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EVALUATION OF NEW COATINGS FOR THE PROTECTION OF ORNAMENTAL CAST IRONWORK EXPOSED IN UNCONTROLLED ENVIRONMENT

Mai Mohamed RIFAI[1*], Zeinab ABDEL HAMID[2],
Saleh Mohamed SALEH[3], Mohamed Mohamed ABDELBAR[3]

[1]Conservation Department, Faculty of Archaeology, Cairo University, Egypt
[2]Central Metallurgical Research and Development Institute, Cairo, Egypt
[3] Conservation Department, Faculty of Archaeology, Fayoum University, Egypt

Abstract

Ironworks constitute a great part of the world cultural heritage of metallic objects. Amongst these only a small part are on display in controlled environments. The rest is often exposed to uncontrolled atmospheres, high humidity and fluctuating temperatures and are usually heavily corroded. The aim of this study is to evaluate the efficiency of organic coating materials and corrosion inhibitors to protect ornamental cast ironwork from corrosion in uncontrolled environment using electrochemical techniques (Potentiodynamic polarization Tafel lines and electrochemical impedance (EIS)) and one year of exposure inside the clock tower of Muhammed Ali's mosque in Salah El-Din Citadel in Cairo (natural ageing). Grey cast iron coupons were prepared to simulate the composition and morphology of the historic cast iron staircase, and treated with different protection systems. Four organic coatings have been studied; a methyl acrylate / ethyl methacrylate copolymer resin (Paraloid™ B-72) dissolved in acetone, an ethylene copolymer wax (Poligen® CE 9), Permalac (N-Butyl acetate-14.0) and Permalac EF (N-Butyl acetate-14.0). The last two have not been commonly used in conservation and restoration treatments. Two corrosion inhibitors have been studied; tannic acid and tannic acid mixed with phosphoric acid. The results indicated that the best protection of cast iron coupons was afforded by Permalac, which protects cast iron from corrosion and the effect of UV. Finally, Permalac was applied on the staircase inside the clock tower of Muhammed Ali's mosque.

Keywords: *Ornamental Cast Ironworks; Corrosion; Conservation; Protection*

Introduction

Ornamental ironwork exposed to the atmosphere represents a considerable conservation problem in terms of protection due to the size and variety of the ancient and historic iron artefacts that require treatment and maintenance [1]. These ironworks constitute a vast number of architectural metal fittings such as paneled doors, window grilles, metal bands, chapels, veils, doorknockers, crescents and chains. In Egypt, iron was extensively used during the reign of Muhammed Ali's Family (1802-1952 AD) for manufacturing architectural metal fittings. Therefore ornamental ironworks became commonplace in the buildings of this period, especially in the royal palaces. In the late eighteenth and early nineteenth centuries, cast iron was increasingly incorporated into ornamental ironwork [2]. Gray cast iron has become a

* Corresponding author: mairifai@hotmail.com

popular cast metal material which is widely applied in modern industrial production, because of its low cost (20–40% less than steel), and wide range of desirable/ achievable mechanical properties such as good castability, convenient machining property and better wear resistance [3]. Common problems encountered today with cast-iron construction include badly rusted or missing elements, impact damage, structural failures, broken joints, damage to connections, and loss of anchorage in masonry.

The susceptibility of cast iron to corrosion is unlike that of steel. Alloying elements can play a dominant role in the susceptibility of cast irons to corrosion attack. The corrosion of cast iron involves thinning, pitting, and graphitic corrosion [4]. Cast iron thinning and pitting occurs in much the same way as in steel, with metal lost to the solution. Graphitic corrosion is unique to cast iron and involves the selective leaching of iron components from the iron-graphite matrix of which cast iron is composed. A matrix of graphite flakes is left, and has a significantly lower structural strength than the original metal. Typically the matrix of graphite flakes is held together by the iron oxide corrosion products, and it may retain the un-corroded shape of the original metal. This graphite-iron oxide structure is commonly referred to as the 'graphitised zone'. These corrosion products are very dense, adherent, strength, and form a barrier against further corrosion [5]. Oxidation, or rusting, occurs rapidly when cast iron is exposed to moisture and air. The minimum relative humidity necessary to promote rusting is 65%, but it can be lower in the presence of corrosive agents, such as seawater, salt air, acids, acid precipitation, soils, and some sulfur compounds present in the atmosphere, which act as catalysts in the oxidation process [6-9]. Rusting is accelerated in situations where architectural details provide pockets or crevices to trap and hold liquid corrosive agents. Furthermore, once a rust film forms, its porous surface acts as a reservoir for liquids, which in turn causes further corrosion. If this process is not arrested, it will continue until the iron is entirely consumed by corrosion, leaving nothing but rust.

