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# Effects of novel additives for zinc-nickel alloy plating

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## ABSTRACT

The development of alternative coating material is important for the corrosion life of metals. Improving the corrosion resistance and decorative appearance of zinc-nickel coatings is gaining importance. Related physical properties can be provided by using various chemicals. Tetraethylamine, triethanolamine, gelatin, and *p*-aminobenzenesulfonic are the chemicals used in this study to evaluate corrosion resistance and decorative appearance.

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## 1. Introduction

Metal coating is a method applied to provide corrosion resistance in many industries. The most common metal coating method is zinc plating. Alloy coating with other metals can also be applied to improve the properties of the zinc coating [1,2]. The most commonly applied form is a Ni and Cu coating [3-5]. Zinc-nickel plating is most preferred owing to the corrosion resistance it provides [6,7].

As the Ni concentration increases, the corrosion resistance of zinc-nickel coatings increases. The amount of nickel can increase the corrosion resistance of the pure zinc coating by up to 10 times [8,9]. However, the passivation process also increases the corrosion resistance. In addition, the pore problem that affects the corrosion life of the pure zinc coating can be largely eliminated by nickel plating [10,11].

Another parameter that increases the corrosion resistance is the coating thickness [12,13]. However, increasing the coating thickness requires better running baths and higher chemical consumption [14,15]. This may also require the use of more toxic materials in the zinc and nickel sealing baths [16,17].

Corrosion life has been reported to increase as the alloy coating content increases [18,19]. Chemical additives applied to alloy coatings increased their corrosion life by up to 140 hours in salt water corrosion tests [20-22]. For example, gelatin, ammonium salts, or amine compounds have been added to Mg coating baths to increase corrosion resistance. On the other hand, corrosion resistance of alloy coatings has been increased by passivation methods such as phosphating [23,24] and chromating [25].

In this study, a zinc nickel-plated bath is used to increase the corrosion life of the specific chemicals used for nickel and zinc coatings. For example, as a complexing agent for the nickel coating, tetraethylenepentamine (TEPA), diethylene triamine (DETA) as a complexing agent in the zinc coating, triethanolamine as a zinc coating bath surfactant (TEA), gelatin as a zinc coating bath gloss, and *p*-amino benzene sulfonic acid are used. Furthermore, the optimum zinc-nickel ratio and coating thicknesses have been determined for longer life.

## 2. Experimental

### 2.1. Selection of chemicals

The main concentrations for the zinc-nickel alloy coating bath were 12.5 g/L ZnO, 130 g/L NaOH, and 6.8 g/L $NiSO_4$. In order to optimize the concentrations, different compositions were studied, as discussed in Sections 2.2 and 2.4.

A buffer solution (pH = 10) was prepared and 100 mL of 0.05 M acetic acid and 50 mL of 0.05 M NaOH were used for

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**Table 1.** Test material blocks for determination of NiZn/Fe parameters, plating thickness, and Ni/Zn contents.

