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ANODIZING OF ALUMINUM-MAGNESIUM ALLOY USING CHROMIC ACID PROCESS

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ABSTRACT

Aluminum-magnesium alloy has been anodized using chromic acid as an electrolyte. The effect of voltage in the range of 15-60V, electrolyte concentration in the range of 20-110 g/l, electrolyte temperature in the range of 30-60 °C and time of exposure in the range 25-85 minutes on the coating weight of the anodic film are studied. The experimental data was fitted in terms of the coating weight and the coefficients of third order polynomial are estimated. Optimum conditions of the studied variables are predicted and found equal to 32V, 85 g/l, 50 °C and 70 minutes.

الخلاصة

تم انودة سبيكة المنيوم-مغنسيوم باستخدام حامض الكروميك كمحلول الكتروليتي. تم دراسة تأثير كل من الفولتية من 15-60 فولت وتركيز المحلول الالكتروليتي من 20-110 غم/لتر ودرجة الحرارة من 30-60 م° وزمن تعرض من 25-85 دقيقة على وزن التغطية. تم ملائمة القيم التجريبية بدلالة وزن التغطية حيث تم ايجاد معاملات معادلة من الدرجة الثالثة ومن ثم استخراج القيم المثلى للمتغيرات ووجدت 32 فولت، 85 غم/لتر، 50 م° و70 دقيقة.

KEY WORDS

Anodizing, Chromic Acid Process, Aluminum Alloy

INTRODUCTION

The main processes in use for the anodizing of aluminum employ solutions of sulfuric acid, chromic acid or a mixture of sulfuric acid and oxalic acid as electrolytes. Other processes have been used in specific applications. The chromic acid process is used where a high resistance to corrosion is required with a minimum loss of metal section. They are also used where an enamel-like decorative finish is required and for the detection of flaws in castings and for the treatment of riveted and other assembled parts (Canning, 1970; Al Anodizing Council 2001).

The chromic acid anodizing process for corrosion protection of structural aluminum alloys was invented and subsequently patented by Bengough and Stuart in 1923. Their process utilized a complex voltage control procedure for time intervals applied to aluminum alloys in a 3-5% by weight chromic acid aqueous solution operated at 38-42 °C, the voltage is increased in steps from 0 to 40/50 volts (Henley, 1982). In 1937, Robert W. Buzzard at the National Bureau of Standards found that by increasing the chromic acid concentration to 10% by weight, the complicated voltage variance cycle could be eliminated and the process time decreased (10% chromic acid process). Their process operated at a temperature of 55 °C and 30 volts (Canning, 1970).

The universal chromic acid anodizing process invented and subsequently patented by Turns and Forrester in 1981. This invention provide a universally acceptable chromic acid anodizing process that could be employed for all of the aluminum alloy parts that were to be anodized. A universal process involves a 3-20% by weight chromic acid. In general the optimum conditions obtained were: 20V, 40 °C and 45 minutes. It should be noted that an applied voltage value of 20V was due to the fact that the alloys used have a relatively high content of total alloying element (7.5%).

Sulfuric acid anodizing requires 600 mg/ft^2 (64.6 mg/dm^2) to provide corrosion resistance equivalent to 200 mg/ft^2 (21.5 mg/dm^2) for chromic acid anodizing as stated in Mil-A-8625 (Defence Dept. USA, 1993). Unlike the sulfuric acid process, in the chromic acid anodizing, any electrolyte remaining after inadequate washing, or due to seepage from flaws in the metal, will leave an easily detected yellow stain. For this reason this process is mandatory for anodized items which will be in contact with explosives, propellants or pyrotechnics and is preferred for anodized items which are to remain in close proximity to explosives, propellants or pyrotechnics (Ministry Of Defence UK, 1997) .

In this investigation the coating weight of anodic film of aluminum-magnesium alloy in chromic acid anodizing process was studied. The effect of the operating conditions on the coating weight were also studied and optimized.

