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INVESTIGATION OF CORROSION PROTECTION BY CHEMICALLY APPLIED PATINA ON ARTISTIC BRONZES

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ABSTRACT

Increase of pollution in recent years, requires monitoring of the corrosion behavior of artistic bronzes coated with syntetic patina, in urban atmosphere.

This present work aims to investigate the corrosion rezistance of various artificial patina currently used in bronze sculpture. Electrochemical and microscopic methods were used to investigate the protective effect of several chemically produced patinas on artistic bronze.

KEYWORDS: bronze, corrosion, patina, polarization curves

1. Introduction

On a bronze sculpture, the color of the surface has the ability to enrich the aesthetic.

The art of patination can be defined as a slip coloring metal surface oxidation, caused by prolonged exposure in the surrounding atmosphere. This definition is actually describing the two patina categories used in the case of bronzes: natural and artificial.

Natural patina is the result of compounds formation after corrosive chemical reactions that occur on the surface of bronze. There is no way to achieve a true natural patina except with time itself. This is very important to natural patina but very impossible for the sculptor, because it requires years to accomplish an end result. Artificial patinas, on the other hand, have the advantage not only of creating similar results of natural patina, they also have the ability to incorporate a wider range of color hue and depth not found in natural patinas, and this is accomplished almost immediately [1].

Making a special color on the surface of bronze art objects requires a mastery of the artist. This work is almost unknown until recently, the secrets being kept by each artist.

The importance of producing artificial patinas on bronze comes from the well known ability of this alloy to react against atmospheric agents by forming different coloured corrosion products of pleasant aspect, which protect the bronze objects from further corrosion [2].

Many factors influence the initial development of the patina, some of them being active throughout the life of a work of art.

The final quality of the patina depends on the alloy composition and on environmental conditions it develops in. From a chemical point of view the patina layer can be described as a hydrated copper oxide stabilized on a copper oxide substrate [2, 7 - 9]. However, the poluants present in urban atmosphere gives birth to various corrosion products on bronze surface. The most damaging are chlorides (especially sodium chloride, which encourages the development of copper chloride), sulfates and oxides, particularly sulfur dioxide [9 - 13].

Increase of pollution in recent years requires monitoring of the patination process that was formerly left to the action of nature.

Artificially produced patina gives to the surface protection against corrosion and aesthetic value and can be formed on bronze surfaces by using chemical reagents or by electrochemical methods [14, 15]. For this reason, finding new artificial patinas to protect works of art cast in bronze is a current concern.

In this context, the main objective of this paper is to study the protective effect of various artificial patinas deliberately produced by sculptors on bronze. The study was conducted under conditions that simulate acid rain.

2. Experimental data

The bronze used in the experiments was chosen to be similar to the bronze monument of Matthias Corvinus in Cluj Napoca which dates back to 1902. The statues of this monument were made of bronze on a metal frame and according to the chemical analysis, the composition of the alloy varies in different parts of the sculptural group; there are variations in the percentage of tin, zinc, lead, but the content of copper exceeds 90% of the alloy in most cases (Table 1).

Table 1. *The chemical composition of the alloy used in the casting of the King Matthias the Ist sculptural group*

	Sn	**Pb**	**Zn**	**Cu**
	[%]			
Sample 1	7.17	0.08	0.36	rest
Sample 2	8.00	0.52	1.30	rest
Sample 3	7.72	0.41	0.21	rest

Consequently the alloy used in electrochemical studies, according to current standards, was chosen CuSn8, whose chemical composition is displayed in Table 2.

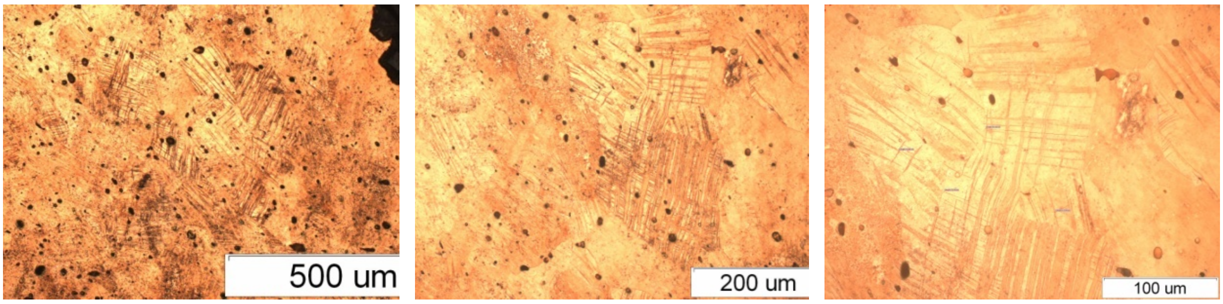
Table 2. *The chemical composition of the used alloy*

