

Electrochemical characterization of organic coatings for protection of historic steel artefacts

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Abstract Electrochemical techniques are mainly known in the field of cultural heritage conservation as a tool for the elimination of corrosion layers or the removal of chlorides. However, these techniques are also a valuable tool for assessing the anti-corrosive efficiency of protective coatings. The aim of this study was to evaluate the performance of different coatings for their use in metallic heritage conservation using polarisation resistance (R_p) and electrochemical impedance spectroscopy (EIS). Carbon steel samples were prepared to simulate the surface composition and morphology of historic steel artefacts, and coated by a conservator–restorer following the common practices in conservation treatments. Three commercial organic coatings have been studied: a microcrystalline wax (Renaissance™) and a methyl acrylate/ethyl methacrylate copolymer resin (Paraloid™ B-72) dissolved in acetone—both them commonly used in conservation and restoration treatments—and an ethylene copolymer wax emulsion in water (Poligen™ ES-91009) that has not been used so far for this purpose. Four commercial corrosion inhibitor additives were added to the Paraloid™ B-72 resin and

Poligen™ ES-91009 wax. The additives were commercial preparations with the following known active components: a blend of triazoles (M435), an ammonium salt of tricarboxylic acid (M370), a calcium sulphonate (M109), and a bis-oxazoline (Alkaterge-T™). R_p and EIS results showed that the best protection of the steel specimens was afforded by Poligen™ ES-91009 when applied in thick layers. None of the additives have shown a clear improvement of the protection properties of the coatings, and one of them impaired the barrier effect of the coating.

Keywords Organic coatings · Conservation · Heritage · Corrosion · Additives · EIS · R_p

Introduction

From a corrosion and protection point of view, archaeological, historic and artistic artefacts differ from industrial objects in that they are usually coated (partly or totally) with corrosion products developed over years or centuries. These corrosion products are part of the history of the object and, in some cases, conserve important information about the original shape, decoration or manufacturing techniques [1]. Therefore, they need to be at least partially preserved and protective coatings should be applied over them rather than on a clean metal surface.

Coatings used for conservation and restoration treatments should meet a number of special requirements, mainly transparency, a good aesthetic appearance, long-term stability and reversibility. The latter is a vital condition for restoration products, since the treatment applied to an object intended to last for centuries will eventually need to be renewed [2]. It is also very important that protection systems be easy to apply to artefacts of different types and

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sizes and be safe both for conservators–restorers and the environment. Moreover, most of these coatings are applied to metals already covered, partly or totally, by corrosion products or patinas.

For all these reasons, corrosion protection systems developed for industrial applications may not be suitable for the protection of archaeological, historic and artistic artefacts, and it is necessary to study the protective properties of suitable coatings using a methodology adapted to their special characteristics and requirements [2, 3]. A recent survey in different countries in the Mediterranean area has showed that Paraloid™ B-72 (a methyl acrylate/ethyl methacrylate copolymer) and microcrystalline waxes are, by far, the most common coatings used for protection of copper- and iron-based historical or archaeological artefacts [4]. However, many failures of the coatings have been reported, and waxes and acrylic resins are usually dissolved in solvents that might be harmful for both the conservators–restorers and the environment. There is a general trend towards the substitution of toxic protection systems by environmentally friendly and low-toxicity products. Solvent-based coatings are being replaced by water-borne ones, in order to reduce the emission of volatile organic compounds. Toxic corrosion inhibitors such as benzotriazole, commonly used in conservation–restoration treatments, are being replaced by less toxic compounds [5]. In this line, corrosion inhibitors from natural products have been extensively studied in recent years [6, 7]. Many extracts from aromatic herb, spices and medicinal plants have been demonstrated to be good corrosion inhibitors for steel [8] and copper [9]. Therefore, there is a need to develop new coatings or test the suitability of already existing ones for their use in this field [2].

Electrochemical techniques are mainly known in the field of cultural heritage conservation in relation with restoration treatments of metallic artefacts, usually the elimination of corrosion layers [10, 11] or the electrochemically aided removal of chlorides [12–15]. However, these techniques are a very valuable tool and a quick method for assessing the anti-corrosive efficiency of protective coatings and films applied to prevent the further degradation of metal objects. Electrochemical impedance spectroscopy (EIS) has been extensively used in the past few decades for the study of organic coatings for metals [16–18]. It has also been used to assess coatings performance after physical- or chemical-accelerated ageing tests [19, 20]. However, their use for the evaluation of coatings for metallic heritage conservation has been much more recent and limited [21–23].

The aim of this paper is to study the protective properties of traditional and innovative (in conservation) organic coatings for their use in conservation and restoration treatments for historic iron artefacts and the effect of doping with four

corrosion inhibitor additives, and the applicability of electrochemical techniques to the assessment of those coatings.

The entire experimental protocol has been developed with the aim of reproducing as close as possible the real conditions of conservation–restoration treatments of metals [2]. Coatings have been selected amongst commercial products already used by conservators–restorers and other commercial products developed for other applications that fulfil the requirements of metal conservation criteria. Coatings have been applied by a conservator–restorer by hand, as they would be applied in real treatments. Authors are aware that this experimental procedure reduces the reproducibility and produces coatings with a greater degree of inhomogeneity, making the interpretation of the EIS spectra more difficult. However, on the other side, it allows for a study of the coatings in conditions that reproduce more closely the real application of the coating in conservation–restoration treatments.

Experimental

Metallic specimens

Three sets of 3-mm-thick sheet steel specimens have been analysed. Set 1 and set 3 consisted of clean steel specimens coated with organic coatings. The difference between both sets was the method for the application of the coating (see below). Set 2 consisted of pre-corroded steel specimens coated with organic coatings and artificially aged.

The composition of the steel, determined using glow discharge-optical emission spectroscopy, was (by weight) 0.13% C, <0.10% Si, 0.53% Mn, 0.010% P, 0.015% S, and balance Fe.

The clean steel specimens (set 1 and set 3) were mechanically polished with successive grades of emery paper down to grade 600, ultrasonically cleaned in ethanol, and stored with silica gel until they were coated.

