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Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

PROTECTION OF ARTISTIC BRONZES BY ARTIFICIAL PATINA AND WAX

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ABSTRACT. The artificial patina is important to the restoration of historical objects or creation of bronze artworks. The main objective of this paper was to study the protective effect of one type of deliberately produced artificial patina on a bronze surface, in presence / absence of wax. Corrosion tests were carried out in a 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5) solution simulating an acid rain. The protective effect of artificial patina with / without wax was comparatively investigated by electrochemical and non - electrochemical methods. The microscopic structure study of the bronze surface with / without artificial patina was conducted through optical and electronic microscopy. The chemical composition and the morphology of the corrosion products layer, formed on the bronze / artificial patina surface were determined by SEM - EDX.

Key words: *bronze, corrosion, artificial patina, polarization curve, wax*

INTRODUCTION

On a bronze sculpture, the patina has the capacity to enrich its aesthetic aspect. Patination art can be defined as a coloring of metal surface by oxidation or by prolonged exposure to the surrounding atmosphere [1 - 4]. That can be the definition of both categories of patina existing in the case of bronze: *natural* and *artificial*.

The natural patina can be observed especially in museums, or on outdoor sculptures and its color is green, yellow or black. As stated by Mattsson [5], "*the atmospheric exposure of copper has generally no detrimental effect, but rather a beneficial one; it develops an interesting and pleasing play of colours on the metal surface excellent for architectural purposes*".

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Because the formation of natural patina requires a long period of time, it is possible to create artificial patina. Production of artificial patina is an important step in the restoration of historical objects and creation of art works of bronze. Artificial patina is obtained by specific treatments (chemical or electrochemical) applied to the surface [1, 6 - 8]. There is a variety of chemicals that can confer a wide palette of colors to the resulting patina [1, 6 - 9]. For additional protection, after application of artificial patina, the surfaces are polished with wax [7, 9]. Nevertheless, the protective properties and the corrosion resistance of different types of artificial patina are insufficiently studied until now, and there are only few papers on this topic [4, 7 - 11].

In this context, the main objective of this paper is to study the protective effect of a green artificial patina, chemically produced on bronze by using sodium thiosulfate and ferric nitrate, in the absence or in the presence of wax. The corrosion behavior of the bronze samples was investigated under conditions that simulated acid rain (0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$, pH = 5 solution).

RESULTS AND DISCUSSION

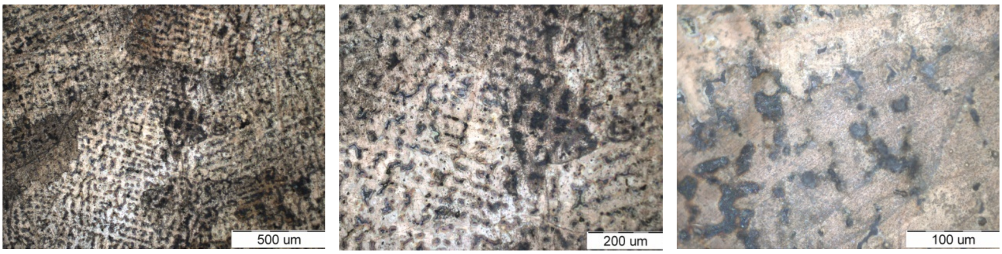
Microscopic structure

To conduct the studies, a contemporary bronze whose chemical composition, displayed in Table 1, is close to the bronze used by sculptors in the early 20th century [12] was selected.

Table 1. The chemical composition of the investigated bronze

Alloy	Cu [%]	Sn [%]	Impurities, [%] max								
			Zn	Pb	Sb	Fe	Al	S	As	Mn	Ni
CuSn8	rest	7-9	0.8	1.0	0.1	0.2	0.02	0.1	0.15	0.2	1.0