EXPERIMENTAL WORK

The specimens used for this study were aluminum-magnesium alloy cut into a dimension of (12 x 1 x 0.24) cm. The analysis of aluminum-magnesium alloy by weight percent as follows: aluminum 98%, copper 0.023%, zinc 0.45%, magnesium 1.51%, lead 0.002% and silicon 0.015%.

The variables studied were: voltage, temperature, acid concentration and time. The first three variables were studied by factorial method and the last variable was studied at the best conditions of the first three. Their arrangement is shown is as shown bellow.

The range of the operating conditions studied were as follow:

X_1 = Voltage (V)	15-60V
X_2 = Acid concentration (C_A)	20-110 g/l
X_3= Temperature (T)	30-60 °C
X_4 = Time (t)	25-85 min.

The relationships between the coded levels and the corresponding real variables as follows:

$$X_{1,coded} = \frac{3(X_{1,actual} - 37.5)}{22.5} \tag{1}$$

$$X_{2,coded} = \frac{3(X_{2,actual} - 65)}{45} \tag{2}$$

$$X_{3,coded} = \frac{3(X_{3,actual} - 45)}{15} \tag{3}$$

$$X_{4,coded} = \frac{2(X_{4,actual} - 55)}{30} \tag{4}$$

Procedure

1- Pretreatment: Prior to anodizing the specimen was treated with the following processes:

- -Chemical Cleaning: Oil, grease and general dirt were properly removed with trichloroethylene at 25 °C. Grease tends to float on surface, which was removed later by filtration. After this stage the specimen rinsed in running water then by distilled water to remove the excess trichloroethylene on the specimen (Ministry of Defence UK, 1995).
- -Stripping Anodic Coating: Defective anodic coatings cannot conveniently be touched up; stripping and re-anodizing are necessary. Anodic coating was stripped in a solution containing

phosphoric acid (3.5 vol.%) and chromic acid (2.0 wt.%) at 99 °C and for 10 min., after this stage the specimen rinsed in running water then by distilled water to remove the excess solution on the specimen (Ministry of Defence UK 1997).

- -*Etching*: 5% by weight sodium hydroxide solution was used with an operating temperature of 40-50 °C. The specimen was placed in the etching solution for a period of 5 min., after this stage the specimen rinsed in running water then by distilled water to remove the excess sodium hydroxide on the specimen (Alubook-Lexical, 2002).
- -*Desmuting*: The specimen was treated in solution contain (30 vol.%) nitric acid and (5 vol%) hydrofluoric acid for about 5 min. at 25 °C to remove the black layer that formed on the surface and to activate the surface for the anodizing afterward the specimen was rinsed with running water followed by distilled water, dried by means of air (Ministry of Defence, UK, 1995).

2- Anodizing: A schematic representation of the experimental apparatus is shown in **Fig. (1).** Two direct current power supplies connected in series were incorporated with the anodizing cell to supply the electrodes a maximum current of 5A and a voltage of 60V. The anodizing cell (one liter capacity) was placed on a magnetic stirrer heater to heat the electrolyte solution and maintains good mixing of the solution to prevent temperature layering in the anodizing cell. A thermostat was connected with power supply heater to control the temperature desired for the solution throughout anodizing time. The aluminum specimen was connected to the positive terminal where it becomes anode, while the stainless steel article was connected to the negative terminal to be the cathode. The two electrodes were held by means of jigs and PVC rack, such only 25 cm^2 of each electrodes surface was immersed. The ammeter and voltmeter were connected to the electric circuit, to measure the current and voltage for the circuit during the process.

