Laboratory and field tests on patinas and protective coating systems for outdoor bronze monuments

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Abstract (English)

Six protective coating systems, commonly used in conservation practice, have been tested both on polished bronze coupons and on selected areas of a bronze statue in similar exposure conditions. Patinas have been characterised both on outdoor exposure on the monument and as developed on the polished bronze coupons. Electrochemical Impedance Spectroscopy measurements, using a specially designed contact probe, have been conducted on coupons and in situ on the bronze statue. Data for the first two years of weathering in a marine environment are reported. The coating performance on the polished coupons and on the corroded bronze monument is discussed.

Keywords: EIS, bronze, in situ characterisation, coatings, patinas, Atmospheric Corrosion

1. Introduction

The conservation of outdoor bronze monuments is widely studied. Several publications have examined the complex interplay between the properties of sculptures and environmental parameters (Drayman-Weisser 1992, Graedel 1987, Strandberg 1998). The number and the range of all the parameters involved produces a very wide range of possible situations, and holistic understanding therefore remains elusive. Several studies for new protective coatings have been undertaken (Brostoff and de la Rie 1997, Pilz and Römich 1997), but typical requirements for cultural heritage objects (aesthetic appearance, reversibility, etc.) seems not to be easily satisfied, and no common accepted solutions have been established for the protection and maintenance treatment

Table 1. Coating systems and application methods, from Letardi and Cozzolino 2002.

	Commercial name	**Description**	**Application method**
[A]	Soter 201 LC	commercial product consisting of 20-24 wt% crystalline wax, BTA and synthetic organic polymer, dispersed in turpentine and ether	Three layers were applied cold with a paint-brush by 24/48 hours intervals. After each application was dried the surface was polished with a soft brush.
[B]	R21	22 w% microcrystalline wax dispersed in white spirit	Three layers applied as above but on the surface warmed with a hairdryer
[C]	Tromm TeCe 3534F	33 wt% microcrystalline wax dispersed in white spirit	One layer was applied as above on a heated surface (100 C on the bronze plates, 50 C on the monument). This wax was used in a higher concentration to obtain a thicker layer since only one layer could be applied hot
[D]	Incralac	commercial product consisting of acrylic lacquer with BTA	Four layers were applied by brush in 24 hours intervals
[E]	Incralac + Soter LC	double-layer system	2 lacquer + 3 wax layers were applied as above
[F]	Incralac + R21	double-layer system	2 lacquer + 3 wax layers were applied as above

strategies have been adopted. Electrochemical methods have received growing interest as tools for metal conservation (Otieno-Alego et al 1998a, D'Ercoli et al. 1999, Letardi 2000, Cicileo et al. 2004).

A project has commenced in 2001 as a cooperation between a research laboratory (CNR), a conservation institution (ICR) and local authorities, (Soprintendenza PSAD Liguria, Museum branch of the local Municipality) (Letardi et al. 2003). The project was planned to compare the behavior of selected coating systems upon natural weathering, both on polished bronze samples and on selected areas of a bronze monument. Six protective coating systems, widely used in conservation practice, were chosen, as summarised in Table 1. Waxes [A] and [B] are widely applied by Italian restorers; wax [C] is largely adopted in Germany. The acrylic-based Incralac [D] has been used worldwide; also the use of coating [D] with a wax topcoat has been widely reported. In this project it was decided to test coating [D] with both [A] and [B] wax topcoat; the coating system [D]+[B] (labelled [F]) has been widely used by Italian restorers.

The bronze statue *Monumento ai Mille* (E. Baroni, 1910) chosen for this study is located in Genoa, right next to the sea. Patina samples from the statue were characterised by XRD (Letardi et al. 2002). The more abundant corrosion products identified are Cuprite, Atacamite, Paratacamite and Mushistonite, with Nantokite, Gypsum and Quartz in some places. Six areas with various patinas were selected on the monument for monitoring and comparison of the coating system behaviour. The patina was evaluated as relatively homogeneous in each area. Four areas (labelled I, II, III, IV) were on the front side facing towards the sea and two (labelled V, VI) were on the rear facing towards the street. On each area, a number of 6 x 4.5 cm zones were cleaned by a restorer and then coated with the above described systems [A] to [F]. One or two zones for each area were left without coating.