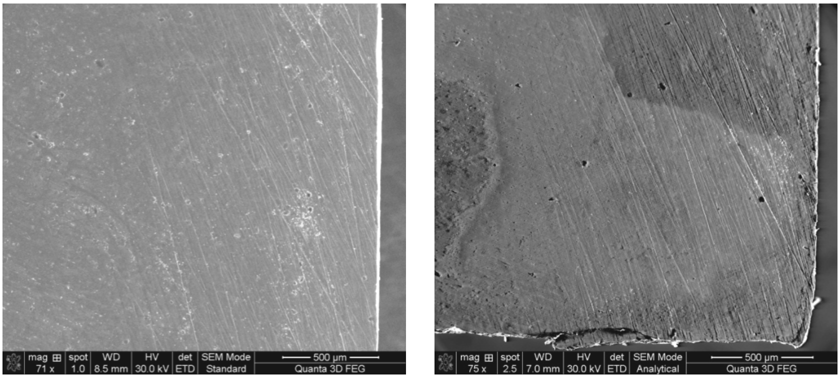
Figure 1 presents the microscopic structures of bare bronze electrodes, magnified at x100, x200, x500, which were subsequently subjected to accelerated corrosion in an environment that simulated an acid rain.



a) b) c)

Figure 1. Microscopic structure of bronze used for electrochemical studies: a) x100; b) x200; c) x500

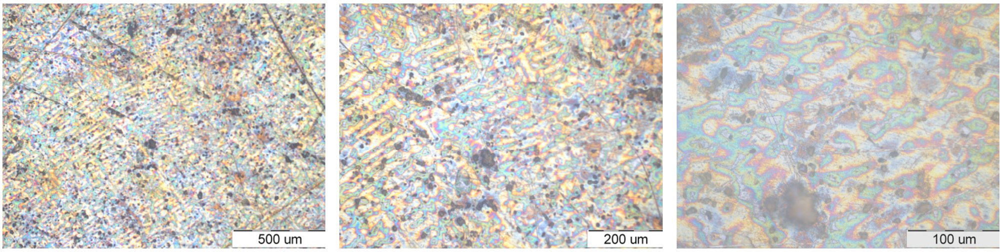
As it can be observed, the images illustrate the dendritic segregation of the α solid solution and interdendritic segregations of eutectoid α + δ in small quantities. Additionally, the images obtained by scanning electron microscopy (Figure 2) show that the cross-sectional appearance of the bronze samples is homogeneous, without stratifications, slag inclusions or foreign material.



a) b)

Figure 2. Images SEM, for the bronze used in the present work: a) x71, b) x75

The optical micrograph images of the artificially patinated bronze (Figure 3) show a discontinuous layer of corrosion products (artificial patina) reproducing the dendritic microstructure of the substrate [13].



a) b) c)

Figure 3. Microscopic structure of bronze used for electrochemical studies covered with artificial patina: a) x100; b) x200; c) x500

Morphological characterization of the corrosion products by SEM - EDX

In order to determine the morphology and the chemical composition of the patina layer formed on the bronze surface, SEM - EDX analysis was performed at different points of the electrode's surface and some results are presented in Figure 4 and Table 2.