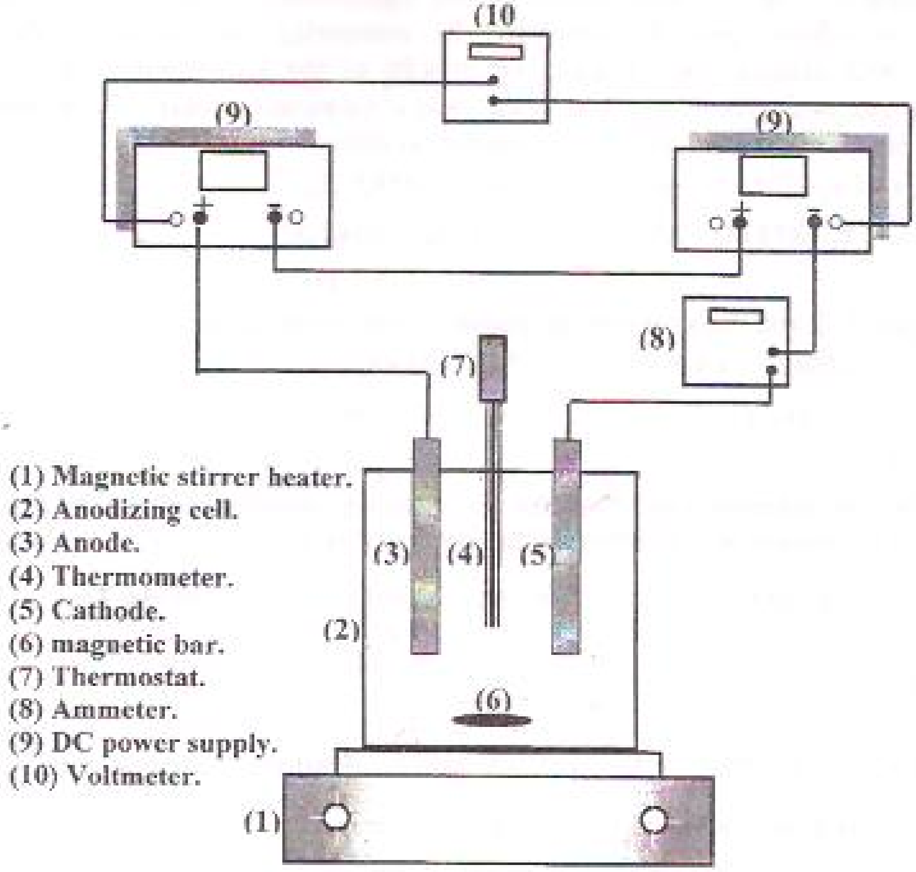

Fig. (1) Schematic diagram for the whole assembly of experimental work.

3- Sealing: The final stage is the sealing process where the specimen was immersed in a one liter solution containing 100 g of potassium dichromate and 18 g of sodium carbonate in distilled water. The solution was kept at temperature 99 °C. The immersion time was 10 min. and the pH of solution was maintained between 6.3-7.4 by the addition of chromic acid or sodium hydroxide (Ministry of Defence UK, 1997).

DISCUSSIONS

A third order polynomial equation is employed for the three variables (voltage"X_1", acid concentration"X_2" and temperature"X_3"). The coating weight is represented by the response Y of the model equation to be constructed. The general form of third order polynomial is written as follows:

$$Y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_4 X_1^2 + a_5 X_2^2 + a_6 X_3^2 + a_7 X_1 X_2 + a_8 X_1 X_3 + a_9 X_2 X_3 + a_{10} X_1^3 + a_{11} X_2^3 + a_{12} X_3^3 + a_{13} X_1 X_2 X_3 + a_{14} X_1 X_2^2 + a_{15} X_1 X_3^2 + a_{16} X_2 X_1^2 + a_{17} X_2 X_3^2 + a_{18} X_3 X_1^2 + a_{19} X_3 X_2^2 \qquad (5)$$

The coefficients of equation (5) can be determined by Quasi-Newton method using software program "STATISTICA, Version 5".

