

Research Article

2-Mercaptobenzimidazole, 2-Mercaptobenzothiazole, and Thioglycolic Acid in an Electroless Nickel-Plating Bath

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The use of three different materials, 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid, was investigated to improve the performance of electroless nickel-plating baths. By changing the concentrations of these materials, sample plates were coated. Optical microscope images were obtained by selecting representative coated plates. From the results of the investigations, the effects of these materials on electroless nickel plating were observed, and the most appropriate amounts of these materials for nickel plating were determined. Moreover, the nickel plating speed observed with the bath solution containing 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid is higher than that in the case of traditional electroless plating baths, but the nickel consumption amount in the former case is lower. In order to minimize the waste water generated from electroless nickel-plating baths, we determined the lowest amounts of the chemicals that can be used for the concentrations reported in the literature.

1. Introduction

There have been several important developments in plating technologies recently. One reason for this is the important functional abilities of plating materials. The development of coating materials may involve high costs, but because coated materials have long lifetimes, this disadvantage can be mitigated. Electroless nickel plating is used for many purposes in the metal industry, and its usage is increasing every year because nickel-plated materials change the functional properties of substrates.

Electroless nickel plating imparts perfect corrosion resistance and abrasive properties to the substrate. It is also independent of the material shape and provides uniform plating thickness. Therefore, electroless nickel plating is used in the petroleum, chemical, plastic, optics, mining, nuclear, automotive and food industries.

Differences in the electroless nickel-plating method compared to other plating techniques include not only electrical current in the electrolyte, but also the presence of nonmetallic materials in the solution, with 88–95% nickel metal bonded onto the metal surface. Because nickel ions and nonmetallic

elements such as phosphorus take part in the plating process, an amorphous layer, which is called the metallic glass layer, is formed. Electroless nickel plating is a chemical reduction technique that is autocatalytic. When the microstructure is observed, crystals are not present in the plating layer, unlike galvanic cells where crystals are formed. Unlike coatings that are plated using other electrolytic techniques, electroless nickel is not sacrificial plating. Because it forms a uniform thickness on the substrate, in contrast to electrolytic coatings that show a difference in thickness with current densities, it behaves as a barrier coating that isolates the substrate from the ambient. This plating method has special features that are unrivalled, and it is also preferred over other plating techniques in many industries.

There are several applications of electroless nickel plating in the metal industry. Yee et al. created a palladium-copper interlayer in nickel plating by adding copper for improving the physical properties of nickel plating [1]. Shao et al. studied a different process by plating nickel on a magnesium alloy [2]. Liu et al. contributed to industrial development by studying the recovery of high-purity ferric phosphate [3]. In another work, Fujii et al. achieved electroless nickel plating on

polymer particles [4]. Rajaguru et al. contributed importantly to the metal plating industry by performing electroless nickel plating for low-volume production of plastic parts [5]. Yim et al. plated nickel electrolessly on pitch-based carbon fiber reinforced composites. These studies showed that physical properties such as hardness were improved [6]. Jin et al. prepared grafted carbon fibers by electrochemically mediated atom transfer radical polymerization. They investigated the adsorption of Ni^{2+} on these grafted carbon fibers in an electroless nickel-plating bath [7]. The process of nickel plating creates an important problem such as the recovery of nickel. Li et al. studied the recovery of nickel in industrial processes [8]. In another study by Shu et al., nickel particles were activated by using thiourea dioxide [9]. Liu et al. determined new methods for the electroless nickel-plating process by using complex salts that contain Li and Fe [10]. Tengsuwan et al. [11] used supercritical carbon dioxide-assisted nickel plating to fabricate polymer particles. An integrated electroless nickel-plating process was developed for CMOS (Complementary Metal Oxide Semiconductor) MEMS (Micro-Electromechanical System) by Lee et al. [12]. From the viewpoint of industrial development, the characterization of electroless nickel-coated cellulose fibers was investigated by Sittisart et al. [13]. Lee et al. presented a new method of recovering nickel that involved electrolysis of spent electroless nickel-plating solutions comprising hexasulfonate salt [14]. Ajibola et al. [15] contributed to industrial development by studying electroless nickel plating using aluminum alloys. The recovery of Ni metal, P, and S from process baths for plated double-hydroxide composites by electroless nickel plating has been studied by Zhu et al. [16]. Another work from the viewpoint of industrial development is a study on arc-discharge-synthesized carbon nanotubes for metal matrix composites; this study was performed by Jagannatham et al. [17].

The recovery of nickel is an important aspect of nickel-plating processes, and there are many studies regarding this. Nickel recovery using a Counter Current Emulsion Flow Extractor is an interesting example in this regard [18].

In the present study, the effects of compositions that contain 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid were investigated to improve physical properties such as corrosion resistance and mechanical strength.

2. Experimental Procedure

In this study, three different chemicals were used in the electroless nickel-plating baths, and the crystal structure of the coated materials and their images were observed so that the most ideal composition can be determined.

2.1. Experimental Procedure

2.1.1. Compounds Used in the Experiments. 2-Mercaptobenzimidazole, 2-mercaptobenzothiazole sodium salt, and thioglycolic acid were used in the study. Optical microscopy of the coated plates was performed using a Leica DMLM Microscope + QWIN Programme Image Analyser.

TABLE 1: Chemical composition of the first main part solution in a nickel-plating bath.