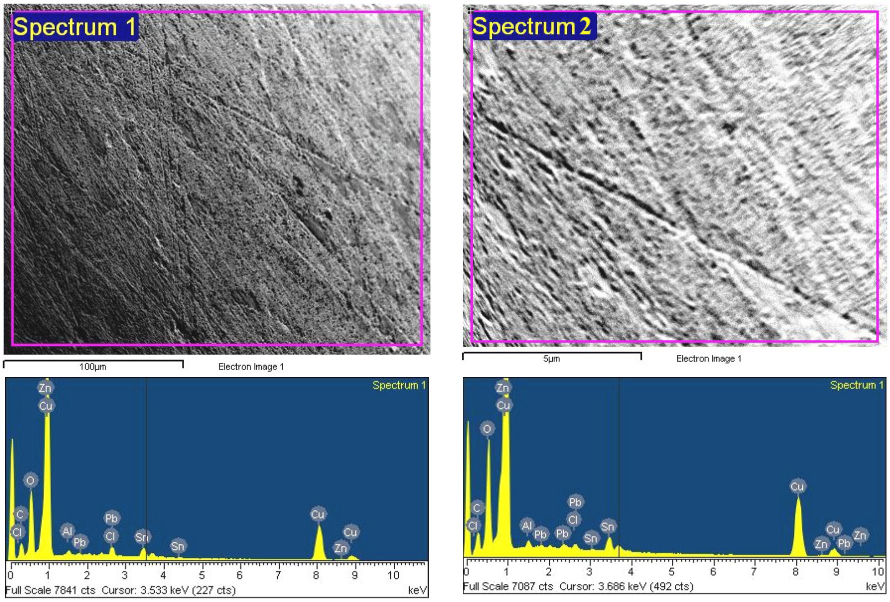


Figure 4. SEM/EDX results obtained on surface of bare bronze after corrosion tests

As can be seen from Table 2, the distribution of the chemical elements is relatively homogenous. The EDX analysis in different points indicated the presence of copper, oxygen, carbon, zinc and tin, whereas aluminum and lead were present as minor elements.

Table 2. Elemental composition [%] of the corrosion products formed at different points of the bronze electrodes, determined by EDX analysis

		C [%]	**O** [%]	**Al** [%]	**Zn** [%]	**Pb** [%]	**Fe** **[%]**	**Sb** **[%]**	**Sn** [%]	**Cu** [%]
Bare bronze		9.42	15.27	0.51	4.24	0.97	-	-	4.02	65.57
		7.82	15.09	0.60	3.79	0.90	-	-	3.71	68.09
Bronze covered with patina	surface	32.46	17.88	4.61	2.27	1.32	2.91	-	2.15	36.40
		30.08	9.35	0.82	3.19	1.11	1.22	-	2.82	51.41
	cross section	7.47	1.76	-	3.82	-	-	-	8.04	78.91
		11.78	1.79	0.33	2.44	1.05	0.85	0.91	11.84	69.01

The presence of zinc in the corrosion products layer in higher concentration than in the bronze substrate could be the sign of dezincification, which is a form of selective corrosion, where one of the components of the alloy is removed or leached out. Previously reported experiments showed that a high content of Sn protects the alloy from Zn loss (dezincification) [14]. On the other hand, the copper content in the corrosion products layer is the result of copper selective dissolution from the alloy (decuprification) [15]. In general, zinc dissolves preferentially, but the zinc / copper ratio is not constant during the dissolution process. Thus, at the beginning, copper and zinc display an analogous trend of dissolution, but afterwards copper remains nearly constant with increasing exposure time [16]. This could be probably due to the set-in of equilibrium between the copper dissolving in the solution and the metal precipitating as corrosion product on the surface.

The presence of C in the corrosion products layer can be explained by the fact that this element enters in the composition of the electrolyte used in the electrochemical tests. The higher Al content than that identified in the composition of the alloy can be explained by the use of aluminum oxide (Al_2O_3) for the samples polishing. It can be also noticed the presence of oxygen in the analyzed corrosion products layer, presuming the formation of cooper oxides (cuprite, Cu_2O) on the bronze surface [7].