The fitted response of the equation (5) is:

$$Y = 273.555 - 8.874 X_1 + 4.5 X_2 + 32.167 X_3 - 6.923 X_1^2 + 0.21 X_2^2 - 8.901 X_3^2 - 3.454 X_1 X_2 + 2.615 X_1 X_3 - 2.83 X_2 X_3 + 0.757 X_1^3 - 0.654 X_2^3 - 2.401 X_3^3 - 0.76 X_1 X_2 X_3 + 0.349 X_1 X_2^2 + 0.41 X_1 X_3^2 - 0.054 X_2 X_1^2 - 0.223 X_2 X_3^2 - 0.554 X_3 X_1^2 - 0.201 X_3 X_2^2 \qquad (6)$$

The analysis of variance (F-test) is used for testing the significance of each effect in equation (6). The significance of effects may be estimated by comparing the value of the ratio a2/(standard errors)2 with critical value $F_{0.95}(1, 44) = 4.06$ of the F-distribution at 95% level of confidence with 1 and 44 degree of freedom. If the ratio $a^2/(\text{standard errors})^2 > 4.06$ then the effect is significant. The new response function is then written as follows:

$$Y = 273.555 - 8.874 X_1 + 4.5 X_2 + 32.167 X_3 - 6.923 X_1^2 - 8.901 X_3^2 - 3.454 X_1 X_2 + 2.615 X_1 X_3 - 2.83 X_2 X_3 + 0.757 X_1^3 - 2.401 X_3^3 - 0.76 X_1 X_2 X_3 - 0.554 X_3 X_1^2 \qquad (7)$$

Employing equations (1, 2 and 3) to convert the coded values to real values as follows:

$$W_C = 995.4 + 3.875 V - 0.2362 V^2 + 0.0018 V^3 + 0.57 C_A - 84.442 T + 2.237 T^2 - 0.019208 T^3 + 0.0134 T C_A + 0.3056 V T + 0.03 C_A V - 0.00137 C_A V T - 0.00199 V^2 T \qquad (8)$$

It is important to find the optimum conditions for the operating variables. Taking the first derivative of equation (8) for the response W_C with respect to each variable and equating to zero as follow:

$$\frac{\partial W_C}{\partial V} = 3.875 - 0.4724 V + 0.0054 V^2 + 0.3056 T + 0.03 C_A - 0.00137 C_A T - 0.00398 V T = 0 \qquad (9)$$

$$\frac{\partial W_C}{\partial C_A} = 0.57 + 0.0134 T + 0.03 V - 0.0137 V T = 0 \qquad (10)$$

$$\frac{\partial W_C}{\partial T} = -84.442 + 4.474 T - 0.0576 T^2 + 0.0134 C_A + 0.3056 V - 0.00137 C_A V - 0.00199 V^2 = 0 \qquad (11)$$

Solving these three equations, it is found that the values were:

$V = 32\ volt$

$C_A = 85\ g/l$

$T = 50\ ^{o}C$

A third order polynomial equation is employed for the time variable (X_4) at best operating conditions.

The coating weight is represented by the response Y of the mathematical model to be constructed. The general form of third order polynomial is written as follows:

$$Y = b_0 + b_1 X_4 + b_2 X_4^2 + b_3 X_4^3 \qquad (12)$$

The fitted response of equation (12) is:

$$Y = 336.086 + 28.8 X_4 - 11.893 X_4^2 + 0.95 X_4^3 \qquad (13)$$

Employing equation (4) to convert the coded value to real value as follow:

$$W_C = 23.8 + 10.289 t - 0.0993 t^2 + 0.0002815 t^3 \qquad (14)$$

Taking the first derivative of equation (14) for the response W_C with respect to t and equating to zero as follows:

$$\frac{dW_C}{dt} = 10.289 - 0.1986t + 84.45*10^{-5} t^2 = 0 \qquad (15)$$

Solving this equation, it is found that the value was: $t = 77$min.