Chemical composition	CAS no.	Concentration (gL^{-1})
Distilled water	7732-18-5	828
Nickel sulfate	7786-81-4	360
Sulfuric acid	7664-93-9	32

TABLE 2: Chemical composition of the second main part solution in a nickel-plating bath.

Chemical compound	CAS no.	Concentration (gL^{-1})
Distilled water	7732-18-5	309
Potassium hydroxide	1310-58-3	220
Maleic anhydride	108-31-6	10
Lactic acid	50-21-5	133
Glycolic acid	79-14-1	133
Sodium acetate	127-09-3	200
Sodium hypophosphite	10039-56-2	320

2.1.2. Bath Solutions Used in Nickel Plating. An acidic bath was used in electroless nickel plating, and the bath was prepared using two main solutions (Tables 1 and 2). From these two solutions, two baths of 75 mL and 1 L were prepared. The pH was adjusted to 4.8 and the solutions were heated to 90°C under working conditions. The chemicals used in this study were obtained from Merck, Istanbul.

2.2. Experimental Procedures. Before plating, the substrate was pretreated by cleaning, then dried, weighed, and labeled. After drying, these material samples were immersed in 2% sulfuric acid for 2–5 s, rinsed in water, and placed in the electroless nickel-plating bath. Plating was then performed at 90°C for 10 min. After plating, all samples were rinsed in tap water, dried, and weighed. Subsequently, the pH was checked and nickel analysis was conducted.

A total of 5 stainless steel substrates were plated, and the plating ratio for each plate was calculated. A total of five plating baths were prepared. Plating baths 1–5 were prepared by diluting 75 mL bath solution to 1 L. The bath compositions and plating results for each bath are shown in Tables 3–7.

Representative samples from the selected substrates were imaged under an optical microscope, and the results are shown in Figures 1(a)–1(e).

2.2.1. Nickel Analysis. A 10 mL bath solution was placed in an Erlenmeyer flask and 100 mL distilled water was added to the solution, and then 5 mL ammonia and approximately 0.5 g murexide were added. It was immediately titrated with EDTA until a purple color was observed, and the consumption of EDTA (S) was recorded.

Calculations are as follows: $(S) * 0.587 = \text{g/L metallic nickel}$ [16].

The pH decreased as the plating progressed. Therefore, the pH was adjusted using dilute ammonia. Nickel sulfate and reduction solutions were prepared for replenishing the material loss during working of the bath. For every 1 g/L

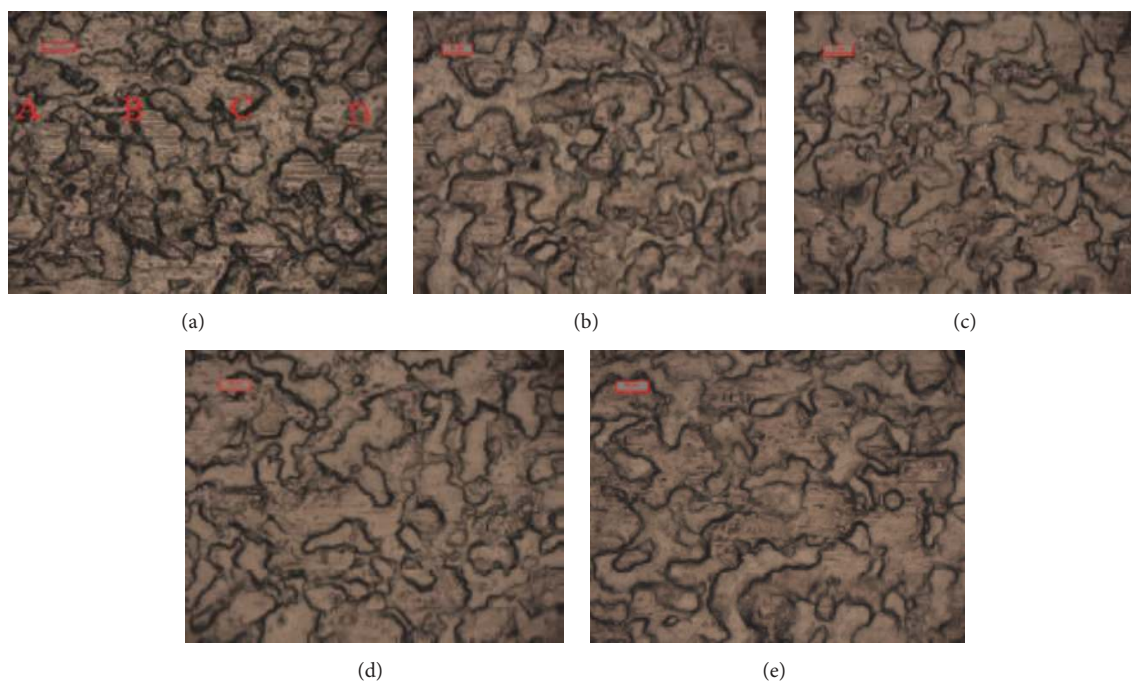


FIGURE 1: (a) Optical microscope image of plated material no. 1. (b) Optical microscope image of plated material no. 2. (c) Optical microscope image of plated material no. 3. (d) Optical microscope image of plated material no. 4. (e) Optical microscope image of plated material no. 5.

