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SYSTEM STUDYING FOR CREATING A STATISTICAL MODEL OF THE ELECTROLESS COPPER PLATING ON TEXTILES

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Abstract

Metallized fabrics are modern composite materials combining the positive physiological and ergonomic properties of a textile-based and screening properties of electroless plated copper layer as protection from electromagnetic interferences.

The chemical method is the most convenient for copper plating on textiles. In a study of the process were identified complex relationships between the electrolyte composition and plating conditions. The complexity of this technology is an important multi-factorial object for investigations.

By conducting of a planned factorial experiment is obtained adequate linear regression model for chemical copper plating on textiles. It allows predicting the thickness of the chemical copper coating on certain values of input parameters (concentrations of copper sulfate and formaldehyde, and time delay) in the investigated factor space, as well a further optimization of the process.

Key words: Electroless copper, metallization of textiles, experimental modelling, control electroless plating

1. INTRODUCTION

One of the first practical applications of chemical plating in the early twentieth century was the manufacture of copper mirrors, which later shifted away from the chemical silver-plate. After the World War II, the rapid development of radio-electronics put to the fore the need for printed circuit boards (PCBs) with plated holes. It turns out that because of their qualities - high conductivity, good soldering and the possibility of plating at room temperature, chemical copper is sought decision.

The chemical plating is electroless deposition by reduction process of copper ions to copper deposition of coating on metal and dielectric surfaces. Interest to this plating increases greatly in relation to the rapid development of radio-electronics and galvanized dielectrics, functional and decorative purposes. Currently, the most extensive area of its application is the manufacture of PCBs. However its importance is great for metal and synthetic fibers, graphite powder, ceramics, glass, plastics and others [1-5].

The chemical method is most convenient for plating on textiles [6]. Major influence on the kinetics of this process play a major concentration of salt, the reducer and plating time.

In a study of the process were identified complex relationships between the electrolyte composition and mode of deposition. The complexity of this technology is important multi-factorial object for study.

The planning of the experiment is a scientific direction for studying of multi-factorial processes. Its application leads to a rapid decision of multi-factorial tasks to clarify the role of input factors (X) on

the output parameters (Y). The main method for investigation of objects for use and management is modelling [7-12].

By means of the obtained mathematical model can be evaluated the impact of each factor separately, and their interaction on the output parameter, and to obtain by this way a reliable estimatation (information) for the object at a minimum number of experiments. Construction of model of the multi-factorial object is a necessary condition for the latter to be studied and researched, but also operated and maintained in the normal (optimum) technological regime [7-6].

For objects where it is very difficult to understand the mechanism of processes taking place in them or is not justified a loss of time, of work and of resources at one technological implementation, particularly convenient way of presentation is by the famous diagram of "black box". Such object can be studied and managed adequately only on the basis of information at its input and output [7-12]. The main method for obtaining information on objects represented by a diagram of the "black box" is the experiment. Collection of experimental data can be done either by active or passive experiment. At the active experiment on the input of the studied multi-factorial object impact only controlled, variable factors. It may be full (FFE) or fraction (FrFE) factorial experiment. Output parameters (Y) characterized the object and their exact defining is the main purpose of the experiment. Factors (X) should be manageable, non-accidental and unrelated to each other in order to manage the experimental research process. If the factors are dependent then the changing of one factor will bring to the change of all those factors that depend on it.

Using statistical methods for modeling of multi-factorial objects can be obtained mathematical models that adequately describe the process of chemical deposition of copper coatings, and to design a corresponding response surfaces. A similar approach was used to study both the chemical and electrochemical plating of metal and alloy coatings [7-13].

2. EXSPERIMENTAL

It is well known that the solutions for chemical deposition of copper are less stable than those for chemical deposition of nickel. Instability of copper baths can be explained by partial reduction of Cu^{2+} to Cu^{+}. These Cu^{+} ions then participate in disproportional reaction at which copper metal (Cu^{0}) particles are obtained, dispersed in the electrolyte.

