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The Influence of Input Factors of Aluminium Anodizing Process on Resulting Thickness and Quality of Aluminium Oxide Layer

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Abstract

In order to optimize the technological process of aluminium anodic oxidation, the possibilities of usage of sodium chloride in the electrolyte has been studied, since very small concentration of sodium chloride allows us to reduce concentration of other components of the electrolyte. Also the influence of sodium chloride concentration in the electrolyte on the final thickness and quality of the formed anodic aluminium oxide (AAO) layer has been investigated in this paper. In contrast to common anodizing experiments, in which the influence of only one separate factor at a time is considered, in our research all relevant factors (four chemical factors) were varied simultaneously according to the methodology of statistical experimental design, i.e. design of experiments (DOE). Based on the evaluation of experimentally obtained data by application of mathematical-statistical methods and theory of neural networks, the relationship between the concentration of sodium chloride in the electrolyte and final thickness of the AAO layer was experimentally determined. Thanks to that it was possible to obtain the predictive model which can determine the final thickness of AAO layer. Moreover, the results of this research allows us to reduce the concentration of other components of the electrolyte up to the level of 25 % of commonly used concentration of these electrolyte components designed for the process of aluminium anodic oxidation.

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Keywords: Anodizing, composition of electrolyte, factors influence, oxide layer.

1. Introduction

Anodic oxidation of aluminium was used for finishing of parts made of aluminium and aluminium alloys since 1923, when it was used as corrosion protection for the first time. Its essence lies in creation of thin layer of aluminium oxide on the surface of a part, which blocks the access of oxygen from the atmosphere and thus to eliminate its corrosive effect [1]. A lot of research was conducted in the area of anodic oxidation of aluminium ever since its first industrial use. Their goal was to clarify the main principle behind the creation of oxide layer on the surface of aluminium part, specify the influences of individual input factors on thickness of oxide layer [2], [3], [4], geometry of oxide layer [4], [5], [6], its properties [7], [8], [9], [10], [11], also how to optimize the process of oxidation [11] and last, but not least, creation of new electrolytes, which could reduce the cost and risks to health and environment [12], [13]. Electrolytes, in which sulphuric acid, oxalic acid and boric acid are the main ingredients, were created thanks to this research. In case of creation of new electrolytes, which would contain lower concentrations of these acids, the addition of sodium chloride seems to be an appropriate solution. So this article is aimed to find optimal operating conditions [14].

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2. Experimental

In order to determine the influence of chemical composition of electrolyte on the resulting oxide layer thickness created during the aluminium anodizing process, an experiment was carried out and statistical analysis of experimentally obtained data was performed. Specifically, the influence of four chemical factors (input factors x_1 , x_2 , x_3 and x_4): the concentration of sulphuric acid, concentration of oxalic acid, concentration of boric acid and concentration of sodium chloride was observed. A circuit diagram for the process of anodizing in a Hull cell is shown in Fig. 1. and the location of the sample during experimental anodizing process is also illustrated in this figure. In the Fig. 1 is shown the sample as the product of experimental anodizing process with deposited AAO layer. The experiment was carried out according to the central composite design based on DOE methodology [15], [16]. Five levels for each input factor were considered during the experimental procedure, as is illustrated in the Table 1. We can see different operating conditions of the experiment, which include the composition of electrolyte (x_1 , x_2 , x_3 and x_4), the electrolyte temperature (x_5), the size of an applied voltage (x_6) and the anodizing time (x_7). The standard operating condition, the center-point, for input factors considered during experimental procedure are defined in Table 2.

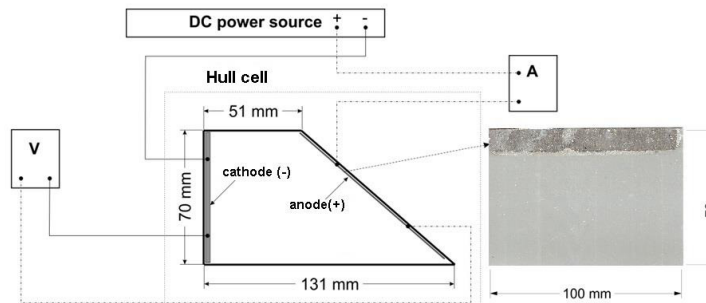


Fig. 1. A circuit diagram for the process of anodizing and location of sample

Table 1. Levels of observed factors.

