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# PRELIMINARY STEP IN FORMULATING THE OPTIMUM ELECTROLESS NICKEL BATH USING TAGUCHI METHOD

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**Abstract.** Electroless nickel plating has been rapidly developed and widely used in many fields due to its superior properties of coating. It is an autocatalytic process in which the deposited nickel is reduced from its ionic state by chemical reducing agent in bath. The basic compositions of the bath and operating condition are $NiSO_4.6H_2O$, $NaH_2PO_2.H_2O$, $(NH_4)_3C_6H_5O_7$, wetting agent and at 50°C. In this preliminary study, Taguchi Robust Design Technique was used to rank several factors that may affect the deposition rate in order to formulate the optimum electroless nickel bath. They were concentration of nickel salt, reducing agent, complexing agent and pH of the bath. The Taguchi orthogonal array $L_9$ was used for the experimental design with three levels of consideration for each factor. Mild steel plates were used as substrates. The deposition process was carried out for half an hour and the rates were obtained by weighing the samples before and after plating. The response (deposition rate) was analysed based on the Taguchi's signal-to-noise ratio (S/N) and analysis of variance (ANOVA). The results showed that the most notable factor influencing the deposition rate was the pH, followed by the concentration of nickel salt, reducing agent and complexing agent. The optimum bath formulation was then predicted based on these results.

*Key words*: Electroless nickel plating; Taguchi's method; Taguchi orthogonal array; deposition rate; optimum bath formulation

**Abstrak.** Teknologi penyaduran nikel secara tanpa elektrik telah berkembang pesat dan diaplikasikan secara meluas dalam banyak bidang industri disebabkan ciri sadurannya yang unggul. Penyaduran tanpa elektrik ialah suatu proses pengautomangkinan iaitu saduran nikel berlaku daripada penurunan garamnya oleh agen penurunan yang hadir dalam larutan tanpa elektrik. Komposisi asas larutan tanpa elektrik nikel di dalam kajian ialah $NiSO_4.6H_2O$, $NaH_2PO_2.H_2O$, $(NH_4)_3C_6H_5O_7$, agen pembasah dan suhu operasinya ialah 50°C. Dalam kajian awal ini, teknik Taguchi telah digunakan untuk menyelidik beberapa faktor yang dapat mempengaruhi kadar saduran supaya larutan elektrolit nikel yang optimum dapat diformulasikan. Faktor-faktor ini ialah kepekatan garam nikel, agen penurunan, agen pengkompleks dan pH larutan. Susunatur ortogonal Taguchi $L_9$ telah digunakan untuk merancang ekperimen dengan tiga paras bagi setiap faktor. Kepingan keluli lembut digunakan sebagai substrat. Proses penyaduran dijalankan selama setengah jam dan kadar saduran didapati dengan menimbang sampel sebelum dan selepas saduran. Data-data yang diperolehi telah dianalisis berdasarkan nisbah isyarat kepada bisingan Taguchi dan analisis varians. Keputusan menunjukkan bahawa faktor pH paling mempengaruhi kadar saduran diikuti dengan faktor kepekatan garam nikel, agen penurunan dan agen pengkompleks. Formulasi larutan elektrolis yang optimum seterusnya dapat diramalkan berdasarkan keputusan ini.

*Kata Kunci*: Penyaduran nikel secara tanpa elektrik; kaedah Taguchi; susun atur ortogonal Taguchi; kadar saduran; larutan tanpa elektrik yang optimum

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## 1.0 INTRODUCTION

Autocatalytic (electroless) plating of nickel-phosphorus alloy on various types of substrates has been used commercially in many industrial fields such as aerospace, automotives, electronics, computers, machinery, oil and gas production and valve industries [1]. Since its discovery by Brenner and Riddell, electroless plating has been studied extensively due to its superior properties of coatings and great commercial value. Electroless nickel coatings not only have remarkable wear and corrosion resistance, but uniform thickness on any area of the substrates exposed to the plating solution regardless the shape of the substrates [2]. Conventional electroplating process does not have this advantage, which its coatings thickness influenced by current density supplied on the substrates.

Many types of electroless nickel baths (plating solutions) had been formulated in order to obtain desirable coating properties with high deposition rate and bath stability [3,4]. Generally, there are two types of electroless nickel baths acidic and basic baths. For most of the published formulations, electroless nickel plating requires operating temperature between 70 and 95°C to obtain satisfied deposition rate [5,6]. Deposition rate is affected by composition of the bath as well as operating temperature and pH. In this research, special attention has been focused on the electroless nickel bath formulation. In order to obtain the optimum performance of the formulated bath, Taguchi method was used for designing the experiments.

