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RESEARCH PAPER

2-Mercaptobenzimidazole, 2-Mercaptobenzothiazole, and Thioglycolic Acid as Additives for Electrolytic Ni Plating

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Abstract In this study, 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid were used as additives in the nickel electroplating bath to improve the physical properties of the plated materials, such as corrosion resistance, electrical resistivity, plating thickness, and adhesion force. Physical tests on the resulting plated materials were conducted using a visible-region spectrophotometer and electron microscope; in addition, the hardness of the nickel plating was investigated using a Falex tester. The problem of wastewater production associated with nickel plating can be eliminated using 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid.

Keywords Electrolytic Ni plating · 2-Mercaptobenzimidazole · 2-Mercaptobenzothiazole · Thioglycolic acid

1 Introduction

Market requirements in the metal plating industry have forced manufacturers and producers to develop new plating processes that increase the corrosion life, electrical properties, hardness, and toughness of the plated materials; attempts have also been made to ensure the widespread application of these processes. The aforementioned requirements necessitate in-depth study of the bath compositions and the nature of the organic compounds used in the process, because these parameters affect plating bath efficiency. In addition, such studies help minimize the equipment/facility cost. Therefore, past research in this regard has largely focused on the development of efficient bath compositions. Three different complex salts were employed to modify the chemical composition of electrolytic plating baths. Gezerman and Çorbacıoğlu (2013, 2014) studied the nickel plating process from the viewpoint of wastewater treatment using an acetylacetonate complex salt (Gezerman and Çorbacıoğlu 2010, 2015).

Several published and patented works on the industrial application of nickel plating have demonstrated the use of electrolyte solutions based on nickel sulfate ($NiSO_4(H_2O)_6$), nickel chloride ($NiCl_2{\cdot}6H_2O$), and nickel sulfamate ($H_4N_2NiO_6S_2$) salts in commercial applications (Tasic et al. 2011). Another prevalent nickel plating process employs a nickel acetate solution; hence, in this study, a nickel plating electrolyte solution is prepared from nickel acetate, nickel chloride, boric acid, and acetic acid rather than using a traditional Watts-type bath (Wendling et al. 2012). An example of an alternative nickel plating bath is the lactate solution prepared by Juzeliunas et al. (2000), wherein lactic acid was used for nickel plating in place of the traditionally used boric acid. The effects of propargyl alcohol (PA), butynediolethoxylate (BEO), and pyridinium sulfobetaine (PPS) on the process requirements for the preparation of a nickel plating bath has been investigated by Patsch et al. (1980). He et al. (2016) investigated the effects of nickel acetate solution in nickel plating baths.

Several research groups have attempted to improve the physical properties of nickel plating on an industrial scale by varying the bath composition using chlorides, nitrates,

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acetate, and nickel methanesulfonic acid (Abubekerov and Diaconescu 2015). Fazli and Bahrololoom (2016) investigated the electrochemical behavior of the Ni–P alloy plating process. Zohari et al. (2015) attempted the fabrication of Ni–TiC nanocomposites in a traditional Watts-type bath as an application of the nickel plating process. As nickel and nickel alloy plating have been widely used in the industry, the investigation by Hadipour et al. (2015) on the thermal resistance of Ni–P plating used as a thermal barrier represents an important development in this area. Yang et al. (2016) used diamine in nickel plating baths. Watts-type nickel plating baths are the most commonly used because the required nickel salts are readily available. This has led to the development of similar processes, such as the nickel sulfite process developed by Lee et al. (2014). The electrolytic and electroless nickel baths developed by Liu et al. (2009) constitute a notable improvement to the nickel plating process in the metal industry. Ni boride plating has also been achieved on boron carbide particles (Zheng et al. 2016), but the variety of platings achieved on multilayer films by Sahin et al. (2013) using the electrolytic method is one of the most important highlights in this field.

In this study, the behavior of 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid as organic additives in electrolytic nickel baths was investigated, and results similar to those obtained using electroless nickel plating baths were observed. The use of these chemicals helps in circumventing the corrosion and adhesion disadvantages as well as the problem of wastewater generation associated with electrolytic nickel plating baths.

2 Experimental Procedure

In this study, three different chemicals were used in the electrolytic Ni-plating baths. The crystal structures and micrographs of the coated materials were evaluated to determine the ideal composition.

2.1 Compounds Used in the Experiments

2-Mercaptobenzimidazole, 2-mercaptobenzothiazole sodium salt, and thioglycolic acid were obtained from Merck, Istanbul, and used in the study.

2.2 Bath Solutions Used for Ni Plating

The acidic bath used in electrolytic Ni plating was prepared from two stock solutions (Tables 1, 2). Two baths of 75 and 1000 mL were prepared from these two solutions. The pH was adjusted to 4.8, and the solutions were heated to 90 °C under working conditions.