Coded scale	Natural scale	Factor level				
		-2.83	-1	0	1	2.83
x_1	$\text{H}_2\text{SO}_4 [\text{g}\cdot\text{l}^{-1}]$	12.57	40.00	55.00	70.00	97.43
x_2	$\text{C}_2\text{H}_2\text{O}_4 [\text{g}\cdot\text{l}^{-1}]$	3.76	6.50	8.00	9.50	12.24
x_3	$\text{H}_3\text{BO}_3 [\text{g}\cdot\text{l}^{-1}]$	4.51	10.00	13.00	16.00	21.49
x_4	$\text{NaCl} [\text{g}\cdot\text{l}^{-1}]$	0.12	0.30	0.40	0.50	0.68
x_5	$T [^\circ\text{C}]$	-5.46	11.00	20.00	29.00	45.46
x_6	$U [\text{V}]$	2.34	6.00	8.00	10.00	13.66
x_7	$t [\text{min}]$	1.72	40.00	30.00	40.00	58.28

Table 2. Standard levels of observed factors.

Factor	H_2SO_4	$\text{C}_2\text{H}_2\text{O}_4$	H_3BO_3	NaCl	T	U	t
Level	200 $[\text{g}\cdot\text{l}^{-1}]$	20 $[\text{g}\cdot\text{l}^{-1}]$	50 $[\text{g}\cdot\text{l}^{-1}]$	0 $[\text{g}\cdot\text{l}^{-1}]$	22 $[\text{C}^\circ]$	10 $[\text{V}]$	30 $[\text{min}]$

The samples used in the experiment were cut out from a sheet of alloy EN AW 1050 H24 with dimensions 100x70x1 mm. Before anodic oxidation in a Hull cell, each applied specimen was degreased in a 38 % solution of sodium hydroxide at temperature of 55 to 60 °C for 2 minutes and stained in a 40 % solution of sodium hydroxide at the temperature of 45 to 50 °C for 30 seconds. Afterwards, the surface of each sample was immersed in a 4 % activation solution of nitric acid bath.

3. Evaluation of experiment

At the end of anodizing process, a map of measuring points was created on each sample, where the response - the thickness of aluminium oxide layer was measured. Measuring points were placed on a sample 1 to 9 cm from left edge with distance of 1 cm and 1 to 4 cm from bottom edge with distance of 1 cm. The relationship between chemical composition of the electrolyte and the thickness of the formed AAO layer was determined by implementation of statistical analysis methods [17], which used significant input factors and their interactions at the chosen significance level of $\alpha=10\%$. Table 3 shows significant factors and

probability of incorrect determination of their significance at the chosen significance level of $\alpha=10\%$ and layer thickness measured on measuring points located 5 cm from the left edge of a sample. The prediction model of the thickness of the formed AAO layer is based on identifying of significant factors. Model was created with a modified third order neural unit [18]. Thanks to the prediction model, it was possible to observe the relationship between input factors and the resulting thickness of aluminium oxide layer on the surface of a used sample.

Table 3. Significant factors at significance level of $\alpha=10\%$.

