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Effect of Stoving and Air Drying Lacquers on Corrosion Resistance and Preserving Decorative Colours on Copper

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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, the most important purpose is to produce various artificial patinas on copper surface and preserving them by applying clear lacquers. Different decorative colours 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 thicknesses of all coatings were almost the same (3–4 μm). The microstructure of coating surface was studied by scanning electron microscope (SEM) and surface composition was identified by X-ray diffraction (XRD). It was shown that the coating surface morphology (rather than its corrosion resistance) is an important factor for having a good protection after applying lacquers. The importance of this finding is the possibility of producing a range of colours by changing the porosity of the surface without reducing its corrosion resistance and even increasing it in some cases. The possibility of fine tuning the colour to the taste of the customer or the artist is its other aspect.

Key Words: Morphology, Lacquers, Patina, Impedance, Salt spray.

INTRODUCTION

Although copper and its alloys are mostly used in industry, but its use in decorative and art application could not be ignored. Patina will be developed on the copper's surface after many years of exposure to atmosphere. Depending on the atmosphere, different colours will be produced and the patina may or may not be protective.

These days, the 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. 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 colour of the patina will be changed and most of the time the change will be unpredictable. So, it is more reasonable to produce the patina artificially (according to the taste of customers) by using different solutions and immersion methods and to preserve it by lacquers. In doing this it is possible to investigate the possibility of producing a set of new colours with changing the morphology of patinas. These new patinas may not be protective before applying the lacquer but their corrosion resistance after applying lacquer is the subject of this investigation.

By adding different salts to a standard bath solution, patinas of different colours have been obtained: brown, green, light blue and violet. Many of them have excellent resistance and aesthetic properties. The patinas formed on copper sheets are mainly composed of Cu_2O and $Cu_4SO_4(OH)_6$ and their formation is accelerated by aeration and temperature increase[1–7].

There are two basic types of clear lacquers, air-drying and stoving. In this study through optimization of bath compositions and conditions (baths Nos. 1, 2 and 3), three different traditional colours were created on the copper surface and both types of clear lacquers were 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).

EXPERIMENTAL

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-area of 1 cm^2 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 and degreased in 1% alkaline solution at 75°C for 10 min and cleaned in 10% H_2SO_4 at 55°C for 1 min and then washed with distilled water and dried in a hot air stream. Then it was immersed in baths Nos. 1 to 3.

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 = 50 g/L	$NiSO_4$ = 100 g/L	$Fe(NO_3)_3$ = 11.5 g/L
$K_2S_2O_8$ = 12 g/L	$Na_2S_2O_3$ = 40 g/L	$Na_2S_2O_3$ = 66.5 g/L
pH = 14	pH = 6	pH = 5
Temperature = 65°C	Temperature = 60°C	Temperature = 95°C
Time = 5 min	Time = 5 min	Time = 5 min

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

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 0.01 Hz with amplitude 5 mV.

The Tafel polarization curves were obtained using a sweep rate of 1 mV s^{-1} from –600 to 100 mV after 30 min immersion in electrolyte at room temperature.

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

Scanning electron microscopy (SEM): The surface microstructure was studied by SEM model Camscan MV2300.

Analysis of the coatings: The solid phases formed on the copper surface were characterized by X-ray diffraction (XRD) Phillips model XPERT with monochromatized CuKα radiation.

Thickness of coatings: The thickness of coatings was assessed by digital leptoskop Model 2015 with ±1 μm accuracy.

RESULTS AND DISCUSSION

Fig. 1 shows the Nyquist plots (100 kHz–0.01 Hz) of the copper electrode in 3.5% NaCl solution without coating (R_{Cu}) and with coating by No. 1 bath (C_1).

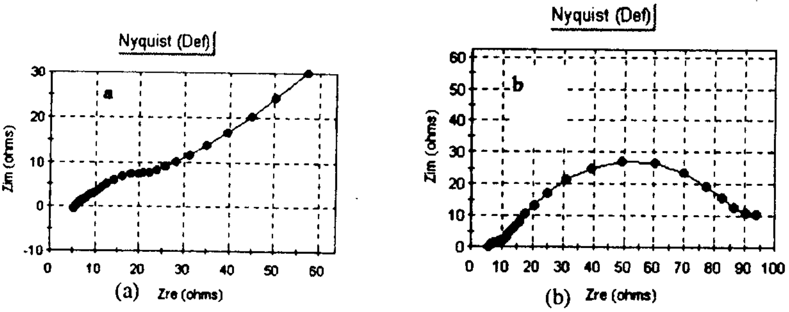


Fig. 1. Nyquist plots of copper electrodes in 3.5% NaCl solution after 30 min immersion: (a) without coating, R_{Cu}, (b) with coating, C_1

For the copper electrode (R_{Cu}) as shown in Fig. 1 (a) , 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) linear portion (0.01–0.5 Hz) is generally believed to be a Nernst diffusion process of soluble copper species ($CuCl_2$) from electrode surface to bulk solution. The (MF) straight line portion (0.5–25 Hz) is related to the diffusion of copper species through an oxide film on the copper surface[10, 11].