Historic exterior ironwork need to be preserved in their present physical condition, to respect their original appearance or the appearance they have acquired during their exposure outdoors, as far as practicable. The main function of coatings for exterior ironwork is protective rather than decorative. Science has been harnessed to develop modern coatings that are both extremely effective in protecting new metal surfaces and are long-lasting. However, as with cleaning, there is a now a need for a reappraisal of the appropriateness of these coatings for historic exterior ironwork. So, the aim of this study is to evaluate the efficiency of organic coatings and corrosion inhibitors to protect ornamental cast ironwork from corrosion in uncontrolled environment using electrochemical techniques (Tafel Polarization curve and EIS) and one year of exposure inside the clock tower of Muhammed Ali's mosque in Salah El-Din Citadel in Cairo (natural ageing).

Experimental

Materials and Methods

The cast iron coupons (10x15x2.5mm) were used in this work. Elemental analysis of the ornamental cast staircase was carried out by carbon /sulfur analyzer in conjunction with inductively coupled plasma (ICP), indicated that it is manufactured from cast iron alloy with a carbon content (3.514 wt.%), besides carbon, containing some additional alloying elements like silicon (2.95 wt.%), phosphorus (0.94 wt.%), manganese (0.96 wt.%) and sulphur (0.073 wt.%) [10]. The chemical compositions (% atom) of the cast iron coupons from which were manufactured similar to the ornamental cast staircase under study, is: C 3.57, Si 1.81, Mn 0.498, P 0.268, S 0.226, Ni 0.0410, Cr 0.0365, V 0.0285, Cu 0.0225, Mo 0.0188, Fe 93.64. To avoid initial testing of the different protection systems on real objects, it was necessary to manufacture pre-corroded metal coupons simulating real object, which could be used all along our experimental work [11]. The cast iron coupons cut with a dimension 10x15x2.5mm and numbered (stamped with punches).

Four organic coatings have been studied; a methyl acrylate/ethyl methacrylate copolymer resin (Paraloid™ B-72) dissolved in acetone, an ethylene copolymer wax (Poligen® CE 9), Permalac (N-Butyl acetate-14.0) and Permalac EF (N-Butyl acetate-14.0). Two corrosion inhibitors have been studied; tannic acid and tannic acid mixed with phosphoric acid.

Permalac (N-Butyl acetate-14.0): is a glossy, crystal clear, durable, air-drying coating that was initially formulated for application on both exterior and interior cast iron [12].

Permalac EF (N-Butyl acetate-14.0)**:** This provides all the UV and abrasion resistance provided by Permalac but contains only 170 grams of VOCs per liter. As this product dries to the touch quickly, it can be re-coated in 30 minutes. After the final coating of Permalac EF has been applied, the finish will fully cure in two hours or less [12].

Poligen CE 9: a Synthetic polyethylene wax is a ready-to-use liquid (ethylene in water) wax. The coating is safe and easy to use since it is applied as a liquid (no solvent is required), and dries within 24 hours [13-15].

Acrylic resin Paraloid B72: a methyl acrylate/ethyl methacrylate copolymer resin, dissolved in acetone, was applied by brush at room temperature and left to dry for 16-24h. It is the most popular protective coating for archaeological or historical copper, iron, silver, and gold alloys in the Mediterranean basin [16].