The statistical analysis of the response function showed that the temperature is the factor which has the largest effect on the coating weight, since its coefficient in equation (6) is greater than the coefficients of the other variables. **Figs. (2 and 3)** show the effect of temperature on the coating weight at different voltages and acid concentrations respectively.

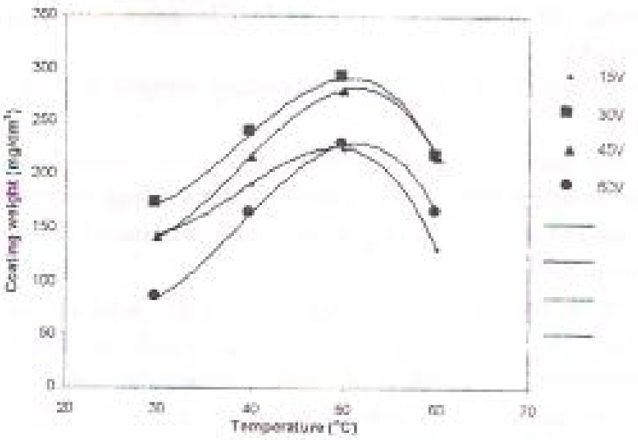

Fig. (2) Effect of temperature on coating weight at different voltages (C_A= 65 g/l, t= 55min.).

Examining these figures one can see that the coating weight or thickness of anodic film increased as the temperature increased in the range between 30-50 °C. But the coating weight decreased as the temperature increased from 50 °C to 60 °C.

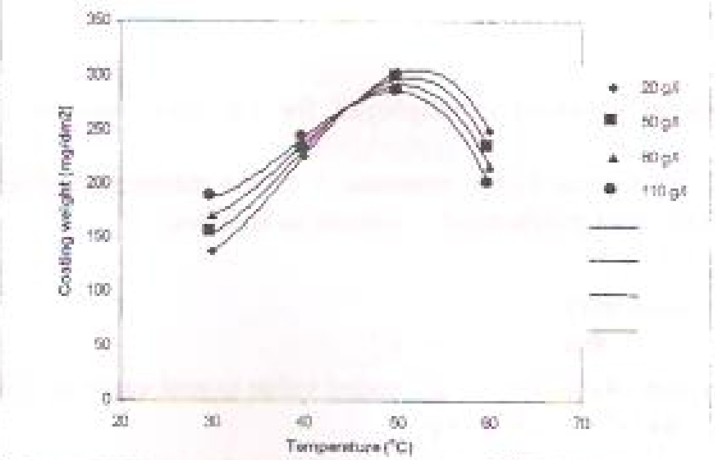

Fig. (3) Effect of temperature on coating weight at different acid concentrations
(V= 37.5V, t= 55min.).

This behavior is due to the effect of increasing temperature on coating weight by two inverse ways. The first way, when the temperature increased, the current density increased therefore the formation rate of anodic coating increased, this behavior is in agreement with Arhenious theory. On the other hand further increase in temperature results in the increase of the dissolution rate of anodic coating increased.

From **Fig. (2)**, it is clear that, increasing the temperature from 30 °C to 50 °C gave an increase in the formation rate of anodic coating larger than the increase in the dissolution rate of anodic coating therefore the positive net from these two factors represented by the increase in the coating weight. On the contrary, increasing the temperature up to 60 °C gave a negative net represented by the decrease in the coating weight.

Figs. (4 and 5) show the effect of voltage on the coating weight at different temperatures and acid concentrations respectively.

Examining these figures one can see that the coating weight increased as the voltage increased from 15V to 30V. Moreover the coating weight decreased as the voltage increased from 45V and higher.

Fig. (4) shows that the gradient in the coating weight was increased as temperature decreased, when increasing the voltage above 30V.