## 2.0 EXPERIMENTAL

The substrate material used in this study was mild steel plate with a dimension of 30 × 40 × 0.5 mm. Before plating, the substrates were pretreated with the following procedures. The substrates were polished with high-grade sand paper before rinsed them with distilled water. The substrates were then chemically cleaned in an alkaline solution for 15 minutes at 60 – 90°C. They were subsequently rinsed with hot water, dried and weighed. Then, the substrates were pickled in 10% HCl solution for 2 minutes followed by water rinsing and electroless plating. The basic compositions of the bath and operating conditions under investigation were as followed: [$NiSO_4.6H_2O$] 30 – 50 g/L, [$NaH_2PO_2.H_2O$] 30 – 50 g/L, [$(NH_4)_3C_6H_5O_7$] 40 – 60 g/L, with wetting agent of 0.4 ml/L, pH 8.0 –10.0 (adjusted with NaOH) and temperature 50°C. The types of chemicals used in this project were analytical grade while the wetting agent was 62A; a commercial wetting agent supplied by Enthone OMI.

The orthogonal array $L_9$ was used to study the influence of four factors which were concentrations of $NiSO_4.6H_2O$ (nickel salt), $NaH_2PO_2.H_2O$ (reducing agent), $(NH_4)_3C_6H_5O_7$ (complexing agent) and pH of the bath against the deposition rate. Each factor was considered at 3 levels. The factors involved and their levels were shown in Table 1. If full factorial experimental design were used, it would require 81(3) trial runs for all possible combinations of these factors [4]. By using Taguchi

**Table 1** Design factors and their levels for orthogonal experiment

| Column | Factors | Level Number | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| 1 | $[NiSO_4.6H_2O]$ g/L | 30 | 40 | 50 |
| 2 | $[NaH_2PO_2.H_2O]$ g/L | 30 | 40 | 50 |
| 3 | $[(NH_4)_3C_6H_5O_7]$ g/L | 40 | 50 | 60 |
| 4 | pH | 8 | 9 | 10 |

orthogonal array $L_9$ for experimental design, the number of trial runs was reduced to 9 simple and effective experiments. It could save experimental cost and time.

The use of Taguchi orthogonal arrays helps determine the minimum number of experiments needed which may produce the most favourable information for a given set of factors. The comparison between full factorial design and Taguchi design was shown in Table 2. Table 3 illustrated the orthogonal array $L_9$ [7]. Since there were four of three levels factors, these factors were assigned to all four columns in the $L_9$ array.

**Table 2** Comparisons of factorial design and Taguchi design

| Factors | Level | Total Number of Experiments | |
|---|---|---|---|
| | | Factorial Design | Taguchi |
| 2 | 2 | 4 ($2^2$) | 4 |
| 3 | 2 | 8 ($2^3$) | 4 |
| 4 | 2 | 16 ($2^4$) | 8 |
| 7 | 2 | 128 ($2^7$) | 8 |
| 15 | 2 | 32,768 ($2^{15}$) | 16 |
| 4 | 3 | 81 ($3^4$) | 9 |

**Table 3** $L_9$ (3[4]) Orthogonal Array [7]

| Trial No. | Column Number | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| 1 | 1 | 1 | 1 | 1 |
| 2 | 1 | 2 | 2 | 2 |
| 3 | 1 | 3 | 3 | 3 |
| 4 | 2 | 1 | 2 | 3 |
| 5 | 2 | 2 | 3 | 1 |
| 6 | 2 | 3 | 1 | 2 |
| 7 | 3 | 1 | 3 | 2 |
| 8 | 3 | 2 | 1 | 3 |
| 9 | 3 | 3 | 2 | 1 |

Interaction effects between factors were not examined in this study and considered insignificant. Nine trial runs with particular combinations of factor levels in the array were carried out and duplication was done ($R_1$ refer to 1$^{st}$ reading and $R_2$ refer to 2$^{nd}$ reading). The deposition process was carried out for half an hour and the rates were obtained by weighing samples before and after plating.

