

## Silver Artefacts Patination and Protection by Nano-alumina Pigmented Coatings

*In the framework of safeguarding movable cultural heritage artefacts, a study of silver alloys is undertaken to find a protective system that could be safely employed, following the ethics of conservation. For this purpose silver drawn sheet coupons were tarnished by different chemical methods to simulate the corrosion patina of aged artefacts. An extensive study of the produced corrosion layers was performed by X-ray diffractometry, scanning electron microscopy and surface analysis as well as optical microscopy. The nano-alumina pigmented acrylic polymer coatings were tested on the clean and artificially aged metal coupons. Electrochemical impedance spectroscopy was employed to check on the integrity of the protective coatings. The proposed method of protection, based on nano-alumina pigmented acrylic resin, seems to be quite sufficient to protect metal surface without compromising the aesthetic aspect of the metal/coating system and it is also reversible.*

### 1. INTRODUCTION

The archaeological and artistic value of objects of silver found in archaeological sites makes their preservation of primary importance. These objects undergo an atmospheric corrosion process leading to the formation of corrosion products termed patinas. The patina is formed spontaneously with a long time exposure to the environment surrounding these items. The structure and the composition of patina are specific to each object. Silver metal artefacts also tarnish readily in urban atmospheres due to sulphides [1,2]. Tarnishing is the formation of  $\text{Ag}_2\text{S}$  on the surface of silver when exposed to a wide range of sulphur containing environments and it is accelerated by humidity.

Synthetic or artificial patina layer can be obtained by appropriate surface treatment on bronze or silver alloys [3]. In that way a reproducible patina, simulating the corrosion patina of aged artefacts can be obtained at any moment within a reasonable time.

Many publications concerning patina are devoted to the chemical characterisation and to the crystallographic structure in relation either to the environment to which the metals have been exposed [4] or the consequence of the atmosphere, of soil [5] or marine corrosion [6]. Because of a substantial increase of pollutant concentration in urban

atmosphere, the protective patina formed during a long period of time appears not to be stable, and the patina formation or its dissolution (corrosion process) has been restarted in various sites. It is therefore important to find solutions, which protect metal objects covered by patina.

Polymer nanocomposites have great potential as a class of materials that show unique combinations of thermal and mechanical properties [7]. The aim of this work was to obtain a protective system that could be safely employed on silver objects following the ethics of conservation. The proposed method of protection, based on nano-alumina pigmented acrylic resin [8], seems to be quite promising to protect metal surface without compromising the aesthetic aspect of the metal/coating system.

### 2. EXPERIMENTAL

#### 2.1. Silver patination

Silver drawn sheet coupons (2cm x 5cm x 0.04 cm) with a composition Ag 92.5 % and Cu 7.5 % were tarnished by different chemical methods so as to produce corrosion layers similar to the ones produced on the metal artefacts either by saline environment, containing mainly AgCl or urban environment, containing  $\text{Ag}_2\text{S}$  [9]

*AgCl silver patina:* Silver coupons were immersed in the hot solution of  $\text{CuCl}_2$  50 g/l (50–60°C) for 20 min. The corrosion-patination layer developed gradually and the color changed to brownish purple. The samples were removed, washed in warm water and allowed to dry in air. An even

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corrosion layer consisting mainly of AgCl has been produced.

*Ag<sub>2</sub>S silver patina:* The silver samples were immersed in cold (RT) BaS 5 g/l solution for 24 hours, producing a slightly uneven dark brown Ag<sub>2</sub>S corrosion layer

## 2.2. Protective coatings

The applied coatings consist of an acrylic resin as the binder, the solvent and the pigment. Paraloid® B-72 100% acrylic resin (a copolymer of ethyl methacrylate and methyl acrylate by Rohm and Haas) was tested as a binder. The pigment added in the Paraloid coatings was  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanopowder (40-47nm). Toluene was used as the solvent. A 15% wt Paraloid®B-72 solution in toluene was brushed onto the metal surface, and after the solvent evaporation, a film formed with thickness 5 – 10  $\mu$ m. alumina nano-powder was added at 10% weight percent vs. Paraloid® B-72.

## 2.3. Electrochemical Impedance Spectroscopy

The characterization of the Paraloid-alumina system, in terms of the electrical properties of the film has been evaluated through impedance measurements. A three-electrode cell was used for the EIS measurements. The counter electrode was Pt foil and the reference electrode was saturated calomel electrode. The EIS was performed by a Gamry CMS300 computer controlled system with commercial software for the data analysis. Impedance spectra were recorded in the frequency range from

5000 to 0.06 Hz by applying a sinusoidal signal of 10mV amplitude at the open circuit potential,  $E_{oc}$ , as a function of the pigment load in the 0.1M NaCl solution.