Steel specimens for set 2 were pre-corroded in a climate cabinet. They were supported on a poly-methyl-methacrylate rack at an angle of 60 degrees from the horizontal and exposed to a 3-day cycle consisting of 100% relative humidity (RH) at 30 °C for 24 h followed by 24 h in a laboratory environment (55–60% RH and 25–30 °C), and finally, a further 24 h at 100% RH and 30 °C. This protocol has been developed for the preparation of steel specimens with some corrosion pits on the steel surface to resemble the corrosion originated on historic and artistic objects over years or centuries [2, 24].

It should be noted that the type of cleaning applied to historic objects during conservation–restoration treatments seeks to remove certain bulky and loose corrosion products but not to completely eliminate the entire corrosion product

layer. Surface information on the object (decoration, tool marks, etc.) is, in many cases, preserved by corrosion products, and conservation ethics therefore require the maintenance of this material.

After the pre-corroding treatment, the steel specimens were partly cleaned by a restorer using a protocol similar to that used for the cleaning of objects of historic and artistic value. The specimens were first wiped using cotton swabs wetted with ethanol, to remove powdery corrosion products, and then polished with rotary natural bristle brushes. This procedure did not completely remove all the corrosion products; therefore, some corrosion products remained on the surface before the application of the coating.

Coatings

Table 1 summarises the organic coatings tested. Two commercial coatings commonly used in conservation and restoration treatments were studied, namely Renaissance™ wax (a microcrystalline wax) and Paraloid™ B-72 (a

methyl acrylate/ethyl methacrylate copolymer). A new (in conservation treatments) organic coating, Poligen™ ES-91009, a ready-to-use liquid wax (ethylene copolymer wax emulsion in water), was also studied. Four commercial corrosion inhibitor additives were added to the Poligen™ ES-91009 and the Paraloid™ B-72. The additives were commercial preparations with the following known active components: a blend of triazoles (Cortec Corporation M435), an ammonium salt of tricarboxylic acid (Cortec Corporation M370), a calcium sulphonate (Cortec Corporation M109) and a bis-oxazoline (Dow Chemical Alkaterge-T™) (see Table 1).

Coatings for set 1 were applied by brushing in two criss-cross layers, allowing 24 h for drying between layers. Coatings for Set 2 were applied by immersion and artificially aged in a climate cabinet, a Voetsch Industrietechnik VC 4034 system, for 30 daily cycles of 90% RH at 35 °C for 16 h and 55% RH at 23 °C for 8 h. To compare the protective properties of the different coatings before and after artificial ageing, seven reference specimens (coated but not artificially aged, Cx-N in column six of Table 1)

Table 1 Characteristics of colourless organic coatings and corrosion inhibitors applied on the steel surface

Organic coating	Clean surface—brushing (set 1)			Pre-corroded surface—immersion (set 2)			Clean surface—immersion (set 3)		
	Specimen	Thickness μm	Standard deviation	Specimen	Thickness μm	Standard deviation	Specimen	Thickness μm	Standard deviation
Without organic coating	0	–	–	C0	–	–	–	–	–
Renaissance™ ^a	1	1	0	C1-N	4	2	X1	3	1
				C1-A	16	7			
Poligen™ ES-91009 ^b	2	1	1	C2-N	27	15	X2	23	15
				C2-A	42	26			
Poligen™ ES-91009+M435 ^c	2a	3	3	C2a-N	62	39	–	–	–
				C2a-A	79	38			
Poligen™ ES-91009+M370 ^d	2b	4	4	C2b-N	33	19	–	–	–
				C2b-A	33	22			
Paraloid™ B-72 ^e	3	7	4	C3-N	6	4	X3	7	1
				C3-A	7	2			
Paraloid™ B-72+M435	3a	6	4	–	–	–	–	–	–
Paraloid™ B-72+M109 ^f	3b	6	4	C3b-N	12	5	–	–	–
				C3b-A	7	2			
Paraloid™ B-72+Alkaterge-T ^g	3c	10	5	C3c-N	6	3	–	–	–
				C3c-A	8	4			

C pre-corroded specimen, coated by immersion, N non-artificially aged coating, A artificially aged coating, X clean specimen, coated by immersion

^a Renaissance™ is a microcrystalline wax from the Picreator Enterprises Company

^b Poligen™ ES-91009 is an ethylene wax in water (liquid) from the BASF Company

^c M435 is a corrosion inhibitor a blend of triazoles from the Cortec Corporation

^d M370 is a corrosion inhibitor an ammonium salt of tricarboxylic acid from the Cortec Corporation

^e Paraloid™ B-72 is a 15% (by volume) acrylic resin in acetone (liquid) from the Rohm and Haas Company

^f M109 is a corrosion inhibitor a calcium sulphonate from the Cortec Corporation

^g Alkaterge-T is a corrosion inhibitor a bis-oxazoline from the Dow Chemical Company

and seven artificially aged specimens (Cx-A in Table 1) were tested. Figure 1 shows the two samples of set 2 as they were tested. Finally, to investigate the effect of the coating procedure, clean samples were coated by immersion with the three coatings without additives (set 3). These samples were not aged.

Table 1 also summarises the thickness of the organic coatings, measured with an Elcometer 300 thickness gauge, using a probe for magnetic materials based on electromagnetic induction. The reported thickness is the average of 20 points in different areas of two different specimens.

Electrochemical techniques

Three different electrochemical tests were performed: corrosion potential (E_{corr}), polarisation resistance (R_p) and EIS. A classic three-electrode configuration cell was used. The working electrode was the surface (4.15 cm^2) of the steel specimen exposed to the electrolyte, the counter electrode was a large surface area platinum mesh and the reference electrode was a saturated calomel electrode (SCE). Experiments were performed after 1 h of stabilisation of the E_{corr} . After that time, the potential remained stable. It should also be pointed out that the coatings under study were intended to be used for indoor protection of metals, and therefore, long immersion times were not considered to be representative of the real conditions of exposure of the coatings. Figure 2 shows a scheme of the electrochemical cell used.