Alloy	**Cu**	**Sn**	**Impurities,** [%] max										
	[%]		Zn	Pb	Sb	Fe	Al	S	Bi	Mg	As	Mn	Ni
CuSn8	rest	7-9	0.8	1.0	0.1	0.2	0.02	0.1	0.01	0.01	0.15	0.2	1.0

For microscopic study, the electrodes were polished on the 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).

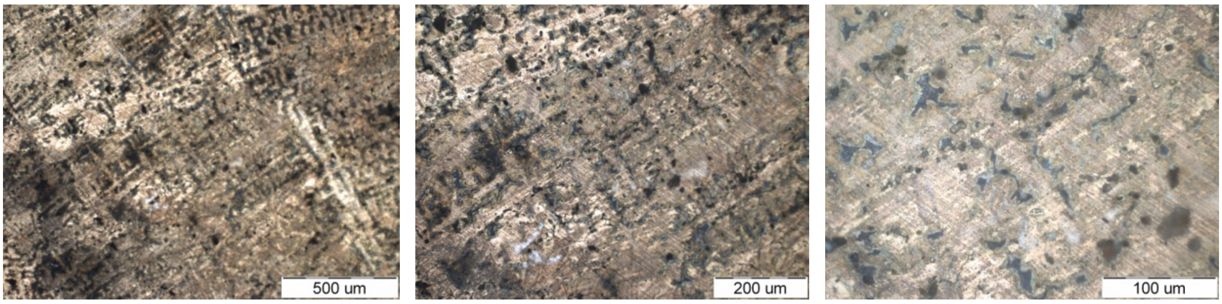
The metallographic analysis revealed the existence of a homogeneous structure, the crystals having polyhedral appearance with macles (Fig 1).

Crystalline grain size is between 50-200 µm, which gives the alloy a high resistance to corrosion [16].



a) b) c)

Fig. 1. *Microscopic structure of alloy use in the casting of King Matthias I sculptural group: a – x100; b – x200; c – x500*



a) b) c)

Fig. 2. *Microscopic structure of bronze used for electrochemical studies: a – x100; b – x200; c – x500*

Figure 2 presents the microscopic structures of electrodes, magnified at x100, x200, x500, which were subjected to accelerated corrosion in an environment that simulated acid rain.

The images in Figure 2 display the dendritic segregation of the α solid solution and interdendritic segregations of eutectoid α + δ in small quantities. The eutectoid α + δ is formed in a Cu - Sn alloy and results from the decomposition of phase γ at a temperature of 520 ° C (see the equilibrium diagram Cu - Sn). According to the picture displayed in the Metallurgic Atlas, the structure is the specific one for a cast bronze. 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, a saturated calomel electrode (ECS) as reference electrode and a platinum counter electrode.

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 = 1.76cm^2. For electrical contact a metal rod was attached (Figure 3).

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

***Fig. 3.** The electrodes used during the experiments*

The study was conducted on three electrodes covered with an artificial patina: electrode (1) was treated with flowers of sulfur; electrode (2) was treated with a solution containing copper sulfate and potassium permanganate and electrode (3), with sodium thiosulfate and ferric nitrate.

3. Results and discussion

The experiments started with measuring the potential of the working electrode in an open circuit for a period of 3600s, the records being presented in Figure 4.

As shown in figure 4, for all studied electrodes, in the first minutes of immersion in the corrosive solution, the potential in open circuit evolves towards more positive values, reaching a stationary value after approx. 35 minutes. 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, hydroxisulfate and/or hydroxycarbonate [19].

