

Comparison of the Protective Effect of Lacquers on Preserving Decorative Colors on Copper

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Abstract

These days, the formation of patinas on copper surface is a subject of great interest, because of its aesthetic aspect and its protecting properties against the more diverse ambient conditions. In this study, first of all, different decorative colors have been produced by optimization of available conversion coating bath composition. Then, their corrosion resistances were evaluated in 3.5% NaCl solution before and after applying protective lacquers (stoving and air-drying) by using various techniques including electrochemical impedance spectroscopy, potentiodynamic polarization methods and salt spray test. The thickness of all coating were the same (3-4 μm). The microstructure of coating surface were studied by Scanning Electron Microscopy (SEM) and surface composition were identified by X-Ray Diffraction (XRD). It was shown that the coating surface properties (rather than it's corrosion resistance) are important for having a good overall protection after applying lacquers.

Keywords

Microstructure, Lacquers, Patina, Impedance, Salt spray

Introduction

These days, formation of patinas on copper surface is a subject of great interest, not only because of its aesthetic aspect but also because of its protecting properties against the more diverse ambient conditions[1-5].

Chlorides, sulphates, oxides and hydroxides, which consolidate with exposure time, constitute patinas, and may protect the metal from further corrosion.

Patina formation is strongly linked to the air composition and the pollution content. It takes many years for the patina to appear. During these years the color of patina will change and in most cases the change will be unpredictable, hence, it is more reasonable to produce the patina artificially (according to the customer's need) by using different solutions and immersion methods and to preserve it by lacquers.

By adding different salts to a standard bath solution, patinas of different colors have been obtained: brown, green, light blue and violet. All have excellent resistance and aesthetics properties. The patinas formed on copper sheets are mainly composed of Cu_2O and $\text{Cu}_4\text{SO}_4(\text{OH})_6$ and their formation is accelerated by aeration and temperature increase [6-8].

Lacquers are used for three purpose: To protect sensitive surfaces that would otherwise deteriorate in appearance because of atmospheric attack or handling.

To provide decorative effect such as high gloss or a particular colour.

In combination with phosphating to provide a composite functional finish which has



extremely high corrosion resistance. There are a number of air-drying lacquers, the earliest of which, known as gun lacquers, and based on natural resins, are characterized by a low viscosity and the ability to impart a bright glossy finish to both polished and unpolished metals. Today by far the most important air-drying lacquers are the cellulose type based on nitrocellulose, with synthetic resins and other ingredients added to impart good adhesion, improve gloss and resistance to wear, and provide other required properties. The ease with the properties of nitrocellulose can be modified which gives this class of lacquer a versatility that has yet to be surpassed by other types of film former.

There are also air-drying lacquers, based solely on synthetic resins, the most widely used being vinyls and acrylics; they offer different combinations of properties that make them appropriate for various applications, and their use is increasing.

These are invariably based on synthetic resins, the most important classes of which are urea-formaldehyde, melamine-formaldehyde, epoxy and acrylic. Here again it is usual for other resins to be incorporated in the formulae to make the lacquer more generally useful, and all these lacquers are characterized by a hardness, durability under adverse conditions[9].

In this study through optimization of bath compositions and condition (baths No. 1, 2 and 3), three different traditional colors are created on copper surface and both types of clear lacquers (air-drying & stoving) are used for protecting these patinas. The corrosion resistance of these coatings was evaluated in 3.5% NaCl solution before and after applying protective lacquers, using electrochemical impedance spectroscopy, potentiodynamic polarization methods and salt spray test. The surface microstructure was studied by Scanning Electron Microscopy (SEM), and the composition of patinas was studied by X-Ray Diffraction (XRD).

1- Experimental

2-1- Specimens

The present study has been carried out with samples of commercial ETP copper. Table 1.

Table (1) Composition of copper specimen (ppm).

P	S	Te	As	Se	Sb	Cr	Pb	Sa	Bi	Ag	Zn	Ni	Co	Fe	Cu
22	22	22	22	22	22	22	22	22	22	8	23	22	22	25	rest

A copper rod with cross-sectional area of 1 Cm² was embedded in a Teflon holder and used for electrochemical measurements. The copper surface was first polished with SiC abrasive papers of grade 300-1200, rinsed with distilled water, degreased in %1 alkaline solution at 75°C for 10 min, cleaned in %10 H₂SO₄ at 55°C for 1 min and then washed with distilled water and dried in a hot air stream. After that, it was immersed in baths No. 1 to 3.

