OPTIMIZATION OF ELECTROLESS NI-P COATING BATH AND ITS IMPACT IN THE INDUSTRIAL APPLICATIONS

Refaie Omar¹, Mohmoud A. El-Sharief²

¹Assist. Professor of Department of Mining and Metallurgical Engineering, Assiut University, Assiut, Egypt. Email: dr_refaie@aun.edu.eg

²Assoc. Professor of Department of Mechanical Engineering, Assiut University, Assiut, Egypt. Email: msharif@aun.edu.eg

Received 30 November 2020; Revised 31 December 2020; Accepted 6 January 2021

ABSTRACT:

Electroless Ni-P coating is widely used in industrial engineering applications due to its ability to alter and improve the surface properties of the steel substrates. Electroless nickel coating introduce an excellent combination of surface properties, where, it could add brightness, luster, and good appeal. The final coating layer also possess a very good adhesion with the coated substrates, this is the reasons for using such layer as an ‘undercoat’ for other coatings. The ability to produce a very homogenous composition and produce coating with a high corrosion resistance are mainly based on the plating bath composition. The present work investigates the influence of bath compositions, which included nickel sulphate, sodium hypophosphite and tri-sodium citrate, on the process of electroless Ni–P coating. The deposition rate (Dr) as well as the bath stability were monitored to optimize the plating bath conditions with the different composition. The results of this work showed that
the deposition rate of coating layer increase with the increase of nickel source and reducing agent while; sodium citrate concentration in the plating bath has adverse effect on the deposition rate of coating.

**Keywords:** Ni-P electroless plating, reducing agent, complex agent, bath stability.

## 1. Introduction

Brenner and Riddell introduced the electroless coating technique for first time in 1945 [1]. The method was new as they do not require any external electricity. Since then and until today, it has evolved into a mature subject of research and development due to its wide range of applications [2]. The old processes were used to deposit the metallic coating without external current usually involve immersion plating or homogenous chemical reduction process (silvering) [3]. In immersion plating process, the base material is dissolved into the solution; meanwhile, the metallic ions in the solution are reduced on the surface of the base material. Such processes did not accepted for practical applications, as their result coating has weak adherence and poor properties [3]. Electroless nickel coating technique reactions involves nickel ions reduction and film deposition result from oxidation of a reducing agent present in the plating bath, which provides an internal electrons needed for coating [2, 3]. Electroless Nickel-Phosphorus (Ni-P) coatings have been used increasingly in various industries since the early 1980’s. Some of the outstanding characteristics of these coatings are superior corrosion and wear resistance, excellent uniformity, wide range of thickness as well as good mechanical and physical properties, good solderability, and surface lubricity [2-7]. In addition, compared to conventional electroplating methods, electroless nickel coatings can be applied on different substrates (conductive and nonconductive) since no external current is applied to the component [8]. Electroless nickel plating produces an amorphous deposit in the as-plated condition. Since the deposit is not dependent on current distribution, it is almost uniform in thickness, regardless of the size or shape of the plated surface [7, 9, 10]. Table 1 shows the main components of electroless plating and function of each component [3, 4, 7].
Table 1 Components and parameters of bath and their functions.

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source of metal</td>
<td>Metal ions source</td>
</tr>
<tr>
<td>Reducing agent</td>
<td>Supplying electrons to reduce the metal ions</td>
</tr>
<tr>
<td>Complexing agent</td>
<td>To control the free nickel available to the reaction</td>
</tr>
<tr>
<td>Accelerators</td>
<td>Accelerate the reducing agent and increase the deposition</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>Stabilizing the bath from decomposition</td>
</tr>
<tr>
<td>Buffers</td>
<td>Sustaining the pH for long time</td>
</tr>
<tr>
<td>pH regulators</td>
<td>adjusting the pH value</td>
</tr>
<tr>
<td>Temperature</td>
<td>Energy for deposition</td>
</tr>
</tbody>
</table>

The current study will focus on optimization of bath composition for the electroless Ni-P coating including nickel source, reducing agent, and the complexing agent.

2. Experimental Work

2.1 Specimens Preparation
Steel specimens (1030 steel) were used for the electroless Ni-P plating experiments. The specimens shape was disk with two flat surfaces (12 mm in diameter and 6 mm height).

The specimen flat surface was polished up to 1200 grit with silicon carbide papers, followed by 3 and 1µm diamond-paste polishing respectively. Specimens surfaces were then cleaned in ethanol ultrasonic bath for 10 minutes followed by degreasing in 10% NaOH solution for another 10 minutes at 60 ºC. The final ultrasonic cleaning was applied on the sample for another 10 minutes in ethanol. Specimens washed with deionized water after each step. The weight of the substrate before coating (w1) determined and its surface was activated into a hydrochloric acid (40 vol.% HCl) for 30 seconds and specimen delivered to the coating bath.