Samples both of un-coated bronze and coated with the coating systems [A] to [F], were placed on an exposure rack in the urban marine environment at a site inside the Genoa Harbour, not far from the *Monumento ai Mille*. Exposure commenced in late June 2001, as soon as the treatment on the areas on the monument was completed. Orientation and position according to ISO 9223 standard were selected: the samples were facing south exposed skyward in the position of 45 degrees from horizontal level.

The application of several laboratory and field measurement techniques is in progress, in order to provide a wide characterisation of alloys, patinas, and coatings both on the coupons and on the monument. This paper will report the characterisation on coating thickness and coupons patina composition, and will mainly focus on the Electrochemical Impedance Spectroscopy measurements both on the samples and on Area III on the monument (Figure 1).

2. Experimental Procedure

The bronze samples for the natural weathering program were obtained from cast ingots with the composition Cu 90%, Sn 8%, Pb 2%. Coupons (size 3x3 or 6x6 cm, 3 mm thickness) were polished using SiC metallographic grinding paper 1200 grit in water, washed in ethanol and dried in air.

The conservator-restorer (I.Reindell) treated test areas on the *Monumento ai Mille*. Each selected zone was outlined with scotch tape and was cleaned by rotating brush, washed with water and acetone and dried.
The coatings were brush-applied by the restorer, following the standard methodology used in conservation, both

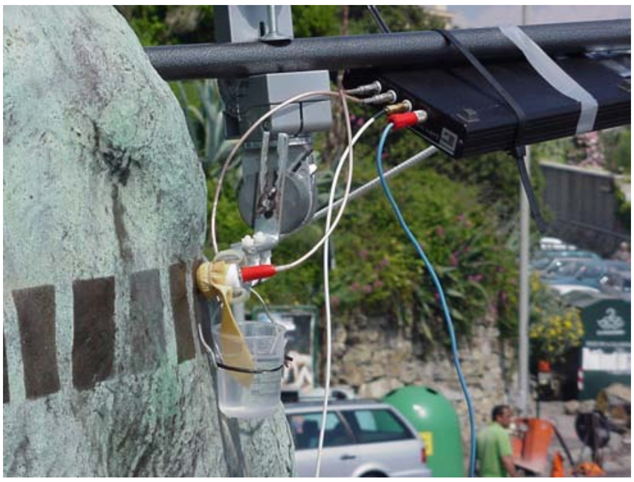

Figure 1 Electrochemical Impedance Spectroscopy measurement with the contact probe on *Monumento ai Mille* (test area III). From left to right, the visible 6x4.5 cm test zones are the ones for [B], [C], no coating, [E], and [F].

on coupons and on the monument zones. This was chosen in order to stay as close as possible to practical restoration world. Details on coatings and their application methods are reported in Table 1 (Letardi and Cozzolino 2002).

Coupons not exposed to weathering as well as after removal from the exposure rack have been stored in a sealed cabinet with silica gel.

2.1 Thickness measurements

Patina and coating thickness have been measured by Eddy Current technique [(Namicon DuoCheck with QE2 probe (0-1500μm)]. As the Eddy Current probe marks the waxy coatings, in order to check samples homogeneity, each coupon was weighted before and after coating application, and the weight gain per unit area has been computed for each sample. Coating thickness has been measured on two 3x3 and two 6x6 coupons for each coating system; for each series samples for measurement were chosen as the ones with the higher and the lower weight gain per unit area upon coating application. On each sample, 9 or 16 measurements on 3x3 and 6x6 coupons respectively were conducted, evenly distributed on the sample surface. Samples with waxy coatings have been cleaned and coated again after thickness measurement (Letardi et al. 2003). Unfortunately no characterisation of the coating thickness was possible on the Monument.