Table 1 Chemical composition of the first main solution in a Ni-plating bath

Chemical composition	CAS no.	Concentration (g/L)
Distilled water	7732-18-5	750
Nickel sulfate (99.9%)	7786-81-4	200
Sulfuric acid (99.9%)	7664-93-9	50

Table 2 Chemical composition of the second main solution in a Ni-plating bath

Chemical compound	CAS no.	Concentration (g/L)
Distilled water	7732-18-5	200
Potassium hydroxide (99.9%)	1310-58-3	200
Maleic anhydride (99.0%)	108-31-6	5
Lactic acid (90.0%)	50-21-5	100
Glycolic acid (98.0%)	79-14-1	100
Sodium acetate (99.9%)	127-09-3	250
Sodium hypophosphite (99.9%)	10039-56-2	145

2.3 Electroplating Procedure

Before plating, the substrate was cleaned, dried, weighed, and labeled. After drying, the samples were immersed in 2% sulfuric acid for 2–5 s, rinsed with water, and placed in the Ni-plating bath. Plating was performed at 90 °C for 10 min under a current density of 0.3 A/cm^2. After plating, all samples were rinsed with tap water, dried, and weighed. The pH was then checked and Ni analysis was conducted. Twelve stainless steel substrates were plated, and the plating ratio for each plate was calculated. Four plating baths were prepared. Plating baths 1–4 were prepared by diluting 75 mL of the bath solution to 1 L. The bath compositions and plating results for each bath are shown in Tables 3, 4, 5 and 6. Representative samples from the selected substrates were imaged under a scanning electron microscope (SEM), and the results are shown in Figs. 1, 2, 3 and 4.

2.4 Ni Analysis

10 mL of the bath solution, 100 mL distilled water, 5 mL ammonia, and approximately 0.5 g murexide were placed in an Erlenmeyer flask. The solution was immediately titrated with ethylenediaminetetraacetic acid (EDTA) until a purple color was observed, and the consumption of EDTA (S) was recorded. The consumption of EDTA (S) was converted to the concentration (g/L) of metallic Ni using the following equation (Gezerman and Çorbacıoglu 2015):

Table 3 Plating performed in bath solution No.1 and results

Material no.	Chemical additive	Weight before plating (g)	Weight after plating (g)	Plating speed (μm/h)
01	1.0 mL 2-mercaptobenzimidazole	35.2589	35.2589	0
02	1.0 mL 2-mercaptobenzothiazole	36.0253	36.0253	0
03	1.0 mL thioglycolic acid	34.9852	34.9852	0

Table 4 Plating performed in bath solution No.2 and results

Material no.	Chemical additive	Weight before plating (g)	Weight after plating (g)	Plating speed (μm/h)
04	2.0 mL 2-mercaptobenzothiazole	32.1256	33.8974	26.18
05	2.0 mL 2-mercaptobenzimidazole	32.5412	33.9632	31.96
06	2.0 mL thioglycolic acid	33.4123	34.2589	25.67

Table 5 Plating performed in bath solution No.3 and results

Material no.	Chemical additive	Weight before plating (g)	Weight after plating (g)	Plating speed (μm/h)
07	3.0 mL thioglycolic acid	31.4757	32.5289	0.31
08	3.0 mL 2-mercaptobenzimidazole	33.9652	34.0972	11.62
09	3.0 mL 2-mercaptobenzothiazole	31.8231	31.8231	0

Table 6 Plating performed in bath solution No.4 and results

Material no.	Chemical additive	Weight before plating (g)	Weight after plating (g)	Plating speed (μm/h)
10	4.0 mL thioglycolic acid	31.6235	31.8964	0.32
11	4.0 mL 2-mercaptobenzimidazole	33.6598	33.8963	13.62
12	4.0 mL 2-mercaptobenzothiazole	34.4585	34.4585	0

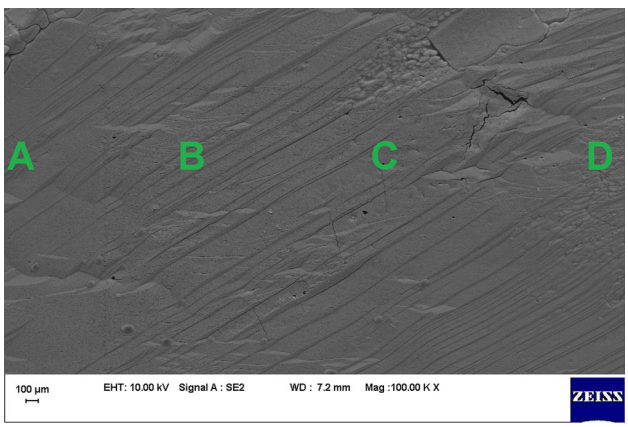


Fig. 1 SEM image of plated material (3 mL/L of 2-mercaptobenzimidazole + 4 mL/L of thioglycolic acid + 2 mL/L of 2-mercaptobenzothiazole in Ni-plating bath)