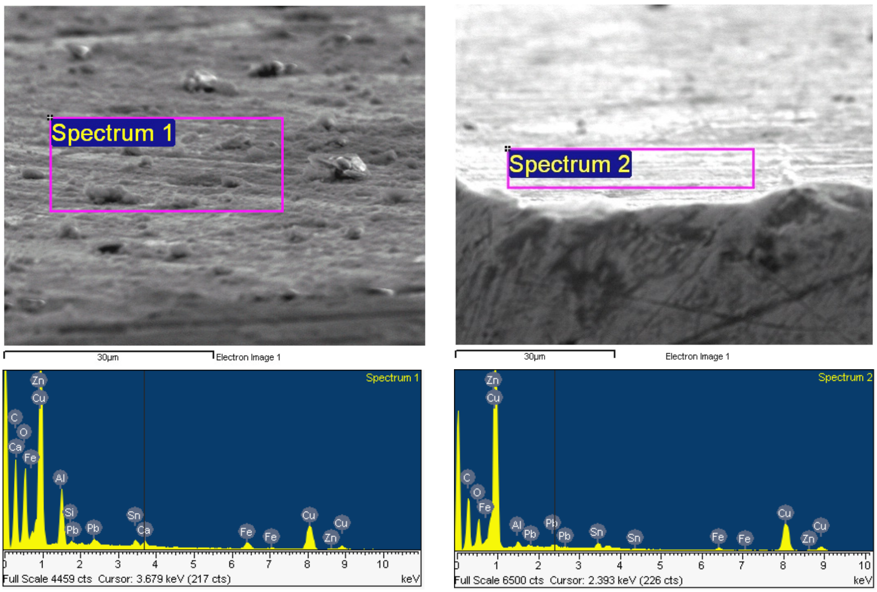


Figure 5. SEM/EDX results obtained on surface of bronze electrode covered with green artificial patina, after corrosion tests

In order to determine the morphology and the chemical composition of the patina layer formed on the surface of bronze covered with green artificial patina, SEM-EDX analysis was performed at different points of the electrode's surface and some results are presented in Figure 5 and Table 2.

In this case the EDX analysis at different points indicated the presence of copper, oxygen, carbon, zinc and tin whereas iron, aluminum and lead were present as minor elements.

The patina was analyzed also in cross-section (Figure 5 and Table 2).

Analyzing the SEM images from Figure 5 it can be noticed that the original surface is well preserved and no porosities are observed at the alloy / patina interface. As can be seen from Table 2, the EDX analysis at two different points on cross-section of bronze electrode covered with green artificial patina, indicated the presence of oxygen, in smaller quantities than on its surface (1.76 – 1.79 %). This can presume an internal oxidation, possibly with formation of tin species, which stabilize the patina layer [17]. As it can be observed, the elemental composition of the patina is relatively the same at the surface and in depth (cross-section) of the layer covering the bronze surface. Nevertheless, the Cu and the Sn content is higher in the depth of the patina layer, due to the proximity of the bronze substrate.

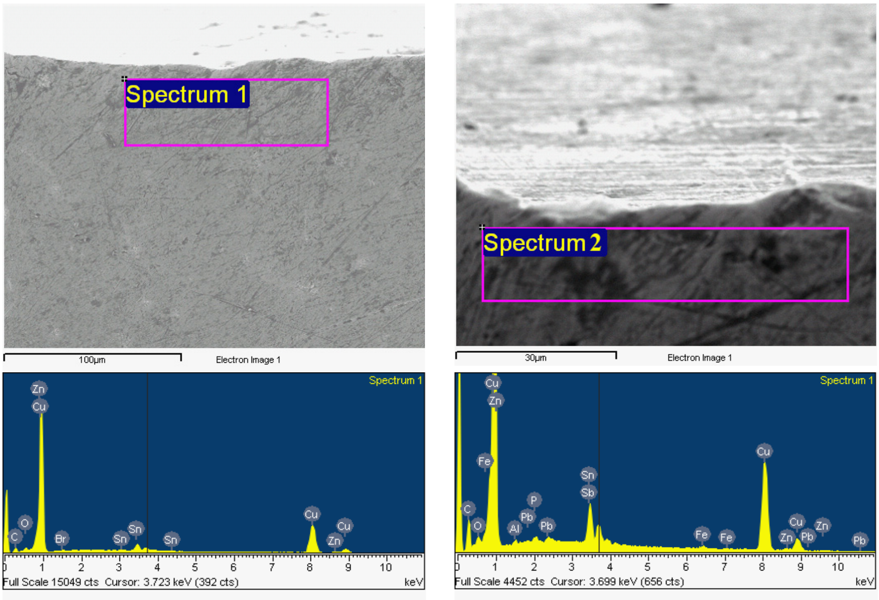


Figure. 5. SEM/EDX results obtained on cross-section of bronze electrode covered with green artificial patina.

Polarization measurements

In order to characterize the protective effect of the green patina, electrochemical corrosion measurements were carried out.