## 3.0 RESULTS & DISCUSSION

The results of the nine trial conditions, with two run per trial condition are shown in Table 4. The deposition rates were measured in term of weight gains (mg). In the Taguchi analysis, there are three types of quality characteristics with respect to the target design, they are 'smaller is better', 'nominal is better' and 'bigger is better' [7]. In this study, the higher value of deposition rate is desirable. Thus, it was categorised in the 'bigger is better' quality characteristic. All of the results were transformed into signal to noise ratio (S/N) in the last column of Table 4. Column four was assigned as the Mean Squared Deviation (MSD). For the 'bigger is better' quality characteristic,

$$MSD = (1/R_1^2 + 1/R_2^2) / 2 \tag{1}$$

**Table 4** Experimental results and their S/N ratios

| Trial No. | Weight Gain/mg | | MSD | S/N |
|---|---|---|---|---|
| | $R_1$ | $R_2$ | | |
| 1 | 52.6 | 51.2 | 3.715E-04 | 34.30 |
| 2 | 62.7 | 64.5 | 2.474E-04 | 36.07 |
| 3 | 89.6 | 87.3 | 1.279E-04 | 38.93 |
| 4 | 96.2 | 98.1 | 1.060E-04 | 39.75 |
| 5 | 51.1 | 49 | 3.997E-04 | 33.98 |
| 6 | 98 | 95 | 1.075E-04 | 39.69 |
| 7 | 77.8 | 77.7 | 1.654E-04 | 37.81 |
| 8 | 111.6 | 113.6 | 7.889E-05 | 41.03 |
| 9 | 85 | 84.4 | 1.394E-04 | 38.56 |
| | | | **Mean (m)** | **37.79** |

The signal to noise ratio was computed as follows:

$$S/N = -10 \log (MSD) \tag{2}$$

The average effects of the factors for each level were shown in Table 5. For an example, the pH factor was at level three for trial condition 3, 4 and 8 in the array. In other words, number 3 appeared at trial 3, 4 and 8 in Column 4 of Table 3. Computation for average effect of pH at level 3, which was denoted by $m_{D3}$ is shown below:

**Table 5** The average effects of factors for each level

| Column | Factors | Average Effects | | |
|---|---|---|---|---|
| | | Level 1 | Level 2 | Level 3 |
| 1 | $[NiSO_4.6H_2O]$ | 36.43 | 37.81 | 39.13 |
| 2 | $[NaH_2PO_2.H_2O]$ | 37.29 | 37.03 | 39.06 |
| 3 | $[(NH_4)_3C_6H_5O_7]$ | 38.34 | 38.13 | 36.91 |
| 4 | pH | 35.61 | 37.86 | 39.9 |

$$m_{D3} = 1/3\ (S/N_3 + S/N_4 + S/N_8) \qquad (3)$$

$$= 1/3\ (38.93 + 39.75 + 41.03)$$

$$= 39.90$$

where $S/N_3$, $S/N_4$ and $S/N_8$ were the signal to noise ratio values listed in the last column of Table 4 corresponding to their trial number. The others were computed in the same manner as $m_{D3}$. Note that there had been gradually increased in average effects started from level 1 to level 3 for factors $[NiSO_4.6H_2O]$, $[NaH_2PO_2.H_2O]$ and pH and gradually decreased in average effects for factor $[(NH_4)_3C_6H_5O_7]$. These observations indicated that the deposition rate would be increased when the concentration of nickel salt, reducing agent and pH become higher. On the contrary, when the concentration of complexing agent increased, the deposition rate will become lower.

Different factors affect the deposition rate to different degrees. The relative effect of the different factors can be obtained by the decomposition of total variation into its appropriate components, which is commonly called analysis of variance (ANOVA). ANOVA is also needed for estimating the error variance. The results of ANOVA were shown in Table 6.

Column 4 in the ANOVA table was defined as Sum of Squares. For example, sum of squares due to pH factor was computed using the following formula [7]:

**Table 6** ANOVA table

| Column | Factors | DOF | Sum of Squares (SS) | Variance | F | Percent |
|---|---|---|---|---|---|---|
| 1 | $[NiSO_4.6H_2O]$ | 2 | 10.94 | 5.47 | – | 22.11 |
| 2 | $[NaH_2PO_2.H_2O]$ | 2 | 7.32 | 3.66 | – | 14.8 |
| 3 | $[(NH_4)_3C_6H_5O_7]$ | 2 | 3.58 | 1.79 | – | 7.24 |
| 4 | pH | 2 | 27.63 | 13.82 | – | 55.85 |
| | All Others/Error | 0 | – | – | | – |
| | **Total** | **8** | **49.47** | | | **100** |

$$SS_{pH} = 3(m_{D1} - m)^2 + 3(m_{D2} - m)^2 + 3\,(m_{D3} - m)^2 \quad (4)$$

$$= 3(35.61 - 37.79)^2 + 3(37.86 - 37.79)^2 + 3(39.90 - 37.79)^2$$

$$= 27.63$$

where $m_{D1}$, $m_{D2}$ and $m_{D3}$ refer to the average effects correspond to pH factor for each level as listed in Table 5. Sum of squares of other factors were computed in the same manner and respectively tabulated in the same column. The variance of each factor was determined by dividing sum of square for each factor with its degree of freedom (DOF). The degree of freedom associated with a factor equals to one less than the number of levels. For a factor with 3 levels, level 1 data can be compared with level 2 and level 3 data but not with level 1 itself. Thus the 3 levels factor has 2 DOF [7]. The variance ratio (F) is the ratio of variance due to the effect of a factor and variance due to the error term.