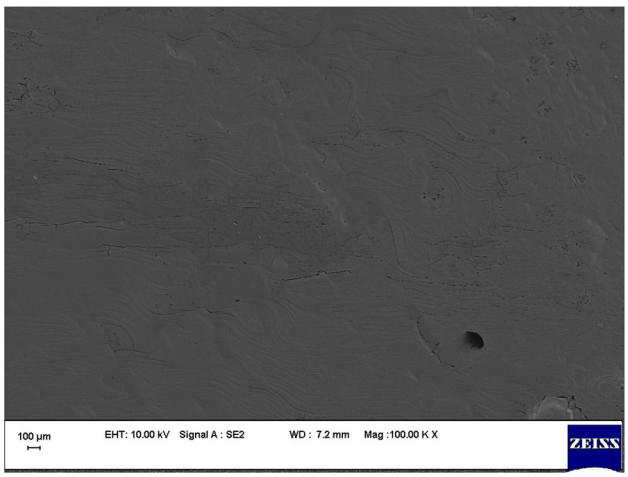


Fig. 2 SEM image of plated material (3 mL/L of 2-mercaptobenzimidazole in Ni-plating bath)

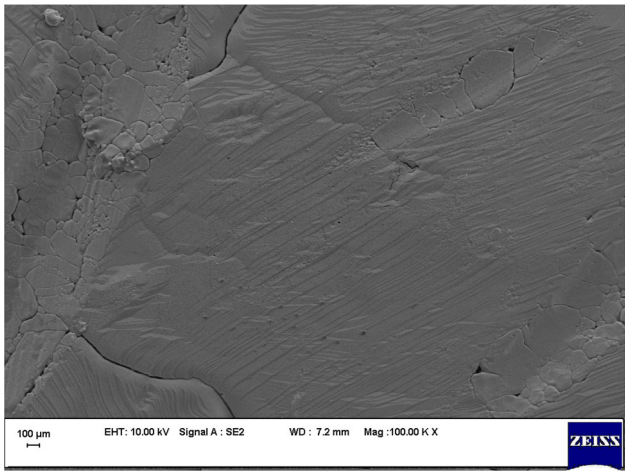


Fig. 3 SEM image of plated material (4 mL/L of thioglycolic acid in Ni-plating bath)

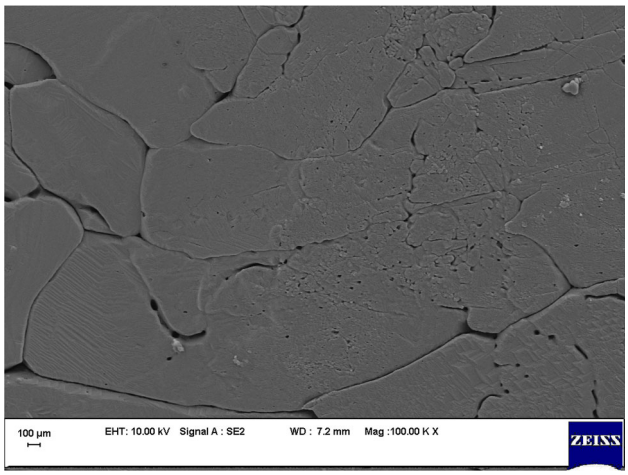


Fig. 4 SEM image of plated material no.4 (2 mL/L of 2-mercaptobenzothiazole in Ni-plating bath)

$(S) \times 0.587 =$ g/L metallic Ni.

The pH decreased as the plating progressed and hence was adjusted using dilute ammonia. Ni sulfate and reduction solutions were prepared for replenishing the material lost during electroplating. For 1 g/L Ni, 10 mL of the Ni sulfate solution was added. After this addition, for each 10 mL of the Ni sulfate solution, 8 mL of the reduction solution was added.

2.5 Replenishing Solutions

Buffer solutions were prepared to replenish the basic components in the Ni-plating bath. The bath was composed of two main solutions: the Ni sulfate solution and the hypophosphite solution. This buffer solution is known as the reduction solution. Ni sulfate (45 g) was diluted in distilled water to 100 mL. This solution was used for replenishing Ni in the plating bath. The compounds shown in Table 7 were mixed in a beaker and diluted to 100 mL. The resulting solution was used for replenishing the hypophosphite.

3 Results and Discussion

3.1 Physical Properties of Ni-Plated Layer

Electrolytically plated Ni materials have a glassy and homogeneous metallic structure, known as metallic glass, in which microvoids are absent. Heat treatment, however, results in the formation of microvoids (Yu and Kyoungdoc 2015). The amount of phosphorus, which depends on the chemical composition of the bath, changes the plating rate, layer formation, and mechanical strength. Hence, the structure of the plated Ni layer also changes. The layer structure of the electrolytically plated Ni was investigated by shear tests (Dage Series 4000 Bond tester) (Yu and Kyoungdoc 2015). The shear height was determined to be 100 µm at a shear rate of 550 µm/h. After shear tests, the fracture surfaces were investigated using SEM (Zeiss Supra 55).

3.2 Plating Thickness

Uniform plating layers with the required thicknesses between 2.5 and 25 µm can be achieved. For parts that require higher corrosion resistance, a plating thickness of 25–75 µm is preferred. The surface roughness increases as the plating thickness increases. The thickness of the deposited electrolytic Ni plating was measured using an X-ray apparatus (Fischer Instruments GmbH, 2002); the results are shown in Table 8.