Tannic acid ($C_{76}H_{52}O_{46}$): is a specific commercial form of tannic, a type of polyphenol. Solutions of tannic acid stronger than 10 percent are much too concentrated and recommends that several coats of diluted 2-10 percent solution of tannic acid is effective; (with the addition, if necessary, of sufficient concentrated phosphoric acid H_3PO_4 to achieve a pH of at least 2.4) be brushed on the object. Regardless of whether tannic or phosphoric acid is used, it is highly recommended that a sealant, such as microcrystalline wax, be applied over the film formed on the object, The wax will provide a vapor barrier, which the film does not, and will also contribute some strength to corrosion layers on the metal [17].

Electrochemical Measurements

Potentiodynamic polarization Tafel lines

The corrosion study was carried out using anodic and cathodic Tafel lines. The electrochemical measurements were performed using IviumStat instrument (supplied by Ivium Technologies, Eindhoven, the Netherlands). The IviumSoft software (Netherlands) can be used to control IviumStat instrument, by means of a personal computer (PC). The personal computer (PC) is used to specify the parameters of the measurement, to display the measured curves and to calculate the results of the measurements. The software allows the calculation of the Corrosion Current I_{corr} and Tafel slopes automatically or manually depending on the shape of the Tafel lines. For the manual mode, the operator has to set the suitable potential markers to determine the most linear straight lines in the anodic as well as in the cathodic part. On the other hand, in the automatic mode, the software will set the potential range markers for each, and the model analysis usually gives the most reliable result. In all cases, we tried both the automatic and the manual modes to determine the linear parts in order to obtain the most reliable values of Icorr. The electrochemical measurements were performed on rectangular specimens as working electrodes; each has an apparent surface area of 1.0 cm^2. The reference electrode that all potentials are referred was $Hg/Hg_2Cl_2/Cl^-$ saturated calomel electrode (SCE) of E^o = 240mV versus reference hydrogen electrode (RHE) and the auxiliary electrode was a platinum sheet. The electrolytes used were 0.6M NaCl solution prepared using triply distilled water. The polarization was started from the cathodic part and then the anodic part; first, the electrode was put in the test solution until the open circuit potential was reached (E_{corr}) [18-20]. The polarization was started from this point down to -500mV in the cathodic direction, and then, the polarization was reversed from the open circuit potential up to +500 mV in the anodic direction. The corrosion current (I_{corr}) was calculated from the intersection of the linear parts of the anodic and cathodic lines at zero polarization. All experiments were carried out in 3.5 % NaCl solutions at room temperature of 25 ± 1 °C.

Electrochemical impedance spectroscopy (EIS)

EIS measurements were also carried out at the OCPs (open circuit potentials) by applying a 10-mV sinusoidal potential through a frequency domain from 35 kHz down to 100 mHz. All experiments were carried out in 3.5 % NaCl solutions at room temperature (25 ± 1 °C). The inhibition efficiency is calculated from the EIS data using the following equation:

$$I_{EIS}(\%) = [(R_p - R_0)/R_p] \times 100 \quad (1)$$

where R_p and R_0 are the polarization resistances of the samples with and without organic coating, respectively.

Artificial Ageing Methods

The artificial ageing of the metal analogues aimed at reproducing the corrosion layers found on historic objects. Cast iron coupons were hanged in desiccators, exposed to: 24h at 30 °C/100% RH; + 24h at 25 °C/50-60% RH; + 24h at 30 °C/100%RH) [11, 13, 21, 22]. Then cast iron coupons were exposed to the solution containing 1.6 mol $FeCl_2.4H_2O$ and 0.4 mol NaOH and were hanged in desiccators [23]. The artificially aged coupons were further cleaned mechanically by scalpels and fine sand papers, so as to reproduce fully the surface of real ironworks ready for application of protection systems (coatings and corrosion inhibitors) [14]. Final preparation of the cast iron coupons, cotton swab moisture with ethanol rolled lightly over the surface to collect the powdery and non adherent corrosion products.

Coating Preparation and Application

All coatings were applied by brush, as this method is the most appropriate for application on the staircase under study. Table 1 shows the conditions of application of the selected protection systems. During application, the coupons were placed with an inclination of 20 degrees to the vertical in a beaker (with silica gel) and were totally covered by the coating materials. The beaker was covered with a glass dish, in order to minimize evaporation of the solvent. All handling was performed with clean talc free gloves and tongs.