## 3. RESULTS & DISCUSSION

### 3.1. Silver patina

*AgCl silver patina:* By immersing silver coupons in the hot CuCl<sub>2</sub> solution, a relatively even 3-3.5  $\mu$ m thick corrosion layer has been produced. Main corrosion products identified by XRD analysis are chloroargyrite, AgCl and probably nantokite, CuCl. Table 1 presents SEM images and XRD diffractograms of the AgCl aged silver coupons.

*Ag<sub>2</sub>S silver patina:* After immersion in the BaS solution, slightly uneven dark brown 2-6 $\mu$ m thick corrosion layer is created on the silver coupon surface. On the back scattered electron image (Tab. 2) three different areas can be noticed: white one of the almost clean metal, gray one of silver rich and black one of the copper rich corrosion products. The results of EDS analysis disclose that apart from Ag<sub>2</sub>S, on the sample surface the presence of CuS as well as Ag<sub>2</sub>O and/or Cu<sub>2</sub>O can not be excluded. In the Table 2 are presented SEM images and XRD diffractogram of the Ag<sub>2</sub>S aged silver coupons.

Table 1 - SEM and XRD analysis of the AgCl aged silver coupons

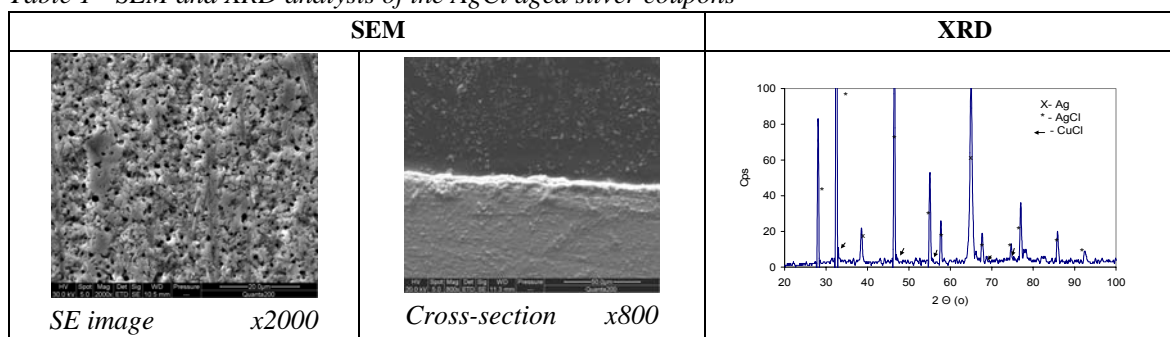
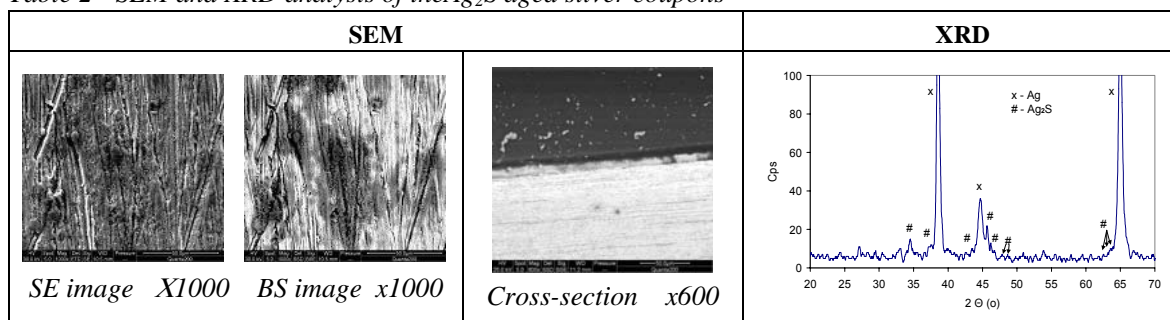


Table 2 - SEM and XRD analysis of the Ag<sub>2</sub>S aged silver coupons



### 3.2. Electrochemical Impedance Spectroscopy

The impedance measurement were performed in the 0.1M NaCl solution for plain and 10 % alumina pigmented Paraloid® B-72 protective coatings on the clean, Ag<sub>2</sub>S and AgCl aged silver surface. The samples were first left at the open circuit potential for one hour before starting the experiments. In order to interpret the data and to evaluate the role of the alumina pigment in the overall performance of the coating, the data were fitted to the equivalent electrical circuit presented in Fig. 1. The results are presented in Table 3.