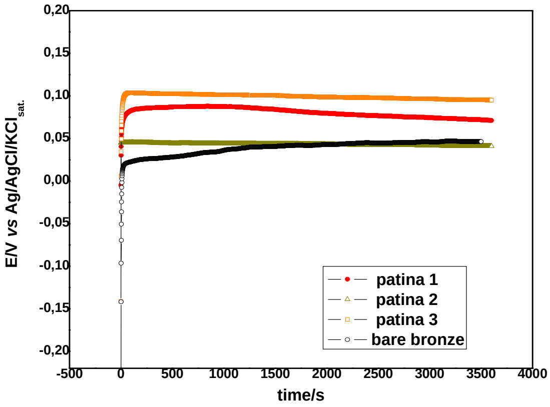


***Fig. 4**. Time variations of the open circuit potential of the bronze electrodes immersed in 0.2g/L Na_2SO_4 + 0.2g/L $NaHCO_3$ (pH = 5)*

It can be noticed that the open circuit potentials of the coated electrodes 1 and 3 are more positive than that of bare bronze, suggesting an interaction of the patina with the anodic process (metal dissolution), while the open circuit potential of electrode 2 is the same with that of bare bronze suggesting a weak protection effect of the corresponding patina.

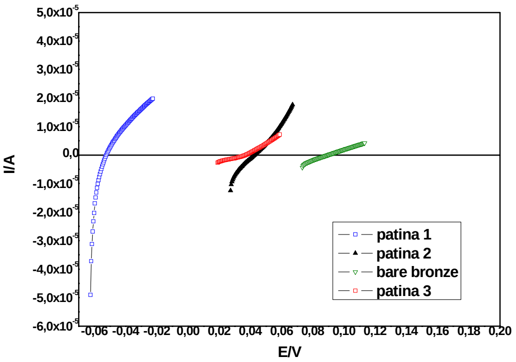


***Fig. 5.** Linear polarization curves (± 20 mV vs. ocp) for the studied electrodes immersed in 0.2g/ L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH = 5)*

To determine the polarization resistance of the electrodes, linear polarization curves were recorded, in the potential domain of ± 20 mV around the value of the open circuit potential (ocp) (Figure 5). The polarization resistance values for each electrode, calculated as the inverse of the slope of each curve, are shown in Table 3.

Tabel 3. *The value of polarization resistance (R_p = 1/p, p is the slope of the curve)*

Electrode	**Slope** (p)	**R_p=1/p** [Ω]
Patina 1	7.25×10^{-4}	1380
Patina 2	2.25×10^{-4}	4444
Patina 3	1.87×10^{-4}	5348
Bare bronze	3.24×10^{-4}	2060

As can be seen from Table 3, the highest value for R_p was noticed in the case of the electrode (3), treated with a solution containing sodium thiosulfate and ferric nitrate.

To determine the kinetic parameters of the corrosion process, polarization curves were recorded in the potential range of ± 200mV *vs.* ocp (Figure 6).

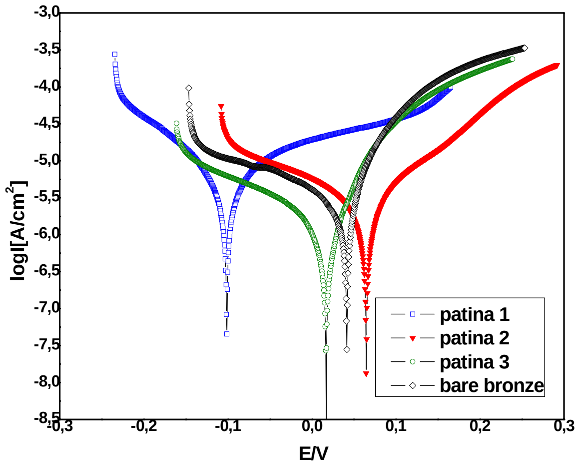


Fig. 6. *The polarization curves (± 200 mV vs. ocp) for the studied electrodes immersed in 0.2g/L Na_2SO_4 + 0.2g/L $NaHCO_3$ (pH = 5)*

The kinetic parameters of the corrosion process were determined from the Tafel interpretation of the polarization curves and the results are presented in Table 4.