Table 1. The conditions of application of the selected protection systems.

Protection System	Protection System type	Chemical Composition	Composition	Conditions of application
Permalac	Coating	(N-Butyl acetate-14.0)	Used as supplied ready to use to obtain a level and smooth seal	Three layers were applied with a paint-brush: two applications one criss and one cross. Drying time: less than 5 minutes
Permalac EF	Coating	(N-Butyl acetate-14.0)	Same as above	Same as above.
Poligen CE 9	Coating	an ethylene copolymer wax	Used as supplied	Three layers were applied with a paint-brush in a criss-cross manner. Setting time: 2-3h depending on the atmospheric conditions.
Tannic acid 5%	CI	$(C_{76}H_{52}O_{46})$	5 percent tannic solution (50 g tannic, 1 liter water, 150 ml. ethanol)	Four layers were applied by brush in 24 hours intervals
Tannic acid mixed with phosphoric acid	CI	$(C_{76}H_{52}O_{46})$ + (H_3PO4)	100 g tannic + 900 ml. deionized water + 50 ml. ethanol + 2 ml. dilute phosphoric acid	Four layers were applied by brush in 24 hours intervals
Tannic acid 5% + Paraloid™ B-72 3% in acetone	CI + Coating	a methyl acrylate/ethyl methacrylate copolymer resin (Paraloid™ B-72)	same as above followed by Paraloid ™ B-72 3% in acetone	Four layers of tannic acid 5% were applied by brush in 24 hours intervals, followed by two layers of paraloid B72 3% in acetone were applied by brush
Tannic acid mixed with phosphoric acid + B 72 3% in acetone	CI + Coating	Same as above.	same as above followed by Paraloid ™ B-72 3% in acetone	Four layers of tannic acid mixed with phosphoric acid were applied by brush in 24 hours intervals, followed by two layers of parloid B723% in acetone were applied by brush

After application, the coupons were placed horizontally in order to ensure even film formation. To create aeration on the back side of the coupon, each coupon was placed on two small ceramic bases, to minimize the contact point, and was left to dry [13].

Long-Term Testing

The objective of the Long-term testing was to assess further the most effective coatings and corrosion inhibitors from the electrochemical testing [11]. The cast iron coupons (70 x50x2.5mm), once manufactured, were numbered (stamped with punches) as shown in Fig. 1.

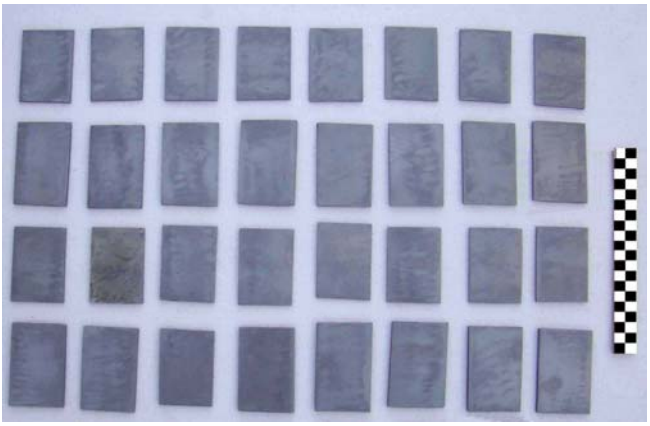


Fig.1. The cast iron coupons after the final preparation.

The protection systems were applied to clean bar metal substrates and all the preparation methodology before coating application was done as shown in Figure 2. The rack with the whole cast iron coupons were exposed inside the clock tower of Muhammed Ali's mosque in Salah El-Din Citadel in Cairo for one year as shown in Figure 3. The corrosion progress was followed along the exposure period, but more specifically once every two months, by visual examination, colour measurements and weighting (once a month). In addition, relative humidity (RH) and temperature (T) were recorded along the exposure period using data logger.

