# MODELLING OF ELECTRODEPOSITION BATH USING THE FLOW ANALYSIS TECHNIQUE

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## ABSTRACT

This study aims to develop coating quality by using Flow Analysis (FA) technique in acid copper coating bath. The coating metal concentration of electrodeposition bath mixture, current density, coating time, distance between anode and cathode, temperature of bath mixture and pH are some of the factors which affect the coating quality. The coating metal concentration is the most important parameter. The metal concentration of electroplating bath solution decreases during the coating so coating quality also decreases. Bath mixture composition has been determined by analysing samples periodically according to the conventional industrial application. Much more time, effort and high financial cost are very necessary for this type of analysis. This paper represents a new method which determines the metal concentration of coating baths with flow analysis technique. The metal concentration is measured on-line with spectrophotometric technique which includes flow through cell according to the new method. This technique is very simple and the results can be taken easily. Firstly, the decrease in metal concentration is determined by the batch technique and then a sufficient amount of stock metal solution is added to the plating bath continuously by on-line system. The metal concentration of coating bath solution is kept at constant concentrations. This means that the coating metal quality does not

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decrease. All data are examined statistically. After reaching optimum conditions, coating results are examined by using Faraday Laws.

**Keywords:** Copper (II), Electroplating, Current Density, On-Line, Electrodeposition, Flow Through Cell

## 1. INTRODUCTION

The coating method protects metal surfaces against metal corrosion. An electroplating metal coating method is offered in industrial applications in many cases. The main components of an electroplating system are anode, cathode, electrolyte, bath mixture concentration and current density. The coating surface can be examined by using the Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-Ray diffraction analysis technique /1,2/. The coating surface should be smooth, stick, resistant against blows and should not be burned. The most effective factors of the coating surface are electroplating bath mixture concentration, current density, temperature, distance between anode and cathode, pH and coating time. Some examples of metal coating are gold, silver, zinc, and chromium. During the electroplating process, the metal concentration in bath mixture decreases. In fact the plating quality also goes down, so the analysis of electroplating bath solution composition plays a very important role in affecting the plating quality. In industrial applications, this analysis is made by taking samples from the electroplating bath solution.

Conventional industrial applications need more time, effort and high cost of analysis. Some new techniques which are based on Flow Analysis (FA) are used to solve this problem. FA is an analytical technique that is virtually ideal for industrial application /12/. It was developed by Ruzicka and Hansen and Steward in the 1970s /3, 6, 9, 10, 11/. In the study "Flow injection determination of Cu (II) in electrochemical bath with potentiometric differential micro detector", flow analysis (FA) is used /7/. According to FA technique, Cu (II) selective membranes are used for determining Cu (II) in copper sulphate plating bath solution /4, 5, 8/. In this study a new technique is described to solve the problem of analysing bath mixture concentration.

# 2. EXPERIMENTAL

## 2.1. Reagents and Sample

All chemicals were analytical reagent grade and supplied by E. Merck. Deionised water was used throughout the work. The copper coating bath solutions were prepared using two different concentrations, 9.93 g $l^{-1}$ Cu(II) and 4.96 g $l^{-1}$ Cu(II). The copper stock solutions 50.9 g $l^{-1}$ Cu(II) and 38.2 g $l^{-1}$ Cu(II) were prepared from $CuSO_4.5H_2O$.

### *2.1.1. Apparatus*

Absorbance measurements were obtained with a UV-150-02-Spectrophotometer (Schimadzu, Kyoto, Japan) using a flow-through cell (volume 1200 μl) with a light path of 1 cm, connected to a computer and strip chart linear recorder. The fluid was impelled with a peristaltic pump (Watson Marlow Pump) and used tygon pumping tubes (0.5mm, i.d.). An Orion Model 920A Ion-Analyzer equipped with a combination glass- calomel electrode was used for pH determination.