2.2 EIS measurements

EIS measurements were performed with a contact probe prototype and a method being developed in order to be applicable for field measurement on outdoor bronze statues (Letardi et al. 1998, Letardi 2002). The area probed in each measurement is 1.77 cm^2. A commercial cleaning-cloth soaked with a mineral water (electrical conductivity 318$\mu S/cm^2$, pH=7.9) is fixed to the contact cell, and the system obtained is then leant on the surface to be measured. The cloth has been immersed in the mineral water for 130min before being fixed to the contact cell; the system has been left to stabilise the open circuit potential for 30min before measurement start. EIS measurements have been made with a Gamry Femtostat, with Framework/EIS300 V3.11 software© 1999, Gamry Instruments. Spectra with 10 point per decade have been acquired in potentiostatic mode with 10mV AC signal level at open circuit potential.

Measurements were made in the frequency range 100KHz - 10mHz. For many exposures, 2 to 4 coupons for each coating system were measured; and 2 to 4 measurements were done in different parts of the 6x6 samples. On the monument it was not possible to record more than 2 to 3 spectra for each zone at each exposure time, especially since favorable weather conditions was necessary in order to take measurements. The average value of the Impedance Modulus |Z| at 10 mHz (low frequency limit) was computed for each coating system at each exposure, both for coupons and monument area III. The low frequency value of Impedance modulus is generally used to quickly assess coating protection ability: the higher is the value, the lower the corrosion rate of the system.

2.3 Patina composition characterisation

A Rigaku diffractometer was used to record X-Ray Diffraction spectra for corrosion product characterisation. The operating condition was: Cu K_α radiation with Ni filter, 40 kV, 30 mA. Spectra were directly measured using the 3x3 coupons.

3. Results

3.1 Patinas

Monitoring of patina thickness on the bare bronze coupons showed quick growth in the first 3 months, with an average value of 10 μm; afterwards the growth measured in the present conditions was slower with an average value of 11μm after 1year and 13μm after two years. Characterisation of patina components by XRD shows Cuprite is abundant from the very beginning of exposure; Atacamite and Paratacamite were present after the first month, then increasing with respect to Cuprite as weathering progresses. Ammonium Phosphate (JCPDF 22-0062) was also identified in the first month, with a slower increase with exposure. Small amounts of Quartz were also identified.

All the EIS measurements on the non-coated zone of Area III of the monument gave similar results during the time, with an average value of the Impedance modulus 0.15 ± 0.05 MΩcm^2. The bronze alloy used for the coupons, soon after polishing, was characterised by a value 0.09 ± 0.02 MΩcm^2, which grows rapidly in the first 3 months exposure, with a value 0.3 ± 0.2 MΩcm^2 after 1 year of exposure.

Table 2. Characterisation of the coatings applied on coupons with the application methods described in Table 1, as weight gain per unit area W and thickness Σ measured with Eddy Current method. The best fit value obtained for the parameters in the equation $W = a\ \Sigma + b$ are reported for each coating, along with the coefficient of determination $\chi 2$.

		W [mg/cm^2]	**Σ [μm]**	a	b	$\chi 2$
[A]	6x6	1.2 ± 0.2	6 ± 3	0.13±0.02	0.63±0.09	0.95
	3x3					
[B]	6x6	1.0 ± 0.1	6 ± 2	0.08±0.02	0.6±0.1	0.81
	3x3					
[C]	6x6	0.8 ± 0.3	4 ± 2	0.19±0.02	0.0±0.1	0.97
	3x3					
[D]	6x6	1.6 ± 0.1	11 ± 3	0.09±0.01	0.52±0.09	0.98
	3x3	1.1 ± 0.1	6 ± 2			
[E]	6x6	2.0 ± 0.2	13 ± 2	0.12±0.03	0.4±0.03	0.95
	3x3	2.3 ± 0.3	6 ± 3	0.12±0.07	1.42±0.04	0.997
[F]	6x6	1.6 ± 0.1	10 ± 2	0.08±0.01	1.0±0.1	0.98
	3x3	1.6 ± 0.2	7 ± 2			