| | **NiZn (µm)** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Blocks | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Mean Value (µm) | 7.98 | 7.61 | 11.7 | 10.7 | 10.7 | 5.71 | 5.63 | 17.2 | 10.8 | 13.9 | 21.5 | 14.8 |
| Meas. Time (s) | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Standard dev. (µm) | 0.82 | 1.19 | 4.94 | 0.42 | 1.42 | 0.36 | 0.42 | 6.90 | 0.65 | 0.76 | 1.54 | 0.98 |
| C.O.V. (%) | 10.23 | 15.58 | 10.23 | 3.96 | 13.25 | 6.35 | 7.52 | | 6.00 | 550 | 7.15 | 6.6 |
| Number of readings | 8 | 9 | 12 | 4 | 10 | 5 | 5 | 15.9 | 3 | 5 | 5 | 5 |
| Range (µm) | 2.2 | 3.3 | 15.2 | 0.9 | 3.6 | 1.0 | 1.0 | 10.7 | 1.3 | 2.0 | 4.2 | 2.4 |
| Min. reading (µm) | 6.7 | 6.4 | 5.2 | 10.2 | 9.1 | 5.3 | 5.1 | 26.6 | 10.2 | 12.6 | 19.4 | 14.1 |
| Max. reading (µm) | 8.9 | 9.7 | 20.6 | 11.1 | 12.7 | 6.3 | 6.1 | | 11.5 | 14.6 | 23.6 | 16.5 |
| | **Ni (%)** | | | | | | | | | | | |
| Blocks | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Mean Value (µm) | 12.6 | 15.2 | 13.5 | 18.0 | 17.2 | 14.4 | 15.8 | 14.3 | 16.7 | 16.1 | 15.1 | 15.6 |
| Meas. Time (s) | | | | | | | | | | | | |
| Standard dev. (µm) | 0.26 | 0.81 | 0.52 | 0.39 | 0.64 | 0.36 | 0.35 | 1.06 | 0.41 | 0.33 | 0.13 | 0.43 |
| C.O.V. (%) | | | | | | | | | | | | |
| Number of readings | 8 | 9 | 12 | 4 | 10 | 5 | 5 | 8 | 3 | 5 | 5 | 5 |
| Range (µm) | 0.8 | 2.3 | 1.6 | 0.9 | 2.1 | 1.0 | 0.9 | 2.8 | 0.7 | 0.8 | 0.3 | 1.1 |
| Min. reading (µm) | 12.2 | 14.3 | 12.7 | 81.5 | 16.5 | 14.0 | 15.5 | 13.1 | 16.5 | 15.6 | 15 | 15.2 |
| Max. reading (µm) | 13.0 | 16.6 | 14.2 | 82.4 | 18.6 | 14.9 | 16.4 | 15.8 | 17.2 | 16.4 | 15.3 | 16.3 |
| | **Zn (%)** | | | | | | | | | | | |
| Blocks | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Mean Value (µm) | 87.4 | 84.8 | 86.5 | 82.0 | 82.8 | 85.6 | 84.2 | 85.7 | 83.9 | 83.9 | 84.9 | 84.4 |
| Meas. Time (s) | | | | | | | | | | | | |
| Standard dev. (µm) | 0.26 | 0.81 | 0.52 | 0.39 | 0.64 | 0.36 | 0.35 | 1.06 | 0.33 | 0.33 | 0.13 | 0.43 |
| C.O.V. (%) | | | | | | | | | | | | |
| Number of readings | 8 | 9 | 12 | 4 | 10 | 5 | 5 | 8 | 3 | 5 | 5 | 5 |
| Range (µm) | 0.8 | 2.3 | 1.6 | 0.9 | 2.1 | 1.0 | .09 | 2.8 | 0.7 | 0.8 | 0.3 | 1.1 |
| Min. reading (µm) | 87.0 | 83.4 | 85.8 | 81.5 | 81.4 | 85.1 | 83.6 | 84.2 | 82.8 | 83.6 | 85 | 83.7 |
| Max. reading (µm) | 87.8 | 85.7 | 87.3 | 82.4 | 83.5 | 86.0 | 84.5 | 86.9 | 83.5 | 84.4 | 84.7 | 84.8 |

the analysis. The solution was then titrated with 0.1 M EDTA using 5 mL of sodium cyanide, 5 mL of formaldehyde, and 0.1 g of the omechrome black T indicator. For the bathing operation, a 0.7 dm$^2$ iron sheet was cleaned with 10% sulfuric acid and coated at 30 °C for 10 min.

### 2.2. NaOH analysis

For the NaOH analysis, 5 mL of the bath sample, 100 mL of distilled water, and two drops of indigo carmine indicator were combined in a flask. The solution was then titrated with 0.05 M HCl and consumption was measured (Total NaOH consumption = 8 g/L HCl).

### 2.3. ZnO analysis

A solution was prepared for ZnO analysis by mixing 5 mL of the plating bath with 1 mL of HCl, 20 mL of buffer solution, and 10 mL of distilled water, where pH = 10.

### 2.4. NiSO$_4$ analysis

Atomic absorption spectrometry was used for NiSO$_4$ analysis and 1, 3, and 5 ppm Ni$^{2+}$ standard solutions were used for calibration. Bath solutions containing 1500 ppm Ni$^{2+}$ were diluted 500 and 1000 times.

### 2.5. Surface analysis

For the purpose of surface analysis, a Jeol 6060 electron microscope was used with 100 nm resolution, 20.0 kV high voltage separation, 9.8 mm working distance, and 50000× magnification. For fracture strength, a force of 14.701 N was applied to the surface of the coating in accordance with the ASTM F519-10 standard [26,27].

