanism for formation of nickel cyanide* 

50-40 mg/AH. As the

cyanide concentration in the solution increases, an iridescent haze developed in the  $1.1-1.7 \text{ A/dm}^2$  (10-15 ASF) range.

#### **Box-Membrane Apparatus**

By eliminating the anode from the electrolyte, conversion of polyamines to nitriles is halted, breaking the pathway for cyanide formation. The current system requires a selectively permeable membrane to be inserted between the anode and cathode, thus forming an anode compartment containing a conductive *anolyte*. The apparatus is illustrated in Figure 5. The use of membranes to separate anodes from the bulk electrolyte has been seen in many plating applications. Membranes have the ability to transfer current, while inhibiting the transfer of certain ions that are undesirable. An illustration of ion-permeability in the current system is shown in Figure 6.

Many membranes have been tested. however. PTFE based membranes better handle the harsh conditions of the plating process: 1) the material withstand the 📖 can highly alkaline plating solution, 2) resistance

current flow is to minimal. and 3) the transport of only desirable ions across the membrane is permitted. The membrane allows permeation by small cations, such as Na<sup>+</sup>,  $K^+$ , and  $H^+$ , while blocking anions such as  $OH^{-}$ ,  $CI^{-}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$  and large materials, such as polyamines.

Cyanide was not detected during the experiment. Also, the consumption rate of the polyamine complexor





Figure 6 – Permeability of PTFE-based membranes.

\*as measured with Method 9010B of U.S. EPA SW-846

was significantly less than with direct anodes. In fact, the complexor was mostly consumed through drag-out at a rate of 8-10 mg/AH. The deposit remained bright throughout the experiment, with no formation of low-current density hazes.

#### Conclusions

Polyamine complexors in alkaline zinc-nickel plating solutions were oxidized at the anode to form nickel cyanide. Not only did its formation raise environmental concerns, but also the presence of cyanide caused low current-density hazes in the deposit. Additionally, the consumption rate of complexor was elevated.

By using a box-membrane apparatus, several improvements were made: 1) the formation of cyanide was halted, 2) the consumption rate of polyamine complexors reduced significantly, and 3) the deposit appearance was greatly improved over the life of the solution.

#### References

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