3.2 Coating systems

On the coupons, weight gain per unit area after coating application showed a good Gaussian distribution for all the coatings. A wider distribution characterised wax [C] and sharper one was obtained for wax [B]; for coating [D] the same application methods produced different results on samples 3x3 and 6x6, and the weight gain per unit area is clearly bimodal. The distribution is quite wide for coating [E] and it appears to be bimodal also, while for system [F] the distribution is narrow. The Eddy Current measurements provide an average value between 4 and 7 μm for all the coatings on the 3x3 samples. The same value is obtained on the 6x6 samples coated with the waxes (coatings [A], [B], and [C]), while the measured thickness is higher for 6x6 samples with Incralac containing coatings ([D], [E], and [F]). In particular it is almost double for coating [D] and [E]. Results are summarised in Table 2.

The linear correlation between the coating thickness Σ and the coupon weight gain per unit area W after coating application has been tested; fitting of data with the curve $W = a\Sigma + b$ (see Table 2) gave very satisfactory results for coatings [A], [C], [D] and for coating [B] the regression results were satisfactory also. For the double layer systems [E], [F] very good fits were obtained, with two different curves for 3x3 and 6x6 samples in the case of coating [E]. It could be easily calculated that this was due to the quite different values obtained for the

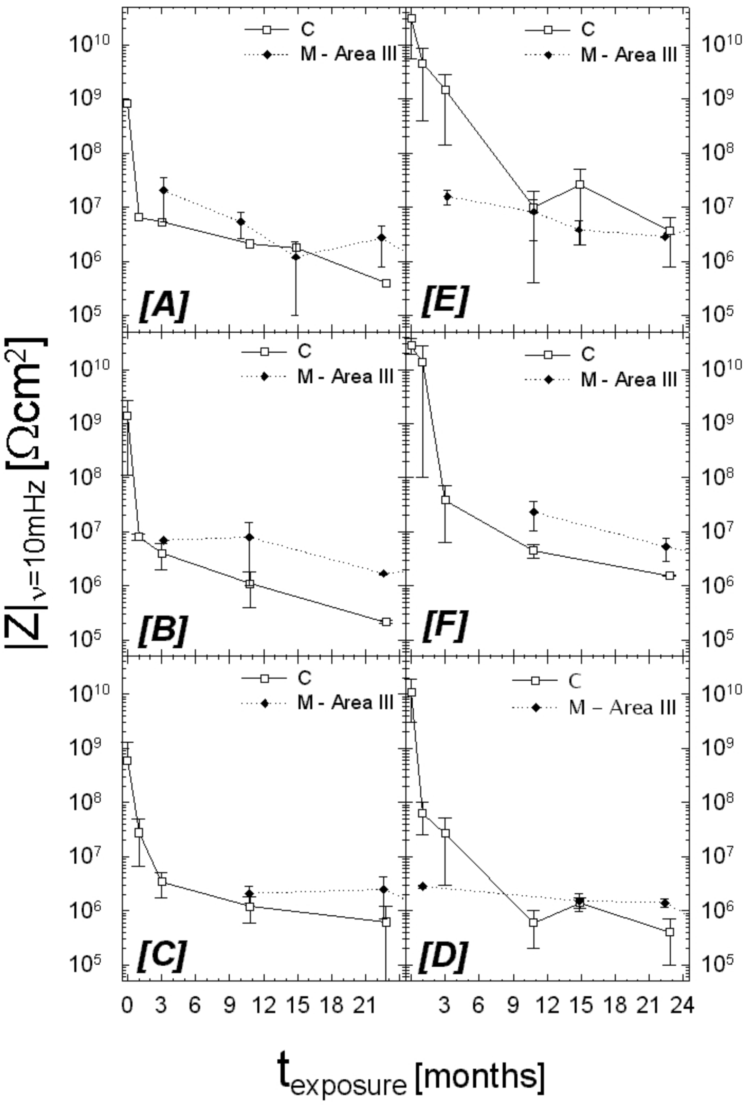

Figure 2 Low frequency value of Impedance modulus as a function of exposure time. Average data are plotted for the six coating systems [A] to [F] under test. Label C is for coupons and label M for monument.