In order to measure the corrosion resistance of the coated materials, salt spray tests were carried out at 35 °C, pH = 6.5-7.2, and 5% NaCl according to the ASTM B 117 standard. Corrosion resistance measurements were taken, and the effects of each of the complexing agents on the alloy bath were observed. According to this procedure, the life of zinc-zinc plated TEPA alloy was measured as 150 hours, TEA added 175 hours, and the TEPA/DETA/TEA combination added 200 hours.

Color analysis was performed as another parameter to evaluate the coating quality. The most important factor determining the quality of the coating is the mixture of *p*-aminobenzene sulfonic acid, 1-(3-sulfopropyl)pyridinium betaine (PPS), propargyl alcohol ethoxylate (PME), and gelatin, used for brightening purposes in the alloy coating bath. The color analysis was performed at 425 nm (the standard) and analyzed with a CIE L * a * (Macbeth CMC-CE7000-XL0339) and CIE Standard Illuminator D65 (equivalent to 6500 K illumination). Two measurements were taken from each sample to confirm the reproducibility and accuracy of the analysis.

### 2.6. X-Ray analysis for alloy coating thickness

X-ray analysis (Fischer Instruments GmbH, 2002) was used to understand the effect of the coating thickness of the chemicals used and the electrolytic solution. The results of the analysis are shown in Tables 1-5. Concentrations of the complexing agents used in the bath were analyzed by Cu monochromatic radiation with X-ray diffractometer (Siemens, Model D 5000) λ = 1.5406 Å (35 mA and 40 kV) (Figure 1).

## 3. Results and discussion

In this study, the effects of pentaamines, ethylene diamine, and ethanol amines added to the zinc nickel alloy coating bath were investigated. Because the reduction potentials of Zn and Ni were high in the electrolysis bath, the chemical materials used did not cause any pollution. For easy dissolution of complexing materials in alkaline environments, the solution medium has to be alkaline [28,29]. For this reason, organic hydroxyl and ammonium salts are used for pH adjustment of zinc-nickel alloy coating baths. In addition, the metallic complexing agents must be known in order to be classified according to their efficiency, and thus know their rate of dissolution in an electrolyte bath.

**Table 2.** Plating thickness of the NiZn/Fe blocks and corresponding Ni and Zn plating percentage.

| | **NiZn (μm)** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Blocks | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Trial 1 | 7.9 | 10.1 | 20.6 | 10.9 | 10.0 | 5.3 | 5.1 | 23.5 | 11.5 | 12.6 | 19.4 | 14.1 |
| Trial 2 | 6.7 | 9.8 | 18.3 | 10.4 | 9.9 | 5.5 | 5.6 | 19.0 | 10.2 | 13.9 | 21.1 | 16.5 |
| Trial 3 | 7.5 | 9.7 | 12.8 | 10.2 | 9.8 | 5.7 | 5.4 | 26.6 | 10.8 | 14.6 | 23.6 | 14.3 |
| Trial 4 | 7.2 | 9.9 | 12.0 | 11.1 | 12.7 | 6.3 | 5.4 | 24.2 | | 13.9 | 22.0 | 14.4 |
| Trial 5 | 8.4 | 11.2 | 9.7 | 10.8 | 12.3 | 5.7 | 6.1 | 10.7 | 10.7 | 14.4 | 21.4 | 14.9 |
| | **Ni (%)** | | | | | | | | | | | |
| Blocks | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Trial 1 | 12.3 | 11.9 | 12.3 | 17.8 | 17.1 | 14.3 | 15.7 | 15.1 | 16.5 | 16.1 | 15.0 | 15.5 |
| Trial 2 | 12.6 | 12.0 | 12.6 | 17.6 | 17.4 | 14.0 | 15.5 | 14.1 | 16.5 | 16.4 | 15.0 | 16.3 |
| Trial 3 | 12.5 | 12.1 | 12.5 | 18.2 | 17.3 | 14.5 | 15.9 | 15.8 | 17.2 | 15.6 | 15.2 | 15.4 |
| Trial 4 | 12.6 | 11.8 | 12.6 | 18.5 | 18.6 | 14.9 | 16.4 | 15.7 | | 16.3 | 15.0 | 15.2 |
| Trial 5 | 12.2 | 12.1 | 12.2 | 18.4 | 17.8 | 14.2 | 15.7 | 13.1 | | 16.3 | 15.3 | 15.4 |
| | **Zn (%)** | | | | | | | | | | | |
| Blocks | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Trial 1 | 87.7 | 87.6 | 87.7 | 82.2 | 82.9 | 85.7 | 84.3 | 84.9 | 83.5 | 83.9 | 85.0 | 84.5 |
| Trial 2 | 87.4 | 87.8 | 87.4 | 82.4 | 82.6 | 86.0 | 84.5 | 85.9 | 83.5 | 83.6 | 85.0 | 83.7 |
| Trial 3 | 87.5 | 87.3 | 87.5 | 81.8 | 82.7 | 85.5 | 84.1 | 84.2 | 82.8 | 84.4 | 84.8 | 84.6 |
| Trial 4 | 87.4 | 87.1 | 87.4 | 81.5 | 81.4 | 85.1 | 83.6 | 84.3 | 84.2 | 84.4 | 85.0 | 84.8 |
| Trial 5 | 87.8 | 87.6 | 87.8 | | 82.2 | 85.8 | 84.3 | 86.9 | 85.8 | 83.7 | 84.7 | 84.6 |