3.3 Uniformity of the Plated Ni Layer

Uniform plating is important for achieving the desired material performance. During electroplating, the thickness changes depending on the material configuration, geometry, and distance to the anodes (Gezerman and Çorbacıoğlu 2010). It is therefore possible to achieve a uniform plating thickness on every part of the material through electrolytic plating (Tasic et al. 2011). In the present study, the plating thicknesses were uniform over the entire material surface. As such, these conditions are suitable for ensuring plating uniformity on the surface. As shown in Fig. 1, four different points were selected for SEM imaging of the plated material. The thicknesses measured at these points were similar for the entire surface of a sample (Table 9).

Table 7 Components of a reduction solution

Chemical compound	CAS No.	Concentration (g/L)
Potassium hydroxide (99.9%)	1310-58-3	10
Maleic anhydride (99.0%)	108-31-6	0.5
Lactic acid (90.0%)	50-21-5	6.7
Glycolic acid (98.0%)	79-14-1	6.7
Sodium acetate (99.9%)	127-09-3	6.7
Sodium hypophosphite (99.9%)	10039-56-2	16.7
2-Mercaptobenzimidazole (98.0%)	583-39-1	
2-Mercaptobenzothiazole (99.0%)	149-30-4	
Thioglycolic acid (98.0%)	68-11-1	

Table 8 Interdependence of physical parameters in the plating process

Adhesion force (kg/cm^2)	Thickness of the Ni plating (μm)
0	0
2	10
2.2	11
2.4	12
2.6	12
2.8	14
3.0	15

Table 9 Selected points in the plated material in Fig. 1

Signed point	Thickness of the Ni plating (μm)
A	10.5
B	11.1
C	10.7
D	10.3

3.4 Melting Point

Electrolytically plated Ni is a eutectic alloy that has a wide range of melting points. The change in the melting range depends on the phosphorus content of the alloy: as the phosphorus content decreases, the melting range increases. The thermal properties of electrolytic Ni are different from those of pure Ni. One such difference is the high-temperature resistance to oxidation. The melting point of pure Ni is 1455 °C. However, the melting point of electrolytic Ni decreases significantly when different compounds are added to the plating bath. In this study, the melting point of electrolytic Ni that was plated from a bath containing 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid was determined to be 1060 °C according to the refractory-metallized areas method (Feng et al. 2015).

3.5 Density

The density of electrolytic Ni decreases as the phosphorus content increases. The densities of electrolytic Ni with low and high phosphorus contents were 8.5 and 7.75 kg/cm^3, respectively (Tasic et al. 2011). In this study, the density of the electrolytic Ni plating was measured using the associated dimensional changes (Xie et al. 2015). The thickness of the plated Ni was between 10 and 15 μm on the thin side. The mass and dimensions of the test material were measured using a three-coordinate measuring machine. The plating thickness was determined under a graduated-scale microscope after metallographic polishing. In this study, the density of the plated electrolytic Ni plating was found to be in the range of 7.01–7.15 g/cm^3.

3.6 Electrical Resistivity

The change in the electrical properties of the substrate depends on the Ni-plating layer. Layers that have a high phosphorus content are less conductive than copper. The resistivity of a layer with low phosphorus content was 20 μΩ cm (Cao et al. 2015). For applications that require low electrical resistivity, thin plating layers are deposited. Heat treatment and bath composition can affect resistivity. Heat treatment of the Ni layer resulted in phosphorous precipitation and a corresponding doubling of the conductivity. Phosphorus also affects the thermal expansion of the Ni layer (Tasic et al. 2011). The electrical resistivity was measured using a super-mega ohmmeter-type electrometer (Model RM 170) (Table 10). These results indicate that the electrical resistivity increases with the addition of 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid.

3.7 Mechanical Properties of Electrolytic Ni Plating

Electrolytic Ni has similar properties to other electroplated amorphous materials in that it has mechanical and corrosion resistance and is elastic. The testing methods and

Table 10 Electrical resistivity of the plated material

Bath solution	Electrical resistivity (μΩ cm)
1	19
2	20
3	18
4	17

results for the determination of several physical properties such as penetration, hardness, tensile strength, and elongation are explained below.

3.8 Penetration

Penetration of the Ni layer is perfect on several substrates (Sahin et al. 2013). Microscopic particles on the substrate were cleaned using a bath solution, creating a metallic bond between the Ni layer and the substrate surface. The initial reaction occurred on all catalytic materials. However, penetration decreased on non-catalytic metals. The reaction was initiated by applying a very thin electroplated Ni layer. On aluminum substrates, hydrogen in the Ni layer was released by baking at 130–200 °C for 1–4 h. Diffusion of the Ni layer into the substrate increased the bond strength. The adhesive strength between the Ni layer and the steel was 85–100 MPa. Here, the adhesion strength of the Ni was measured by a heat-quench test (Xie et al. 2015), wherein the plated materials were heated at 250 °C for 2 h and quenched in air. No cracks, blisters, discoloration, or peeling of the plating was observed after testing (Xie et al. 2015).

