

THE CONTRIBUTION TO COATING QUALITY EVALUATION BY STATISTICAL METHODS

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Preliminary Note – Prethodno priopćenje

The paper deals with evaluation of quality of electrolytic coating by statistical methods. Electrolytic solution was created by $ZnCl_2$ within interval of $0,062 \text{ mol} \cdot \text{l}^{-1}$ to $1,01 \text{ mol} \cdot \text{l}^{-1}$, $NaCl$ ranging from $7,01 \text{ mol} \cdot \text{l}^{-1}$ to $60,66 \text{ mol} \cdot \text{l}^{-1}$, H_3BO_3 ranging from $0,11 \text{ mol} \cdot \text{l}^{-1}$ to $0,89 \text{ mol} \cdot \text{l}^{-1}$. Physical conditions of the experiment are represented by the electrolyte temperature ranging from $-3,78 \text{ }^\circ\text{C}$ to $43,78 \text{ }^\circ\text{C}$, electroplating period ranging from 3,11 to 26,98 min and voltage ranging from 1,62 V to 6,38 V. Steel S355J0 was used as an experimental material. The results showed that zinc chloride volume contained in the electrolyte does not produce any influence on resulting quality of zinc coating.

Key words: coating, galvanic zinc coating, quality, statistical analysis, design of experiments

INTRODUCTION

Galvanic zinc coating as an anticorrosion protection belongs to usually applied electrochemical procedures applied to steel products surface finishing, especially in automobile industry [1]. Its main advantage consists in simplicity and price availability [2, 3]. Galvanic zinc coating ensures cathode and barrier protection [4] of ferrous, non-ferrous metal alloys and non-metallic conducting materials as well [5]. It reduces a friction factor and ensures a series of optical properties [6]. The coating does not contain heavy metals or hexavalent chrome, therefore this technology is environmentally friendly [7]. It appears as a suitable replacement for cadmium in many application areas [7]. The properties of a deposited zinc coating depend on range of factors that include the following: current density, electrolyte temperature, electrolyte pH value, chemical composition of electrolyte, additives and impurities in electrolyte.

In the paper, the method of deposited zinc coating quality evaluation method is presented from the point of view of its appearance and morphologic properties. The authors try to describe the coating quality by only one number and subsequently to define the influence of chemical and physical factors on final visual properties of the coating. The main aim of the paper is to understand mutual connections between visual characteristics of the coating and the factors that influence the process of galvanic zinc coating, as well as a potential prediction of these relations.

COATING QUALITY EVALUATION METHOD

There is the same standard dimension of a sample intended for electroplating in a Hull cell for all experiments, $100 \times 70 \times 0,5 \text{ mm}$. The sample plated is shown on Figure 1, where the basic characteristics used in a deduction of the methods for surface evaluation are defined.

The dimension of an elementary square S_a that is of area of 25 mm^2 for the specific case, is the basis for the surface quality methods evaluation deduction. It will be calculated according to the formula:

$$S_a = a^2 \quad (1)$$

For further calculation, the quality of coating deposited on the sample under the defined conditions of electroplating needed to define. The basic qualitative types of coatings that occur most commonly are shown on Figure 2.

The qualitative types of coating are characterized by their quality number (n_q) and by their scale (s_q).

Subsequently, the basic areas S_a are assigned a qualitative number of a deposited coating type. The area of specific type of deposited coating in mm^2 that corre-

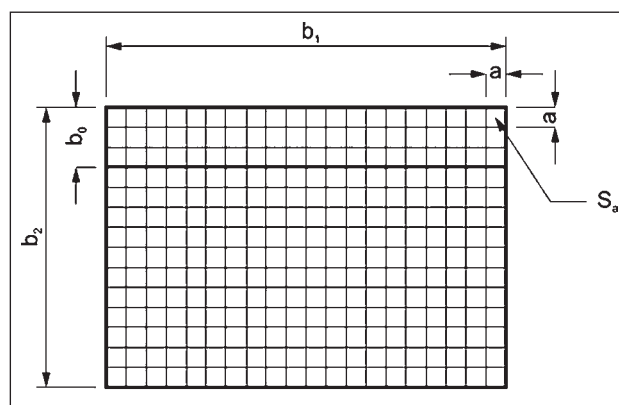


Figure 1 Sample Diagram

M. Badida, L. Sobotova, Technical University of Kosice, Faculty of Mechanical Engineering, Slovakia, M. Gombar, J. Kmec, D. Kucerka, The Institute of Technology and Business in České Budějovice, Czech Republic, R. Hrmo, Dubnica Institute of Technology in Dubnica nad Váhom, Slovakia