For solving of the aimed task was used classical and active planned experiment in the deposition of copper coatings on ABS and textiles from trilonic electrolyte.

From the preliminary comparative measurements on these two materials have been carried out and found that the data obtained were within the error. This gave us a reason after that for greater precision to work with ABS only.

Samples presented mechanically cut ABS-sized substrates 1X1 cm. The electroless deposition of copper coatings on samples of ABS is performed by the following technological scheme:

1. Pre-activation in 3 M HCl
2. Activation by colloidal activator
3. Acceleration in alkaline solution
4. Chemical copper plating in trilonic electrolyte

Trilonic electrolyte contains copper sulphate, formaldehyde and complexone III, at work conditions pH = 12,8÷13; T = 45°C. Complex-forming agents, buffer agents, stabilizers and others have been added to the electrolyte.

The thickness of coatings obtained by us on ABS in trilonic electrolyte is measured by X-ray fluorescence analysis.

To obtain the copper coatings with appropriate properties an active full factorial experiment with two levels of variation of the factors has been carried out. An attempt to obtain mathematical model adequately describing the process of chemical deposition of copper coatings on textile substrates and the respective response of the surfaces has been made.

As independent variables were chosen: concentration of copper sulphate ($\widetilde{x}_1$, g/l), the reducer (formaldehyde) concentration ($\widetilde{x}_2$, g/l) and time delay ($\widetilde{x}_3$, min). The levels of variation were determined by preliminary experiments.

Controlled output parameter was a copper deposition rate ($\overline{Y}$, μm).

Conditions of planning of the experiment are given in Table 1.

The number of experiments is $N = 2^3 = 8$. To improve the accuracy of the study, the experiments have been doubled. The total number of observations were $N_T = 2.2^3 = 16$.

Table 1: Conditions of planning of the experiment

CONDITIONS OF PLANNING	NATURAL VALUES OF THE FACTORS		
	$\widetilde{x}_1$	$\widetilde{x}_2$	$\widetilde{x}_3$
Basic level, $\widetilde{x}_{oi}$	15	7	17
Interval of variation, I_i	10	5	13
Upper level, $\widetilde{x}_{i\max}$	25	12	30
Lower level, $\widetilde{x}_{i\min}$	5	2	4

For description of the quantity relationships between input and output parameters the next regression equation has been used:

$$Y= b_0 + b_1 \widetilde{x}_1 + b_2 \widetilde{x}_2 + b_3 \widetilde{x}_3 + b_{12} \widetilde{x}_1 \widetilde{x}_2 + b_{13} \widetilde{x}_1 \widetilde{x}_3 + b_{23} \widetilde{x}_2 \widetilde{x}_3 + b_{123} \widetilde{x}_1 \widetilde{x}_2 \widetilde{x}_3 \quad (1)$$

Matrix of the planned experiment was constructed as the natural values of the factors were converted in coded (dimensionless) form, then the table was filled with a strictly defined sequence (Table 2).

Table 2: Matrix of the planned experiment

EXPERIMENTS	CODED VALUES OF THE FACTORS							
	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$
1	+1	-1	-1	-1	+1	+1	+1	-1
2	+1	+1	-1	-1	-1	-1	+1	+1
3	+1	-1	+1	-1	-1	+1	-1	+1
4	+1	+1	+1	-1	+1	-1	-1	-1
5	+1	-1	-1	+1	+1	-1	-1	+1
6	+1	+1	-1	+1	-1	+1	-1	-1
7	+1	-1	+1	+1	-1	-1	+1	-1
8	+1	+1	+1	+1	+1	+1	+1	+1

x_0 – fictive factor for calculating the "b_0"

"+1" – top level of the coded factors ($x_{i\max}$)

"-1" – low level of the coded factors ($x_{i\min}$)

Matrix is orthogonal and symmetric, covering all factors and their interactions, and x_0 is included for the calculation of the coefficient b_0.