Table 4. *Corrosion process parameters for the examined samples*

Electrode	**Ocp**	**E_{cor}**	**i_{cor}**	**β_a**	**β_c**
	[mV *vs* SCE]		[µA/cm^2]	[mV]	
Patina 1	-48	-101	3.25	91	77
Patina 2(brown)	95	65	1.87	85	134
Patina 3(green)	41	17	1.33	55	164
Bare bronze	51	46	5.36	46	284

β_a and β_c are the Tafel coefficients

As shown in Table 4, all the patinas determine a decrease of corrosion current density of the bronze sample. Among them the coated electrode 1 is the less resistant to corrosion and it presents accelerated corrosion in comparison with the other two synthetic patinas. Treatment 3 seems to be the best among the treatments tested; however, the amelioration of corrosion rate is not significant. Moreover, no definite trend was observed in the shift of β_a and β_c values in the case of different patinas. A comparison between the corrosion current density and of the polarization resistance values of investigated electrodes is shown in Figure 7. The electrodes surfaces after the accelerated corrosion tests are presented in Figure 8.

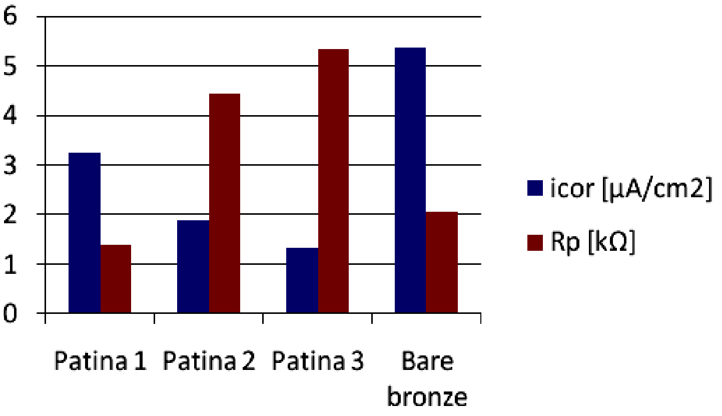


Fig. 7. *Variation of corrosion current density and of polarization resistance for the investigated electrodes*

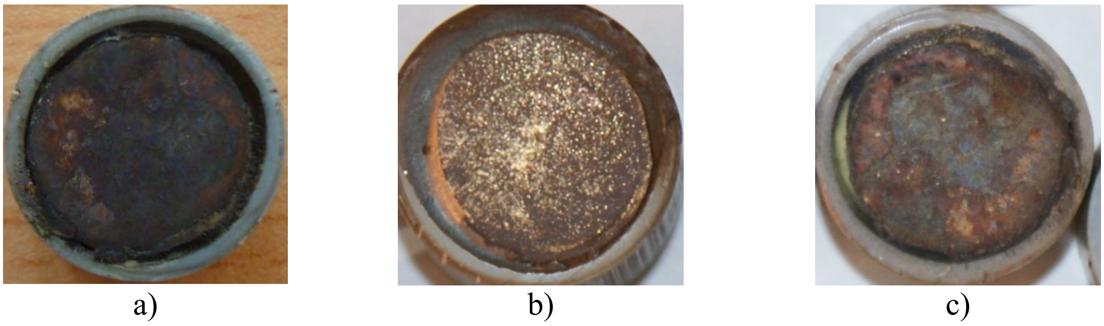


Fig. 8*. The electrode surfaces after the corrosion test performed in a solution containing 0.2g/L Na_2SO_4 + 0.2g/L $NaHCO_3$ (pH = 5), a) patina 1, b) patina 2, c) patina 3*

4. Conclusions

In this paper we compare the corrosion resistance of the patina obtained by using traditional flowers of sulfur with new synthetic, chemically obtained patinas on bronze. Corrosion tests were conducted in an environment that simulates acid rain.

Bronze coated with new synthetic patinas have a higher corrosion resistance than the traditional one prepared with sulfur.

In future we intend to investigate some new recipes and new methods of corrosion protection of artistic bronzes.

Acknowledgments

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References

[1]. **P. Kipper -** *Patina for Silicon Bronze*, Regal Printing, Hong Kong, 2003.

[2]. **B. Rosales, R. Vera, G. Moriena -** *Evaluation of the protective properties of natural and artificial patinas on copper. Part I. Patinas formed by immersion*, Corrosion Science, vol. 41, 1999, pg. 625-651

[3]. **R. Picciochi**, **A.C. Ramos s.a** - *Influence of the environment on the atmospheric corrosion of bronze*, Journal of Applied Electrochemistry, vol. 34, 2004, pg. 989-995.