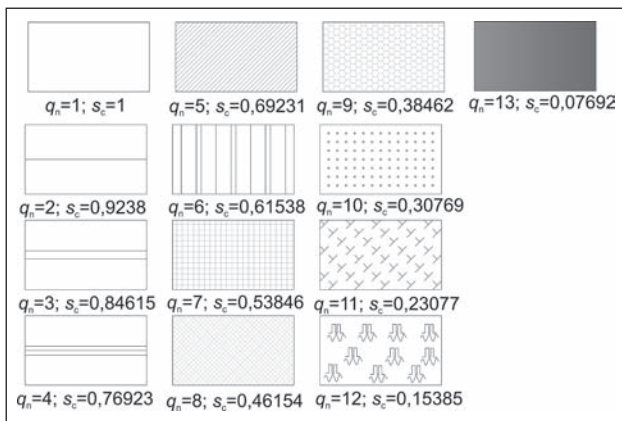


Figure 2 Basic qualitative types of coatings (1 – mirror polished, 2 – shiny without reflection, 3 – reduced gloss, 4 – semi gloss, 5 – matte, 6 – stripped, spotted, 7 – ‘burnt’ – coarsed – grained, 8 – powder, sponge, 9 – blisters, 10 – porous, 11 – coating is spontaneously bursting, 12 – embossed , corrugated, 13 – coating did not segregate

sponds to the given qualitative number q_n can be calculated by following formula:

$$S_{p,i} = S_a \cdot f_i \tag{2}$$

where $i = q_n = 1, 2 \dots 13$, f_i means the number of basic areas of i - qualitative type of coating on a sample. Total evaluated area of the sample we will obtain by following formula:

$$S_H = (b_2 - b_0) \cdot b_1 = \sum_{i=1}^{13} S_{p,i} \tag{3}$$

Taking the experimental method of the coating formation in a Hull cell, in addition to total evaluated area S_H , there is also an area on the sample that was not electroplated and it will be assigned the zero qualitative number. The area of non-evaluated surface of the sample will be determined by the formula:

$$S_0 = b_0 \cdot b_1 = a^2 \cdot f_{q_n} = 0 \tag{4}$$

Total area of the sample is then defined as:

$$S_T = b_1 \cdot b_2 = S_H + S_0 \tag{5}$$

A percentage of a specific (i - th) quality of deposited coating on the sample is defined by following formula:

$$P_{H,i} = \frac{S_{p,i}}{S_T} \cdot 100 \tag{6}$$

If it multiplies a specific quality percentage value of the deposited coating by the relevant quality scale of the coating (Table 1), it obtains total percentage scale ratio of i - th quality of the coating deposited on the sample:

$$P_{Q,i} = P_{H,i} \cdot s_{c,i} \tag{7}$$

Overall quality of the deposited coating can be expressed by following formula:

$$Q_T = \sum_{i=1}^{13} P_{Q,i} \tag{8}$$

The computing result is a value matrix enabling to apply mathematic and statistical methods that enable us

to analyse the dependencies and to predict a monitored parameter – the deposited coating quality.

CONDITIONS OF EXPERIMENTAL VERIFICATION

Experimental verification of deposited coating quality evaluation methods was carried out in a Hull cell. It was used NaCl-based electrolyte. The experiment conditions are given in Table 1.