2-2- Immersion Baths and conditions

The optimized compositions of three immersion baths are given in Table 2.

Table (2) Plating bath compositions and operating conditions.

No.1[8]	No.2[9]	No.3[9]
NaOH=50g/l	NiSO ₄ =100g/l	Fe(NO ₃) ₃ =11.5g/l
K ₂ S ₂ O ₈ =12g/l	Na ₂ S ₂ O ₃ =40g/l	Na ₂ S ₂ O ₃ =66.5g/l
PH=14	PH=6	PH=5
Temp=65°C	Temp=60°C	Temp=95°C
Time=5min.	Time=5min.	Time=5min.

The plating baths are prepared by using Merk chemicals (extra pure) dissolved in distilled water.

2-3- Electrochemical Measurements

Impedance measurements were carried out at the open circuit potential (E_{oc}), using a computer-controlled potentiostat/Galvanostat 263A (EG&G) Princeton Applied Research and HF Response Model 1025.

Experiments were performed in a conventional three-electrode cell assembly with a Pt-counter electrode (CE) and a saturated calomel reference electrode (SCE).

The impedance spectroscopy was conducted in 3.5% NaCl aqueous Solution after 30 min immersion in electrolyte at room temperature. The alternating current frequency range extended from 100 KHz to 0.01Hz, with Amplitude of 5mV.

The Tafel polarization curves were obtained by using a sweep rate of 1 mvs⁻¹ from -600 mv to 100 mv after 30 min immersion in electrolyte at room temperature.

2-4- Salt Spray Testing

The corrosion resistance of coatings before and after applying lacquers were evaluated by using salt spray test according to the ASTM B-117 standard procedures.

2-5- Scanning Electron Microscopy (SEM)

The surface microstructure was studied by SEM model Camscan MV2300

2-6- Analysis of the coatings

The solid phases formed on the copper surface were characterized by X-Ray diffraction (XRD) Phillips, model X'PERT with monochromatize Cu k α radiation.

2-7- Thickness of coatings

The thickness of coatings were assessed by digital Leptoskop Model 2015 with $\pm 1\mu\text{m}$ accuracy.

3- Results and discussion

Fig 1 shows the Nyquist plots (100 KHZ-0.01 Hz) the copper electrode in 3.5% NaCl solution without coating (R_{Cu}) and with coating by No.1 bath (c_1)

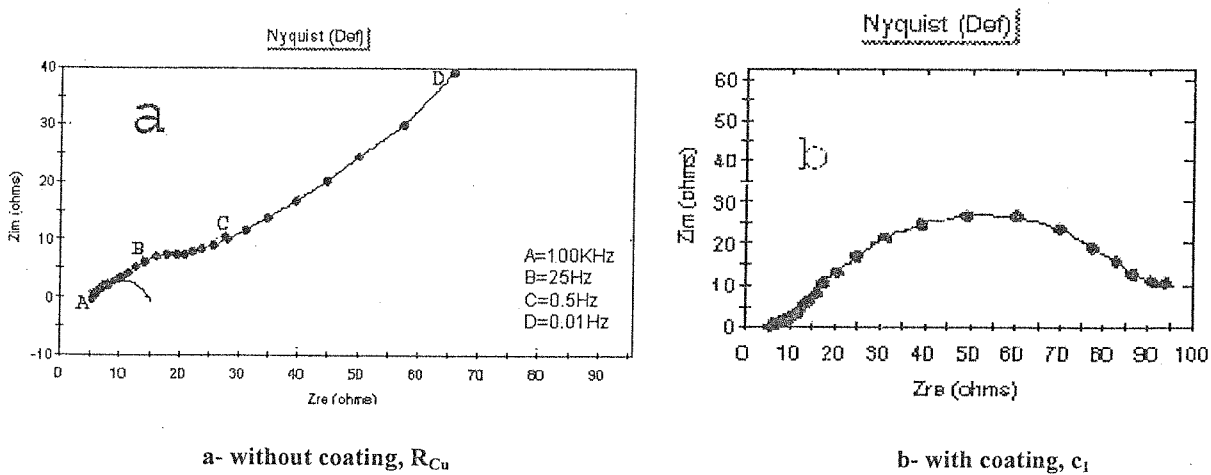


Figure (1) Nyquist plots of copper electrodes in 3.5% NaCl solution after 30 min immersion

For the copper electrode (R_{Cu}) as shown in Fig. 1a, two straight line portions in the low-frequency (LF) and the middle-frequency (MF) regions, and a small high-frequency (HF)

semicircle were observed. The (LF from C to D) linear portion (0.5Hz-0.01Hz) is generally believed to be a Nernst diffusion process of soluble copper species (CuCl_2) from electrode surface to bulk solution.