[4]. **L. Robbiola**, **J.M. Blengino** - C. Fiaud, *Morphology and mechanisms of formation of natural patinas on archaeological Cu-Sn alloys*, Corrosion Science, vol. 40, 1998, pg. 2083 – 2111.

[5]. **L. Robbiola**, **R. Portier** - *A global approach to the authentication of ancient bronzes based on the characterization of the alloy – patina – environment system*, Journal of Cultural Heritage, vol. 7, 2006, pg. 1-12.

[6]. **K.P. FitzGerald**, **J. Nairn**, s.a. - *Atmospheric corrosion of cooper and the colour,structure and composition of natural patinas on copper*, Corrosion Science, Vol. 48, pg. 2480-2509, 2006

[7]. **F.J.R. De Oliveira**, **D.C.B. Lago**, s.a. - *Study of patina formation on bronze specimens*, Materials Chemistry and Physics,vol. 115, 2009, pg. 761–770.

[8]. **C. Chiavari**, **A. Colledan**, s.a. - *Corrosion evaluation of traditional and new bronzes for artistic castings*, Materials Chemistry and Physics, vol.95, 2006, pg. 252-259.

[9]. **G.M. Ingo**, **T. De Caro**, **Riccucci C.**, **Khosroff S.** - *Uncommon corrosion phenomena of archaeological bronze alloys*, Applied Physics A, Material Science & Processing, Vol. 83. 2006, pg. 581-588.

[10]. **A. Domenic-Carbo, M.T. Domenic-Carbo, I. Martinez-Lazaro** - *Electrochemical identification of corrosion products in archaeological artefacts. A case study*, Microchimica Acta, Vol.162, 2007, pg. 351-359.

[11]. **J.D. Chelaru, V.F. Soporan, O. Nemeş** - *Time analysis of King Matthias The I Sculptural Group*, International journal of conservation science, Vol.1, 2010, pg. 69-74.

[12]. **M.P. Casaletto, G.M. Ingo, M. Albini, A. Lapenna, I. Pierige, C. Riccucci, F. Faraldi** - *An integrated analytical characterization of corrosion products on ornamental objects from the necropolis of Colle Badetta-Tortoreto (Teramo, Italy)*, Applied physics a: materials science & processing, Vol 100, 2010, pg. 801-808.

[13]. **I. Sandu, A. Dima, I.-G. Sandu** - *Restauration and conservation of metal objects*, Corson Publishing House, Iaşi, 2002.

[14]. **I. Sandu** - *Deterioration and degradation of the cultural patrimony treasures. Supply of inorganic materials,* vol. I, „Alexandru Ioan Cuza” University Publishing House, Iaşi, 2008.

[15]. **L. Mureşan, S. Varvara**, **s.a**. - *Protection of bronze covered with patina by innoxiouus organic substances*, Electrochimica Acta, vol.52, 2007, pg. 7770-7779.

[16]. **V., Cândea, C. Popa**, *Iniţiere în ştiinţa metalelor,* Editura Vega, ISBN 973-951-70-3-0, Bucureşti, 1995

[17]. **A.Vlasa, S. Varvara, L. Mureşan** - *Electrochemical investigation of the influence of two thiadiazole derivatives on the patina of an artchaeological bronze artefact using a carbon paste electrode*, Studia Universitatis BABEŞ – BOLYAI, vol.2, 2007, pg. 63 -71.

[18]. **J.D. Chelaru, V.F. Soporan, O. Nemes, T. Koloszi, V. Duca** - *The influence of the enviromental factors on the King Matthias Sculptural Group*, „International Conference 16th Building Services, Mechanical and Building Industry Days”, 2010, pg. 265-272.

[19]. **N. Souissi, L. Bousselmi, s.a.** - *Electrochemical behavior of an archaeological bronze alloy in various aqueous media: New method for understanding artifacts preservation*, Material and Corrsion, vol. 54, 2003, pg. 318-325.

[20]. **T. Koloszi, A. Pasat, R. Moraru, O.M. Gui, J.D. Chelaru** - *Digital techniques in reinforcement and conservation of a large sculptural group. Case study: the sculptural group of Mathias I in Cluj Napoca, Romania, 5th International Conference on Interdisciplinarity in Education - ICIE'10*, Tallinn, 2010, Estonia.