3.9 Hardness

Hardness is the most important feature of electrolytically plated Ni. The microhardness of the plated Ni layer was 500–700 (HV100). This value is equal to approximately 45–58HR (Rockwell), which is identical to that of hardened alloy steel (Xie et al. 2015). High-temperature treatment could not be applied because the thermal properties of the constituent materials such as brass, copper, and stainless steel, as well as the specific properties of the substrate, were heat sensitive. In this case, if treatment was performed at a lower temperature for a longer time, the required hardness could have been obtained. A Rockwell hardness of 950–1000 was obtained after heat treatment at 340 °C for 4–6 h or at 290 °C for 10–12 h. A lower hardness was obtained upon heat treatment at 260 °C. A small increase was obtained upon heat treatment at temperatures below 230 °C. Hardening treatment is not preferred at lower temperatures. As such, heat treatment was performed for 2–4 h at 180–200 °C to increase the adhesive strength between the substrate and the plated material. The heat treatment was also performed to decrease the tension by removing hydrogen from the plating layer. The microhardness of Ni was measured using a diamond indenter (Xie et al. 2015). The Vickers hardness value was obtained under a load of 50 g by averaging four measurements from each bath. The microhardness of the Ni layers before heat treatment was in the range 760–785 HV. An increase in Vickers hardness from 188 to 294 HV was observed after heat treatment at 230 °C for 2 h.

3.10 Tensile Strength

High tensile strength of the electrolytic Ni layers inhibits any damage to the plating. Different methods, such as that based on residual stress measurement, have been developed to determine the tensile strength (Withers and Bhadeshia 2001). In this study, the pull test was used for determining tensile strength.

3.11 Pull Test for Tensile Strength

Materials electroplated from each of the four bath solutions were subjected to a pull test using a universal testing machine for measurement of the tensile strength (Xie et al. 2015). The test was deemed successful if there was no separation of the Ni coating from the substrate and if the coating had a tensile strength force of approximately 3500 N. The tensile strength values of the plated materials were examined over the range 3650–3800 N.

3.12 Elongation

The elongation changed with changes in the plated Ni material composition. The resistance to elongation was higher than some engineering materials such as zinc and copper. Thin electrolytic Ni platings are quite flexible, and unlike an electroplated layer, do not crack upon bending. As the thickness of the electroplated layer increases, the brittleness also increases. Therefore, electrolytic Ni plating can be performed on all shapes. However, it cannot be applied on substrates that require bending, as small deformations can cause corrosion and low abrasion resistance. Low phosphorus ratios or sulfur-containing agents can increase the resistance to rupture. Elongation was evaluated using the "Pressure Bulge Test for Thin Film Characterization" (Çam 2009). In this test, a digital oscilloscope (Nicolet, model 40, bandwidth 100 MHz) was used for recording the pressure loading signal. After pressure loading, images were collected with a CCD camera (Sony, XC-75). According to the results of this experiment, the elongation of the plated layer changed from 1.1 to 2.4%.

3.13 Wear and Resistance to Abrasion

Abrasion implies the removal of material from the surface. Electrolytically plate Ni shows significant resistance to abrasion. Laboratory experiments show that resistance to abrasion for heat-treated Ni is the same as hard chromium platings. This result suggests the need for high alloy materials or hard chromium platings for any surface. The abrasion resistance of the Ni-plated materials in this study was evaluated according to ASTM D2670-67 (Somers et al. 2016), using a Falex machine. The test results for each sample under the maximum applied load are listed in Table 11. The maximum load listed for samples 1–2 was recorded without breaking. However, the maximum load for samples 3–4 was recorded just before breaking. These results suggest that if the amount of the organic additives is increased, the plated layers show increased abrasion resistance in all four baths.

3.14 Friction Characteristics

The friction coefficient of the lubricated and unlubricated layers was 0.13 and 0.6, respectively, which could prevent overheating when using the material. Small friction coefficients also prevent effects like over-expansion and contraction due to heating and cooling by friction. The friction characteristics of the Ni layers were tested on a fully computerized microtribometer (Model UMT-2) (Shu et al. 2015) equipped with a friction counterpart, a cemented carbide ball of diameter 5 mm. A load of 5 N and sliding speed of 2 mm/s were used. The total elapsed time for each plated material was 15 min.

3.15 Soldering and Welding on Electrolytic Ni Plating

The electroplated Ni in this study could be soldered easily. In the electronics industry, Ni-plated metals such as aluminum are prepared using electrolytic processes. The welding point of Ni alloys is lower than that of pure Ni. Additionally, alloy impurities such as phosphorus diffuse and embrittle the steel, which makes welding difficult. A different process has been reported using high-purity stainless steel anodes (Xie et al. 2015).

Electrolytic Ni-plated layers are easily soldered using an acidic flux. Without the flux, heat treatment can make soldering difficult. A solderability test was designed to evaluate the solderability and wettability of the soldering material to the electrolytic Ni layer. The test was performed by soldering the plated materials and evaluating the soldering points using a pull test for mechanical characterization of the soldering interface. Each test material was prepared from two pieces that were plated with approximately 20 μm of electrolytic Ni. After plating, the two pieces were placed on an aluminum jig and heated on a hot plate to the melting temperature of the solder (350–400 °C) to fill the 0.2 mm gap with the solder. After cooling, each piece was removed from the screws of the jig and the soldering parts were machined (Xie et al. 2015).