Two electrolytes were tested to simulate the type of pollutants found in museum environments: a 0.1 M NaCl solution and a dilute Harrison's electrolyte (0.35 wt.%

$(\text{NH}_4)_2\text{SO}_4 + 0.05 \text{ wt.}\% \text{ NaCl}$ in distilled H_2O) [25], using a volume of 20 ml.

Both electrolytes (NaCl and Harrison) have been used for R_p measurements of set 1. Since no significant differences were observed between the two electrolytes, EIS measurements of set 1 and R_p and EIS measurements of set 2 were carried out using a 0.1 M NaCl electrolyte only.

An EG&G PARC 273A potentiostat was used for R_p measurements. The potential was swept from $E_{\text{corr}} \pm 10 \text{ mV}$ at a scan rate of 0.16 mV/s. A Solartron 1250 Frequency Response Analyser connected to an EG&G PARC 273A potentiostat was used for EIS measurements, applying a logarithmic sweeping frequency of five steps per decade, from 64 kHz to 64 mHz. Impedance measurements were performed at the E_{corr} , imposing a sinusoidal signal of 10 mV rms.

Results and discussion

The visual appearance of the specimens is an important parameter to take into account when dealing with coatings intended for use in cultural heritage conservation and restoration treatments. Although this is a subjective matter, it is very important that a coating applied to a metal does not alter its visual aspect. It is desirable to have little (if any) colour change. From this point of view, the three studied organic coatings performed well, since they are transparent.

In the case of bare metals, the metallic shine also needs to be preserved. In this respect, some differences were

Fig. 1 Aspect of the steel specimens of set 2, after pre-corrosion, partial cleaning and coating



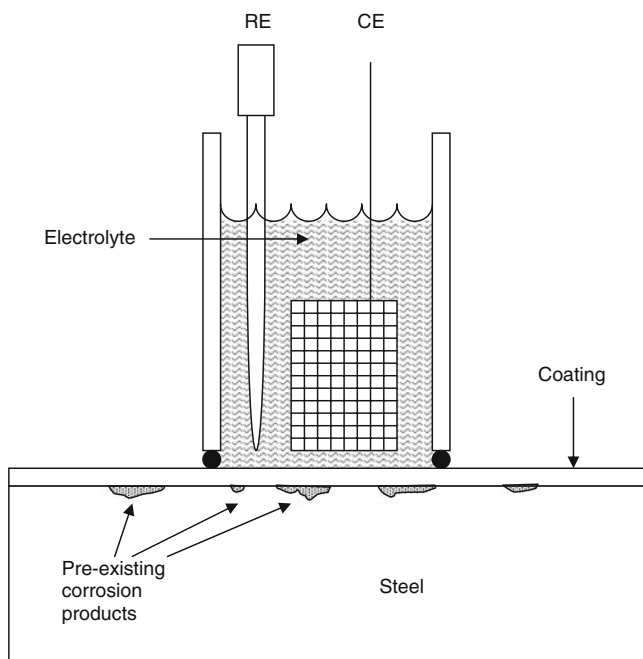


Fig. 2 Scheme of the electrochemical cell used for the experiments

observed. The best appearance was afforded by the Renaissance™ coating, since the aspect of the steel is “ideal” (no changes were observed). In contrast, the Paraloid™ B-72 coating yields a very glossy, plastic-like aspect, and it is difficult to get a visually uniform coating. The visual appearance of the specimens coated with Poligen™ ES-91009 is half-way between the Renaissance™ and Paraloid™ B-72 coatings. The aspect is slightly glossy, but the coating is more uniform than with Paraloid™ B-72.

Table 1 (column three) shows the thickness of the coatings applied by brushing to clean samples (set 1). Important differences can be observed in the thickness of the coatings, and this parameter should therefore be taken into account when comparing the protective properties of the different coatings. There is also considerable scatter, with a high standard deviation (see column four), in the thicknesses measured in different areas of the specimens.

Figure 3 shows the E_{corr} for the different specimens (set 1) after 1 h in contact with the NaCl and Harrison electrolytes. It can be seen that the application of the coatings shifts the E_{corr} towards more noble values (i.e., less negative potentials), except in the case of specimen 1 (Renaissance™ wax), which yields potential values similar to the uncoated specimen. The highest E_{corr} value is shown by specimen 2a (Poligen™ ES-91009+M435 corrosion inhibitor).

Figure 4 shows the R_p measurements for the different specimens (set 1). It can be seen that specimen 1 (Renaissance™ wax) showed poor protective properties, yielding a similar R_p value to the uncoated steel

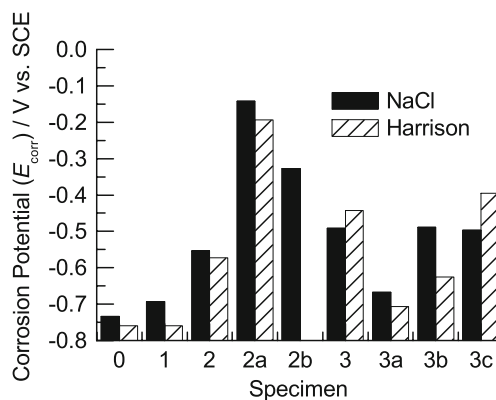


Fig. 3 Corrosion potential (E_{corr}) measurements of the different specimens (set 1) after 1 h of immersion in the electrolyte

($\sim 10^3 \Omega \text{ cm}^2$). Specimens coated with Poligen™ ES-91009 showed better protection, especially when doped with M435 and M370 corrosion inhibitors (specimens 2a and 2b), yielding an R_p value of $\sim 10^6 \Omega \text{ cm}^2$. However, it should be taken into account that specimens 2a and 2b are much thicker than specimen 2, so the increase in the barrier effect due to the thickness increase might also play an important role in the increase of the R_p values. Specimens coated with Paraloid™ B-72 resin also afford good protection ($\sim 10^5 \Omega \text{ cm}^2$), although in this case, the addition of a corrosion inhibitor does not improve the protective effect in all cases (protection higher for specimen 3b but similar for specimen 3c). In the case of specimen 3a, the M435 corrosion inhibitor greatly impairs the protective properties of the Paraloid™ B-72 resin. Since all the Paraloid™ B-72-based coatings have similar thicknesses, the differences between them can be attributed to the effects of the additives.