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 (μ /h)
01	No addition	33.4517	33.8962	21.40
03	2 mL 2-mercaptobenzimidazole	33.5632	33.5632	0
04	2 mL 2-mercaptobenzothiazole	33.4147	33.4147	0
05	2 mL thioglycolic acid	33.7166	33.3940	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 (μ /h)
13	0.5 mL 2-mercaptobenzothiazole	33.9627	34.7547	25.42
14	0.5 mL 2-mercaptobenzimidazole	33.4948	34.5026	32.35
15	0.5 mL thioglycolic acid	33.6508	34.4758	26.48

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 (μ /h)
25	0.3 mL thioglycolic acid	33.0866	33.8744	25.29
26	0.3 mL 2-mercaptobenzothiazole	32.8369	33.4808	20.67
27	0.3 mL 2-mercaptobenzimidazole	33.2579	33.9064	20.82

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 (μ /h)
54	0.1 mL 2-mercaptobenzothiazole	33.0866	33.8744	25.29
55	0.1 mL thioglycolic acid	32.8369	33.4808	20.67
56	0.1 mL 2-mercaptobenzimidazole	33.2579	33.9064	20.82

TABLE 7: Plating performed in bath solution no. 5 and results.

Material no.	Chemical additive	Weight before plating (g)	Weight after plating (g)	Plating speed (μh)
84	0.2 mL thioglycolic acid	32.6090	33.3158	34.03
85	0.2 mL 2-mercaptobenzothiazole	32.6960	33.3498	31.48
86	0.2 mL 2-mercaptobenzimidazole	32.5083	33.0693	27.01

TABLE 8: Components of a reduction solution.

Chemical compound	CAS no.	Concentration ($\text{g}\cdot\text{L}^{-1}$)
Potassium hydroxide	1310-58-3	10
Maleic anhydride	108-31-6	0.5
Lactic acid	50-21-5	6.7
Glycolic acid	79-14-1	6.7
Sodium acetate	127-09-3	6.7
Sodium hypophosphite	10039-56-2	16.7
2-Mercaptobenzimidazole	583-39-1	
2-Mercaptobenzothiazole	149-30-4	
Thioglycolic acid	68-11-1	

nickel, 10 mL nickel sulfate solution was added. After this addition, for each 10 mL of nickel sulfate solution, 8 mL of reduction solution was added (the reduction solution is described in Section 2.2.2).

2.2.2. Replenishing Solutions. Buffer solutions were prepared to replenish the basic components in the nickel-plating bath, which contained the two main solutions. One of these was the nickel sulfate solution and the other was the hypophosphite solution. This buffer solution is known as the reduction solution.

Nickel sulfate (45 g) was diluted in distilled water and made up to 100 mL. This solution was used for replenishing the nickel in the plating bath. Compounds as shown in Table 8 were mixed in a beaker and diluted to 100 mL, and the resulting solution was used for replenishing the hypophosphite.

2.3. Characterization of Physical Properties of Electrolessly Nickel-Plated Layer

2.3.1. Layer Structure. Layer structure of the electroless nickel was investigated by shear testing [19], which was conducted using a Dage Series 4000 Bond tester. The shear height was determined as 100 μm at a shear rate of 550 $\mu\text{m}\cdot\text{h}^{-1}$. After shear testing, the fracture surfaces were investigated using SEM (Zeiss Supra 55 scanning electron microscope). An SEM image of the nickel plating formed after the addition of thioglycolic acid is shown in Figure 3(a), while an SEM image of the plating formed after the addition of 2-mercaptobenzothiazole is shown in Figure 3(b). Finally, an SEM image of the plating formed after the addition of 2-mercaptobenzimidazole is shown in Figure 3(c).

2.3.2. Plating Thickness. It is possible to deposit a uniform plating layer with the required thickness, which typically

TABLE 9: Interdependence of physical parameters in the plating process.

Adhesion force ($\text{kg}\cdot\text{cm}^{-2}$)	Thickness of the nickel plating (μm)
0	0
2	10
2.2	11
2.4	12
2.6	12
2.8	14
3.0	15

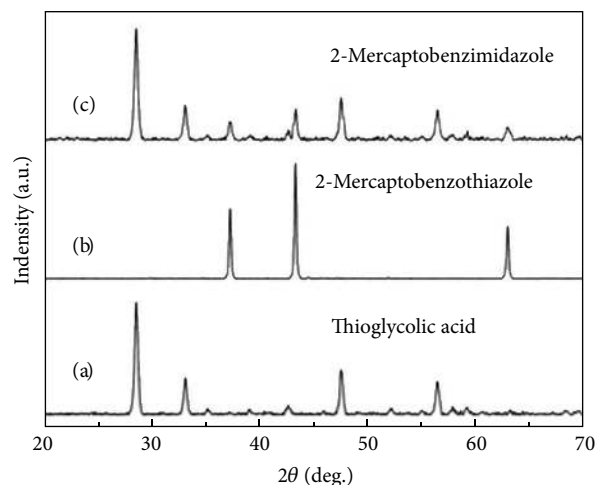


FIGURE 2: XRD patterns of 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid in electroless nickel-plating baths.

lies between 2.5 and 25 μm . For parts that require higher corrosion resistance, a plating thickness between 25 and 75 μm is preferred. If the plating thickness increases, the surface roughness increases. The thickness of the deposited electroless nickel was measured using X-Ray Fluorescence (XRF), and the results are shown in Table 9.

2.3.3. Density. In this study, the density of electroless nickel plating was measured using the associated dimensional change [20]. The thickness of the plated nickel 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, and plating thickness was determined under a graduated-scale microscope after metallographic polishing.