2.2 Samples coating
All chemicals used were analytical reagents (AR) and purchased from Sigma-Aldrich and deionized water (>17 MΩ.cm) were used. The
plating cell was consisted of a 200 ml double wall beaker heated by digitally controlled circulated water baths feed. Magnetic stirrer with 300 rpm with a PTFE coated magnetic rod (3 cm) was used. After plating at 80±1°C for 1 hr, the specimen washed in DI water and ethanol respectively dried with nitrogen gas and w2 was then determined, and the deposition rate (Dr) calculated by weight gain method according to equation (1) [11].

\[
\text{Deposition rate (Dr)} = \frac{w_2 - w_1}{\rho \times A \times t} \ \text{µm h}^{-1} \ \text{.................(1)}
\]

Where: ‘\(\rho\)’ is the density of nickel, ‘A’ is the surface area of the specimen and ‘\(t\)’ is the coating time.

3. Results and discussion

The electroless Ni–P solution consists mainly of a source of nickel ions, a reducing agent, and a complexing agent. This study aims to investigate the three main components of bath and optimize them according to the deposition rate and the stability of the solution with using tri-sodium citrate as a complexing agent. Sodium citrate is one of the most common complexing agents used in electroless nickel coating [11-15]. The reason for such wide usage is due to its high stability to limit reaction with the substrate surface and to inhibit the decomposition of bath solutions [16]. In the current study, for nickel ions source nickel sulfate was used, sodium citrate was used as a complexing agent and sodium hypophosphite as a reducing agent. To minimize the total number of trials, experiments arrangement as well as the results were designed and fitted to \(L9\) orthogonal array (Taguchi analysis). Each component concentrations and samples arrangement, as well as the operating conditions, are summarised in Table 2.
Table 2 Arrangement of samples and operating conditions

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Nickel sulfate, M</th>
<th>Sodium hypophosphite, M</th>
<th>Sodium citrate, M</th>
<th>Coating thickness, µm</th>
<th>Operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.05</td>
<td>0.15</td>
<td>0.05</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>0.05</td>
<td>0.25</td>
<td>0.10</td>
<td>0</td>
<td>pH 4.7±0.15</td>
</tr>
<tr>
<td>S3</td>
<td>0.05</td>
<td>0.35</td>
<td>0.10</td>
<td>0</td>
<td>1 mg L⁻¹ thiourea</td>
</tr>
<tr>
<td>S4</td>
<td>0.10</td>
<td>0.15</td>
<td>0.10</td>
<td>3.8</td>
<td>Temperature 80±1°C</td>
</tr>
<tr>
<td>S5</td>
<td>0.10</td>
<td>0.15</td>
<td>0.15</td>
<td>1.3</td>
<td>Bath Volume 200 ml</td>
</tr>
<tr>
<td>S6</td>
<td>0.10</td>
<td>0.35</td>
<td>0.05</td>
<td>12.8</td>
<td>Stirrer Speed 300 rpm</td>
</tr>
<tr>
<td>S7</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>S8</td>
<td>0.15</td>
<td>0.25</td>
<td>0.05</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>S9</td>
<td>0.15</td>
<td>0.35</td>
<td>0.10</td>
<td>15.1</td>
<td></td>
</tr>
</tbody>
</table>

3.1 Effect of bath composition on the deposition rate (Dr):
The deposition rate for each bath composition was calculated and plotted by Minitab program according to Taguchi orthogonal array L9 for design of the experiment [17-20], as shown in Fig.1. It is noticeable that, the increase of nickel sulphate and sodium hypophosphite concentrations in the plating bath, increase the deposition rate.

Nickel sulfate is the source of nickel ions to be plated and sodium hypophosphite is the reducing agent that introduces the electrons required for deposition process according to the electrochemical mechanism (equations 1 to 3). This mechanism considered that Ni plating is resulted from anodic and cathodic reactions. The anodic reaction is the oxidation of hypophosphite with water, which generates electrons needed for cathodic reactions according to the equation 1 [4, 5, 21-23]:

\[
H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H + 2e^- \quad E^* = 0.50 \text{ V.} \quad (1)
\]