The (MF from B to C) straight line portion (25Hz-0.5 Hz) is related to the diffusion of copper species through an oxide film on the copper surface [10,11]

The (HF from A to B) semicircle (100kHz-25Hz) is attributed to the time constant of charge transfer (R_t) and double-layer capacitance (C_{dl}), which were estimated to be $15 \mu\text{cm}^2$ and $630 \pm 5 \text{ F/cm}^2$, respectively.

The polarization resistance (R_p) is determined from the low frequency limit of the impedance at Z_{Re} axis ($R_p = 65 \text{ cm}^2$) or from linear polarization (LP) measurements.

For the copper electrode with coating by No. 1 Bath (c_1) as shown in Fig. 1 b, the (MF) straight line observed in Fig. 1a disappeared, and a depressed semicircle was observed with a diameter of about 95 cm^2 . The double-layer capacitance decreased too. The large semicircle observed from high to low frequencies indicates that the charge-transfer resistance becomes dominant in the corrosion process due to the formation coating on the copper surface. However, a Warburg impedance at the low-frequency region is still visible from (0.01 Hz-0.03 Hz), indicating that the corrosion process was controlled by a mixed charge-transfer and diffusion in solution. Therefore an equivalent circuit was purposed to represent the corrosion interface of coating covered copper in 3.5% NaCl solution, as shown in Fig. 2, where R_s is the solution resistance, R_t is the charge transfer resistance and C_{dl} is the double-layer capacitance, and Z_d represents the diffusion impedance appearing in the low-frequency region.

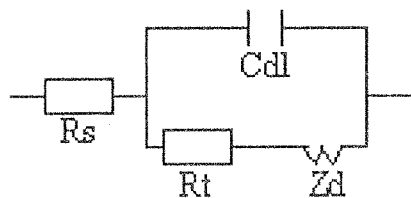


Figure (2) The equivalent circuit for c_1

The quality of the coating was evaluated by the polarization resistance (R_p), capacitance (C_{dl}), and maximum phase-angle (ϕ_{MAX}) of the impedance. The more densely packed the coating, the larger the diameter of the semicircle, which results in higher R_p and lower capacitance values [12].

In Fig: 3 the Nyquist plots and polarization curves of c_1 , c_2 , c_3 were compared with reference (R_{Cu}), that shows corrosion resistance of c_1 and c_2 coatings increase relative to R_{Cu} but the corrosion resistance of c_3 coating decreases.

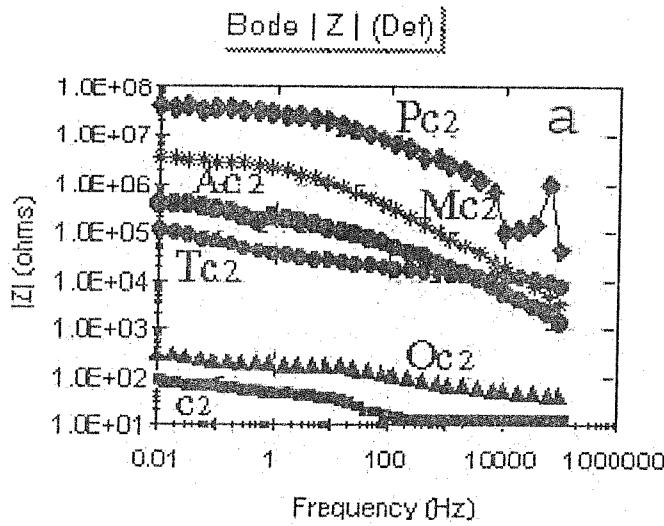
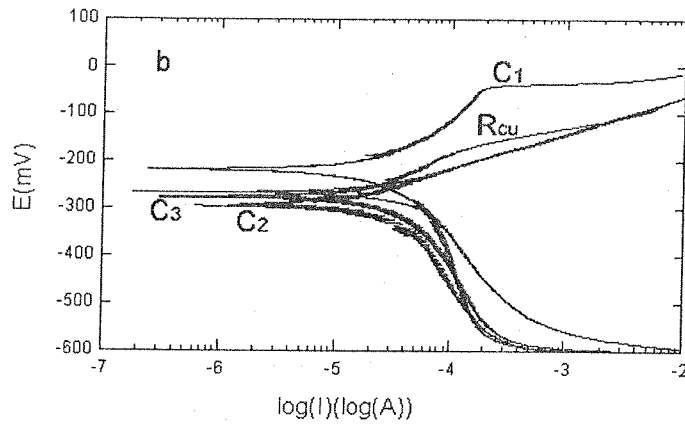


Figure (3) The comparison
 a-Nyquist plots of c_1, c_2 and c_3 with R_{cu} b-Polarization curves of c_1, c_2 and c_3 with R_{cu} .