input	x_2	x_3	x_4	x_5	x_7	x_1^2	$x_1 \cdot x_2$	$x_1 \cdot x_3$	$x_1 \cdot x_5$	$x_1 \cdot x_6$
p	< 0.0001	< 0.0001	0.0005	< 0.0001	< 0.0001	< 0.0001	< 0.0001	0.0105	0.0004	0.0023
input	$x_1 \cdot x_7$	x_2^2	$x_2 \cdot x_4$	$x_2 \cdot x_5$	$x_2 \cdot x_6$	$x_2 \cdot x_7$	x_3^2	$x_3 \cdot x_4$	$x_3 \cdot x_5$	$x_3 \cdot x_7$
p	0.0397	< 0.0001	< 0.0001	0.0001	0.0155	< 0.0001	0.0004	0.0105	0.0015	< 0.0001
input	x_4^2	$x_4 \cdot x_5$	$x_4 \cdot x_6$	$x_4 \cdot x_7$	x_5^2	$x_5 \cdot x_7$	x_6^2	x_7^2	x_1^2	$x_1^2 \cdot x_2$
p	0.0026	< 0.0001	0.0059	0.0001	0.0373	< 0.0001	0.0054	0.0016	0.0001	< 0.0001
input	$x_1^2 \cdot x_3$	$x_1^2 \cdot x_4$	$x_1^2 \cdot x_5$	$x_1^2 \cdot x_6$	$x_1^2 \cdot x_7$	$x_1 \cdot x_2 \cdot x_3$	$x_1 \cdot x_2 \cdot x_4$	$x_1 \cdot x_2 \cdot x_5$	$x_1 \cdot x_2 \cdot x_6$	$x_1 \cdot x_2 \cdot x_7$
p	0.0721	< 0.0001	< 0.0001	0.0028	< 0.0001	0.0001	< 0.0001	< 0.0001	0.0235	0.0007
input	$x_1 \cdot x_3 \cdot x_4$	$x_1 \cdot x_3 \cdot x_5$	$x_1 \cdot x_3 \cdot x_6$	$x_1 \cdot x_4 \cdot x_5$	$x_1 \cdot x_4 \cdot x_6$	$x_1 \cdot x_4 \cdot x_7$	$x_1 \cdot x_5 \cdot x_7$	$x_1 \cdot x_6 \cdot x_6$	$x_1 \cdot x_6 \cdot x_7$	$x_1 \cdot x_7^2$
p	0.0006	0.0009	< 0.0001	0.0012	0.0989	< 0.0001	< 0.0001	0.0888	< 0.0001	0.0039
input	$x_2^2 \cdot x_5$	$x_2 \cdot x_3 \cdot x_4$	$x_2 \cdot x_3 \cdot x_6$	$x_2 \cdot x_3 \cdot x_7$	$x_2 \cdot x_4 \cdot x_5$	$x_2 \cdot x_4 \cdot x_6$	$x_2 \cdot x_4 \cdot x_7$	$x_2 \cdot x_5^2$	$x_2 \cdot x_5 \cdot x_6$	$x_2 \cdot x_6^2$
p	< 0.0001	0.0001	0.0836	0.0065	< 0.0001	< 0.0001	< 0.0001	0.0025	0.0002	0.0002

4. Results and discussion

Fig. 2, Fig. 3, Fig. 4, Fig. 5 show a relationship between chemical factors (x_1, x_2, x_3 and x_4) and thickness of aluminium oxide layer. This relationship is shown individually for each of observed factors continuously from level - 2.38 to level 2.38, while factor level of all other factors is set to 0.

Specifically, Fig. 2 shows the dependence of factor x_1 on thickness of aluminium oxide layer where factors $x_2, x_3, x_4, x_5, x_6, x_7$ are set to factor level 0. Based on the shown graph, there is an obvious positive influence of factor x_1 (concentration of sulphuric acid) on resulting thickness of aluminium oxide layer. The halt of growth in aluminium oxide layer thickness in area of factor levels -1 to 1 is caused by interactions of factors x_1, x_2 and x_3 .

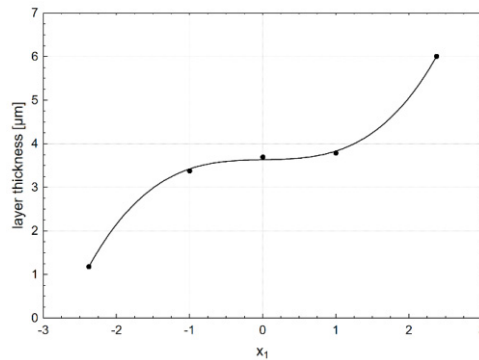


Fig. 2. Influence of factor x_1 on layer thickness.

Fig. 3 shows dependence of factor x_2 on aluminium oxide layer thickness where factors $x_1, x_3, x_4, x_5, x_6, x_7$ are set to factor level 0. Fig. 4 shows dependence of factor x_3 on aluminium oxide layer thickness where factors $x_1, x_2, x_4, x_5, x_6, x_7$ are set to factor level 0. Fig. 3 and Fig. 4 shows a graph where with an increase from factor level - 2.38 to factor level 1 (Fig. 3) and factor level 0 (Fig. 4) also decreases the thickness of created aluminium oxide layer. This state is caused by a difference in the amount of dissociated ions in electrolyte and the aggression of environment (electrolyte), in which the layer is located during the oxidation. It gets to a state where the aggression of environment causes dissolution of the created aluminium oxide layer which is faster than the speed of creation of the layer, which is influenced by the amount of dissociated ions in electrolyte. Subsequent increase of factor level above 1 shown in Fig. 3 (and subsequently above factor level 0 – Fig. 4) causes an increase in aluminium oxide layer thickness, because the speed of layer creation is greater than speed of dissolution of layer back into the electrolyte – electrolyte contains enough dissociated ions which participate in the creation of oxide layer [2]. Fig. 5 shows dependence of