The (HF) semicircle (25 Hz–100 kHz) is attributed to the time constant of charge transfer (R_t) and double-layer capacitance (C), which were estimated to be 15 and 630 ± 5 $\mu F/cm^2$, respectively.

The polarization resistance (R_P) is determined from the low frequency limit of the impedance at Z_{Re} axis ($R_P = 65\ \Omega\ cm^2$) 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. 1 (a) disappeared and a depressed semicircle was observed with a diameter of about 95 Ω 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 of coating on the copper surface. However, a Warburg impedance at the low-frequency region is still visible from 0.01 to 0.03 Hz, indicating that the corrosion process was controlled by a mixed charge-transfer and diffusion in solution. Therefore an equivalent circuit was proposed 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, C_{dl} is the double-layer capacitance and Z_d represents the diffusion impedance appearing in the low-frequency region.

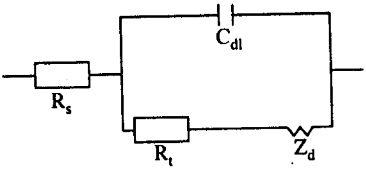


Fig. 2 The equivalent circuit for C_1

The quality of the coating was evaluated by the polarization resistance (R_P), capacitance (C) and maximum phase-angle (θ_{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}) which shows that corrosion resistance of C_1 and C_2 coatings increases relative to R_{Cu}, but the corrosion resistance of C_3 coating decreases.

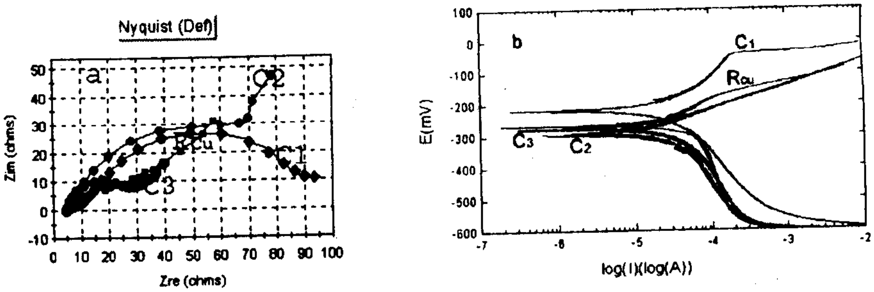


Fig. 3. The comparison of (a) Nyquist plots of C_1, C_2 and C_3 with R_{Cu}, (b) polarization curves of C_1, C_2 and C_3 with R_{Cu}

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 kinds of stoving lacquers used in this study are alkyl 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).

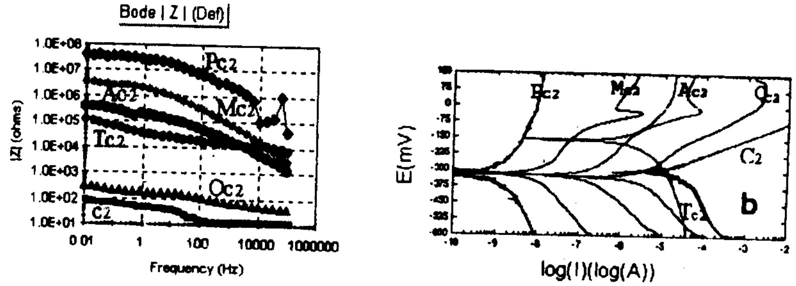


Fig. 4. The comparison of (a) Bode plots, (b) polarization curves of different lacquers used on C_2

As are represented, two component polyester of air drying lacquers group has the most protection; for this reason, comparisons are based on P, M and A lacquers.

The inhibition efficiency of corrosion (η %) after applying coatings (C_1, C_2, C_3) and lacquers (A, M, P) is calculated by polarization resistance[13] as follows.