It should be noted that, being commercial preparations, and therefore having an unknown exact composition, it is difficult to establish the reason for the failure of the coating 3a, since many components of the product may interact with the polymer or with the metal itself, or they may

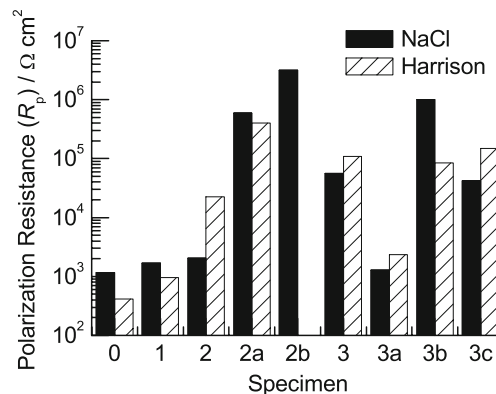


Fig. 4 Polarisation resistance (R_p) measurements of the different specimens (set 1)

interfere with the adhesion of the coating to the substrate. M435 is, according to the manufacturer, a blend of triazoles. The mechanism of inhibition of triazoles is based on its adsorption on the metal surface. Therefore, the efficiency of this corrosion inhibitor additive greatly depends on the ability of the electrolyte to transport the inhibitor to the coating–metal interface. These additives are effective only if their solubility is in the right range: if it is too low, insufficient inhibitor molecules will reach the metal surface to be effective; if it is too high, the additive will be leached from the coating and/or cause osmotic blistering or delamination [26]. Triazole is very soluble in water, and it is known to cause blistering of organic coatings when in contact with moisture and, therefore, is not suitable to be used for organic coatings unless it is modified to control its solubility [27]. The geometry of the defects and the composition of the electrolyte have also been demonstrated to have a significant effect of the efficiency of inhibitor-doped coatings [28]

Figures 5 and 6 show the Bode plots obtained using EIS data for the steel specimens with and without organic coatings (set 1). It can be seen that, on specimens 1 and 2, the coatings do not provide significant protection to the base steel since the impedance modulus ($|Z|$) values (see Fig. 5a) are quite close to those of the uncoated specimens. On the other hand, on specimens 2a and 2b, the coatings

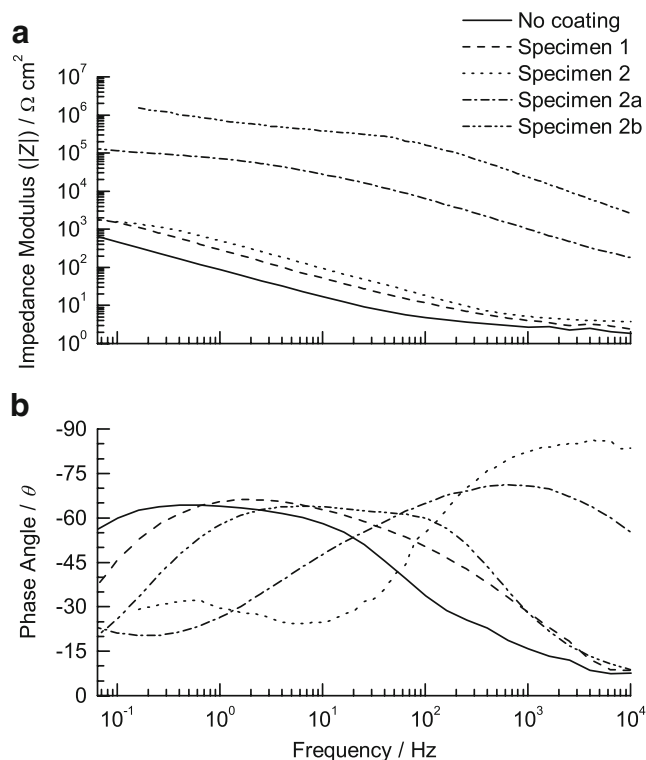


Fig. 5 Bode plots obtained from specimen without coating and with specimens 1, 2, 2a and 2b (set 1) (a, b)

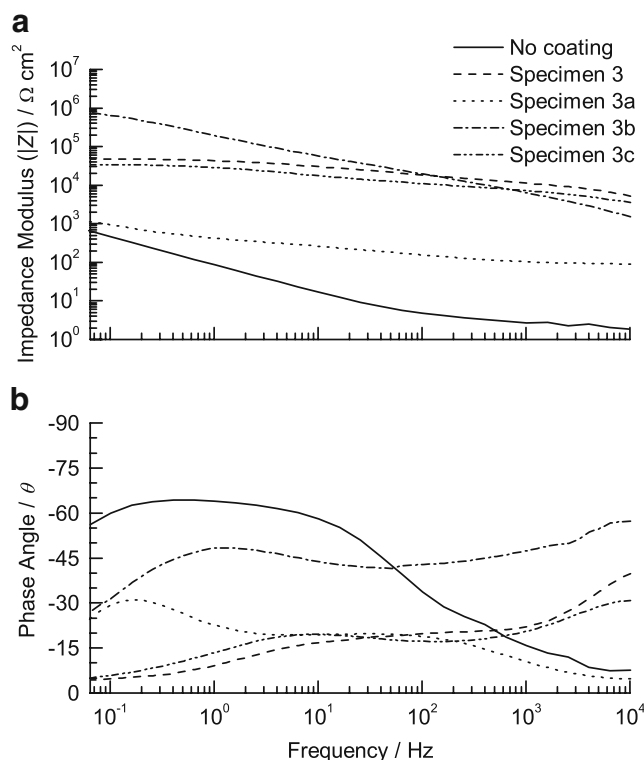


Fig. 6 Bode plots obtained from specimen without coating and with specimens 3, 3a, 3b and 3c (set 1) (a, b)

yield an increase of two to three orders of magnitude in the $|Z|$ values. The coatings on specimens 3, 3b and 3c show good protective properties (see Fig. 6), but the addition of corrosion inhibitor additives decreases their protective properties. Table 2 lists the values of the electrical parameters of the different elements used to fit the EIS data, according to the equivalent electrical circuit in Fig. 7.