The proposed equivalent circuit takes into account diffusion processes within pores in the paint film, which are modeled by the inclusion of a Warburg or pseudo impedance placed in series with

polarization resistance. Diffusion control is a very common process in electrochemistry and since the coating impedes the movement of chemical species, not unexpected with coatings. The chemical species associated with diffusion in coatings are oxygen and ions (from the electrolyte) diffusing toward the metal and corrosion products diffusing away from the metal. It can be noticed (Tab. 3) that the Warburg impedance of the 10 % nano-alumina pigmented Paraloid® B-72 is higher than that of the plain coatings and both of them exhibit superior values on the clean Ag than on the Ag<sub>2</sub>S and AgCl aged silver surface. Also, B-72-Al<sub>2</sub>O<sub>3</sub> coatings show significantly lower coating capacitance as well as double layer capacitance on the all substrates than plain Paraloid® B-72 coatings.

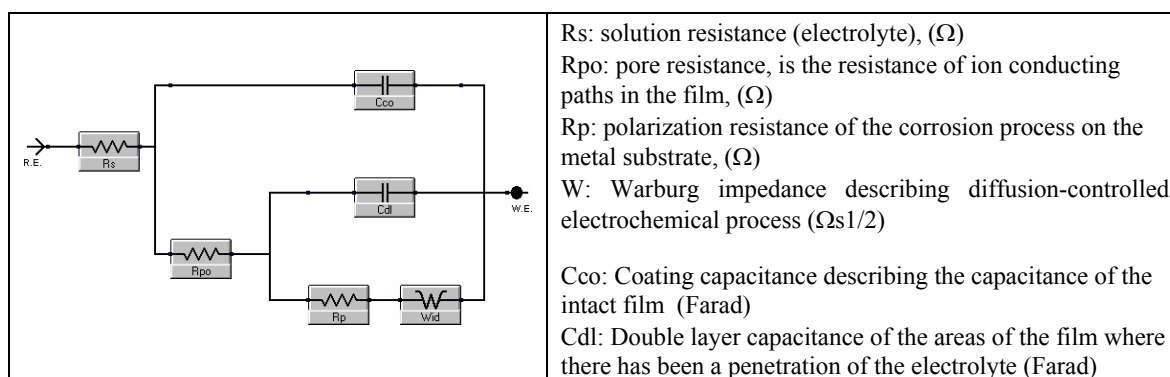


Figure 1 - Equivalent electrical circuits for modelling the behaviour of the tested coatings

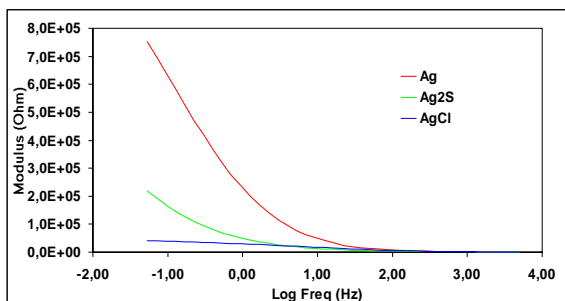
Table 3 - Analysis of the EIS spectra for the plain and 10% nano-alumina pigmented B-72 coating recorded after 1 hour immersion in the 0.1 M NaCl solution.

Substrate	R <sub>po</sub> , k $\Omega$	W, k $\Omega s^{1/2}$	R <sub>p</sub> , k $\Omega$	C <sub>co</sub> , $\mu F/cm^2$	C <sub>dl</sub> , $\mu F/cm^2$
Plain B72					
Clean Ag	10.47	286.2	158.4	0.133	0.181
Ag <sub>2</sub> S	3.74	88.8	12.6	0.0881	0.217
AgCl	3.40	5.80	3.7	0.862	0.859
10 % nano-alumina pigmented B72-Al <sub>2</sub> O <sub>3</sub>					
Clean Ag	8.17	811.6	125.1	0.0379	0.0491
Ag <sub>2</sub> S	3.74	202.2	375.0	0.0182	0.0369
AgCl	3.40	9.32	10.1	0.153	0.756