**Table 3.** X-ray analysis results of plating from a bath containing TEPA.

| **Concentration of TEPA (g/L)** | **Ni ratio in Zn-Ni alloy plating (%)** | **X-ray measurement no** |
|---|---|---|
| 10 | 18.0 | 4 |
| 20 | 17.2 | 5 |
| 30 | 15.8 | 7 |
| 40 | 16.1 | 10 |
| 50 | 16.7 | 9 |

**Table 4.** X-ray analysis of plating from a bath containing TEA.

| **Concentration of TEA (g/L)** | **Ni ratio in Zn-Ni alloy plating (%)** | **X-ray measurement no** |
|---|---|---|
| 10 | 15.6 | 12 |
| 15 | 15.2 | 2 |
| 20 | 15.1 | 11 |

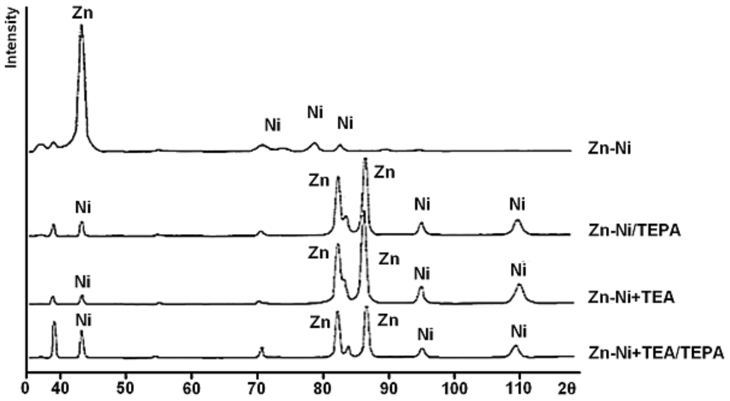


**Figure 1.** X-ray diffraction patterns of Zn-Ni alloy electrodeposits.

The complexing agents help to fill the micro-cracks on the surface of the alloy-forming metals in alloy coating baths. Thus, they increase the corrosion resistance of the metal. However, it has been reported that a high flow density of complex substances can also be effective [30-32].

The coating bath parameters affecting the quality of the metal coating for the alloy coatings are related to the corrosion life, the effect on the microstructure, and the electrolytic potentials of the metals. The electrolytic potential depends on the amount of direct current applied by a regulator [18]. Chemical substances used in the coating bath may cause pollution in the bath. The electric current applied by the regulator can be adjusted to dissolve these substances and avoid pollution.

Selection of complexing agents is important for alloy coating baths because the adhesion performance of metals to the cathode surface can be directly affected by these agents. However, the high current density and the metal concentration in the electrolyte solution also directly affect the coating quality [33,34].

In this study, the performance of the coating materials was evaluated based on their corrosion resistance. Like the contribution of Zn coating to corrosion resistance, this feature reveals the importance of the alloy coating enhancers. The corrosion life was analyzed according to the salt water corrosion test. Initial oxidation of the alloy coating is apparent by its white color owing to the presence of zinc metal. As the applied salt water duration increases, the white color changes to red owing to the presence of iron in the base metal content.