### *2.1.2. Recommended Procedure for the Electrodeposition Bath*

The schematic diagram of the experimental set-up is shown in Figure 1. Copper was deposited from sulphate electroplating bath. In each experiment, 50 cm a copper plate as anode electrode and graphite electrode rod as cathode electrode were used. When copper was deposited from a sulphate bath, the metal concentration of electrodeposition bath was decreased. The bath solution was carried toward the flow-through cell in the spectrophotometer by peristaltic pump and detected, whereby Cu (II) ion was selectively monitored at 810 nm and recorded. So that the decrease of concentration bath mixture was controlled continuously as Cu (II) concentration started to decrease in the coating bath, the tap of the tank, which was connected by a magnetic valve sensitive to absorbance signal by a signal amplificatory, was opened, and the required amount of Cu(II) solution was added to flow into the coating bath. The absorbance value was limited between two marked values for the magnetic valve which was programmed to open and close between these two required values; so Cu (II) ion concentration was fixed by transport to the copper solution in the coating bath mixture.

## 2.2. Methology of Plating Bath

The acid copper plating bath composition was worked using two different types of methods.

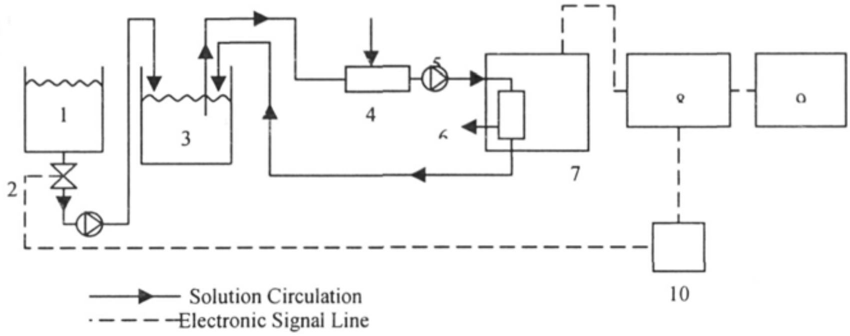

**Fig. 1**: The schematic diagram is conditions for current injection on-line of plating bath.; (1) Stock Cu(II) solution tank, (2) Magnetic valve, (3) Electrolyte cell, (4) current injection, (5) Pump, (6) Sink, (7) U.V.

### *2.2.1 Batch method*

The basic bath solution composition and operating conditions were prepared. The first studies were examined by batch technique to determine the optimum conditions. The determination of Cu (II) in plating bath solution was changed quantitatively. Calculation of the amount of stock solution that must be added to the bath per minute is shown in Equation 1.

$$M_1 V_1 = M_2 V_2 + M_3 V_3 \tag{1}$$

$M_1$: The initial concentration of plating bath solution (Cu (II) g $l^{-1}$)
$V_1$ : The initial volume of plating bath solution, (l)
$M_2$ : Concentration of stock solution (Cu (II) g $l^{-1}$)
$V_2$ : Stock solution volume, (l)
$M_3$ : The last concentration of plating bath solution (Cu (II) g $l^{-1}$)
$V_3$ : The last volume of plating bath solution, (l)

Calculation of approximate values is shown in Table 1. The optimum parameters in Table 1 are shown graphically in Figure 2.

**Table 1**
**Stock solution concentration and adding stock volumes**

| Bath conc. Cu(II) (g $l^{-1}$) | Condition number | Distance between anode-cathode (cm) | Approx. change in absorbance (in 1 min) | Current density (A $dm^{-2}$) | Stock sol. conc. (g $l^{-1}$) | Adding stock volume/ minute Cu(II) (ml $min^{-1}$) |
|---|---|---|---|---|---|---|
| 9.93 | 1 | 12 | 0.00030 | 0.8 | 50.9 | 0.2 |
| | | 12 | 0.00070 | 1.6 | 50.9 | 0.5 |
| | | 12 | 0.00118 | 2.4 | 50.9 | 0.8 |
| | | 12 | 0.00144 | 3.2 | 50.9 | 1.0 |
| | II | 4 | 0.00023 | 0.8 | 50.9 | 015 |
| | | 4 | 0.00072 | 1.6 | 50.9 | 0.5 |
| | | 4 | 0.00166 | 2.4 | 50.9 | 1.0 |
| | | 4 | 0.00144 | 3.2 | 50.9 | 1.0 |
| 4.96 | III | 12 | 0.00150 | 0.8 | 38.2 | 0.5 |
| | | 12 | 0.00252 | 1.6 | 38.2 | 0.8 |
| | | 12 | 0.00392 | 2.4 | 38.2 | 1.3 |
| | | 12 | 0.00415 | 3.2 | 38.2 | 1.4 |
| | IV | 4 | 0.00130 | 0.8 | 38.2 | 0.4 |
| | | 4 | 0.00267 | 1.6 | 38.2 | 0.9 |
| | | 4 | 0.00415 | 2.4 | 38.2 | 1.4 |
| | | 4 | 0.00442 | 3.2 | 38.2 | 1.5 |