parameter "a" of the coatings [D] and [A], which forms the double layer [E]. On the contrary, the value "a" for the wax [B] has almost the same value than for coating [D], so the corresponding double layer [F] is characterised by a single straight line for both 3x3 and 6x6 coupons. Except for wax [C], the parameter "b" is different from 0, as one could expect. Possible explanations for this behavior could be the way coatings are conforming to surface roughness and/or could be unevenly distributed on the sample border.

EIS measurements for 0, 1, 3, 11, 23 months exposure time were performed on coupons for all the coating systems under test (Figure 2, solid lines). At the beginning the average value of the Impedance modulus is about 1 GΩcm^2 for the three waxes, one order of magnitude higher for coating [D] and a bit higher for the double layer systems. Apart the double layer [E], all the other coatings showed a very quick decrease in the first three months, with values two order of magnitude or more lower than the initial ones; after 23 months only the double layer systems [E] and [F] had values over 1 MΩcm^2.

Measurements on coatings on the monument at the beginning of exposure was not advisable since solvents need to evaporate. Soon after the environmental conditions were not completely suitable, and only a few measurements were possible. A wider characterisation was then commenced after 10 months weathering (Figure 2, dotted lines). After three months both waxes [A], [B] and the double layer [E] gave average value in the range of 10 MΩcm^2; notwithstanding an high scatter of data, a similar trend is observed upon weathering, with values

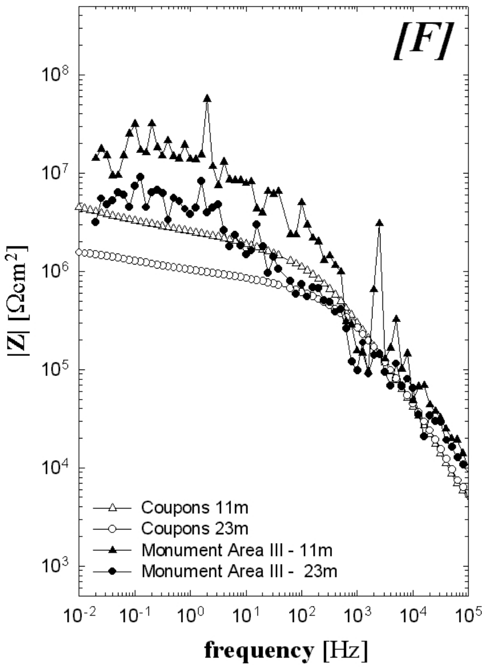

Figure 3 Impedance Modulus for coating [F] measured on coupons and on monument area III.

of a few MΩcm^2 after 23 months. The few data on wax [C] seem to suggest a slow variation, with values around 2 MΩcm^2 both at 11 and 23 months. Coating [D] also seem to present a slow variation, with a value around 3 MΩcm^2 after only one month, which became around 1 MΩcm^2 after 23 months. The double layer [F] presents the higher values, with about 20 MΩcm^2 after 11months and 5 MΩcm^2 after 23 months.