Table 11 Falex testing results of electrolytic Ni-plating bath solutions

Plated material in each bath solution	Maximum load (Nm)
1	350.1
2	400.2
3	350.1
4	110.3

3.16 Corrosion Resistance

Electrolytic Ni plating can isolate the substrate from the ambient environment. As such, the electrolytic Ni layer can impart corrosion resistance to the substrate material. This corrosion resistance depends on the phosphorus ratio, the thickness, surface pre-treatment, final treatment after plating, and the substrate itself. This resistance is due to its chemical passiveness, which is also a function of the phosphorus ratio (Xie et al. 2015). Because it provides superior corrosion resistance, it can be used for designing a plating material. The material should not become harder after plating, because it can lower the corrosion resistance (Xie et al. 2015). Electrolytic Ni results in a more amorphous structure compared with electroplating. Heat treatment can decrease the phosphorus content in Ni layers that affects the corrosion resistance and the properties of the amorphous structures. Small active/passive corrosion cell points appear in the Ni-plating layer and diffuse into the entire layer. The amorphous structures convert into structures with micro-cracks because of physical changes. The corrosion resistance of the Ni layer decreases if its hardness increases during heat treatment. Therefore, heat treatment should be avoided if the corrosion resistance of the material has to be retained (Xie et al. 2015). To evaluate the resistance of the electrolytic Ni plating in a corrosive atmosphere, an accelerated corrosion test was performed. The plated material was placed in a 5% NaCl solution at pH 7.0 and the time required for the discoloration of Ni during corrosion was recorded. To evaluate the corrosion performance of plated materials in this study, immersion in a 5% NaCl solution for 96 h was sufficient. If there was no discoloration on the plated surface in the stipulated time, the test was terminated. In this study, the plated material showed discoloration after 5 days in 5% NaCl solution.

Thus, it was concluded that the solderability of the electrolytic Ni plating is excellent.

3.17 Electron Microscopy Analysis

Electron microscopy analysis was conducted to understand the physical properties of the plated materials and to evaluate their appearance. The following device parameters were used: resolution, 100 μm; high-voltage separation, 10.0 kV; working distance, 7.2 mm; and magnification, 100×. The visible quality of the Ni layer was investigated when 3 mL/L of 2-mercaptobenzimidazole, 4 mL/L of thioglycolic acid, and 2 mL/L of 2-mercaptobenzothiazole were used.

3.18 Color Analysis

A color analysis was performed using a spectrophotometer to observe the effects of 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid on the plated metal surfaces. The color of the metal plate was examined in the CIE (Commission Internationale Del'éclairage/The International Commission on Illumination) L × a × b color space (Luo 2015) using a visible wavelength spectrophotometer (Macbeth CMC-CE-7000-XL0339) at 325 nm and CIE Standard Illuminant D65, which is equivalent to 6500 K illumination. These values are in accordance with the European and Japanese standards. Two measurements were performed for each plate surface. Our aim was to achieve high sensitivity in the visible color region and to supply the closest values to market requirements. Visible color spectrophotometry is not currently used for color analysis in the metal plating industry. However, this technique was used in this study because of the sensitive viewing properties of 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid in the Ni plating. This system enables a comparison of the measured color values. The individual effects of organic compounds such as 2-mercaptobenzimidazole, thioglycolic acid, and 2-mercaptobenzothiazole, which are added for improving the physical properties of Ni plating, were evaluated. The effects of 3 mL/L of 2-mercaptobenzimidazole (Fig. 5), 2 mL/L of 2-mercaptobenzothiazole (Fig. 6), and 4 mL/L of thioglycolic acid (Fig. 7) were evaluated. In addition, the optimum concentrations of these organic compounds were determined (Fig. 8).

3.19 Charpy Impact Test

A Charpy impact test was also conducted using a ZBC2000 device (Sans, China) according to the ASTM E23 standard. A force of 3 kg/cm^2 with a fall speed of 5.5 m/s was applied to the metal surface. Adhesion forces were measured in the high current density area, which had a high Ni coating thickness (10–15 μm), and in the low current density area, which had a low Ni coating thickness (1–5 μm).

4 Conclusion

The use of electrolytic Ni plating has increased rapidly in the last few years. Attributes such as thickness uniformity, material coating compatibility, corrosion resistance, abrasion resistance, and high hardness make it suitable for