In this study two kinds of lacquers (air-drying and stoving lacquers) are used. Three air-drying lacquers that are used in this investigation are oil-lacquer (O), Thinner lacquer (T) and two component polyester lacquer (P), that are based solely on synthetic resins, the most widely used being vinyls and acrylics. Two kind of stoving lacquers are used in this study are Alkyd Melamine (M) and Acrylic (A), based on synthetic resins Melamine-formaldehyde, and Acrylic.

Fig 4, shows that all used lacquers increase the corrosion resistance of coating c_2 , (almost the same results were obtained for c_1 and c_3 coatings).

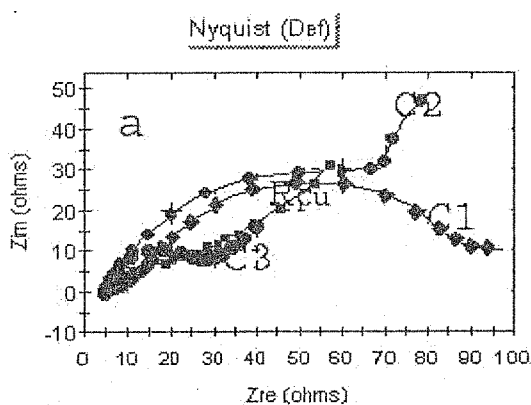
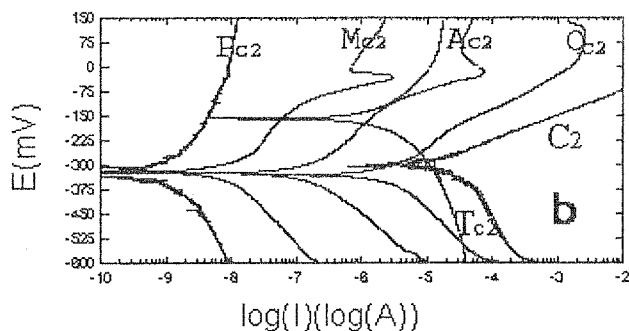


Figure (4) the comparison, a-Bode plots b-polarization curves of different lacquers used on c_2 with c_2

As represented, two component polyester of air-drying lacquers groups have the most protection, so for this reason, comparison is based on P, M and A lacquers.

The inhibition efficiency of corrosion ($\eta\%$) after applying coatings (c_1, c_2, c_3) and lacquers (A, M, P) is calculated by polarization resistance as follows [13].

$$\eta\% = \frac{\frac{1}{R_0} - \frac{1}{R_1}}{\frac{1}{R_0}} \times 100 \quad (1)$$

Where R_0 and R_1 are the polarization resistance values without and with coating and lacquers, respectively.

The impedance parameters derived from this investigation are given in table 3 (a, b).

Table (3) a- Inhibition efficiency of coating c_1, c_2 , and c_3 respect to R_{cu}

Coating	c_1	c_2	c_3
$\% \eta$	33	30.8	-

Table (3) b-Inhibition efficiency of coatings after applying lacquers (P, M, A) with respect to R_{cu}