Table 1 Conditions of experimental verification

K.F.	Factor	Factor Level				
		- 2,37	- 1	0	1	2,37
x_1	$m(\text{ZnCl}_2)$	0,06	0,33	0,53	0,73	1
x_2	$m(\text{NaCl})$	7,01	22,6	33,8	45,1	60,7
x_3	$m(\text{H}_3\text{BO}_3)$	0,1	0,32	0,49	0,65	0,87
x_4	U	1,62	3	4	5	6,38
x_5	T	- 3,78	10	20	30	43,78
x_6	T	3,11	10	15	20	26,89

K.F. – factor code, $m(\text{ZnCl}_2)$ – zinc chloride molar concentration in $\text{mol}\cdot\text{l}^{-1}$, $m(\text{NaCl})$ – sodium chloride molar concentration in $\text{mol}\cdot\text{l}^{-1}$, $m(\text{H}_3\text{BO}_3)$ – boric acid molar concentration in $\text{mol}\cdot\text{l}^{-1}$, U – voltage in Volts, T – electrolyte temperature in $^\circ\text{C}$, t – time range of coating in min.

Within the experimental verification, there was a constant molar concentration $m(\text{C}_7\text{H}_5\text{O}_2\text{Na})$ at the level of $0,0138 \text{ mol}\cdot\text{l}^{-1}$ for all 46 experiments. Material of the cathode, the sample was S355J0. Chemical composition of experimental material is given in Table 2.

The plated samples were pre-treated by chemical degreasing in 40 %, solution of NaOH at temperature of $55 \text{ }^\circ\text{C}$ for period of 10 min. Subsequently, the samples were rinsed in demineralized water of temperature $22 \text{ }^\circ\text{C}$ for period of 1 minute. Then the samples were pickled in 20 % - HCl at temperature of $20 \text{ }^\circ\text{C}$ with exposition time of 5 minutes. Pickled samples were subsequently rinsed in demineralized water of temperature $22 \text{ }^\circ\text{C}$ for period of 2 minutes. Thus pre-treated samples were zinc coated according to conditions given in Table 2.

Table 2 Chemical composition of the experimental material wt / %

C	Si	Mn	P	S	Al
0,2	0,55	1,6	0,05	0,045	0,015

RESULTS AND DISCUSSION

In general, the processes of surface finishing are the complex multifactor systems with significant influence of mutual interactions of physical and chemical factors. Therefore a monitoring of any parameter of the deposited coating, when only one influencing factor changes, often leads to incorrect results and conclusions. In the submitted paper, the results obtained by experimental verification by the process of electrolytic zinc coating in sodium-chloride based electrolyte were processed by methods DoE [8, 9] and in accordance with these meth-

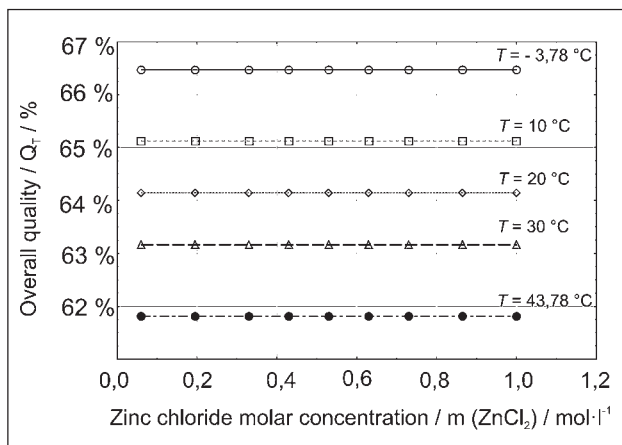


Figure 3 ($m(\text{NaCl}) = 33,8 \text{ mol}\cdot\text{l}^{-1}$; $m(\text{H}_3\text{BO}_3) = 0,49 \text{ mol}\cdot\text{l}^{-1}$; $U = 4 \text{ V}$; $t = 15 \text{ min}$)

ods, the conclusions were stated. A dependence of surface overall quality (OT) on a zinc chloride molar concentration change in an electrolyte at a concurrent change in the electrolyte temperature is shown on Figure 3. It follows from the diagram that zinc chloride molar concentration rise does not result in a change in the surface overall quality. A change in overall quality value can be observed at the increase of electrolyte temperature. The highest values of the surface overall quality are obtained at electrolyte temperature of $-3,78 \text{ }^\circ\text{C}$. The value of overall quality of surface presents $66,47 \%$. Rising the electrolyte temperature to $10 \text{ }^\circ\text{C}$ will result in the overall quality of surface fall-off by $2,03 \%$. If the electrolyte temperature continues to rise, overall quality of surface will fall to $61,81 \%$ at the electrolyte temperature of $43,78 \%$.