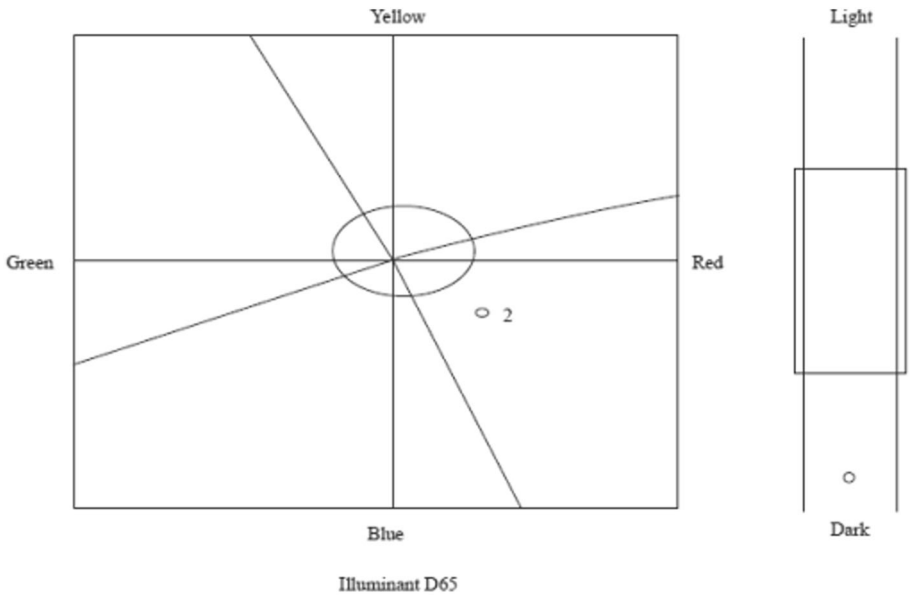


Fig. 5 Color measurement of plated material (3 mL/L of 2-mercaptobenzimidazole in Ni-plating bath; *point marked 2* indicates the value in the second trial)

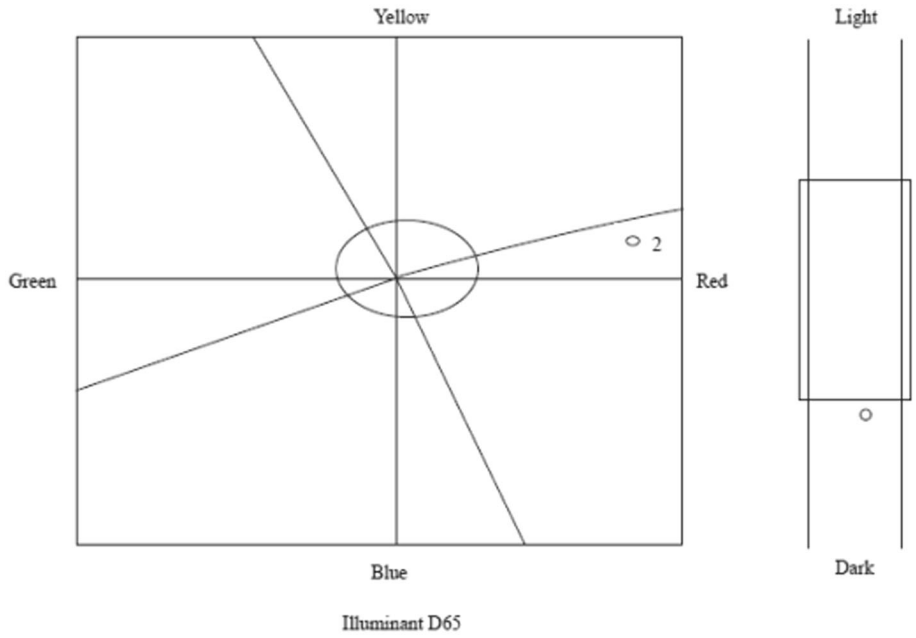


Fig. 6 Color measurement of plated material (2 mL/L of 2-mercaptobenzothiazole in Ni-plating bath; *point marked 2* indicates the value in the second trial)

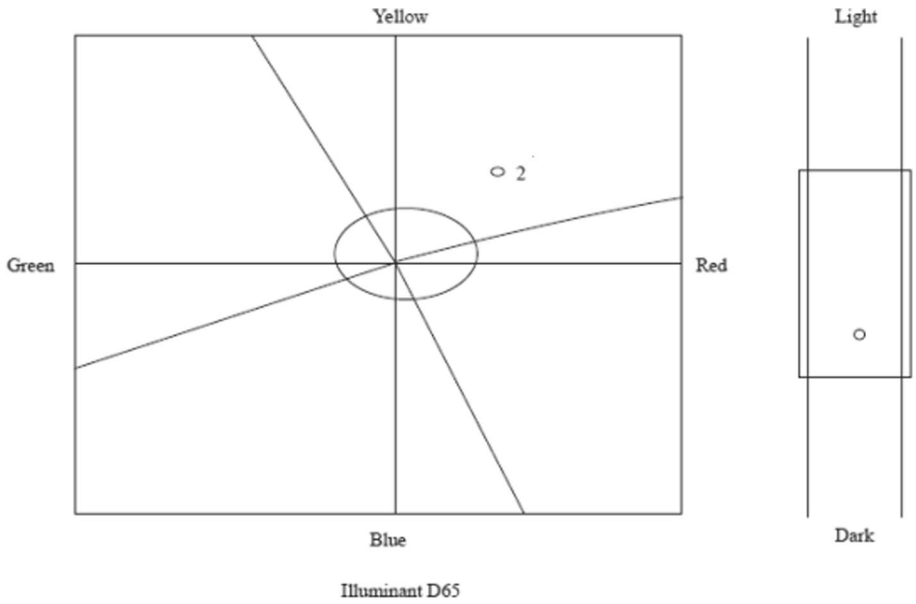


Fig. 7 Color measurement of plated material (4 mL/L of thioglycolic acid in Ni-plating bath; *point marked 2* indicates the value in the second trial)