The review of the 'Percent' column in Table 6 showed that factor pH contributed the highest percentage (55.85%) to the factor effects, followed by [$NiSO_4.6H_2O$] (22.11%), [$NaH_2PO_2.H_2O$] (14.80%) and [$(NH_4)_3C_6H_5O_7$] (7.24%). Since the contribution of [$(NH_4)_3C_6H_5O_7$] was the smallest that is less than 10%, it was considered insignificant. Thus, this factor was pooled (combined) with the error term. This process of disregarding the contribution of a selected factor and subsequently adjusting the contribution of the other factor is known as pooling. The new ANOVA after pooling was shown in Table 7. It was observed that as small factor effect [$(NH_4)_3C_6H_5O_7$] was pooled, the percentage contributions of the remaining factors decreased slightly. But the ranking of factor effects still remained the same. In estimating the performance at optimum condition, only the significant factors were used. An examination of the average effects indicated level 3 of pH factors, [$NiSO_4.6H_2O$] and [$NaH_2PO_2.H_2O$] will be included in the optimum condition. As shown in Table 8, the expected improvement from these factors was 4.72 over the current average of performance 37.79. Since [$(NH_4)_3C_6H_5O_7$] had little significance, it was omitted in the selection of levels

**Table 7** Pooled ANOVA table

| Column | Factors | DOF | Sum of Squares (SS) | Variance | F | Percent |
|---|---|---|---|---|---|---|
| 1 | [$NiSO_4.6H_2O$] | 2 | 10.94 | 5.47 | 3.06 | 14.88 |
| 2 | [$NaH_2PO_2.H_2O$] | 2 | 7.32 | 3.66 | 2.04 | 7.56 |
| 3 | [$(NH_4)_3C_6H_5O_7$] | {2} | {3.58} | – | – | – |
| 4 | pH | 2 | 27.63 | 13.82 | 7.72 | 48.62 |
| | All Others/Error | 2 | 3.58 | 1.79 | | 28.95 |
| | **Total** | **8** | **49.47** | | | **100** |

Note: Insignificant factorial effect is pooled as shown { }

for the optimum condition [3].

The contributions from these factors were calculated by subtracting the current grand average of performance value from the values listed in the last column of Table 5 (Level 3) that correspond to each factor. For an example, the contribution of

**Table 8** Estimate of the optimum condition of design

| Factors | Level Description | Level | Contribution |
|---|---|---|---|
| [$NiSO_4.6H_2O$] | 50 g/L | 3 | 1.34 |
| [$NaH_2PO_2.H_2O$] | 50 g/L | 3 | 1.27 |
| pH | 10 | 3 | 2.11 |
| Contribution from all factors (total) | | | 4.72 |
| Current grand average of performance or Mean | | | 37.79 |
| Expected result at optimum condition | | | 42.51 |

[$NaH_2PO_2.H_2O$] factor was 1.27, which was obtained by subtracting 37.79 (Mean value) from 39.06 (value of the last column and second row of Table 5).

The expected result ($R_{expected}$) at optimum condition in term of S/N ratio can be converted back to scale of units of the original observations by the following steps:

$$42.51 = -10 \log (MSD)$$

$$MSD = 10^{-42.51/10} = 5.6105 \times 10^{-5}$$

$$R_{expected} \cong (MSD)^{-1/2} = 133.51 \text{ mg}$$

## 4.0 CONCLUSIONS

Based on these results, the optimum bath formulation for electroless nickel on mild steel may be predicted in general as follows:

| Factors | Level | Level Description |
|---|---|---|
| [$NiSO_4.6H_2O$] | 3 | 50 g/L |
| [$NaH_2PO_2.H_2O$] | 3 | 50 g/L |
| [$(NH_4)_3C_6H_5O_7$] | 1 | 40 g/L |
| pH | 3 | 10 |

However this prediction just considered the deposition rate, as the ‘bigger is better’ quality characteristic. It did not take bath stability factor into account. Generally, the bath stability will be decreased when concentrations of the nickel salt, reducing agent and pH become higher and concentration of the complexing agent becomes lower.

Thus, a moderate level of the compositions should be considered in bath formulation in order to obtain desirable deposition rate and bath stability. Adding into account, the optimum electroless nickel bath compositions can be predicted and the new bath formulation should not be far away from the values listed above. This formulated bath is believed to give at least 100 mg nickel deposits per half an hour at 50°C.

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