4. Discussion

The use of thickness measurement with the Eddy Current portable instrument on the monument was prone to very wide dispersion of data, due to the high roughness of surface with respect to the probe area; nonetheless the technique could give a rough determination of patinas thickness (Letardi et al. 2003). On the *Monumento ai Mille* average values between 80 and 130 µm were measured on the test areas before cleaning, which reduces to 50 to 110 µm afterwards; in particular 90±33 µm is measured in area III. On the contrary, coating thickness measurement on the monument was meaningless. In fact the coating thickness obtained with the application method adopted, whose measured values on coupons range from 4 to 13 µm, is lower than the dispersion of data obtained in the patina thickness measurements. As the treated zones have an area little less than coupons 6x6, one can guess similar thicknesses are obtained on the monument, even though a characterisation of coatings applied on patinated samples could help in verifying this hypothesis.

The comparison of the corrosion products identified on the monument and on the weathered coupons shows quite a similar composition, apart from the Mushistonite, which is identified on the monument only and Ammonium Phosphate that is identified on coupons only. The more abundant corrosion products identified both on the monument and on the coupons are the typical one reported for marine exposure (Cuprite, Atacamite, and Paratacamite).

The Impedance measurements performed show a fairly wide scattering of data. Many factors, which are not strictly controlled in these natural/field conditions may influence data, and a more detailed analysis of the several measured parameters is under way. The field measurements on the monument are still quite noisy (Figure 3), and further improvement on the data acquisition method are in progress, even though the spectra quality is acceptable for the type of analysis performed.

Notwithstanding the scattering of data, a number of comments can be made. Average values of the low frequency Impedance Modulus are quite similar both on the patina on monument Area III and on the exposed bronze samples after one year. As already noted, these patinas do not have meaningful protective qualities, as the Impedance is only a little higher than for the bare bronze.

Comparison of coatings performance on the coupons and the monument area III is shown in Figure 2:

- Wax [A] performed better on the monument than on the coupons after three months exposure; as weathering continues the difference seems to decrease, even though data at 23m would require further comparison for longer exposure time.
- Wax [B] is characterised by average values systematically higher on the monument than on the coupons.
- Wax [C] has average values higher on the monument than on the coupons.
- Coating [D] is characterised by an average value one order of magnitude less on the monument than on the coupons after one month exposure. The trend observed indicates that values are quite similar on the monument and on coupons around one year exposure, and possibly are higher on the monument than on coupons after 23 months.
- Double layer [E] has an average value two orders of magnitude less on the monument than on the coupons after three months exposure; from 11 months differences are more or less negligible.
- Double layer [F] performs better on the monument than on coupons (Figure 3), with an average value almost one order of magnitude higher on the monument than on the coupon after 11 months.

The results obtained show that after only one year coating [D] offers no advantage with respect to the waxy coatings [A], [B] and [C], which have the advantage of a better accepted aesthetic appearance and are known to give fewer problems concerning reversibility and re-coating. The wax [B], both alone and in the double layer system [F], is the product whose performances on coupons showed the largest differences with respect to the ones on the monument area III. The different trends observed for the selected coatings on the polished bronze coupons and on the monument area III should be considered in more detail. The patina, which is present between the metal and the coatings applied on the monument, is supposed to be the main source for the differences observed on coating behavior with respect to the polished bronze coupons, as indicated by other studies (Otieno-Alego et al. 1998b, Letardi 2004). Further analyses are in progress to better enlighten relevant parameters for conservation purposes.

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Table of Registered Trade Items

Product	**Soter 201 LC**	**R21**	**TECE 3534 F**	**Incralac**
Producer/supplier	Baraldi Lubrificanti Via Decumana, 5 I-40133 Bologna ✆+39-051.381.744	Clariant *(producer)* Phase *(supplier)* Via T.Cremona, 7 I-40139 Bologna ✆+39-051.623.1295	TH.C.Tromm Feuerstrasse, 7-17 D-50735 Köln ✆+49-(0)221974552	Bresciani s.r.l. *(supplier)* Via Socrate 71.3 I-20128 Milano ✆ +39-0227002121