EIS results are usually discussed by means of an equivalent electrical circuit that represents the physical properties of the steel/coating system. The circuit in Fig. 7 includes a resistor (R_s) modelling the resistance of the electrolyte, in series with a constant phase element (CPE_1) in parallel with another resistor (R_1), that model the properties of the coating, and in series with a circuit constituted by CPE_2 and R_2 elements in parallel modelling the double-layer capacitance and the charge transfer resistance, respectively [16, 17, 29–32].

A CPE is commonly used instead of a capacitor to model the behaviour of many electrochemical systems showing depressed semicircles in the Nyquist plot. The impedance of a CPE is defined by the empirical expression: $Z_{CPE} = \frac{1}{Y(j\omega)^\alpha}$, where Y is a constant, $j = (-1)^{1/2}$, $\omega = 2\pi f$ and the exponent α is $-1 \leq \alpha \leq +1$. When $\alpha = 0$, the CPE is a resistor; when $\alpha = 1$, the CPE is a capacitor and when $\alpha = -1$, the CPE is an inductor. Finally, if $\alpha = 0.5$, the CPE is the Warburg impedance, i.e. it models a diffusion process [33, 34]. The

Table 2 Parameters used for the fitting of EIS data (Set 1) using the equivalent electrical circuit of Fig. 7

Specimen	CPE ₁		R ₁ /Ω cm ²	CPE ₂		R ₂ /Ω cm ²
	Y ₁ /F cm ⁻² s ^{-(1-α₁)}	α ₁		Y ₂ /F cm ⁻² s ^{-(1-α₂)}	α ₂	
0	–	–	–	2.8 × 10 ⁻³	0.74	2.7 × 10 ³
1	0.4 × 10 ⁻³	0.80	23	0.3 × 10 ⁻³	0.79	3.0 × 10 ³
2	0.4 × 10 ⁻³	0.76	2.1 × 10 ³	59 × 10 ⁻³	0.51	–
2a	1.2 × 10 ⁻⁶	0.76	82 × 10 ³	2.7 × 10 ⁻⁵	0.58	–
2b	8.9 × 10 ⁻⁹	0.96	281 × 10 ³	8.3 × 10 ⁻⁷	0.47	–
3	3.0 × 10 ⁻⁷	0.56	17 × 10 ³	4.6 × 10 ⁻⁶	0.50	35 × 10 ³
3a	0.4 × 10 ⁻³	0.50	407	1.2 × 10 ⁻³	0.82	1.4 × 10 ³
3b	4.5 × 10 ⁻⁷	0.65	32 × 10 ³	1.0 × 10 ⁻⁶	0.63	1.3 × 10 ⁶
3c	2.1 × 10 ⁻⁷	0.65	8 × 10 ³	7.6 × 10 ⁻⁶	0.54	29 × 10 ³

use of a CPE instead of an “ideal” capacitor is attributed to different reasons, such as surface roughness, inhomogeneous distribution of the reaction rates or the current, or differences in the thickness or properties of a coating (as has been shown in Table 1). Therefore, CPEs with values of the exponent about 0.8 in Table 2 can be interpreted as “non-ideal” capacitors. The CPE₁ and R₁ elements in Fig. 7 may be assigned to the organic coating behaviour, and the “nested circuit” elements CPE₂ and R₂ may be assigned to the steel corrosion process at the bottom of the pores on the coating. The “nested circuit” model is applicable only to coatings that have defects or pores which allow the electrolyte to penetrate the coating down to the steel [16, 17].

Table 2 summarises that the Y₂ and R₂ values for specimen 1 are similar to those of the uncoated specimen 0 and that the coating resistance is extremely low (~23 Ω cm²), indicating poor protective properties of Renaissance™ wax. This result agrees with the R_p results of Fig. 4. SEM images (Fig. 8) of specimen 1 showed that large pores are visible and justify the use of the equivalent electrical circuit of Fig. 7.

In the case of specimens 2, 2a and 2b neither large pores nor cracks were observed by SEM (Fig. 8), but the appearance of two time constants in the EIS spectra indicates that the electrolyte reaches the surface of the metal through microscopic pores or defects of the coating. For such coatings, Skale et al. have proposed that the diffusion of species through the pores of the coating controls the corrosion rate [34], and that this can be modelled using the

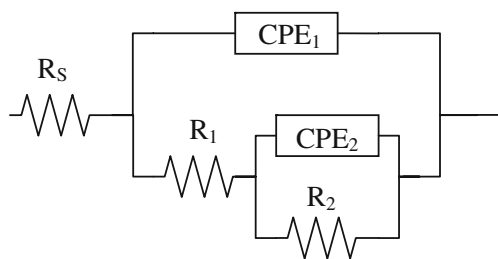


Fig. 7 Equivalent electrical circuit used to fit EIS data

Warburg impedance. In Table 2 (specimens 2, 2a and 2b), the exponent (α₂) of CPE₂ is around 0.5, and therefore, the CPE₂ element is a Warburg impedance. On the other hand, the values of the exponent (α₁) of CPE₁ range from 0.76 to 0.96, and can be attributed to the “non-ideal” capacitive behaviour of the coating. The low value of R₁ for coating 2 (close to the resistance of the uncoated specimen) indicates that coating 2, applied in this small thickness (~1 μm), provides a very low protection, as was already seen in R_p data. The values of R₁ increase from specimen 2 to specimens 2a and 2b, indicating that the latter afford better protective properties. In addition to the effect of the corrosion inhibitor additives, that improvement can also be explained by the higher thickness of the later coatings.