Experiments were carried out by transition from coded in natural values and randomization of the sequence of their implementation.

The results of the tests are processed by standard procedure [7-12].

3. RESULTS AND DISCUSSION

The results of the FFE are presented in Table 3 and each value is average of two experimental data.

Table 3: Experimental results of the planned experiment

PARAMETER	NUMBER OF THE EXPERIMENTS:							
	1	2	3	4	5	6	7	8
Coating thickness ($\overline{Y}$), μm	0.165	0.397	0.257	1.118	0.496	0.961	0.815	1.995

For regression coefficients b_i are calculated the following values:

$$b_0 = +0.776;\ b_1 = +0.342;\ b_2 = +0.271;\ b_3 = +0.291;$$

$$b_{12} = +0.168;\ b_{13} = +0.069;\ b_{23} = +0.068;\ b_{123} = +0.011$$

After calculation of the confidence interval ($\Delta b_i = \pm\ 0.186$), according to the criterion of Student ($|b_i| < \Delta b_i$) insignificant coefficients were:

$b_{12} = +0.168$; $b_{13} = +0.069$; $b_{23} = +0.068$; $b_{123} = +0.011$,

where the regression equation acquires the following form:

$$\bar{Y} = 0.776 + 0.342\, x_1 + 0.271\, x_2 + 0.291\, x_3 \quad (2)$$

From the linear approximation of the regression model, shown on Fig. 1, is evident that the more strongly impact of a factor, the slope of the straight line is steeper (curve x_1).

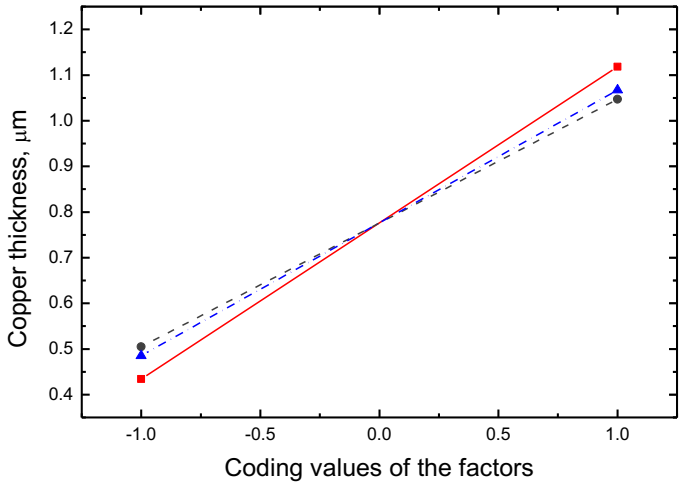


Fig. 1: Single linear approximation, where: (■) is x_1, (●) is x_2, (▲) is x_3

On Fig. 2 is shown that the changes in the concentrations of copper sulphate ($\tilde{x}_1$) and formaldehyde ($\tilde{x}_2$) a stronger influence on the thickness of a top-level time delay $\tilde{x}_3$ (curve 2) and less at a lower level of $\tilde{x}_3$ (curve 1).

The dependence of the thickness of the coatings ($\bar{Y}$) from the input factors - copper sulphate concentration ($\tilde{x}_1$), concentration of formaldehyde ($\tilde{x}_2$) and at fixed upper level of the time delay ($\tilde{x}_3$ = 30 min), defining a factor region (Table 4), according equation (2), is presented in Fig. 3. This graphical relationship of the adequate regression model is a plane in space due to the absence of interactions: x_1x_2; x_1x_3; x_2x_3; $x_1x_2x_3$ (due to insignificance of the regression coefficients b_{12} = +0.168; b_{13} = +0.069; b_{23} = +0.068; b_{123} = +0.011) in the regression model.