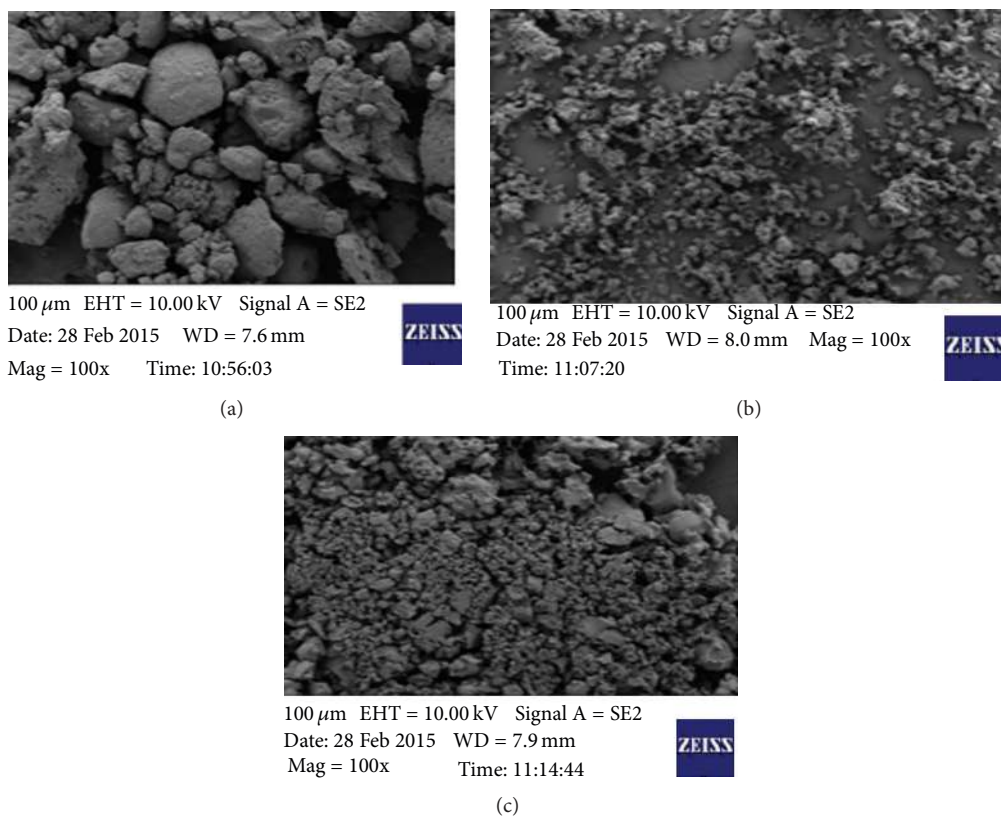


FIGURE 3: (a) SEM image of the nickel plating formed after the addition of thioglycolic acid. (b) SEM image of the nickel plating formed after the addition of 2-mercaptobenzothiazole. (c) SEM image of the nickel plating formed after the addition of 2-mercaptobenzimidazole.

TABLE 10: Electrical resistivity of plated material.

Bath solution	Electrical resistivity (μcm)
1	19
2	20
3	18
4	17
5	17

2.3.4. *Electrical Resistivity.* The electrical resistivity was measured using a super-megaohmmeter-type electrometer (Model RM 170) (Table 10).

2.4. *Mechanical Properties of Electroless Nickel.* Electroless nickel has similar properties to other amorphous platings in that it has high resistance and is elastic. The testing methods and results of the determination of several physical properties such as penetration, hardness, tensile strength, and elongation are explained below.

2.4.1. *Penetration.* Here, the adhesion strength of the electroless nickel plating was measured by a heat-quench test [21]. In this test, plated materials were heated at 250°C for 2 h and quenched in air.

2.4.2. *Hardness.* The microhardness of electroless nickel was measured using a diamond indenter [21]. Vickers hardness was obtained by taking the average of the results of five measurements for plating from each bath with a load of 50 g. The microhardness of electroless nickel before heat treatment was in the range of 760–785 HV. An increase in Vickers hardness by 188 to 294 HV was observed after heat treatment at 230°C for 2 h.

2.4.3. *Tensile Strength.* Tensile strength of the electroless nickel plating prevents any damage to it, and different methods have been developed to measure the tensile strength. In this study, the pull test was used for determining tensile strength.

2.4.4. *Pull Test for Tensile Strength.* Materials plated using the five bath solutions were subjected to a pull test using a universal testing machine for measuring the tensile strength [21]. The test was successful when there is no separation of the nickel coating from the substrate and it 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.

2.4.5. *Elongation.* Elongation is detected using the “Pressure Bulge Test for Thin Film Characterization” [20]. In this

test, for recording the pressure loading signal, a digital oscilloscope (Nicolet, model 40, bandwidth 100 MHz) was used, and for recording images after pressure loading, a CCD camera (Sony, XC-75) was used. According to the results of this experiment, the elongation of the plated layer changed from 1.1 to 2.4%.

2.4.6. Optical Images of Electroless Nickel-Plating Layer. Leica DMLM Microscope + QWIN program Image Analyser was used for obtaining optical microscope images of the plated nickel layer.

2.4.7. Wear and Resistance to Abrasion. Abrasion resistance of electroless nickel-plated materials in this study was evaluated according to ASTM D2670-67 [22]. For this analysis, a Falex machine was used.