For specimens 3, 3a, 3b and 3c (see Table 2), the low values of the α₁ exponent do not allow a classic interpretation of the CPE₁ element. SEM images (Fig. 8) showed that, in this case, the coating is not as uniform as in the case of specimens 2, 2a and 2b, showing some cracks and irregularities. The values of the α₂ exponent are close to 0.5 (Table 2), indicating a diffusion process, probably through the corrosion products inside cracks, pores and/or defects in the coating. The highest resistance value (R₁), and therefore, the best protective property, is yielded by specimen 3b. In contrast, the R₁ value of specimen 3a is lower than that of the coating without any corrosion inhibitor (specimen 3). As has already been mentioned, the R₁ value is attributed to the resistance of the electrolyte in the ionically conducting paths across the coating. Its low value in specimen 3a indicates, therefore, that the barrier effect of the coating is almost completely lost.

Table 1 (column six) shows the average thickness of the different coatings applied by immersion to the pre-corroded steel surface (set 2). Some differences can be observed between those with Paraloid™ B-72 as opposed to Poligen™ ES-91009, with or without corrosion inhibitor additives. There is also considerable scatter in the thickness measured across the specimen surface; see the standard deviations shown in Table 1 (column seven).

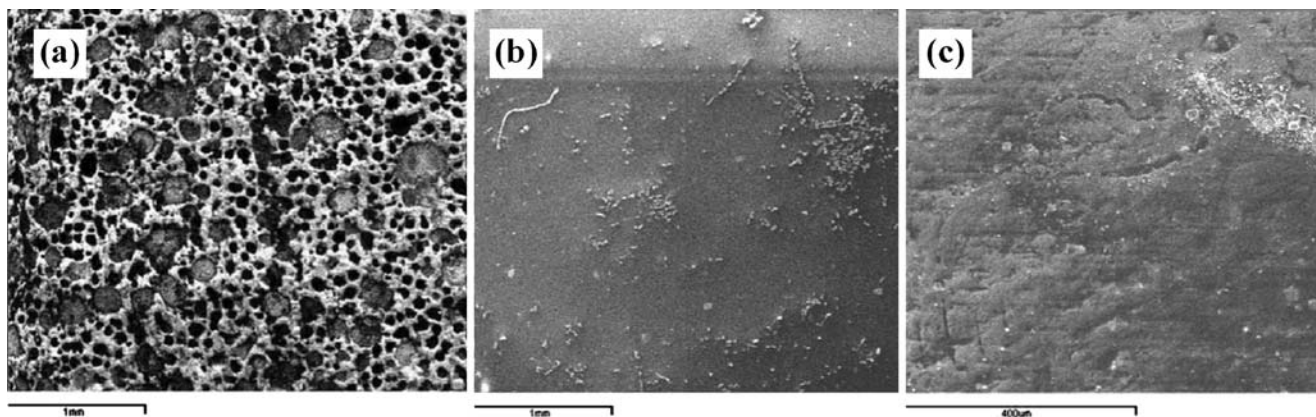


Fig. 8 SEM images of coating 1 (a), coating 2 (b) and coating 3 (c) (see Table 1), applied on the steel samples

Figure 9 shows R_p measurements using NaCl electrolyte for pre-corroded specimens with and without ageing (set 2). For the Poligen™ ES-91009 coatings, the aged specimens seem to perform slightly better than the reference ones. On the other hand, the Paraloid™ B-72-based coatings show a decrease in R_p values with ageing that cannot be attributed only to thickness differences between the specimens.

As for the clean steel surface specimens (Fig. 4, Set 1), the lowest protection was afforded by the Renaissance™ wax (specimens C1-N and C1-A). The highest R_p value (i.e. the best protective properties) is afforded by the Poligen™ ES-91009 coating without corrosion inhibitor additives (specimens C2-N and C2-A). In this case, the addition of corrosion inhibitors to the Poligen™ ES-91009 wax yielded poor protection (specimens C2a-N, C2a-A, C2b-N and C2b-A). The differences with specimens of set 1 (coatings 2a and 2b), where the additives improved the protection properties of the coating, can be explained by the differences in the thickness of the coating: at high thicknesses, the predominant effect is the physical barrier effect, but at low thicknesses, the barrier effect of the coating is lower and its higher permeability to the electrolyte favours the

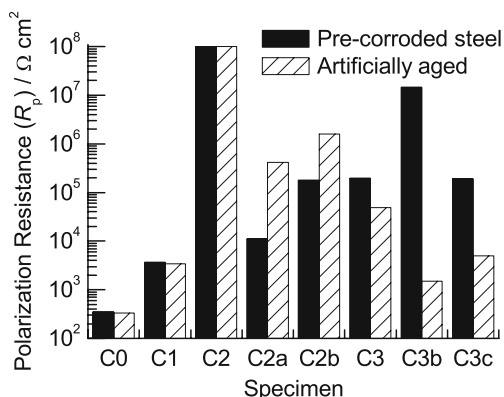


Fig. 9 Polarisation resistance (R_p) measurements of the different specimens (set 2)

solubility of the inhibitor and its transport to the surface of the metal [35].

Paraloid™ B-72 coatings also provide good protection. Although they show lower R_p values than Poligen™ ES-91009, it should be taken into account that, in this set of specimens, the thickness of the Paraloid™ B-72 coatings was much lower than that of the Poligen™ ES-91009 coatings, making a direct comparison between them difficult. For Paraloid™ B-72, corrosion inhibitor additives did not improve the protective properties of the coating. Even though specimens C3b-N and C3c-N show a high R_p compared to specimens C3-N, after artificial ageing, the R_p of the coatings with both corrosion inhibitor additives (C3b-A and C3c-A) is more than one order of magnitude lower than that of the coating without corrosion inhibitor (C3-A).

Figure 10 shows Bode plots obtained using EIS data for the pre-corroded steel specimens with and without organic coatings (set 2) without ageing. EIS spectra have been modelled using the equivalent electrical circuit shown in Fig. 7. The values obtained for the different elements of the circuit are shown in Table 3.

The behaviour of these specimens is very similar to that of set 1. The main difference appears in the sample without coating, where two processes can be observed. In this case, the second process, which does not appear in specimen 0 of set 1, can be attributed to the effect of the corrosion products on localised areas of the surface. The effect of those corrosion products is not visible in the coated samples, where only the response of the coating (R_1 -CPE₁) and the dissolution of the metal (R_2 -CPE₂) can be observed. The EIS response of the corrosion products and inhibitor additives is probably concealed by the other processes.