The experiments started with measuring the open circuit potential (OCP) of the bare bronze and of electrodes covered with green artificial patina, in the absence or in the presence of wax, during 3600 s. The OCP for all studied electrodes increased in the first minutes of immersion in the corrosive solution, reaching a stationary value after approx. 25 minutes. These values were 51 mV / SCE for bare bronze, 15 mV / SCE for bronze covered with green artificial patina and 41 mV / SCE for electrodes covered with green artificial patina polished with wax, respectively. This behavior can be attributed to the chemisorption of oxygen on the surface of the dissolved bronze, along with the formation of surface oxide layers, hydrosulphate and / or hydroxycarbonate [18].

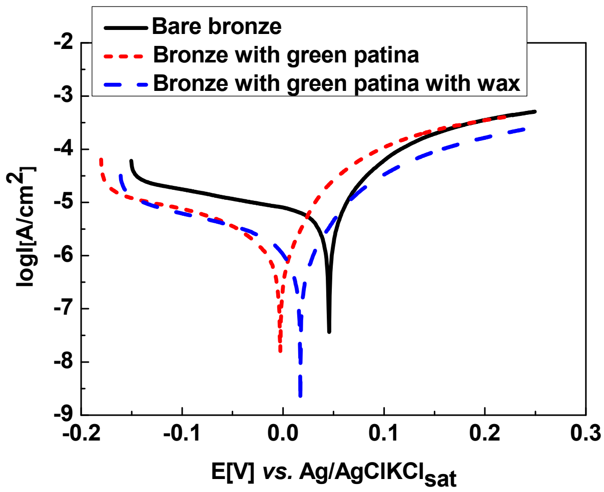


Figure 6. The polarization curves (± 200 mV *vs.* OCP) for the studied electrodes immersed in 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5); scan rate, 10 mV / min.

To determine the kinetic parameters of the corrosion process, polarization curves were recorded in the potential range of ± 200 mV *vs.* OCP (Figure 6). The Tafel interpretation of the polarization curves led to the results presented in Table 3.

Table 3. Corrosion process parameters for the examined samples

Electrode	E_{corr} [mV *vs* SCE]	i_{corr} [μA/cm^2]	β_a [mV]	$-\beta_c$ [mV]	R_p [kΩcm^2]
Bare bronze	62	0.71	44	162	2.98
Bronze with green patina	-3	0.68	33	73	4.48
Bronze with green patina and wax	17	0.45	56	35	5.58

β_a and β_c are the Tafel coefficients [mV]

The analysis of the data from Table 3 reveals that the highest corrosion resistance is exhibited by the electrode covered with green artificial patina in presence of wax (R_p=5.58 [kΩcm^2], i_{corr}=0.45 [μA/cm^2]), followed by the bronze with green patina.

The corrosion current density calculated from Tafel representation and the polarization resistance was used to evaluate the efficiency of wax used for the protection of bronze. The protection efficiencies (PE) conferred by green artificial patina in the absence or in the presence of wax were determined using the equation 1.

$$PE[\%] = \frac{R_{p\ patina/wax} - R_{p\ without.patina/wax}}{R_{p\ patina/wax}} x100 \quad (1)$$

The best results were obtained, as expected, in the case of bronze covered with patina in the presence of wax (approximately 50%).

CONCLUSIONS

The corrosion behavior of an artistic bronze was investigated in the presence of chemically formed patina and wax.

Based on the SEM / EDX analysis of bronze surface it can be concluded that the green patina deliberately formed on bronze has a moderate protective effect.

The tests carried out in an environment that simulated acid rain on bronze showed that the best protection efficiency was exerted by green patina with wax (approximately 50 %).

EXPERIMENTAL

The working electrodes made of bronze CuSn8, cylindrical shaped, were placed in a PVC tube, while the sealing was assured with epoxy resin. In this way, the surface of the electrode exposed to the solution was disk - shaped, with a surface S = 2.00 cm^2. For electrical contact a metal rod was attached (Figure 7).

Figure 7. The electrodes used during the experiments

For the microscopic study, the electrodes were polished on the sample polishing machine with alumina paste, after which the surface was washed with ammoniacal cupric chloride. The study of the surface was conducted through optical microscopy (OLIMPUS GS 51) and electronic microscopy (electron microscope FEI Quanta 3D)

SEM studies were performed with a Scanning Jeol JEM5510LV (Japan) coupled with Oxford Instruments EDX Analysis System Inca 300 (UK) at 15kV and spot size 39 µm.

