

where n is the number of electrons exchanged, D the diffusion coefficient of O_2 , and C_{O_2} the concentration of O_2 in the electrolyte. Identical results were established within certain limits by Rozenfeld (6) and Mansfeld (5), although they have found $i_L \delta = \text{Const}$, since the concentration of electrolyte was kept approximately constant during the experiments. In the present experimental conditions, the electrolyte changes to a more concentrated one with the drying time, the solubility of oxygen diminishes, thus a non constant value is to be expected for that product. This fact is observed and the results indicate during the period under study a control of the corrosion process by diffusion of the oxygen through the electrolyte layer.

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ELECTROCHEMICAL PREPARATION OF A COPPER TOOL-ELECTRODE UTILIZED IN ELECTRIC-DISCHARGE MACHINING

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1. INTRODUCTION

The Electric-discharge Machining (EDM) is an important industrial process. In the EDM process the preform or part to be machined is placed into a cell, as anode, opposite to a cathode or tool-electrode, which has the "negative" form of the model which we wish to reproduce. When the current supplied by a D.C. generator flows through the circuit, the preform is dissolved selectively into the bath, with a speed which is proportional to the current density in each superficial zone. This current density is stabilized uniformly while the part to be machined is jointed together facing the tool-electrode.

The electrochemical preparation of the copper tool-electrode utilized in electric-discharge machining (EDM), which will be used as cathode, consists of several paths: (a) making of a negative pattern of the model that we want to reproduce in the EDM process; (b) electrodeposition of a thick copper coating, which properly stripped, will be utilized as tool-electrode (cathode) in the EDM process.

To make the copper tool-electrode the following operations must be carried through: (1) positive pattern surface preparation; (2) negative pattern preparation; (3) negative pattern activation; and (4) copper electrodeposition on activated negative pattern.

In the present work a method for preparation of a copper tool-electrode to be utilized as cathode in EDM process by means of the described paths is examined.

2. EXPERIMENTAL

2.1. Positive pattern preparation

The process was initiated by the cleaning of the positive pattern by means of a proper degreasing solution followed by a

"proper "decasting" applied on the positive pattern surface.

2.2. Negative pattern preparation

Two "Araldite" synthetical hard resins (the "Araldite CW-215" epoxy resin with a "HY-215" hardener and the "Araldite SW-404" epoxy resin with "HY-404" hardener) were chosen for negative pattern preparation. Each resin was properly mixed and then applied on positive pattern surfaces in order to obtain the suitable negative pattern.

2.3. Negative pattern activation

The object of this operation is to confer the "negative" resin surface enough electrical conductivity to permit the ulterior copper deposition on it. The negative pattern surface was coated with an organic lacquer containing silver powder. The organic lacquers assaied were "Demetron-200" and "Demetron-429". The electrical resistivity of the silver coating obtained were tested with an ICE-tester.

Characteristics of negative pattern are shown in Table I.

Table I. Characteristics of negative pattern.

Dimensional characteristics of negative pattern	Specific Electrical resistance (resistivity) of silver coating (in Ohm.cm) after:						
	1 h	2 h	4 h	6 h	8 h	10 h	12 h
Simple shape	+	0	0	0	0	0	0
Complex shape	+	+	+	0	0	0	0
Very complex shape	+	+	+	+	+	+	0

In this table the electrical characteristics of negative patterns are given in relation to time, measuring the disappearance of resistivity in silver coatings. In this table "0" means that the resistivity measured is equal to "electrical specific resistance" (or resistivity) of silver, that is to say: $1,59 \cdot 10^{-6}$ ohm.cm.

2.4. Copper electrodeposition on activated negative pattern.

The best electrolyte in order to obtain a good coating of copper with the appropriate characteristics to be used as negative pattern in Electric-Discharge Machining is shown in Table II (1).

The copper sulfate reagent must be pure, with not less than 24,9% of copper. On the other hand, it must be exempt of chromate

and nitrate anions and organic matter. Also, copper sulfate utilized must not contain more than 0,3% of nickel, 0,075% of iron, 0,02% of chloride, 0,1% of insoluble matter and 15 ppm of arsenic.