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

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 WITH RESPECT TO R_{Cu}

Coating	C_1	C_2	C_3
η (%)	33	30.8	—

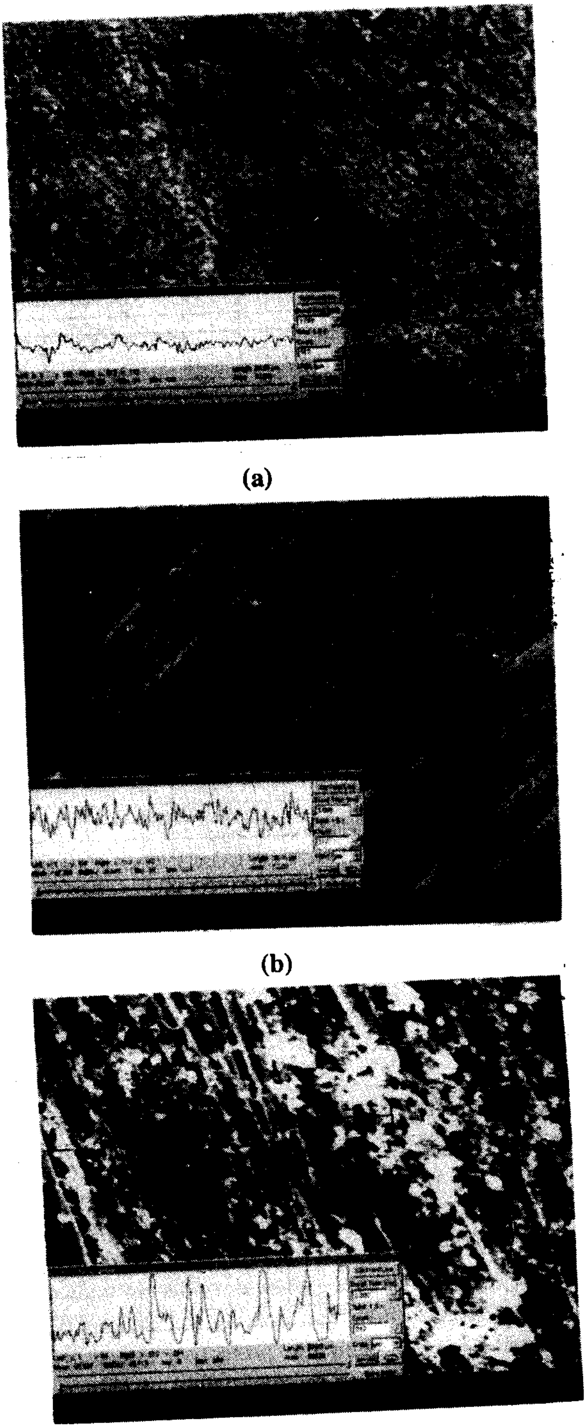
TABLE-3 (b)
INHIBITION EFFICIENCY OF COATINGS AFTER APPLYING LACQUERS (P, M, A) WITH RESPECT TO R_{Cu}

	Ac_1	Ac_2	Ac_3	Mc_1	Mc_2	Mc_3	Pc_1	Pc_2	Pc_3
η (%)	93.538	99.983	99.477	99.957	99.998	99.940	99.997	99.999	99.997

From Table 3 (a and b) it is clear that C_3 (coating bath in No . 3) without lacquer has no protective effect with respect to R_{Cu} , but after applying lacquers, C_3 shows protective effect equal to C_1 and C_2. That is mostly due to the surface morphology which will be discussed when considering microstructures.

Thickness measurements show that coating thicknesses (C_1, C_2 and C_3) are approximately equal (3–4 μ), then the protective effect of C_3 after applying lacquers is considered to be due to microstructure of patinas and is studied by SEM.

Fig. 5 shows the microstructure of the C_1, C_2 and C_3 coatingsby SEM. Topology of each sample is shown on the left corner of Fig. 5.



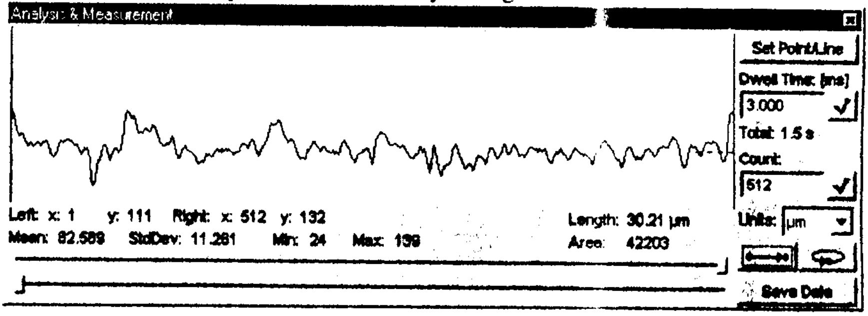
(a)