2.4.8. Friction Characteristics. The friction characteristics of the Ni plating was tested on a fully computerized microtribometer (Model UMT-2) [23], with a friction counterpart of a cemented carbide ball of 5 mm. A load of 5 N and sliding speed of $2 \text{ mm}\cdot\text{s}^{-1}$ were used, and the total elapsed time for each plated material was 15 min.

2.4.9. Soldering and Welding on Electroless Nickel Plating

(1) Preparation of Test Materials. Each test material was prepared from two pieces. These pieces were plated with electroless nickel of approximately $20 \mu\text{m}$ plating thickness. After plating, the two pieces were placed on an aluminum jig and heated on a hot plate to the melting temperature of the solder ($350\text{--}400^\circ\text{C}$) to fill a gap of 0.2 mm with the solder. Each material piece was moved from the screws of the jig, and after cooling, the soldering parts were machined [21].

2.4.10. Corrosion Resistance. To evaluate the resistance of the electroless nickel coating in a corrosive atmosphere, an accelerated corrosion test was performed, and the potentiodynamic polarization curves were determined. The plated material was placed in a 3.5% NaCl solution at a pH of 7.0, and the time required for discoloration of the plating as corrosion occurred was recorded. To evaluate the corrosion performance of plated materials in this study, immersion in 3.5% NaCl solution for 96 h was sufficient (see Figure 4). 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 3.5% NaCl solution. As a result of this experiment, it is concluded that the solderability of the electroless nickel was excellent. It was also resistant to corrosion in 3.5% NaCl at a relative humidity of 95% and temperature of 50°C (i.e., as per the ASTM B 117 standard).

3. Results and Discussion

Electrolessly plated materials show a glassy metallic structure, known as metallic glass, which is homogeneous and

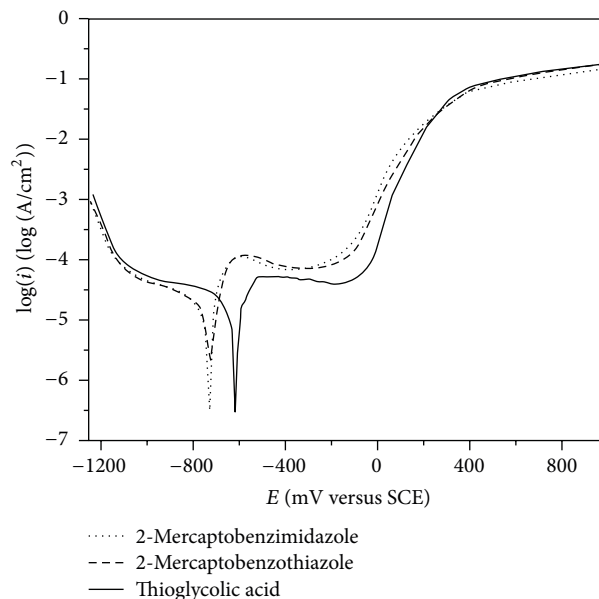


FIGURE 4: Potentiodynamic polarization curves of the nickel platings electrolessly deposited using 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid. The measurements were made after the free-corrosion potentials had stabilized and were performed at room temperature in 3.5 wt% NaCl at a scan rate of 5 mV/s .

does not contain microvoids. Upon heat treatment, it converts to a structure that contains microvoids [19]. If the amount of phosphorus, which depends on the chemical composition of the bath, changes, the plating rate, layer formation, and mechanical strength will change. Hence, the structure of the plated nickel layer will also change. Further, the concentration of phosphor in the electroless nickel plating was 1–10% [5]. Shear tests on the layer structure of the plated materials reveal a shear deposition rate of $100 \mu\text{m}$ at $550 \mu\text{m}\cdot\text{h}^{-1}$. The shear deposition rate in the case of the nickel plating containing 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid is higher than that observed when the plating contained only one of the three additives. The plating deposition rate is higher than previously published or patented values [4]. According to the results of shear testing, the shear deposition rates observed for the plating baths containing only 2-mercaptobenzimidazole, thioglycolic acid, or 2-mercaptobenzothiazole are $70 \mu\text{m}$, $80 \mu\text{m}$, and $95 \mu\text{m}$, respectively. Moreover, when the effects of these three additives on the deposition layers are investigated, interesting results are obtained. The porosity of the material containing one of these three additives decreases in the following order: 2-mercaptobenzimidazole > 2-mercaptobenzothiazole > thioglycolic acid; however, the porosity of the plated material containing the three additives together is much lower than that observed in each of the individual cases stated above.

The plating thickness required for industrial applications ranges between 10 and 20 microns. Electroless plating affords a lower plating thickness than do other plating processes. 2-Mercaptobenzimidazole, thioglycolic acid, and

2-mercaptobenzothiazole used in this study during nickel plating result in a much narrow range of plating thickness (Table 11). While 2-mercaptobenzimidazole, thioglycolic acid, and 2-mercaptobenzothiazole afford plating thicknesses of 10–15 μm , 11–14 μm , and 10–14 μm , respectively, a combination of the three additives gives a plating thickness of 10–12 μm . X-ray measurements indicate that the plating thickness does not show notable changes on the metal surface. When the aforesaid three additives are used in the plating bath, a uniform plating thickness of 10–12 μm is obtained, which is an important advantage of this process, similar to the case of electroless plating. In addition, the effects of 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid on the nickel platings produced were investigated using X-ray diffraction analyses. The XRD pattern of the nickel plating formed after the addition of thioglycolic acid is shown in Figure 2(a); major peaks were seen at 2θ values of 29.10°, 33.120°, 48.230°, and 57.130°. Further, the XRD pattern of the nickel plating formed after the addition of 2-mercaptobenzothiazole, shown in Figure 2(b), contained sharp, high-intensity diffraction peaks at 2θ values of 38.75°, 44.10°, and 64.10°. Finally, the XRD pattern of the plating formed after the addition of 2-mercaptobenzimidazole is shown in Figure 3(c); the diffraction peaks in this spectrum were shifted to higher angles compared to those of the plating produced using a bare bath. This shifting of the peaks to higher diffraction angles was probably owing to the low thickness of the nickel plating. Given the low thickness of the plating, the strain from the epitaxial growth of the plating probably had a significant effect on the plating, resulting in the observed shift in the diffraction peaks.