Nickel ions in the alloy coating bath may precipitate as nickel hydroxide. This is a situation that negatively affects the quality of the coating. Salt complexes such as tetraethylene pentamine are used to prevent the precipitation of Ni ions [35,36].

**Table 5.** X-ray analysis of plating performed using a bath containing DETA.

| Concentration of DETA (g/L) | Ni ratio in Zn-Ni alloy plating (%) | X-ray measurement no |
|---|---|---|
| 0.2 | 14.9 | 6 |
| 0.4 | 14.3 | 8 |
| 0.6 | 12.6 | 1 |
| 0.8 | 13.5 | 3 |

**Table 6.** Concentration of added tetraethylenepentamine (TEPA) and resulting metal contents

| TEPA concentration (g/L) | Zn (%) | Ni (%) | Block no |
|---|---|---|---|
| 10 | 82 | 18 | 4 |
| 20 | 82.8 | 17.2 | 5 |
| 30 | 84.2 | 15.8 | 7 |
| 40 | 83.9 | 16.1 | 9 |
| 50 | 83.3 | 16.7 | 10 |

**Table 7.** Concentration of diethylene triamine (DETA) added to the plating bath and resulting metal contents

| DETA concentrations (g/L) | Zn (%) | Ni (%) | Block no |
|---|---|---|---|
| 0.2 | 85.6 | 14.4 | 1 |
| 0.4 | 85.7 | 14.3 | 3 |
| 0.6 | 87.4 | 12.6 | 6 |
| 0.8 | 86.5 | 13.5 | 8 |

**Table 8.** Zn/Ni ratios used in the plating bath *.

| Material | | Ni (μM) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 |
| | | Zn/Ni (μM) | | | | | |
| Zn (μM) | 9.1 | 6.9 | 7.7 | 8.1 | 8.8 | 9.2 | 9.6 |
| | 9.8 | 6.4 | 7.1 | 7.5 | 8.2 | 8.6 | 8.9 |
| | 10.5 | 6.0 | 6.7 | 7.0 | 7.7 | 8.0 | 8.3 |
| | 11.2 | 5.6 | 6.3 | 6.6 | 7.2 | 7.5 | 7.8 |
| | 11.9 | 5.3 | 5.9 | 6.2 | 6.8 | 7.1 | 7.4 |
| | 12.6 | 5.0 | 5.6 | 5.8 | 6.4 | 6.7 | 6.9 |

* Green: optimum plating thickness and brightness; Blue: high nickel concentration, bright plating; Red: low nickel concentration, matte plating.

Owing to the electrolytic potential, the presence of different metal ions in the alloy bath may trigger the formation of metal pollution due to different salt materials on the cathode surface [37]. For this reason, triethanolamine (TEPA) was used to prevent the precipitation of metal ions such as nickel in salt. Different TEPA concentrations (10, 20, 30, 40, and 50 g/L) were evaluated to determine the optimum amounts of the substances used (Table 6). With increases in TEPA concentration, it was determined that the brightness of the alloy coating decreased. At the optimum concentrations of TEPA (up to 30 g/L), the coating thickness on the plate surface varied between 1-5 microns, and a ratio of 15-18% Ni in the alloy coating was determined.

Increasing the TEPA concentration was found to reduce the diffusion rate of metal ions. In order to avoid this problem, it was necessary to use a second complex salt, and DETA (Diethylene triamine) was selected for this purpose. Experiments were carried out with 0.2, 0.4, 0.6, and 0.8 g/L of DETA added to provide a 10 micron coating containing 15% Nickel. Table 7 shows the nickel plating ratio depending on the concentration of DETA. Accordingly, it was determined that the DETA concentration did not change the coating thickness, and the optimum DETA concentration was chosen as 0.6 g/L. The effect of DETA on the coating thickness of the secondary complexing material for nickel plating in zinc-nickel alloy baths is shown in Table 8.

TEA was used as a complexing salt for the zinc metal in the alloy coating. In order to determine the optimum concentration of TEA in the bath, different concentrations such as 10, 15, and 20 g/L (Table 9) were evaluated and the optimum concentration of 10 g/L was chosen, as the Zn diffusion rate did not change significantly.