(b)

(c)

Fig. 5. SEM images of coatings: (a) C_1, (b) C_2, (c) C_3

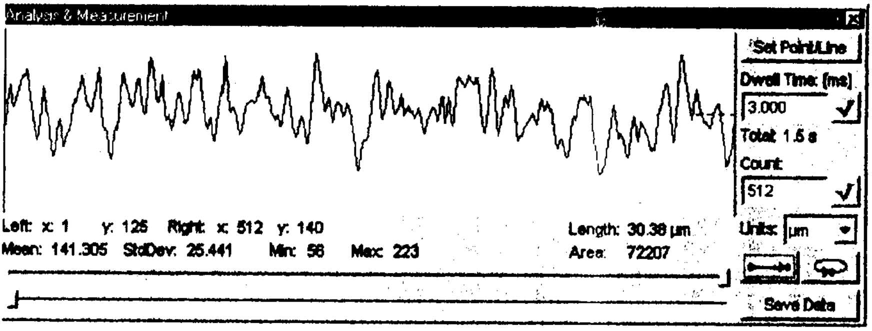
These figures are reproduced for clarity in Fig. 6.



Dwell Time: [ms] 3.000
Total: 1.5 s
Count: 512
Units: µm

Left: x: 1 y: 111 Right: x: 512 y: 132 Length: 30.21 µm
Mean: 82.589 StdDev: 11.281 Min: 24 Max: 139 Area: 42203

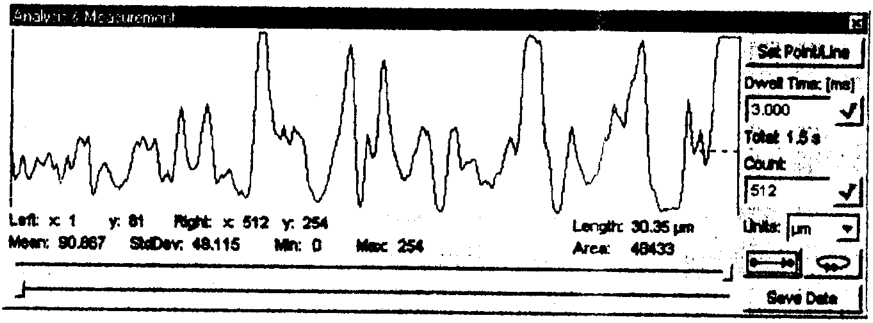
(a)



Dwell Time: [ms] 3.000
Total: 1.5 s
Count: 512
Units: µm

Left: x: 1 y: 125 Right: x: 512 y: 140 Length: 30.38 µm
Mean: 141.305 StdDev: 25.441 Min: 58 Max: 223 Area: 72207

(b)



Dwell Time: [ms] 3.000
Total: 1.5 s
Count: 512
Units: µm

Left: x: 1 y: 81 Right: x: 512 y: 254 Length: 30.35 µm
Mean: 90.867 StdDev: 48.115 Min: 0 Max: 254 Area: 48433

(c)

Fig. 6. Topology image of coatings: (a) C_1, (b) C_2, (c) C_3

The differences between maximum and minimum of data in these figures for each sample are as follows:

$$C_1 = 105, \qquad C_2 = 165 \quad \text{and} \quad C_3 = 254.$$

Even though the topology itself shows the surface roughness and porosity but these differences can be used as criteria for surface roughness and porosity.

It is clear that the porosity of C_1 is less than C_2 and the porosity of C_2 is less than C_3; so it is clear that C_1 is the most dense and homogeneous coating and C_2 is better than C_3. These results are in harmony with Fig. 3 too.

The X-ray diffraction analysis patterns (Fig. 7) of surface chemical composition indicate that C_1 coating is formed from tenorite (CuO) that seems to cover the copper surface completely and XRD result of C_2 composition surface shows nickel sulfide (Ni_3S_2), which covers the surface but not completely. As the C_3 coating could not be analyzed by XRD, so this coating (C_3) is considered to be amorphous and it has much porosity in it.