On Fig. 4 is presented the relationship of the 3D ($\bar{Y}$*, Table 4) as a function of the variation in the concentration of copper sulphate ($\tilde{x}_1$) and formaldehyde ($\tilde{x}_2$), at fixed upper level of the time delay ($\tilde{x}_3$ = 30 min). In this occasion in equation 2 is included the influence of the strongest double interaction, x_1x_2, at which it changes:

$$\bar{Y}^* = 0.776 + 0.342\, x_1 + 0.271\, x_2 + 0.291\, x_3 + 0.168\, x_1x_2 \quad (3)$$

Because of the presence of double interaction ($x_1 x_2$) in equation 3 of the adequate regression model the graphic is a surface in space (Fig.4.).

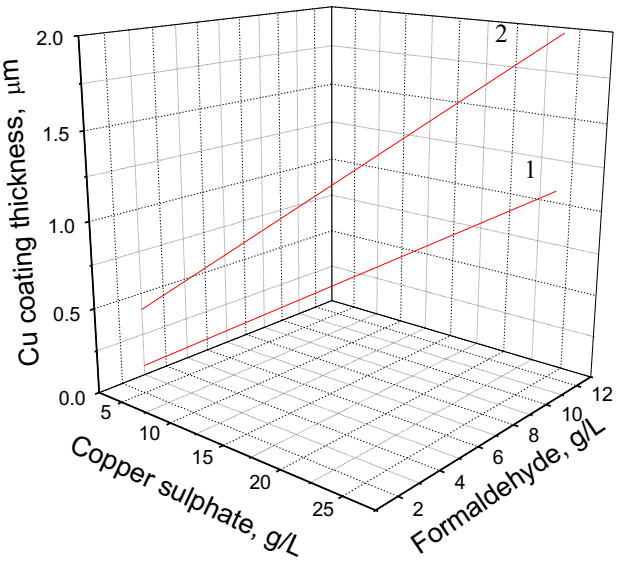


Fig 2: Linear presentation of the output parameter ($\overline{Y}$) at the lower and upper levels of $\widetilde{x}_1$ and $\widetilde{x}_2$ at fixed upper (curve 2) and lower (curve 1) values of $\widetilde{x}_3$

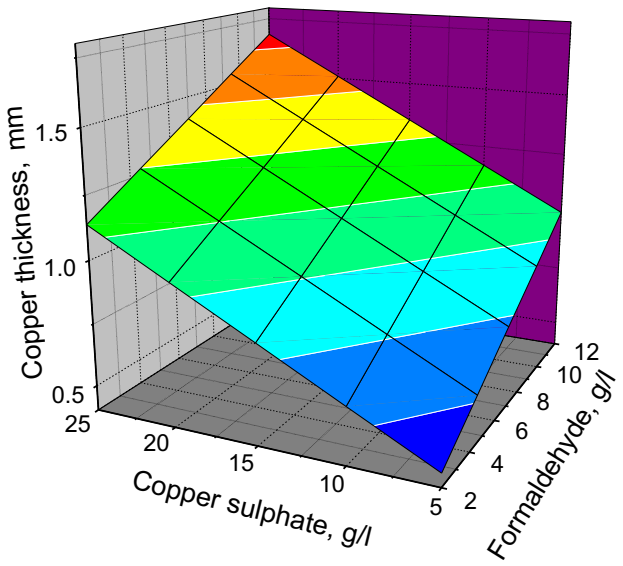


Fig. 3: 3D-Plane

Table 4: Calculated values for the thickness of the coatings, $\overline{Y}$ [μm]