Uniform plating is important for achieving the required material performance. In electroplating, plating thickness changes depending on the material configuration, geometry, and distance to the anodes. Therefore, it is possible to achieve uniform plating thickness on every part of the material through electroless plating [5]. In the present study, the plating thicknesses were quite uniform over the entire material surface. Therefore, it is concluded that suitable conditions ensure plating uniformity on the surface. As shown in Figure 1(a), four different points were selected for optical imaging of the plated material. Thicknesses measured at these points were similar for the entire surface in a sample (Table 11). Electroless nickel is a eutectic alloy that has a wide range of melting points, and it does not have an absolute melting point. The change in the melting range depends on the phosphorus content; as the phosphorus content decreases, the melting range increases. An increase in the phosphorus concentration of 1% increases the melting point of nickel platings by 2.5°C [5].

Thermal properties of electroless nickel are different from the thermal properties of pure nickel such as high temperature oxidation resistance. The melting point of pure nickel is 1455°C, but the melting point of electroless nickel with different added compounds in the plating bath decreases significantly. In this study, the melting point of electroless nickel that contains 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid in the bath was

TABLE 11: Selected points in the plated material in Figure 1(a).

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

determined to be 1060°C according to the eutectic melting bonding (EMB) method [24].

In engineering and automotive industries, high temperature is an important requirement for fuel injection systems, and this necessitates the use of materials that can withstand such temperatures. The melting point of the nickel plating containing phosphorus is 900°C, while the melting points of the nickel plating containing 2-mercaptobenzimidazole, thioglycolic acid, and 2-mercaptobenzothiazole reach 1060°C.

Addition of 2-mercaptobenzimidazole, thioglycolic acid, and 2-mercaptobenzothiazole decreases the density of the plating bath solution to below 7.75 g cm^{-3} [5], which is too low to induce sufficient porosity. Therefore, the surface porosity decreases after plating. The electrical resistivity of the nickel-plated material in this study (30 Ω) is higher than that of the nickel plating containing phosphorus (20 Ω). The electrical resistivity of the nickel plating containing one of the three additives is higher than that of the nickel plating containing phosphorus (22, 24, and 25 Ω when using 2-mercaptobenzimidazole, thioglycolic acid, and 2-mercaptobenzothiazole, resp.); however, the best result for electrical resistivity is obtained in the case of the nickel plating containing all the three additives.

The change in the electrical properties of the substrate depends on the nickel-plating layer. Layers that have a high phosphorus content are less conductive than copper. The resistivity of a layer with low phosphorus was 20 $\mu\text{-cm}$ [25]. For applications that require low electrical resistivity, thin plating layers are deposited. Heat treatment and chemical composition of the plating bath affect resistivity. Conductivity increased by two times because of precipitated phosphorus in the heat-treated nickel plating. Phosphorus affects the thermal expansion of the nickel layer [5]. From these results in Table 10, it is seen that the addition of 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid increases electrical resistivity.

Penetration of the nickel layer is perfect on several substrates [18]. Microscopic particles on the substrate were cleaned using a bath solution, creating a metallic bond between the nickel layer and the substrate surface. The initial reaction occurred on all catalytic materials but not on noncatalytic metals for which penetration decreased. The reaction was initiated by applying a very thin electroplated nickel layer. On aluminum, hydrogen in the nickel layer was released by a baking process at 130–200°C for 1–4 h. Diffusion of the nickel layer into the substrate increases the bond strength. The adhesive strength between the nickel plating and steel was 30,000–60,000 psi. Further, cracks, blisters,

discoloration, or peeling of the plating was not observed after the tests [21].

Studies performed till date show that the adhesion capability of the nickel plating on to the metal surface is better than that of other nickel alloy platings. Charpy impact tests have shown that the addition of 2-mercaptobenzimidazole, thioglycolic acid, and 2-mercaptobenzothiazole results in increased adhesion capability. The most important feature of electroless nickel plating is its hardness. Microhardness of the plated nickel layer was 500–700 HV100. This value is equal to approximately 45–58 HR (Rockwell), which is the same as that for hardened alloy steel [21].

Because of the thermal properties of materials, such as brass, copper, and stainless steel, and the specific properties of the substrate, high temperature treatment could not be applied. In this case, if treatment was performed at a lower temperature for a long 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, while lower hardness was obtained upon heat treatment at 260°C. A small increase was obtained upon heat treatment at 230°C and lower temperatures. 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 plating. It was also performed to decrease the tension by removing hydrogen from the plating layer.

Hardness is one of the most important parameters used in deciding the industrial value of plated materials. Therefore, the hardness obtained in the case of electroless nickel plating, 500–700 HV, is a major disadvantage. In the present study, this problem was solved by increasing the hardness to 785 HV.