### *2.2.2 On-line method*

The optimum conditions were: the bath solution concentration 4.96 g $l^{-1}$ Cu (II), distance of electrodes 12 cm, current density 16 A $dm^{-2}$ and temperature 37±2 °C. The optimum conditions were provided through an on-line system. The results are shown in Figure 3. The new automatic system was sensitive against the absorbance signals from the spectrophotometer. The decrease was determined by the automatic system and then a sufficient amount of stock Cu (II) solution was added to the plating bath. When the plating bath concentration was decreased, the system was stopped automatically to add the stock solution to the plating bath until bath solution concentration again reached the limited value.

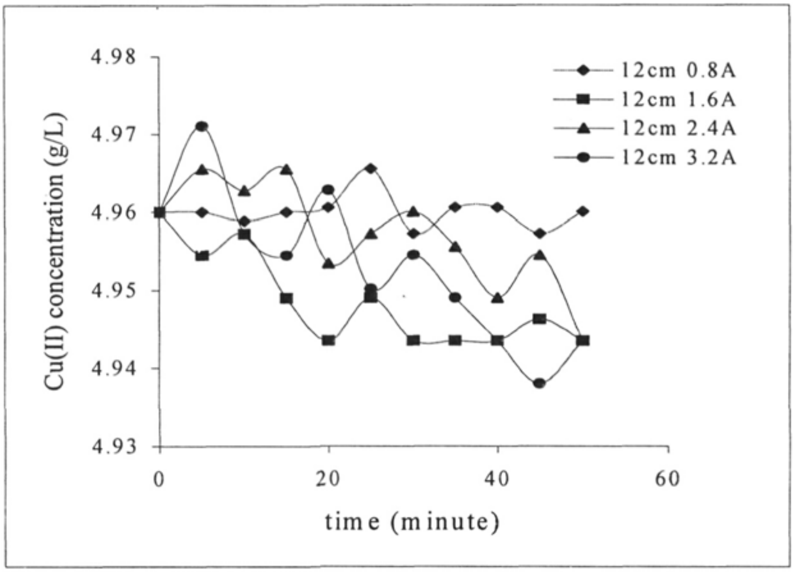

**Fig. 2:** Decrease of the copper concentration in the reaction time as 4.96 g $l^{-1}$ Cu (II) plating bath solution.

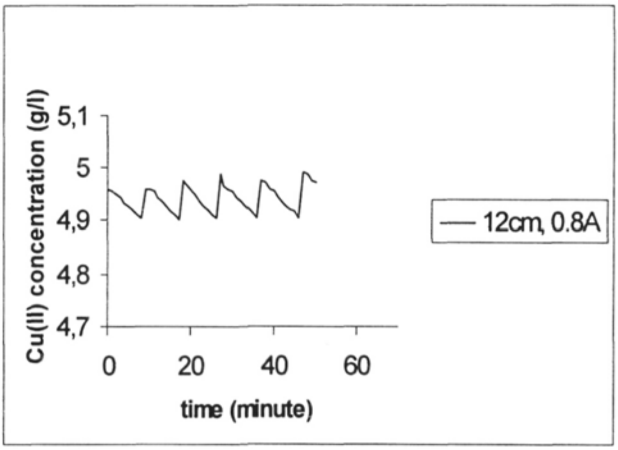

**Fig. 3:** Optimum condition of the copper plating with on-line system as 4.96 g $l^{-1}$ Cu (II), distance of electrodes 12 cm, current density A $dm^{-2}$, temperature 37±2 C°.