### *3.1. p-Aminobenzene sulfonic acid, 1- (3-sulfopropyl) pyridinium betaine (PPS), propargyl alcohol ethoxylate (PME), and the effects of gelatin as brightening agents*

The brightening agent content used for the zinc-nickel alloy bath is shown in Table 10. In order to find the optimum concentrations of *p*-aminobenzene sulfonic acid from the components of the brightening agent, it was studied at varying concentrations ranging from 20-40 ppm, and 30 ppm was determined as the optimum concentration. As other components of the brightening agent, 1-(3-sulfopropyl) pyridinium betaine (PPS) 2 g/L, propargyl alcohol ethoxylate 4 g/L (PME), and gelatin (200 ppm) were used. In order to observe the effects of the brightening material, 1, 2, and 3 g/L concentrations were added. SEM images (Figures 2a, 3a, and 4a) indicated matte (Figure 2b), semi-gloss (Figure 3b), and bright (Figure 4b) finishes were produced by the three respective concentrations, and 3 g/L was determined as the optimum concentration.

Zinc-nickel alloy coating has been guided by its corrosion resistance in bathroom performance and by the desired brightness of the metal plate to be coated. The optimum zinc/nickel ratio was determined in the study to obtain a 10 micron zinc coating and the results are listed in Table 10. In this study, the current density is 2 A/dm$^2$, electrolytic efficiency is 65%. The nickel ratio is 15%, and the zinc ratio is 85%, corresponding to 0.108 g of Ni and 0.612 g of Zn, respectively.

The addition of TEPA as a complexing agent in zinc-nickel plating baths was acceptable up to 30 g/L (Table 6). Beyond this limit, the tendency of the nickel ions to adhere to the cathode surface is reduced. In an alloy bath, different metals adhere to the cathode surface and a complexing material is applied for each metal ion. In this study, TEA was used as the complexing material used for the adhesion of zinc metal ions to the cathode surface. The ratio of the zinc metal coating due to the concentrations of TEA is shown in Table 4, indicating little change for different TEA concentrations. DETA was applied as a second complexing salt to optimize the diffusion rate of nickel ions in the alloy coating bath. In the presence of DETA, nickel ions were found to be homogeneously distributed on the cathode surface (Table 5).

**Table 9.** Concentration of triethanol amine (TEA) added to the plating bath and resulting metal contents

| TEA concentration (g/L) | Zn (%) | Ni (%) | Block no |
|---|---|---|---|
| 10 | 84.4 | 15.6 | 2 |
| 15 | 84.8 | 15.2 | 11 |
| 20 | 84.9 | 15.1 | 12 |

**Table 10.** Concentrations of brightening agent containing *p*-aminobenzenesulfonic acid, 3-sulfopropylpyridinium betaine (PPS), propargyl alcohol ethoxylate (PME), and gelatin, and corresponding visual appearance.

| Concentration of brightening agent (g/L) | Image no | Result |
|---|---|---|
| 1 | 2 | Matte |
| 2 | 3 | Semi-matte |
| 3 | 4 | Bright |