factor x_4 on aluminium oxide layer thickness where factors $x_1, x_2, x_3, x_5, x_6, x_7$ are set to factor level 0. Graph shows an increase of oxide layer thickness during the increase of factor level from -2.38 to 2.38. In this case, growth of aluminium oxide layer is closely related to the conductance of electrolyte, which significantly rises even with addition of small amount (0.5^{-1}) of sodium chloride to the electrolyte. Difference in resulting oxide layer thickness is, from a first glance, only around one micrometre (Fig. 5), however, the concentration of other components of electrolyte is significantly lower.

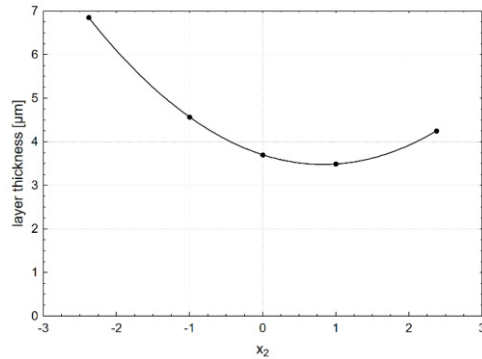


Fig. 3. Influence of factor x_2 on layer thickness.

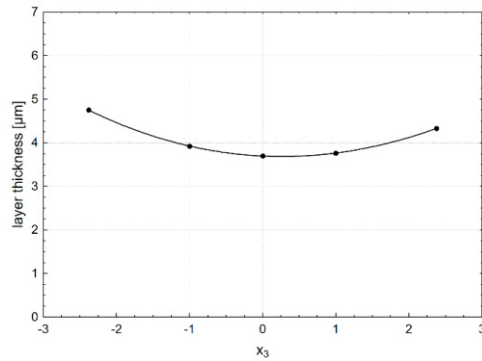


Fig. 4. Influence of factor x_3 on layer thickness.

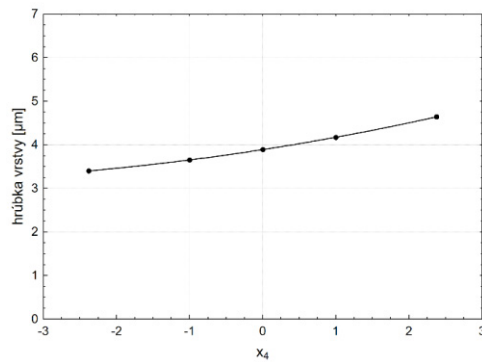


Fig. 5. Influence of factor x_4 on layer thickness.

Fig. 6, Fig. 7 and Fig. 8 show an influence of interaction of chosen factors (x_1 cross x_4 —Fig. 6, x_2 cross x_4 —Fig. 7 and x_3 cross x_4 - Fig. 8) on thickness of created oxide layer. Factors which are not shown in figures Fig. 6, Fig. 7 and Fig. 8 have their factor levels set to 0. All these graphs show a positive influence of sodium chloride on layer thickness (increase in layer thickness of up to 1 to 3 μm) while the concentration in electrolyte is only 0.12 to 0.68 $\text{g}\cdot\text{l}^{-1}$.

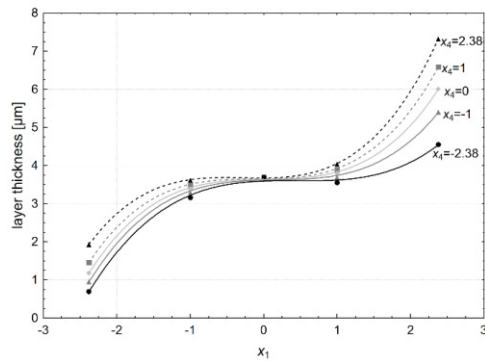


Fig. 6. Influence of factors x_1 and x_4 on layer thickness.