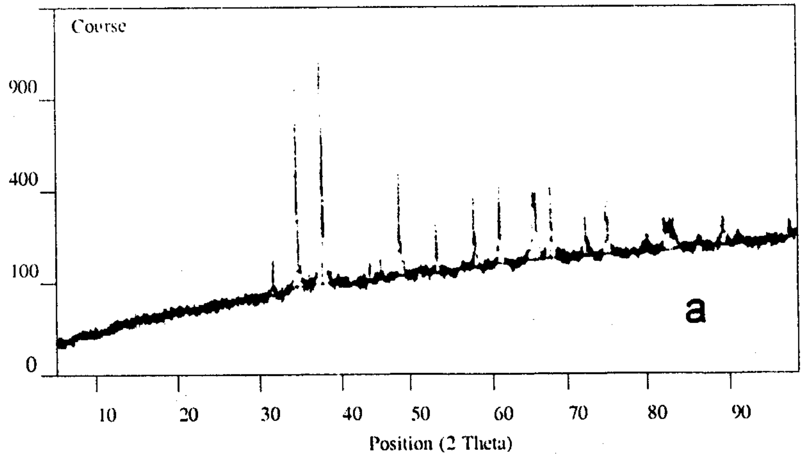


Fig. 7. XRD pattern: (a) C_1 coating, (b) C_2 coating

The results of salt spray test are summarized in Table-4.

TABLE-4
THE DETECTED TIME FOR INITIALIZATION OF CORROSION EFFECT ON COATINGS WITH AND WITHOUT LACQUERS THROUGH THE SALT SPRAY TEST

Specimens	C_1	C_2	C_3	A_{C_1}	A_{C_2}	A_{C_3}	M_{C_1}	M_{C_2}	M_{C_3}	P_{C_1}	P_{C_2}	P_{C_3}
Time (h)	90	44	24	168	192	192	192	192	192	216	240	240

The results of all experimental methods are in good agreement with each other. From these results, this is reasonable that coating surface properties and microstructure rather than corrosion resistance are important for having a good overall protection after applying lacquers and this result is the most important finding of this research. Until now the role of lacquers was to preserve the colour of a corrosion resistant patinas. This finding paves the way for generating many sets of colours by changing the morphology and amount of porosity of the patina which may not be corrosion resistant in itself but may have a very good corrosion resistance after applying lacquers.

The corrosion protection of metallic substrates by organic coating is a complex process and depends mainly[14–17] on the 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. This investigation indicates that even though the C_3 coating before applying lacquers has lower protection but after applying lacquers shows high protection due to morphology of coating. It was shown that surface modification is an important factor which determines electrochemical behaviour. The results of all applied experimental methods show good agreement with each other. According to this finding, it is possible to produce patinas with different porosity and morphology by controlling different parameters (pH, concentration of different species and immersion time) and as a result, create a completely new set of colours and fine tuned them according to the taste of customers or artists.

The equivalent circuit after applying lacquer is shown in Fig. 8. That 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 C_1 coating and C_l and R_l are the double layer of capacitance and charge transfer resistance of lacquer[18].

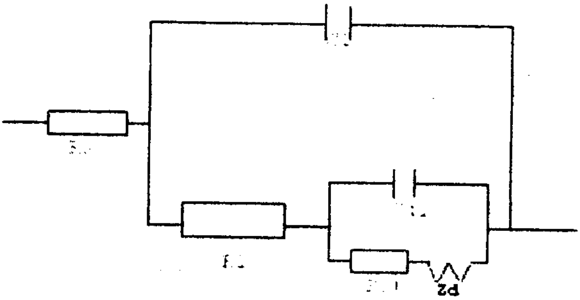


Fig. 8. The equivalent circuit for coating after applying lacquer

Conclusions

1. C_1, C_2 and C_3 coatings which are formed on copper protect the copper surface from corrosion to certain limits. C_3, which is not protecting before applying lacquer and has porosity in its patina, resists corrosion even better than C_2, after applying lacquer.
2. The patina morphology rather than its corrosion resistance before applying lacquer is an important factor for having a good protection after applying lacquers.
3. Applying air drying lacquers (O, T, P) and stoving lacquers (A, M) on coatings increases 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 lacquers of air-drying group are very good and approximately the same. Thus the application of air-drying lacquers to artefacts and decorative industries is recommended due to its low cost and easier application.

5. The most important result is that in natural patina the surface colours are limited and the time for creating patina is very long, but in artificial patina it is being reversed (time is short and the colours are unlimited) which leads to innovation in art and industry. Unlimited colours may be produced not only by creating corrosion resistant patinas but also by producing patinas with different amounts of porosity which may not be protecting but will resist corrosion even better than protecting patinas after applying lacquers.
6. With controlling the amount of porosity, the colour can be fine tuned to the taste of customers.

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