From **Fig. (5)** it can be seen that at low voltage with high acid concentration a good result for coating weight. Beside that the same result can be achieved at high voltage with low acid concentration. This behavior is consistent with operation conditions of known processes (Bengough Stuart process using acid concentration 50 g/l and 40/50 V, 10% chromic acid process using acid concentration 100 g/l at 30V).

Figs. (6, 7) show the effect of acid concentration on the coating weight at different temperatures, voltages respectively. Fig. (6) shows that the coating weight increased as the acid concentration increased for low temperature (30-40 °C), and a large rising is achieved as temperature decreases in this range. On the contrary the coating weight decreased as acid concentration increased for high temperature (50-60 °C) and large gradient is achieved as temperature increases in this range. From **Fig. (3)**, it is clear that the reflection point of this behavior occur at 45 °C.

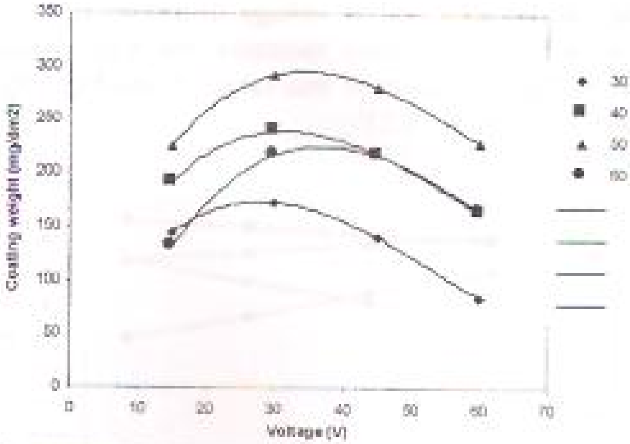

Fig. (4) Effect of voltage on coating weight at different temperatures (C_A= 65 g/l, t= 55 min.).

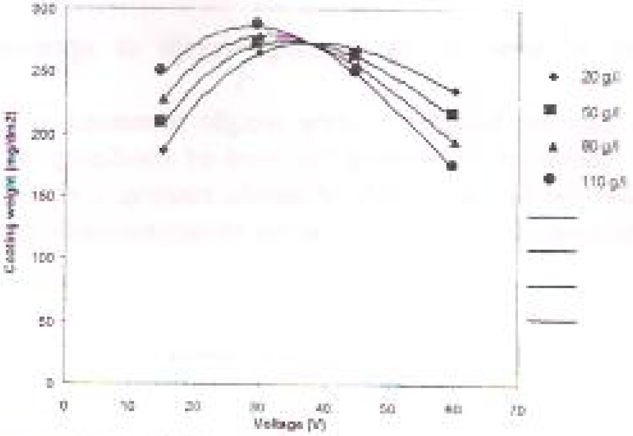

Fig. (5) Effect of voltage on coating weight at different acid concentrations (T= 45 °C, t= 55 min.).

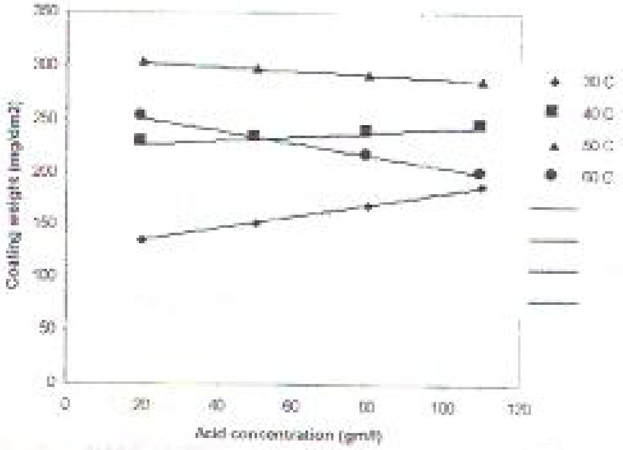

Fig. (6) Effect of acid concentration on coating weight at different temperatures (V= 37.5V, t= 55 min.).