The electrochemical corrosion measurements were performed on a PC – controlled electrochemical analyzer AUTOLAB - PGSTAT 10 (Eco Chemie BV, Utrecht, The Netherlands) using a three electrodes cell containing a working electrode (bronze), an Ag/AgCl electrode as reference electrode and a platinum counter electrode. Anodic and cathodic polarization curves were recorded in a potential range of ± 20 mV and of ± 200 mV *vs.* the value of the open circuit potential, with a scan rate of 10 mV / min, after 1 hour immersion in corrosive solution.

The electrolyte solution for corrosion measurements contained 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5).

Artificial patina

Green artificial patina was prepared on the polished bronze surface in several steps, using the solutions mentioned in Table 3.

The stages in the patination process were: polishing the surface; maintaining in solution (T, t) until the patina layer is formed; neutralization with distilled water; drying with ethyl alcohol; applying of a protective solution containing wax (1 part) and anticorrosive oil (3 parts).

Table 3. Substances used to create artificial patina

Color	Chemical composition of the solution	Chemical formula	Quantity [g/L]	Duration of imersion / temperature	The working electrode
Green patina	Sodium thiosulfate	$Na_2S_2O_3$	45	3 - 5 minutes / 70 ºC	
	Ferric nitrate	$Fe(NO_3)_3$	78		

REFERENCES

1. P. Kipper, Patina for Silicon Bronze, Regal Printing, Hong Kong, **2003**.
2. B. Rosales, R. Vera, G. Moriena, *Corrosion Science*, **1999**, *41*, 625.
3. S. Varvara, L.M. Muresan, K. Rahmouni, H. Takenouti, *Corrosion Science*, **2008**, *50*, 2596.
4. D. De la Fuente, J. Simancas, M. Morcillo, *Corrosion Science*, **2008**, *50*, 268.
5. E. Mattsson, R. Holm, ASTM STP 435, United States, **1968**, 197.
6. I.Z. Balta, S. Pederzoli, E. Iacob, M. Bersani, *Applied Surface Science*, **2009**, *255*, 6378.
7. H. Otmačič-Ćurković, T. Kosec, K. Marušić, A. Legat, *Electrochimica Acta*, **2012**, *83*, 28.
8. K. Marušić, H. Otmačić-Ćurković, Š. Horvat-Kurbegović, H. Takenouti, E. Stupnišek-Lisac, *Electrochimica Acta,* **2009**, *52*, 7106.
9. T. Kosec, H. Otmačič-Ćurković, A. Legat, *Electrochimica Acta*, **2010**, *56*, 722.
10. T. Kosec, A. Legat, I. Milosev, *Progress in Organic Coating*, **2010**, *69*, 199.
11. J.D. Chelaru, L.M. Mureşan, V.F. Soporan, O. Nemeş, T. Kolozsi, *International Journal of Conservation Science*, **2011**, *2*, 109.
12. M.L. Young., S. Schnepp, F. Casadio, A. Lins, M. Meighan, J.B. Lambert, D.C. Dunand, *Anal Bioanal Chem*, **2009**, *395*, 172.
13. L. Guadagnini, C. Chiavari, C. Martini, E. Bernardi, L. Morselli, D. Tonelli, *Electrochimica Acta,* **2011**, *56*, 6598.
14. L. Campanela, O. Colacicchi Alessandri, M. Ferretti, S.H. Plattner, *Corrosion science*, **2009**, *51*, 2183.
15. L. Robbiola, J.M. Blengino, C. Fiaud, *Corrosion Science*, **1998**, *40*, 2083.
16. E. Bernardi, C. Chiavari, C. Martini, L. Morselli, *Applied physics a: materials science & processing*, **2008**, *92*, 83.
17. L. Robbiola, R. Portier, *Journal of Cultural Heritage*, **2006**, *7*, 1.
18. N. Souissi, L. Bousselmi, S. Khosrof, E. Triki, *Material and Corrsion*, **2003**, *54*, 318.