A change in the surface overall quality (QT) in dependence on a change in sodium chloride molar concentration is shown on Figure 4. At the same time, during the experiment, the electrolyte temperature was changing. It follows from Figure 5 that rising sodium chloride molar concentration induces a fall of the surface overall quality value QT by $7,54 \%$ on an average, regardless of the electrolyte temperature.

The highest values of the surface overall quality are obtained at minimal sodium chloride molar concentrations in the electrolyte. At electrolyte temperature of $-3,78 \text{ }^\circ\text{C}$, the value of surface overall quality equals to $68,98 \%$ at molar concentration of sodium chloride in electrolyte of $7,01 \text{ mol}\cdot\text{l}^{-1}$. If the electrolyte temperature rises to $10 \text{ }^\circ\text{C}$, while sodium chloride molar concentration in the electrolyte remains the same, the surface overall quality value falls to $67,63 \%$. A fall in the surface overall quality is $1,96 \%$. Additional electrolyte temperature rise to $20 \text{ }^\circ\text{C}$ will induce a fall in the surface overall quality to $66,65 \%$. Generally, it is possible to state that temperature rise by $1 \text{ }^\circ\text{C}$ will induce a fall of the surface overall quality by $0,14 \%$. Similarly, sodium chloride molar concentration in electrolyte rise by $1 \text{ mol}\cdot\text{l}^{-1}$ will induce a fall of the surface overall quality by $0,14 \%$ as well. This effect of a decrease of the surface overall quality, which represents the visual and

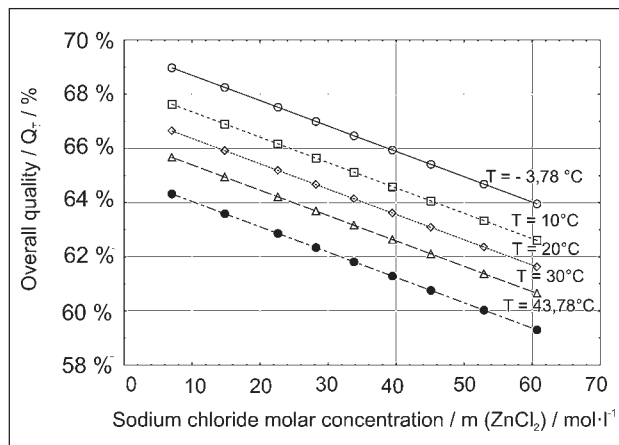


Figure 4 ($m(\text{ZnCl}_2) = 0,53 \text{ mol}\cdot\text{l}^{-1}$; $m(\text{H}_3\text{BO}_3) = 0,49 \text{ mol}\cdot\text{l}^{-1}$; $U = 4 \text{ V}$; $t = 15 \text{ min}$)

morphologic characteristics of coating, can be attributed to the mechanism of a zinc coating formation. A rise of sodium chloride molar concentration in electrolyte induces a rise in its conductivity, what results in a rise of overall current density at the given zinc coating time and thus, coarse-grained coatings are formed. Similarly, electrolyte temperature rise induces its conductivity rise.

CONCLUSION

The submitted paper deals with the application of evaluation methods of visual properties of galvanically deposited coatings in a Hull cell. The principle consists in a scale assignment to particular types of deposited coatings pursuant to Figure 2 and Table 1 to real samples. The application of planned experiments enables the application of advanced statistical methods in processing of measured results and thereby an objectification of achieved conclusions taking into account the influence of mutual interactions between influencing factors in the process of galvanic surface finishing. They especially serve as methods for corrections of a technological process. Under real conditions, their successfulness amounts to almost 96% . Thus, it can be summarized the major advantages as it follows:

- High accuracy of corrections of technological process,
- Simple applicability under real conditions,
- Reliability at observing of DoE conditions,
- Applicability to various technologies of galvanic surface finishing treatments.

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