The best protection according to EIS results is provided by coatings C2 (Poligen™) and C2b (Poligen™+M370), which yield the higher resistance of the coating and very low pseudo-capacitance (in the order of $10^{-10} \text{ F cm}^{-2} \text{ s}^{-(1-a_1)}$), which may be attributed to the high thickness of the layer.

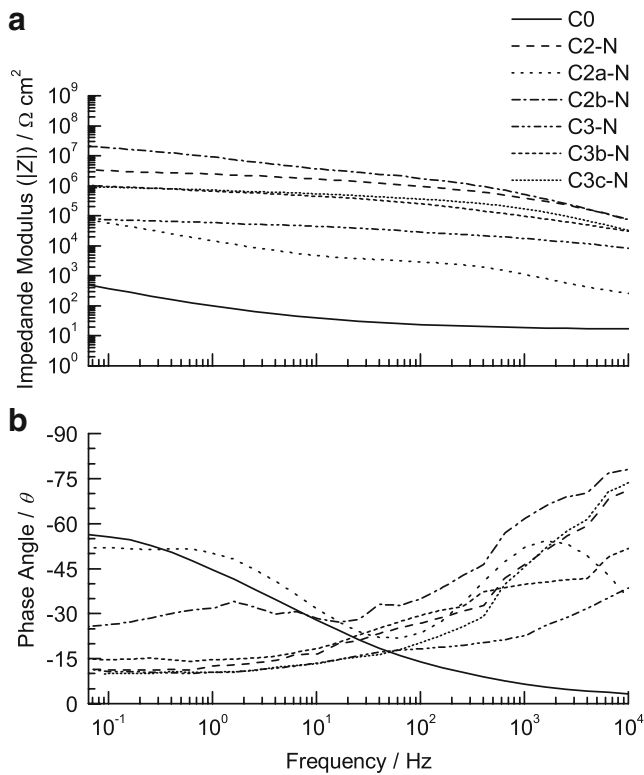


Fig. 10 Bode plots obtained from pre-corroded specimens coated by immersion (set 2) without artificial ageing (**a**, **b**)

The differences in thickness and in the coating application method (brush or immersion) make it difficult in some cases to compare the results between the coatings applied on a clean steel surface (set 1) or a pre-corroded steel surface (set 2). In order to investigate the effect of the application method, few additional measurements (set 3) were made on clean specimens coated by immersion with Renaissance™ wax (specimen X1), Poligen™ ES-91009 (specimen X2) and Paraloid™ B-72 (specimen X3). Table 1 shows, in the last three columns, the average and standard deviation of the thickness of the coatings. Results are very similar to those of set 2, showing that the immersion method produces a thicker layer for Renaissance™ wax and

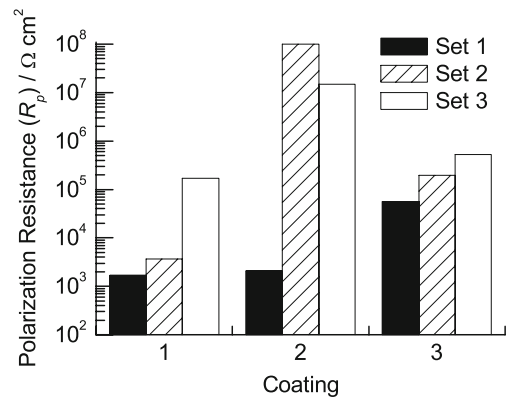


Fig. 11 Polarisation resistance (R_p) measurements of Renaissance™ wax (coating 1), Poligen™ ES-91009 (coating 2) and Paraloid™ B-72 (coating 3) applied in different conditions (sets 1, 2 and 3)

Poligen™ ES-91009, while the thickness is similar regardless of the application method for Paraloid™ B-72.

Figure 11 shows R_p results of the coatings applied by brushing on clean samples (set 1, specimens 1, 2 and 3), by immersion on pre-corroded samples (set 2, specimens C1, C2 and C3) and by immersion on clean samples (set 3, specimens X1, X2 and X3). In the case of Renaissance™ wax, the increase in the coating thickness on the specimens in set 3 produced a significant increase in the resistance of the coating. However, when applied on pre-corroded samples (set 2), it did not lead to a similar increase in R_p values, and only a slight improvement was observed.

Paraloid™ B-72-based coatings have similar thicknesses in the three sets: ~5–10 μm . All these coatings present higher R_p values on specimens coated by immersion (set 2 and Set 3). Since the coating thickness is similar in specimens of all sets, this improvement in protective properties may be attributed to the different application methods. Application by immersion (set 2 and set 3) seems to produce a more uniform layer than application by brushing (set 1), which, in the case of Paraloid™ B-72, produces a non-uniform layer where the brush strokes can be seen, leaving, therefore, weak points where the thickness of the coating is lower.

Table 3 Parameters used for the fitting of EIS data (set 2) using the equivalent electrical circuit of Fig. 7

Specimen	CPE ₁		$R_1 / \Omega \text{ cm}^2$	CPE ₂		$R_2 / \Omega \text{ cm}^2$
	$Y_1 / \text{F cm}^{-2} \text{ s}^{-(1-\alpha_1)}$	α_1		$Y_2 / \text{F cm}^{-2} \text{ s}^{-(1-\alpha_2)}$	α_2	
C0	1.2×10^{-3}	0.67	31	2.2×10^{-3}	0.71	6.0×10^3
C2-N	2.5×10^{-10}	0.96	140×10^3	7.8×10^{-8}	0.37	3.3×10^6
C2a-N	3.5×10^{-7}	0.88	2.7×10^3	2.3×10^{-5}	0.64	930×10^3
C2b-N	4.7×10^{-10}	0.92	1.1×10^6	5.2×10^{-8}	0.42	65×10^6
C3-N	7.3×10^{-8}	0.64	2.0×10^3	1.5×10^{-6}	0.54	31×10^3
C3b-N	1.5×10^{-8}	0.68	100×10^3	7.5×10^{-7}	0.25	2.1×10^6
C3c-N	8.8×10^{-10}	0.94	65×10^3	5.5×10^{-7}	0.23	1.4×10^6