Cathodic reaction:

\[
\begin{align*}
Ni^{++} + 2e & \rightarrow 2Ni \quad E^* = -0.25 \text{ V.} \quad (2) \\
H_2PO_2^- + 2H^+ + 2e & \rightarrow P + 2H_2O \quad E^* = -0.50 \text{ V.} \quad (3)
\end{align*}
\]
The concentration of sodium citrate shows a negative effect on the deposition rate, as the citrate concentration increases in the bath, the complexed nickel ions increase, and the remained nickel ions used in plating decrease (equation 4). When a coordination site of a metal ion is complexed, that site is not as reactive since it is no longer coordinated with a weakly bound water molecule. Since the electroless plating reaction only takes place at vacant or ‘free’ coordination sites, the concentration of complexing agents in the plating bath is very important to control these vacant sites as follows [16]; When a complexing agent (L) is in solution, the free (M^{z+}) and complexed (ML_m^{(z-nm)}) sites reach a state of equilibrium according to the following:

\[ \text{M}^{z+} + \text{mL}^{-n} \leftrightarrow \text{ML}_m^{(z-nm)} \]  

(4)

Where ML_m^{(z-nm)} denotes the metal complex, M^{z+} the free metal ions and L^{-n} the free complex [24]. The calculated deposition rate was tested and confirmed by SEM imaging for a coated sample with a maximum coating thickness of 15 µm as shown in Fig 2. The SEM cross-section image confirms the thickness calculation with a reasonable error.
3.2 Effect of bath composition on the buffering capacity (ΔpH/g)

It is well known that, for Ni deposition, the H⁺ are generated according to the atomic hydrogen mechanism. The atomic hydrogen is produced from hypophosphite reduction with water, and is then desorbed at the catalytic surface according to the equations below [23]:

\[
H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H_{ads}
\]  

(5)

At the catalytic surface, the adsorbed hydrogen reduces Ni²⁺ according to the reaction:

\[
2H_{ads} + Ni^{++} \rightarrow Ni + 2H^+
\]  

(6)

Finally, atomic hydrogen combines and evolves as a hydrogen bubble. The accumulation of hydrogen ions (H⁺) in the plating bath lowers the pH of the solution. It is well known that when the pH decreases, the rate of electroless coating deposition decreases [22, 25-28]. The amount that the pH changes as a result of the formation of H⁺ is related to the buffer capacity of the solution components [16]. Fig. 3 shows the effect of each bath component on the buffering capacity of the plating solution.
Figure 3 Effect of bath composition on the bath stability (ΔpH/g)

From Fig 3, it can be remark that the plating bath becomes more stable and the bath buffering has been improved (smaller variation in solution pH) at concentration of 0.5 M for tri-sodium citrate.

4. Conclusions and Recommendations

The investigating results include the deposition rate as well as the stability of the coating bath. The results can be concluded as follow:
- The electroless Ni-P coating deposition rate can be maximized by controlling the coating bath composition.
- The increase of nickel source and reducing agent increases the deposition rate remarkably while; sodium citrate concentration in the plating bath decreases the deposition rate of coating.
- The bath stability should be taken in consideration during applications in industrial scale as it indicates the bath life and ability to reused for many times.
- Bath stability can be maximized with sodium citrate with concentration of 0.1 M in the coating bath.
References


الظروف المثالية لمحلول الطلاء اللاكهرباءي بالنيكل ومردوده في التطبيقات الصناعية

ملخص البحث:

يستخدم الطلاء اللاكهرباءي بالنيكل على نطاق واسع في الكثير من الصناعات الهندسة نظرًا لقدره على تغيير وتحسين خصائص أسطح المشغولات المصنوعة من الصلب وسياصه. إذ يقدم هذا النوع من الطلاء مزيجًا ممتازًا من خصائص الأسطح للمنتجات المطلية ويمكن أن يضيف السطوع واللمعان وكذلك المظهر الجيد للسطح النهائي. تتميز طبقة الطلاء النهائية أيضًا بالالتصاق الجيد جدًا مع الأسطح المطلية، وللهذا فكثيرا ما يستخدم الطلاء اللاكهرباءي بالنيكل كطبقة طلاء أولى لأنواع أخرى من الطلاءات. انتاج طبقة طلاء متجانسة التركيب لها مقاومة عالية للتأكأل يعتمد بشكل أساسي على تركيبة محلول الطلاء المستخدم. لذلك يدرس هذا البحث تأثير تركيبات محلول الطلاء المختلفة، والتي تتضمن كبريتات النيكل وهيبوفوسفيت الصوديوم وسترات الصوديوم، على جودة طبقة الطلاء المستخدم. وقد استخدم كلا من معدل الترسيب للطلاء (Dr) وكذلك ثبات حامضية محلول الطلاء مقارنة وضعيب مثالية المتغيرات للعملية مع التركيزات المختلفة لمكونات محلول الطلاء. أظهرت نتائج هذا العمل أن معدل ترسيب طبقة الطلاء يزداد مع زيادة مصدر النيكل والعامل المختزل بينما تركيز سترات الصوديوم في محلول الطلاء له تأثير سلبي على معدل الترسب.