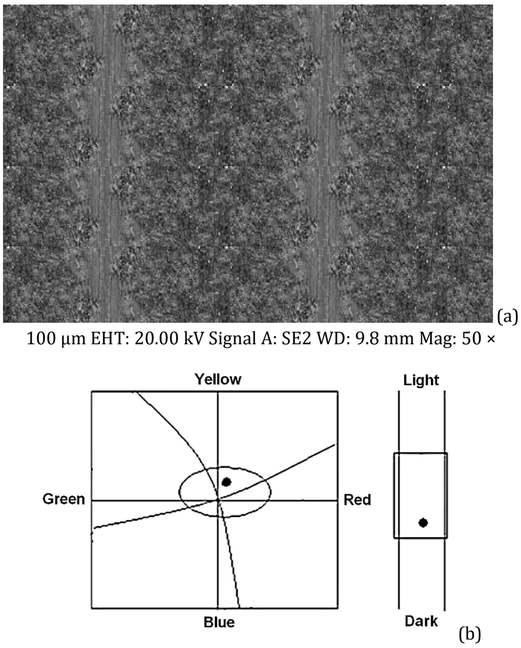


**Figure 2.** (a) SEM image and (b) color measurement of the Zn-Ni plating prepared with 1 g/L of brightening agent.

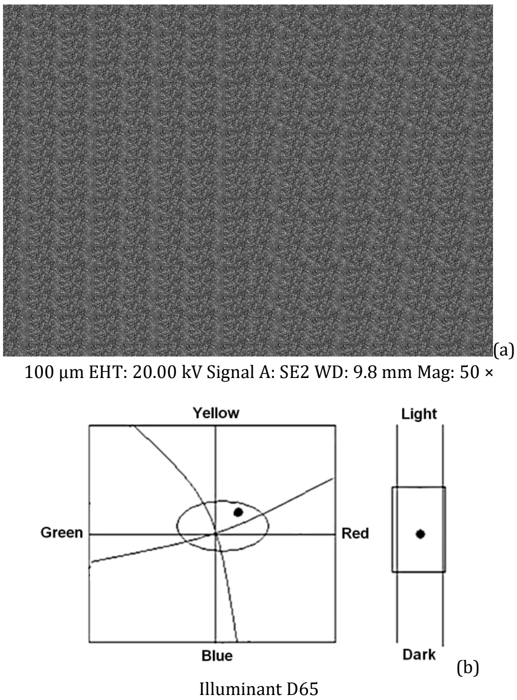
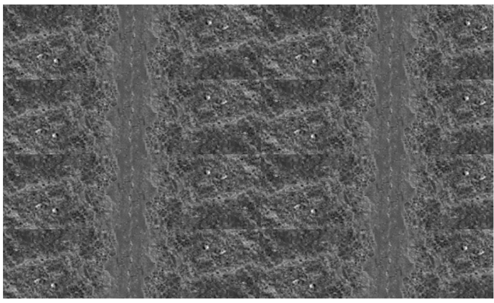
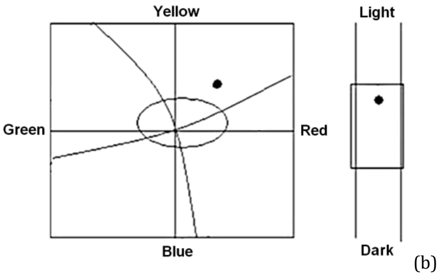


**Figure 3.** (a) SEM image and (b) color measurement of the Zn-Ni plating prepared with 2 g/L of brightening agent.



100 µm EHT: 20.00 kV Signal A: SE2 WD: 9.8 mm Mag: 50 ×



Illuminant D65

**Figure 4.** (a) SEM image and (b) color measurement of the Zn-Ni plating prepared with 3 g/L of brightening agent.

The effect of the chemicals used on the alloy coating was examined for thickness, corrosion resistance, and brightness. TEPA was used as the complexing salt for nickel plating at 20, 30, and 40 g/L concentrations, and 5, 10, and 15 micron coating thicknesses were obtained. For the zinc coating complexing salt, TEA was used at concentrations ranging from 10, 15, and 20 g/L, and the corresponding zinc coating thicknesses were measured as 5, 10, and 15 microns (Table 9).

The SEM images based on brightening agent listed in Table 4 are as shown in Figures 2-4. The results of the addition of 1 g/L of brightening agent for zinc-nickel baths are shown in Figure 2 (matte). The effects of a 2 g/L brightening agent are shown in Figure 3 (semi-matte), and the 3 g/L brightener concentration effects are shown in Figure 4 (bright). As can be seen from the SEM images in Figures 1-3, it was determined that the brightness of the zinc-nickel alloy coating increased as the brightener concentration increased.

## 4. Conclusion

The effects of complexes such as TEA and TEPA on corrosion resistance were investigated for zinc-nickel alloy coating baths. After plating, X-ray, SEM, refraction tests, and the effects of brightening agents such as *p*-aminobenzene sulfonic acid, PPS, and PME on the coating material and the optimum concentration of these substances (3 g/L) were determined. The optimum bath conditions determined were comprised of the a 10 g/L concentration of metallic zinc for the zinc-nickel bath a nickel sulfate concentration of 1.5 g/L in the electrolyte solution, 30.0 g/L of TEPA, 12.0 g/L of TEA, 0.6 g/L of DETA, 20-30 °C bath temperature, 1-3 A/dm$^2$ current density, and 0.3 micron/min coating rate.

With the brightening agent composition suggested in this study, the embrittlement problem for Zn-Ni alloy plating was resolved, enabling its application in the automotive industry. The embrittlement tests indicate that the hardness, microstructure, and tensile compression of the Zn-Ni alloy plating should be considered in future Zn-Ni plating studies.

## Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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