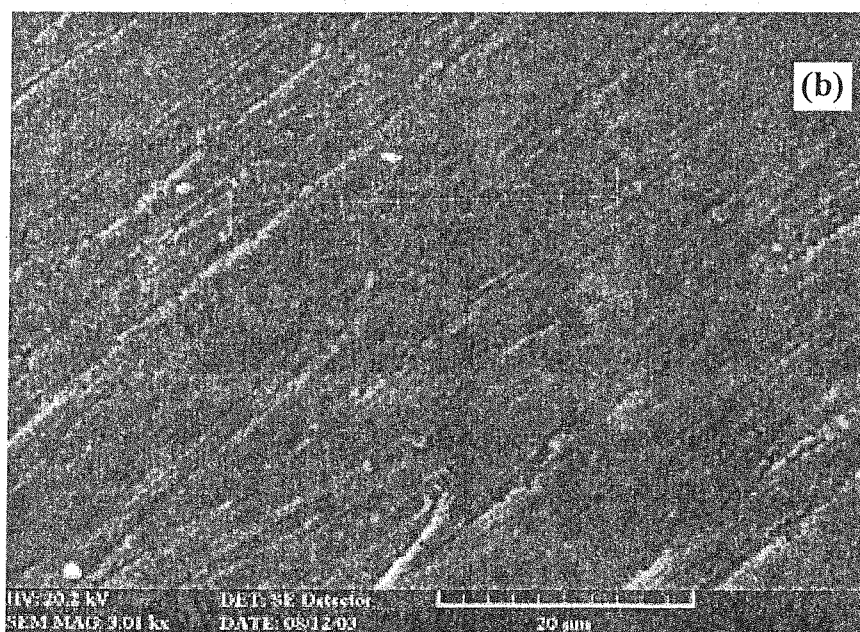
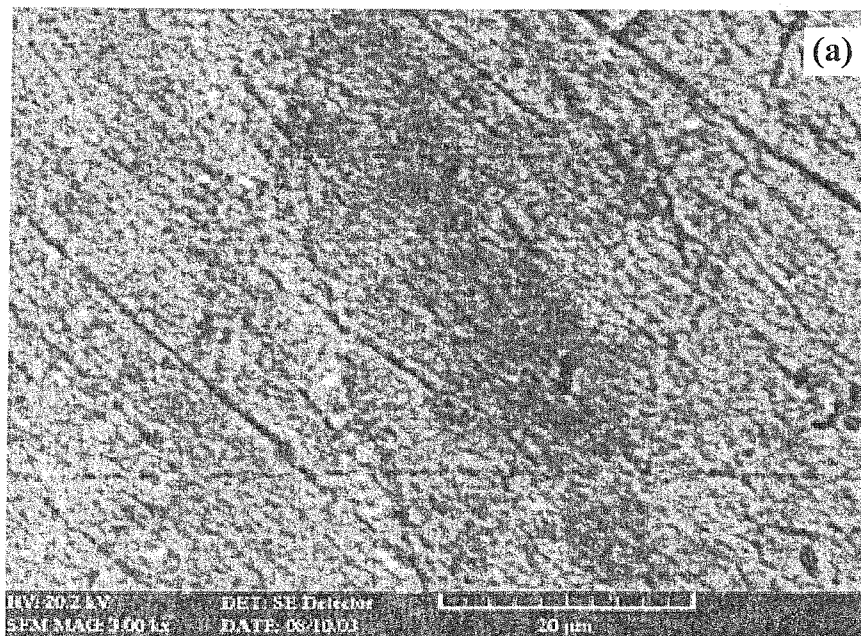
	A_{c1}	A_{c2}	A_{c3}	M_{c1}	M_{c2}	M_{c3}	P_{c1}	P_{c2}	P_{c3}
$\eta\%$	93.538	99.983	99.477	99.957	99.998	99.940	99.997	99.999	99.997

Tables 3a and 3b shows that c_3 (coating in No. 3 Bath) without lacquer has no protection effect with respect to R_{cu} , but after applying lacquers, c_3 shows protection effect equal to c_1

and c_2 . this may be due to the microstructure and thickness of coatings.

Thickness measurements show that coating's Thickness (c_1 , c_2 and c_3) are approximately equal (3-4 μm).

Fig 5 shows the microstructure of the c_1 , c_2 and c_3 coatings by SEM.