## 2.3. The Application of Faradaic Laws

In optimum conditions, two different processes (online and batch) were examined by using Faradaic Laws. The weight of Cu (II) which could be coated on the plate of surface was calculated theoretically by using Equation 2.

$$G=A_e\, F\, i\, t\, n_k \qquad (2)$$

G : Deposited amount of Cu (II) on the cathode (g)
i : Current density (A $dm^{-2}$)
t : Coating time (h)
$A_e$ : Theoretical amount of Cu (II) deposited on the cathode in 1 A $h^{-1}$
F : The surface of the cathode ($dm^2$)
$n_k$ : Cathode efficiency

The parameters of processes were examined by using Faradaic Laws and the results are shown in Table 2. The plate was coated within 5 minutes by using on-line technique with the usage of stock Cu (II) solution. After the process was completed, the efficiency percentage between the experimental coated copper and theoretical coated copper was calculated. The time differency was investigated as 15 minutes, 30 minutes and 45 minutes. The same calculations were performed. All same studies were examined again batch technique at 5 minutes, 15 minutes, 30 minutes and 45 minutes. The efficiency percentage of coated plate between experimental and theoretical coated copper was calculated. All results obtained above were noted in Table 2 as on-line and batch study.

## 3. RESULTS AND DISCUSSION

Initially, the optimum conditions were determined with batch technique; all parameters including plating quality, distance between anode and cathode, statistic results and stock solution concentration were evaluated. The optimum conditions were found to be (Table 1): bath solution concentration 4.96 g $l^{-1}$ of Cu (II), the distance between anode - cathode 12 cm, the current density 0.8 $Adm^{-2}$ the stock solution concentration 38.2 g $l^{-1}$ of Cu (II) and the temperature 37±2 °C. Other conditions found are shown in Table 1. We also saw that the plating surface did not stick to plate strongly and the coatings were burnt at high current density.

The optimum parameters obtained in the batch processing were used in the second step in an on-line process which was shown in Figure 1, and the results were shown in Figure 2. The results obtained from the on-line process were graphed in Figure 3. It was seen clearly that the maximum and minimum concentration values were in a certain range and the process never went out of this range during the on line process.

Table 2 shows that the on-line process was more useful from the aspect of the Faradaic Laws. Efficiency percentage was about 95.5 % with the on-line process. On the other hand, the efficiency percentage was about 65% with the batch process. Therefore the coating quality increased and the process was controlled more precisely by using the on-line process including the on-line Flow Analysis method.

**Table 2**

The relationship between the theoretical and the practical amounts of copper on the plate

| Study time (minute) | Theoretical amount of coating copper (g) | Practical amount of coating copper (g) | Efficiency Percentage |
|---|---|---|---|
| **On-Line Study** | | | |
| 5,000 | 0.0772 | 0.0769 | 99.6 |
| 15,000 | 0.2324 | 0.2193 | 94.4 |
| 30,000 | 0.4649 | 0.4328 | 93.1 |
| 45,000 | 0.6974 | 0.6632 | 95.1 |
| **Batch Study** | | | |
| 5,000 | 0.0772 | 0.0771 | 99.8 |
| 15,000 | 0.2324 | 0.1297 | 55.8 |
| 30,000 | 0.4649 | 0.3156 | 67.8 |
| 45,000 | 0.6974 | 0.4451 | 63.8 |

## CONCLUSION

The determination of Cu (II) metal ions is very important for the electrodeposition industry of our region. The quality of electrodeposited products depends partly on the composition of the metal ions in the plating bath. The analysis of metal ions not only allows accurate control of industrial waste water quality, but also makes it possible to obtain the required product with needed chemical composition.

The aim of the present study is the optimization using a stopped-flow injection system for the determination of Cu (II) ion in the plating bath solution. Both batch and on-line analytical procedures were studied. The linear relationships were assumed between the metal concentration and: 1. The absorbance changes in the course of reaction time, and 2. The adding solution needed to obtain a fixed absorbance change. This methodology was found to work well for the fixed concentration of metal.

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