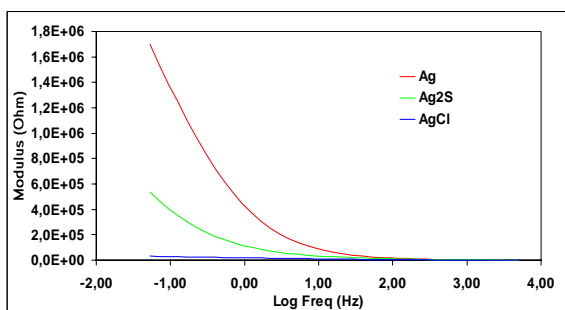
In Figure 2 are presented comparative EIS spectra (Modulus vs. frequency) for the plain and 10% alumina pigmented Paraloid® B-72 on the clean, Ag<sub>2</sub>S and AgCl aged silver surface after 1h immersion in the 0.1 M NaCl electrolyte. It is obvious from Figures 5a and 5b that both plain and alumina pigmented Paraloid® B-72 coatings exhibit greater overall impedance and consequently better protective properties on the clean Ag than on the Ag<sub>2</sub>S

and AgCl pre-aged silver surface. It should be also pointed out that the overall impedance of the B-72-Al<sub>2</sub>O<sub>3</sub> coatings, at low frequencies, on the clean and Ag<sub>2</sub>S aged silver surface is almost three-fold higher than of the plain coatings. The situation is different in the case of the AgCl aged silver coupons. Both B-72 and B-72-Al<sub>2</sub>O<sub>3</sub> display low impedance values. It seems that the AgCl corrosion layer on the silver surface significantly reduces

protection characteristics of the applied protective systems in the investigated corrosion conditions. Thus, it should be taken into account that when the corrosion layers contain chlorides, the appropriate cleaning process should be applied beforehand and followed by a complementary coating, which will properly isolate and seal the metal surface from any contact with air and moisture.



(a) Plain B72



(b) 10% nano-alumina pigmented B72- $\text{Al}_2\text{O}_3$

Figure 2 - Comparativa EIS spectra of Modulus vs. frequency, for the plain (a) and 10% alumina pigmented Paraloid® B-72 (b) on the clean Ag,  $\text{Ag}_2\text{S}$  and  $\text{AgCl}$  aged silver surface after 1h immersion in 0.1 M NaCl electrolyte (initial condition)

## CONCLUSIONS

A reference silver sheet alloy containing 7.5 wt.% Cu has been employed for carrying out different accelerated degradation tests to simulate as best as possible, the specific corrosion conditions of the archaeological silver objects. The use of SEM-EDS and XRD analytical techniques have provided good insight into the nature of the created surface corrosion products. The applied protective system is based on the barrier protection offered by  $\text{Al}_2\text{O}_3$  nanopowder pigmented paraloid coatings. Preliminary results on the characterization of the coatings efficacy, through electrochemical measurements, have shown that the  $\text{Al}_2\text{O}_3$  pigmented Paraloid B72 coatings exhibit enhanced protective

properties, in the investigated corrosion conditions, than the plain ones. The proposed protective treatment is open to argument as the polymeric material may, in the long run, turn out to be an unsatisfactory coating, largely because of water permeability. Incorporated water may lead to swelling that in its turn may disfigure the coating structure in a way favourable for the permeability of more moisture as well as other aggressive ions of the environment. Anyway, the treatment is completely reversible and therefore always accessible to more sophisticated methods of preservation.

## REFERENCES

- [1] C. Dervos, P. Vassiliou, 'Corrosion of silver electrical contacts: the substrate influence', Corrosion Reviews, Vol. 18 No 2-3, 2000, pp. 267-293.
- [2] P. Vassiliou, C.T. Dervos, 'Corrosion of Contacts in A saline environment', Anticorrosion Methods and Materials, Vol. 46, No.2, pp.85-94, 1999.
- [3] R. Hughes and Michel Row, *The Colouring, Bronzing and Patination of Metals*, Thames and Hudson, London, 1982.
- [4] L. Robbiola, J. M. Blengino, C. Fiaud, Corros. Sci. 40 (1996) 1641.
- [5] Kratschmer, L. Odneval, I. Wallinder, C. Leygraf, Corros. Sci. 44 (2002) 425
- [6] Climent-font, G. Demortier, C. Palacio, I. Montero, J. L. Ruvalcabil, D. Diaz, Nuclear Instruments and Methods in Physics Research, B134 (1998) 229
- [7] Th. Skoulikidis, P. Vassiliou, 'Corrosion and Conservation of the Building Materials on the Monuments; The Acropolis Case', Corrosion Reviews, 1999
- [8] B. J. Ash, D. F. Rogers, C. J. Wiegand, L. S. Schadler, R. W. Siegel, B. C. Benicewicz and T. Apple, "Mechanical Properties of  $\text{Al}_2\text{O}_3$ /Polymethyl-methacrylate nanocomposites", Polymer Composites, Vol. 23 (2002) No 6, pp. 1014-1025
- [9] Vassiliou, P. and Novakovic, J.: "Silver Metal Artefacts Protection By Nano-Alumina Pigmented Coatings", Proceedings of the 7<sup>th</sup> European Conference "SAUVEUR", Prague, Czech Republic, May, Vol.2 (2006) pp. 863-865