Table II. Aqueous copper electrolyte.

CuSO ₄ ·5H ₂ O	200 g/l
H ₂ SO ₄	70 g/l
Depolarizer (NaCl)	0,04 g/l
Brightener	0,1 g/l
Leveller	0,05 g/l
Internal stress Depressor	0,1 g/l
Wetting agent	0,5 g/l

The operating conditions of copper electrolyte are shown in Table III.

Table III. Operating conditions of copper plating bath.

Temperature	25 °C
Cathode current density	5 A/dm ²
Cathode current density during first 8 h.	2 A/dm ²
Anode-cathode distance	8-10 cm
Anode-cathode ratio	1:1
Anode	Copper with 0,02-0,6%P
Cathode agitation speed	5 m/min
Filtration	Continuous
Cathode efficiency	96-98%
Throwing power (with Haring-Blum cell)...	18-19%
Rate of deposition (5 A/dm ²)	0,8 m/min
Rate of deposition (2 A/dm ²)	0,3 m/min

Normally, this electrolyte has a high tolerance to impurities, but when substantial quantities of arsenic, antimony, iron, chromium and lead are present, rough deposits can be caused.

Operating technique is as follows:

The negative pattern to be coated with a copper film is immersed, as cathode, into the copper plating bath, always under cu-

current. At the beginning, a low current density must be applied (between 1-2 A/dm², but, after 6-8 hours, we can apply higher current densities (up to 5 A/dm²) until the desired thickness of copper is obtained. The process takes between 6 to 8 days to obtain 1 mm thickness of copper on hollow parts and 5 mm thickness of copper on external parts of the negative pattern.

3. RESULTS AND DISCUSSION

Operating under the mentioned conditions a suitable coppered negative pattern, which can be used as copper tool-electrode, as been obtained. This electrode has the properties that are shown in Table IV.

Table IV. Copper tool-electrode properties.

Density	8,7-8,9 g/cm ³
Thermal conductivity	0,735 cal/cm.s.°C
Electrical conductivity (with respect to Ag)...	98%
Hardness	170 HV
Ductility	21%
Internal stress	800 pounds/inch ²
Thickness (internal zones).....	1 mm
Thickness (external zones).....	4-5 mm

These characteristics are good enough in order to utilize this coppered negative pattern as proper tool-electrode in Electric-Discharge Machining.

In order to test it, as "galvano", this tool-electrode was placed as cathode in an EDM machine. It was an ONA machine model BA-T.

The results obtained were excellent.

On the other hand, copper electrodeposited through the mentioned electrolyte was bright, with good crystalline structure and exempt of dendritic or powdery growth, as well as exempt of internal stress.

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MESURES ÉLECTROCHIMIQUES POUR L'ÉVALUATION DES INHIBITEURS DE LA CORROSION

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1.- INTRODUCTION

Les inhibiteurs organiques de corrosion agissent, en général, par adsorption sur la surface des métaux que l'on désire protéger. Le processus d'adsorption des inhibiteurs s'accompagne d'une série de transformations sur la zone de contact du métal et de la solution, ce qui fait le mécanisme de corrosion complexe. Cette complexité limite, parfois, l'emploi de techniques pour son évaluation.

Dans le présent travail on étudie le mécanisme d'une famille d'inhibiteurs organiques avec différents degrés de substitution, à l'aide de techniques électrochimiques.

2.- Procédé Expérimental

Les échantillons employés sont en acier doux avec une surface utile de travail de 10 cm². Le milieu se composait d'acide chlorhydrique 2 M, et les inhibiteurs étaient une série des amines alifatiques: butylamine, dibutylamine et tributylamine. Les concentrations essayées ont varié entre 10⁻⁴ et 1 M. La durée des essais a été de 96 heures et la température de 288 K. Les Techniques électrochimiques employés furent celles d'impédance, la méthode de résistance de polarisation et les courbes de polarisation.