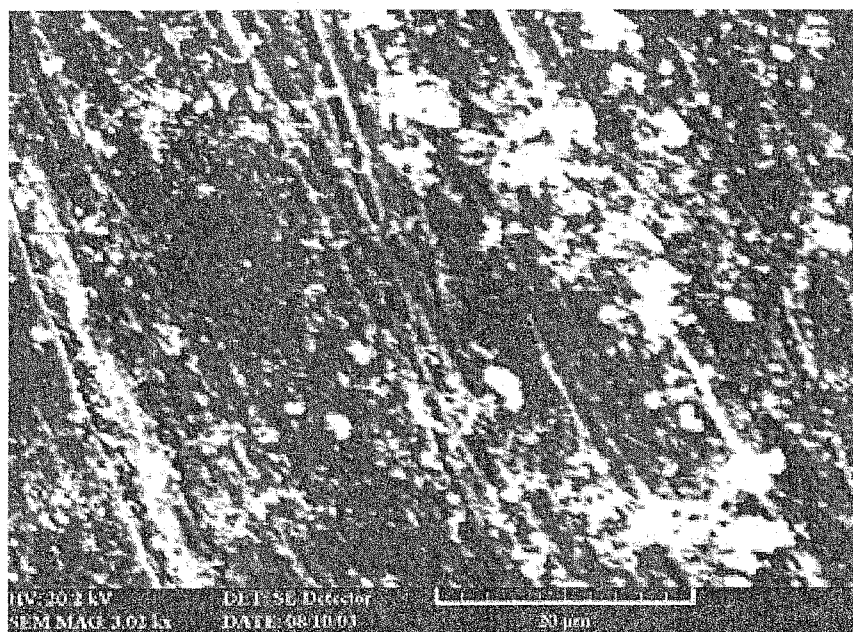


Figure (5) SEM image of coatings : a)c₁, b)c₂, c)c₂ (c)

In Fig 5, the porosity is shown in the SEM images of coatings. It is clear that the porosity of c₁ is less than c₂ and the porosity of c₂ is less than c₃. So it is resulted that c₁ is the most densely and homogenous coating and c₂ is better than c₃. These results are obtained from electrochemical experiments (Nyquist & Polarization), too.

The X-Ray Diffraction analysis of surface chemical composition indicates that c₁ coating is formed from Cuprite (Cu₂O) and Tenorite (CuO) [8], that seems to cover the copper surface completely, and XRD results of c₂ composition surface shows Nickel Sulfide (S₂ Ni₃), that is homogenous but less than c₁. The c₃ coating was amorphous and could not be analyzed by XRD.

The results of salt spray tests are summarized in table 4.

Table (4) The time of initial corrosion effect on c₁, c₂ and c₃ coatings without and with lacquers through the salt spray test.

Specimens	c ₁	c ₂	c ₃	A _{C1}	A _{C2}	A _{C3}	M _{C1}	M _{C2}	M _{C3}	P _{C1}	P _{C2}	P _{C3}
Time(h)	90	24	24	168	192	192	192	192	192	216	240	240

The corrosion protection of metallic substrates by organic coating is a complex process and depends mainly on electrical, chemical and mechanical properties of polymers, adhesion of the coating to the substrate, adsorption characteristics of coating (water and oxygen uptake), ion penetration through the coating and surface characteristics of the metal substrates [14-17]. The results of this investigation show the c₃ coating before applying lacquers has lower protection but after applying lacquers, due to surface properties (porosity) of coating, indicates high protection. It was shown that surface modification is an important factor which determines electrochemical behavior. The results of all experimental methods show the good agreement with each other.

The equivalent circuit, after applying lacquer, is shown in Fig.6. R_s is the solution resistance, R_{ct} is the charge transfer resistance and C_{dl} is the double-layer capacitance, and Z_d represents the diffusion impedance appearing in the low-frequency region for coating, C_1 and R_1 are the double layer of capacitance and charge transfer resistance of lacquer [18].

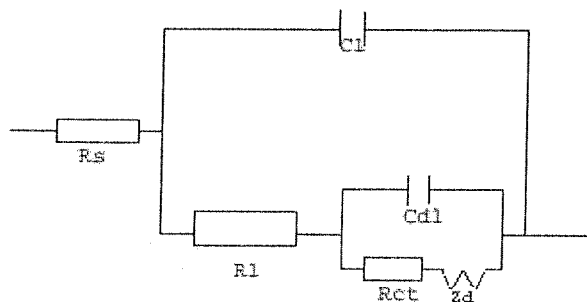


Figure (6) The equivalent circuit for coating after applying lacquer.

4- Conclusion

- 1- c_1, c_2 and c_3 coatings which are formed on copper, protect its surface from corrosion to certain limit.
- 2-The coating surface properties are more important than its corrosion resistance for having a good overall protection after applying lacquers.
- 3-Applying air-drying lacquers (O, T, P) and stoving lacquers (A, M) on coatings increase the protection efficiency, but two-component polyester lacquer of air-drying group gives the best result.
- 4-The protection efficiency of stoving lacquers Acrylic (A) and Melamine (M) and two component Polyester lacquer of air-drying group are very good and approximately the same. Thus, application of air-drying lacquers in the artifacts and decorative industries is recommended because of its low cost and easier application.

5-Acknowledgements

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