The elongation changed with change in the nickel-plating composition, and the resistance to elongation was higher than several engineering materials such as zinc and copper. A thin electroless nickel plating is quite flexible and, unlike an electroplated layer, does not crack upon bending. However, with increased thickness of an electrolessly plated layer, brittleness increases. Therefore, electroless plating can be performed on all shapes. However, it cannot be applied on substrates that work by bending, because small deformations can cause corrosion and low abrasion resistance. Low phosphorus ratio or sulfur containing agents increase the resistance to rupture. An increase in the phosphorus concentration of 1% in electroless nickel platings results in an elongation of 1.2% [5]. Tensile strength is another parameter that must be closely monitored for ensuring the suitability of using nickel platings in industrial applications. As compared to the nickel plating containing phosphorus (3500 N), the phosphorus-free plating obtained in this study had a higher tensile strength of 3800 N. A phosphorus concentration of 1% ensures a tensile strength of 100 N.

The density of electroless nickel plating decreases as the phosphorus content increases; the density of electroless nickel with low phosphorus content was $8.5 \text{ kg}\cdot\text{cm}^{-3}$, whereas the density of electroless nickel with high phosphorus content was $7.75 \text{ g}\cdot\text{cm}^{-3}$ [5]. According to these results, an

TABLE 12: Falex testing results of electroless nickel bath solutions.

Plated material in each bath solution	Maximum load (Nm)
1	338.9
2	451.9
3	338.9
4	107.3
5	158.1

increase in the concentration of phosphorus in the nickel-plating bath of 1% increases the density by $0.75 \text{ g}\cdot\text{cm}^{-3}$. In this study, the density of the plated electroless nickel was found to be in the range of $7.28\text{--}7.32 \text{ g}\cdot\text{cm}^{-3}$.

The elongation in the case of electroless nickel plating changes with the composition of the plated layer. Nickel alloy shows better resistance to elongation than does zinc. While the elongation is 1.2% in other nickel-plating processes, the elongation of our nickel-plating ranges between 1.1% and 2.4%.

Optical microscopic studies performed on five plated materials obtained using plating baths with different compositions show that the plating thicknesses in all the cases are almost the same. The bath compositions used are listed in Tables 3–7. It is seen that as the porosity increases, the plated layer is deformed. Effective precleaning of the porous metal surface results in a uniform plating that is well adhered to the substrate. The plating thicknesses of the samples with different pore shapes are almost the same, 10–12 μm . The optical microscope images showed differences depending on the bath composition and the layer topography. It is possible to adjust the bath solution to obtain both matte and bright finishes. A mirror-plating layer can be deposited on the polished surface to obtain a mirror finish. Such brightness cannot be achieved on sandblasted, polished or cast surfaces. If corrosion protection, perfect elongation, low stress, and thick plating are required, the plating should not be bright [26]. Abrasion implies the removal of material from the surface. Electroless nickel plating imparts perfect resistance to abrasion. Laboratory experiments show that resistance to abrasion of the heat-treated electroless plated nickel is the same as hard chromium plating. This shows the need for high alloy material or hard chromium plating for any surface.

The abrasion resistance of the samples in this study is confirmed to be excellent by the Falex method. Hence, no other protective layer such as chrome plating is necessary on the nickel plating. The Falex testing results for each sample are listed in Table 12 for the maximum load applied. The maximum load listed for examples 1–3 was without breaking, while the maximum load for examples 4–5 was just prior to breaking.

As seen from the Falex results (Table 12), it is observed that if the amounts of organic additive increases, the plated layers have more strength during the Falex abrasion test for all five baths.

The most significant mechanical property in the case of electroless nickel plating is the friction characteristic. The friction coefficient in the case of traditional electroless

nickel plating is 0.13. The friction coefficient obtained for the nickel plating in this study is 0.13, 0.12, and 0.115 for the addition of 2-mercaptobenzimidazole, thioglycolic acid, and 2-mercaptobenzothiazole, respectively, and 0.11 when all the three additives are added to the plating bath.

The friction characteristics of the electroless nickel-plated layer were perfect. The friction coefficient of the lubricated layer was 0.13, and it was 0.6 for the unlubricated layer. This prevents over heating during the working of the material and prevents negative effects like overexpansion and contraction created because of the heating and cooling by friction. The electroless nickel plated in this study could be soldered easily. In particular, in the electronics industry, nickel-plated metals such as aluminum are prepared using electroless nickel plating. Because the welding point of nickel alloy is lower than pure nickel and impurities such as phosphorus in the alloy diffuse into steel, the steel becomes brittle, making welding difficult. Increasing the phosphor concentration by 1% increases the melting point of nickel platings by 50°C.

Using high purity stainless steel anodes, a different process has been reported in literature [21]. Electroless nickel-plated layers are easily soldered using an acidic flux, without which heat treatment can make soldering difficult. A solderability test was designed to evaluate the solderability and weldability of the soldering material to the electroless nickel plating. 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.

Solderability and weldability of the nickel plating play an important role for engineering applications. The nickel plating in our study shows superior soldering properties as compared to the traditional electroless nickel plating and hence can be used in electronic circuits, which in turn can be used to produce electronic cards. Because traditional nickel plating involves the use of phosphorus, the solderability is weak; the solderability, however, increases with a decrease in the phosphor concentration ($10\% > P > 1\%$) in the plating. The solderability and weldability of our nickel plating are superior to those in traditional electroless plating because (1) phosphorus is not used and (2) the combination of 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid increases the welding point of the nickel plating.