many industries. In this study, three different organic additives, including 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid, were used for improving the efficiency of the electrolytic Ni-plating technique. These results suggest that 2-mercaptobenzimidazole improves the performance by disrupting the crystal structure. However, 2-mercaptobenzothiazole had the most pronounced effect on brightness. Thioglycolic acid helped the formation of the crystal structure. During electroplating, crystal growth was observed; the plating layer had a matte finish, and the plating speed decreased. The concentration of these chemical components in the bath did not exceed 5 mL/L. Higher concentrations resulted in decreased plating speeds. Upon replenishing the bath, if the amounts of these chemical compounds were more than 5% of the initial amounts, plating ceased entirely. If the concentration of each chemical was less than 2.5 mL/L, the bath could function without replenishment for 2 h. These data suggest ideal concentrations between 1.5 and 2.5 mL/L. Based on these results, the optimum mixture includes 3 mL/L of 2-mercaptobenzimidazole, 4 mL/L of thioglycolic acid, and 2 mL/L of 2-mercaptobenzothiazole. Thioglycolic acid did not affect the color of the Ni plating, which is useful in maintaining the decorative properties of

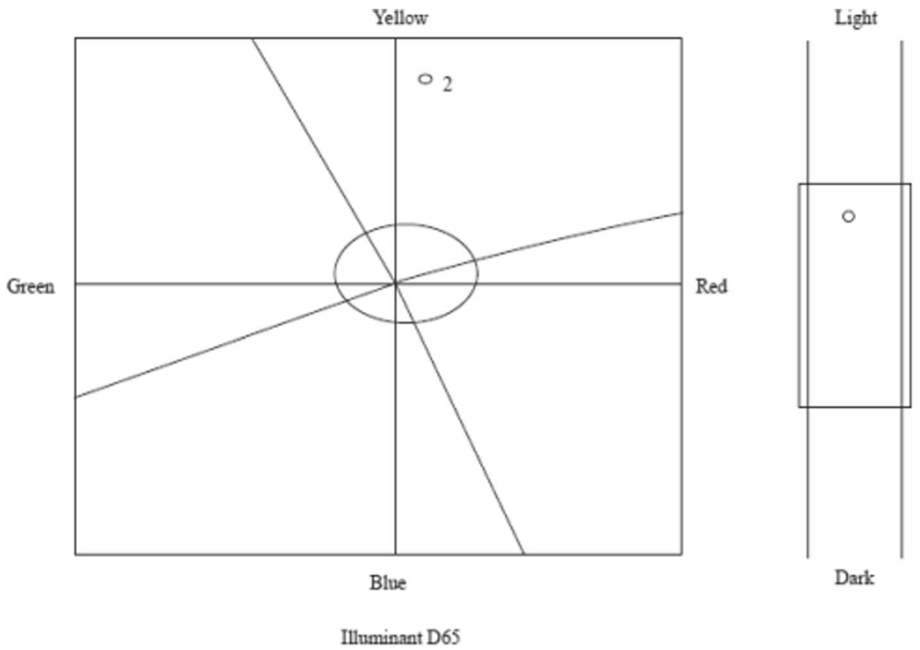


Fig. 8 Color measurement of plated material (3 mL/L of 2-mercaptobenzimidazole + 4 mL/L of thioglycolic acid + 2 mL/L of 2-mercaptobenzothiazole in Ni-plating bath; *point marked 2* indicates the value in the second trial)

the plating. At the same time, its addition improved the physical properties of Ni. A thioglycolic acid concentration of 4 mL/L and a current density of 0.4 A/cm^2 were required to realize a plating thickness of 0.25 μm. In this study, several properties of electrolytic Ni plating were improved. For example, cheaper and more easily available organic compounds were employed, slower deposition rates were achieved, welding characteristics were improved, analytical control of the bath chemicals was easier, throwing power was improved, and uniform coatings were observed. At the same time, the hardness increased to 480 HV, which is higher than that of electrodeposited Ni at 200 HV. The plating hardness could also be increased to 1050 HV by heat treatment at 400 °C for 1 h. Other improvements include higher wear resistance, solderability, brazeability, about 1–3% elongation, and higher corrosion resistance versus traditional Ni and Ni alloy plating. In the studies performed, the optimum concentrations of 2-mercaptobenzimidazole and 2-mercaptobenzothiazole used in the Ni-plating bath were determined to be 3 and 2 mL/L, respectively. A bath temperature of 90 °C, current density of 0.3 A/cm^2, and deposition speed of 0.4 μm/min were determined to be the optimum experimental parameters. In this study, the mechanical and physical properties of the plated material were investigated thoroughly. In addition, fewer chemical additives were used which decreased the amount of potential wastewater generation. As a result, the investment and production costs for manufacturers were also significantly lowered.

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