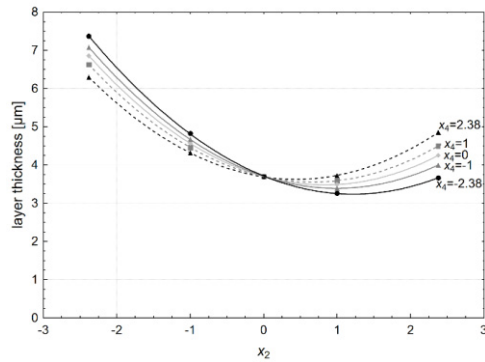


Fig. 7. Influence of factors x_2 and x_4 on layer thickness.

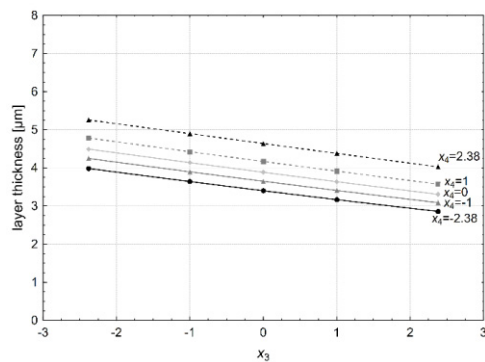


Fig. 8. Influence of factors x_3 and x_4 on layer thickness.

The influence of chemical composition of the electrolyte on the resulting thickness of the formed aluminium oxide layer and the influence on the final quality of the surface of the oxidized sample were investigated. Fig. 9 shows a couple of selected surface disorder types on samples during the process of aluminium oxidation. Fig. 9-A shows sample surface which was not damaged during the process of aluminium oxidation and thus, it does not contain any surface disorders. Fig. 9-B shows us the surface damage due to very small openings, which protrude to greater depth under the surface of oxidized sample. In a way, this surface damage made during the anodic oxidation process closely resembles pitting corrosion effect. In cases shown in Fig. 9-C and Fig. 9-D, the sample surface is covered with craters of larger dimensions, which are concentrated around the edges of sample (Fig. 9-C), or evenly distributed across the whole surface of the sample.

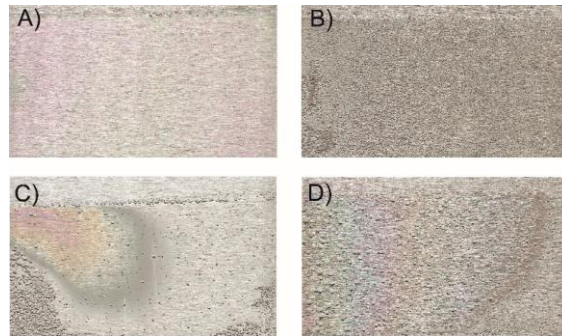


Fig. 9. Sample surface quality.

Fig. 10 and Fig. 11 show the expected occurrence of surface defects on a sample during the process of anodic oxidation of aluminium. This surface damage of a sample is due to aggressive effects of electrolyte environment during the process of anodic oxidation of aluminium. Values for surface damage are calculated using the created prediction model. It is necessary to note that prediction model only determines the rate of surface defect occurrence on oxidized sample. Current prototype of prediction model is unable to determine the type of surface defect created on the sample. Created prediction model also can't yet predict the geometric distribution of defects occurring on the sample surface. Resulting surface quality of oxidized sample is influenced by several factors during the aluminium oxidation process. As stated above, they are aggressive effects of electrolyte, which is defined by its chemical composition, and also operating parameters of the process, such as electrolyte temperature and total oxidation time of the sample. Fig. 10 and Fig. 11 show an influence of sodium chloride on ratio of sample surface damage occurrence. Influence of sodium chloride on sample quality was selected because very little research has been done on its contents in electrolytes. So, Fig. 10 shows the effects of sodium chloride (concentration rises from $0.12 \text{ g}\cdot\text{l}^{-1}$ to $0.68 \text{ g}\cdot\text{l}^{-1}$) in combination with electrolyte temperature, which rises from -5.46°C to 45.46°C . Sulphuric acid concentration is at $55.00 \text{ g}\cdot\text{l}^{-1}$, oxalic acid concentration is at $8.00 \text{ g}\cdot\text{l}^{-1}$, boric acid concentration is at $13.00 \text{ g}\cdot\text{l}^{-1}$, connected voltage level is at 8 V and oxidation time is 30 min . It can be seen on Fig. 10 that while the concentration of sodium chloride increases, the sample damage is minimal for low electrolyte temperatures. With increasing temperature (11°C to 29°C) also increases the defect occurrence rate; these defects cover from 5% to 20% of total oxidized sample surface.