Electroless plating isolates the substrate from the ambient entirely. Electroless nickel plating imparts corrosion resistance to the material depending on the phosphorus ratio in the electroless nickel layer, plating thickness, surface pre-treatment, final treatment after plating, and the substrate. It provides resistance because of its passiveness, which changes depending on the phosphorus ratio [21].

Because it provides perfect corrosion resistance, it can be used for designing a plating material. The plated material should not become harder after plating, because it lowers the corrosion resistance [21].

Electroless nickel plating results in a more amorphous structure than electroplating. Heat treatment affects the corrosion resistance provided by nickel plating because the phosphorus ratio decreases in heat-treated nickel layers, and the amorphous structures lose their properties. An

investigation of the corrosion resistance to salt spray showed that a phosphor concentration of 1% increases the corrosion life by 5 h [5]. Active/passive small corrosion cell points occur in the nickel-plating layer and they diffuse into the entire layer. The amorphous structures convert into structures with microcracks because of physical changes. Corrosion resistance of the nickel layer decreases if its hardness increases because of heat treatment. Therefore, if corrosion resistance of the material has to be retained, heat treatment should not be performed [21].

Electroless nickel plating has been widely used in the metal industry because of advantages such as high hardness, excellent abrasion resistance, uniform plating thickness, and superior corrosion resistance. The high corrosion resistance required for nickel plating is generally realized by means of Ni-Alloy plating, but such alloys are not required to achieve high corrosion resistance in the present study. High corrosion resistance is obtained by using very small amounts of 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid. The corrosion resistance life in our nickel plating is twice that observed with conventional processes, as revealed by salt spray tests.

2-Mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid were used in different concentrations in nickel-plating baths. It was found that, when used separately in high concentrations, they yielded good results.

When 2-mercaptobenzothiazole is used in concentrations higher than 5 g/mL, it results in bright nickel platings. 2-Mercaptobenzothiazole can also reduce the brittleness of nickel platings when used in a concentration of approximately 4 g/mL. Further, these chemical additives are also suitable for reducing the waste water generated from nickel-plating baths and for decreasing the amounts of chemicals used in the baths.

Thioglycolic acid is used for varying the pH. It can also be used for decreasing the energy consumption rates corresponding to 2-mercaptobenzothiazole and 2-mercaptobenzimidazole. For instance, the use of thioglycolic acid changes the energy-consumption rate for 2-mercaptobenzothiazole to 1000 A h and that for 2-mercaptobenzimidazole to 1500 A h.

4. Conclusion

The use of electroless nickel plating began in the last few years and its usage has increased rapidly. The uniform plating thickness realized, suitability of Ni plating on all materials, corrosion resistance, abrasion resistance, and high hardness make Ni plating applicable in many industries.

In this study, three different materials—2-mercaptobenzimidazole, 2-mercaptobenzothiazole, and thioglycolic acid—were used for improving the electroless nickel-plating technique. The effects of these components were investigated, and it was observed that 2-mercaptobenzimidazole improved performance by disrupting the crystal structure. Further, although the other components also affected brightness, the effect of 2-mercaptobenzothiazole was most significant. Thioglycolic acid helped in the formation of the crystal structure. As the plating process proceeded, crystal growth occurred, resulting in matte plating, and the plating speed reduced. The

individual concentrations of the three chemical components in the electroless nickel-plating bath were not more than 5 mL/L; if this amount was increased, the plating speed decreased. Moreover, upon replenishing, if the amounts of these chemical compounds were more than 5% of the initial amounts, plating stopped. If each chemical compound was 2.5 mL/L or less, the baths could work without additional chemicals for 2 h. It is determined that the most appropriate amounts of organic chemicals are between 1.5 and 2.5 mL/L. Based on these results, the optimum amounts of chemical compounds in the electroless nickel-plating baths should be 3 g/L of 2-mercaptobenzimidazole, 4 g/L of thioglycolic acid, and 2 g/L of 2-mercaptobenzothiazole.

Thus, in this study, several properties of electroless nickel were improved by using cheaper and easily available organic chemicals. Further, lower deposition rates compared to traditional electroless nickel bath were achieved, welding characteristics were improved, analytical control of the bath chemicals was made easier, uniform coating thickness on complex objects was achieved, and the hardness of plated materials was increased to 480 HV, which is higher than that in the case of electrodeposited nickel (200 HV). In addition, the plating hardness could be increased to 1050 HV by heat treatment at 400°C for 1 h. Other improvements include about 1–3% elongation and higher wear resistance, solderability, brazeability, and corrosion resistance than those in the case of traditional nickel and nickel alloy plating.

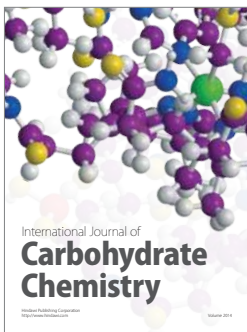
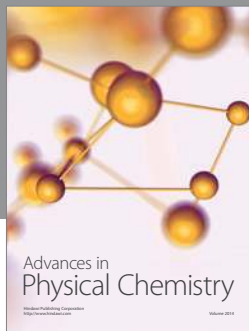
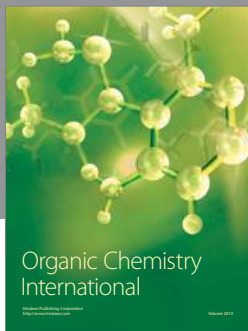
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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