SERIAL NUMBER	$\widetilde{x}_1\,(x_1)$ Copper sulphate, g/L	$\widetilde{x}_2\,(x_2)$ Formaldehyde, g/L	$\widetilde{x}_3\,(x_3)$ Time delay, min	$\overline{Y}$ ($\overline{Y}$ *) Coating thickness, μm
1	5(-1.0)	12(+1.0)	30(+1.0)	0.996 (0.828)
2	10(-0.5)	12(+1.0)	30(+1.0)	1.167 (1.083)
3	15 (0.0)	12(+1.0)	30(+1.0)	1.338 (1.338)
4	20(+0.5)	12(+1.0)	30(+1.0)	1.509 (1.593)
5	25(+1.0)	12(+1.0)	30(+1.0)	1.68 (1.848)
6	5(-1.0)	9.5(+0.5)	30(+1.0)	0.861 (0.777)
7	10(-0.5)	9.5(+0.5)	30(+1.0)	1.032 (0.990)
8	15(0.0)	9.5(+0.5)	30(+1.0)	1.203 (1.203)
9	20(+0.5)	9.5(+0.5)	30(+1.0)	1.374 (1.416)
10	25(+1.0)	9.5(+0.5)	30(+1.0)	1.545 (1.629)
11	5(-1.0)	7(0.0)	30(+1.0)	0.725 (0.725)
12	10(-0.5)	7(0.0)	30(+1.0)	0.896 (0.896)
13	15(0.0)	7(0.0)	30(+1.0)	1.067 (1.067)
14	20(+0.5)	7(0.0)	30(+1.0)	1.238 (1.238)

15	25(+1.0)	7(0.0)	30(+1.0)	1.409 (1.409)
16	5(-1.0)	4.5(-0.5)	30(+1.0)	0.590 (0.674)
17	10(-0.5)	4.5(-0.5)	30(+1.0)	0.761 (0.803)
18	15(0.0)	4.5(-0.5)	30(+1.0)	0.932 (0.932)
19	20(+0.5)	4.5(-0.5)	30(+1.0)	1.103 (1.061)
20	25(+1.0)	4.5(-0.5)	30(+1.0)	1.274 (1.190)
21	5(-1.0)	2(-1.0)	30(+1.0)	0.454 (0.622)
22	10(-0.5)	2(-1.0)	30(+1.0)	0.625 (0.709)
23	15(0.0)	2(-1.0)	30(+1.0)	0.796 (0.796)
24	20(+0.5)	2(-1.0)	30(+1.0)	0.967 (0.883)
25	25(+1.0)	2(-1.0)	30(+1.0)	1.138 (0.970)

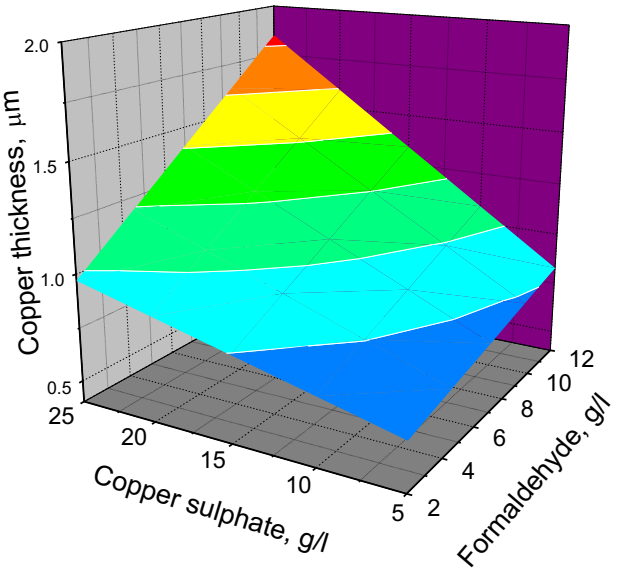


Fig4: 3D-surface

4. CONCLUSION

Proposed is an adequate mathematical model describing the dependence of deposition rate as a function of the variation in the concentration of copper sulphate, formaldehyde and a time delay.

The model allows control, management and prognosis of the thickness of the chemical copper coating (Y) at defined values of the input parameters (x_i).

The model allows optimization the thickness of the copper coating ($\overline{Y}$) by moving along the gradient to the maximum values.

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