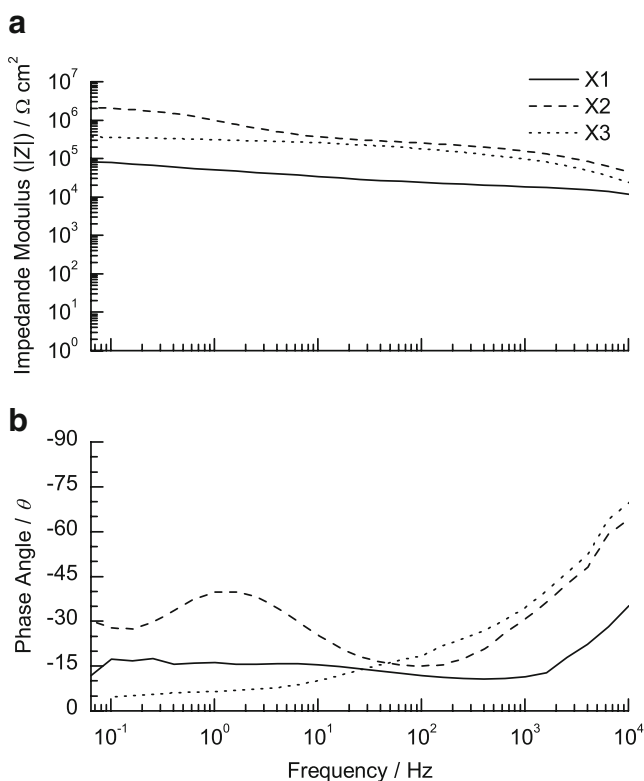


Fig. 12 Bode plots obtained from clean specimens coated by immersion (set 3) (a, b)

In the case of the Poligen™ ES-91009-based coatings, there is a large difference in thickness, and the coatings are much thicker on the specimens coated by immersion (set 2 and set 3). In this case, the increase in thickness produces a three-orders-of-magnitude increase in the protective properties of the coating for the Poligen™ ES-91009 without corrosion inhibitor additives, for both clean and pre-corroded samples. However, in the case of coatings with corrosion inhibitor additives (specimens C2a and C2b), there is no increase in the R_p values with the thickness. This may be explained because, in these cases, the protection afforded by the barrier effect (which increases with the thickness) is not the only protection mechanism. The presence of corrosion inhibitor additives may have two opposing effects: on one hand, they may increase the protective properties of the coating due to their inhibitive effect, but on the other hand, corrosion inhibitor additives

may interact with the coating itself, affecting the cross-linking of the coating [36], or affecting the wetting properties of the binder emulsion with respect to the substrate or the pigments [37, 38]. A detailed study of the effects of the additives on the properties of the coating would require further research that is out of the scope of this paper.

Figure 12 shows Bode plots obtained using EIS data for the specimens of set 3. EIS spectra have been modelled using the equivalent electrical circuit shown in Fig. 7. The values obtained for the different elements of the circuit are shown in Table 4. There is a good agreement between EIS and R_p data, and similar features to the fitting of set 2 EIS data (Table 3) can be observed: CPE_1 values show very low pseudo-capacitances, as can be expected from these thick coatings, and R_1 values are in the range of a few tenths to a few hundred kilo-ohms, slightly higher than those obtained for the pre-corroded samples. As with specimens from set 2, α_2 values are close to 0.5, showing a significant contribution of diffusive effects.

In general, the EIS results agree with results obtained using the R_p technique. The main advantage of the R_p method is that the interpretation of R_p results is usually easier than that of EIS results. However, EIS provides much more in-depth information on the behaviour of the organic coating and the corrosion processes that take place, including mass transport processes.

Conclusions

According to electrochemical tests, the best protection for the steel specimens is afforded by Poligen™ ES-91009 when applied by immersion, producing thick layers ($\sim 40 \mu\text{m}$). When the thickness of the coating is one order of magnitude lower, its protective properties decrease sharply but continue to provide significant protection. The addition of corrosion inhibitor additives did not lead to a clear improvement in protection. Poligen™ ES-91009 is also favoured for its uniform appearance and more natural aspect, which is an important factor to be taken into account for coatings used in conservation–restoration treatments.

The worst protection is provided by Renaissance™, which only increased the R_p and impedance values of the

Table 4 Parameters used for the fitting of EIS data (Set 3) using the equivalent electrical circuit of Fig. 7

Specimen	CPE_1		$R_1/\Omega \text{ cm}^2$	CPE_2		$R_2/\Omega \text{ cm}^2$
	$Y_1/\text{F cm}^{-2} \text{ s}^{-(1-\alpha_1)}$	α_1		$Y_2/\text{F cm}^{-2} \text{ s}^{-(1-\alpha_2)}$	α_2	
X1	4.7×10^{-9}	0.85	17×10^3	8.2×10^{-6}	0.45	85×10^3
X2	2.3×10^{-9}	0.83	200×10^3	3.0×10^{-7}	0.66	3×10^6
X3	1.2×10^{-9}	0.92	67×10^3	3.3×10^{-7}	0.50	250×10^3

specimens by a very small amount when applied by immersion with a thickness of $\sim 10 \mu\text{m}$. When applied in a very thin layer ($\sim 1 \mu\text{m}$) on the clean specimens, no protection was provided.

The performance of Paraloid™ B-72 fell in between that of the Poligen™ ES-91009 and Renaissance™ coatings. However, its appearance was the worst (it has a more “plastic-like” aspect than Poligen™ ES-91009). The addition of M109 and Alkaterge-T corrosion inhibitor additives to Paraloid™ B-72 produced an initial increase in the protective properties of the coatings but, after artificial ageing, the behaviours of the coatings were worse than the Paraloid™ B-72 without corrosion inhibitor additives. The addition of M435 corrosion inhibitor sharply decreased the protection of the coating, yielding R_p and EIS values similar to those of uncoated steel. When applied by immersion, the coating is more uniform and the protection attained is better than when applied by brushing.

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