Fig. (7) shows that the coating weight increased as the acid concentration increased for low voltage (15-30V) and a large rising can be achieved as voltage decreases in this range. Farther more the coating weight decreased as acid concentration increased for high voltage (45-60V) and a large gradient can be achieved as voltage increases in this range. From **Fig. (5),** it can be noted that the reflection point of this behavior occurs at 37.5V.

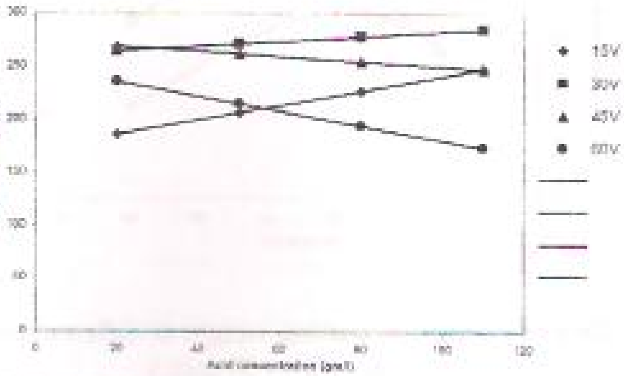

Fig. (7) Effect of acid concentration on coating weight at different voltages (T= 45 °C, t= 55 min.).

Fig. (8) shows the effect of time on the coating weight at optimum operating conditions (32V, 85 g/l, 50 °C).

Examining this figure one can see that the coating weight increased as the time increased in the range between 25-70 min. Moreover increasing the time of anodizing more than 70 min. had no significant effect. In this case the formation rate of anodic coating is equal to the dissolution rate of the anodic coating. Thus the time 70 min. is taken as the recommended optimum time.

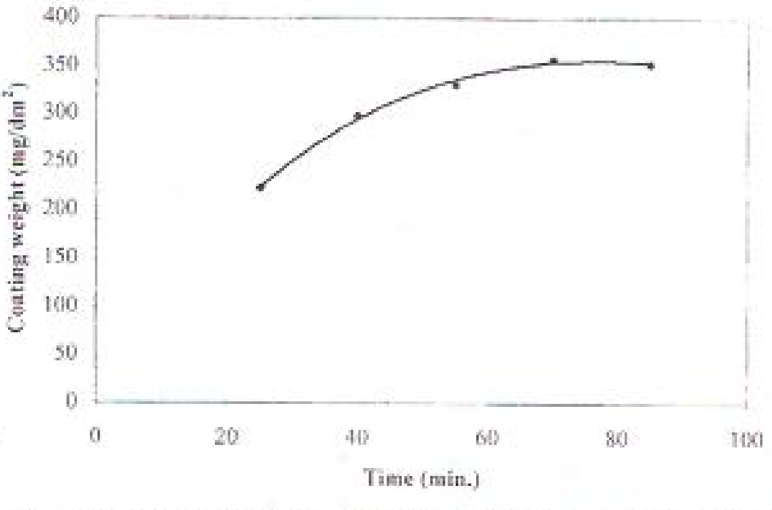

Fig. (8) Effect of time on coating weight (C_A= 85 g/l, V= 32V, T= 50 °C).

While, the mathematical optimum time is equal to 77 minutes. This time value is obtained due to that a small change in coating weight between 70 and 85 min. gave a maximum point at 77 min.

CONCLUSIONS

A third order polynomial of the objective function (coating weight) gave adequate description of the process in terms of temperature, acid concentration and applied voltage (equation 8). While equation 14 describe the process variation with time at optimum values of temperature, concentration and voltage. And these are given below.

It was, also, found that the recommended operating conditions for anodizing aluminum alloy by chromic acid process were:

a- Temperature: 50 °C.
b- Voltage: 32V.
c- Acid concentration: 85 g/l.
d- Time: 70 min. (during the first ten minutes the voltage gradually raised at a rate of 3.2V/min.).

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