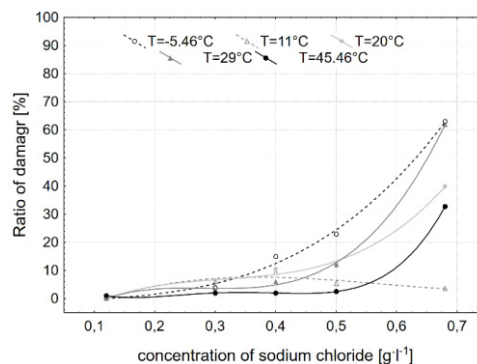


Fig. 10. Effect of sodium chloride and temperature on surface.

Fig. 11 shows the influence of sodium chloride (concentration in electrolyte increases from $0.12 \text{ g}\cdot\text{l}^{-1}$ to $0.68 \text{ g}\cdot\text{l}^{-1}$) in combination with oxidation time, which increases from 1.72 min to 58.28 min. Sulphuric acid concentration is at $55.00 \text{ g}\cdot\text{l}^{-1}$, oxalic acid concentration is at $8.00 \text{ g}\cdot\text{l}^{-1}$, boric acid concentration is at $13.00 \text{ g}\cdot\text{l}^{-1}$, electrolyte temperature is at $20 \text{ }^\circ\text{C}$ and connected voltage level is at 8 V. It is possible to see in Fig. 11 that with increase of concentration of sodium chloride in electrolyte also rises the extent of damage on sample surface. However, these defects cover at most 10 % of oxidized sample surface if concentration of sodium chloride in electrolyte does not exceed $0.50 \text{ g}\cdot\text{l}^{-1}$, and if the sample is oxidized for less than 40 min., significant surface damage occurs only after the concentration of sodium chloride exceeds $0.50 \text{ g}\cdot\text{l}^{-1}$ or if sample is oxidized for more than 40 min.

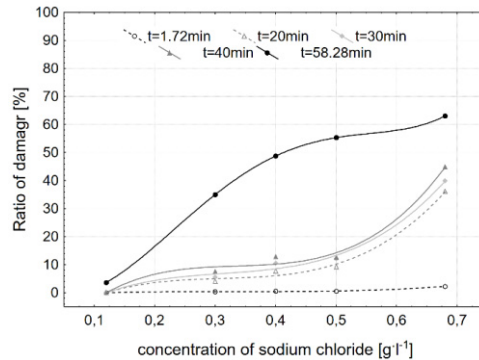


Fig. 11. Effect of sodium chloride and time on surface.

5. Conclusion

As reported in this article, the chemical composition of electrolyte used during the aluminium anodizing process has significant influence on the final thickness and quality of the formed anodic aluminium oxide (AAO) layer. The research was focused on the observation of the effect of amount of sulphuric acid, oxalic acid, boric acid and sodium chloride in the electrolyte on the response. Based on the evaluation of experimentally obtained data by application of mathematical-statistical methods, we obtained some important results, which proved, that the usage of very small amount of sodium chloride can reduce the amount of sulphuric acid, oxalic acid and boric acid needed for the process, moreover in some cases by up to 75 %. The experimental results evidently indicated that the addition of sodium chloride to electrolyte significantly reduces the consumption of other chemical components used in the process of anodic oxidation of aluminium. We can see that when changing chemical components in the electrolyte from high level to low level we get a different impact on the response, i.e. on the thickness and quality of the formed AAO layer. The main advantage of the usage of sodium chloride in the electrolyte is the fact that the decrease of concentration of components used in the electrolyte allows us to create the resulting oxide layer with the same value of the thickness as at the standard levels of concentration of electrolyte components during aluminium anodizing process. The secondary benefit of reducing the concentration of electrolyte components is to reduce costs and claims for disposal of waste water and less impact on the environment. It is important to recall that each model as a result of experimental process is a simplification of some small aspects of reality, and that it will never be 100% perfect. However, with a sufficiently good model, we have an efficient tool for manipulating a small part of reality in a desired direction.

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