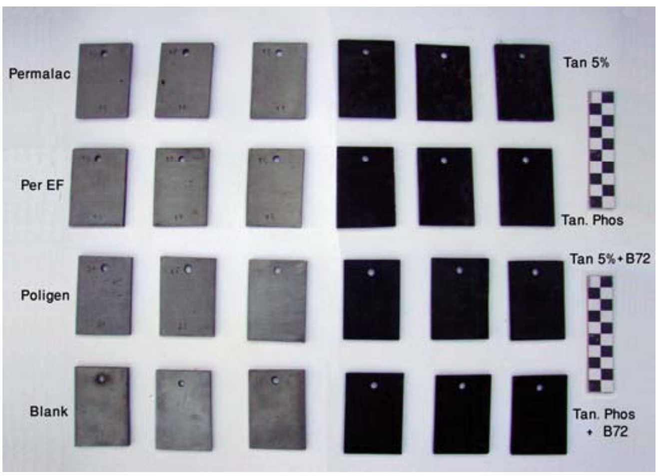


Fig. 2. The cast iron coupons after applied the protection systems.

Fig. 3. The rack with the whole cast iron coupons were exposed inside the clock tower of Muhammed Ali's mosque in Salah El-Din Citadel in Cairo.

Color Measurements were performed by Macbeth color eye 7000 (U.S.A.) UV Spectrophotometer. On each coupon, three measurements were performed on the same test spot of 5×7cm coupons, evenly distributed on the samples surface. Color changes data of the samples were calculated according to the CIE L*a*b* color space. The L* scale measures lightness, and varies from 0 (black) to 100 (perfect white). The a*-scale measures red-green component; +a means more red, -a means green. The b*- scale measures yellow-blue component; +b meaning more yellow, -b more blue. In the CIE L*a*b* system, which has the properties of an Euclidean space, the distance between any two-color points represents their color difference (ΔE*) and it is calculated from the differences of its component ΔL*, Δa*, and Δb* [24]:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (2)$$

Results and Discussion

Electrochemical Measurements

Potentiodynamic polarization Tafel lines

The corrosion resistance of cast iron (metallic cultural heritage) uncoated and coated with different organic coatings or inhibitors was investigated using potentiodynamic polarization Tafel lines and EIS measurements in 0.6M NaCl. The experiments were carried out in aerated solutions at 25 °C after the OCP (open circuit potential) value is reached. Figures 4 and 5 show Tafel lines for uncoated cast iron compared with cast iron coated with different organic coatings and for uncoated cast iron compared with cast iron coated with different inhibitors in 0.6M NaCl, respectively. From Figure 4, it is clear that the polarization Tafel lines for cast iron electrodes coated with Permalac or Permalac EF shift toward less corrosion current density values and its corrosion potentials get less negative compared to uncoated cast iron.

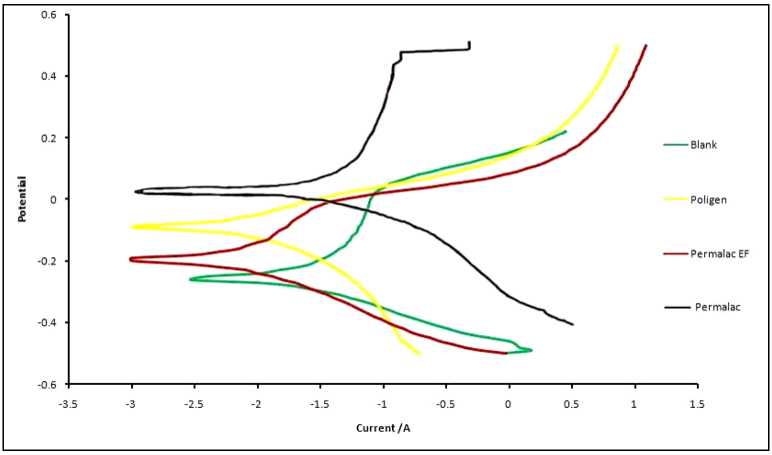


Fig. 4. Polarization curves of cast iron samples treated with different coatings compared with untreated sample.

Cast iron electrodes coated with Poligen® CE 9 have a slightly high corrosion current density compared with uncoated cast iron. This means that Poligen® CE 9 increased the corrosion rate more than the unprotected coupon; this may have resulted due to applying it on pre-corroded surface. The electrochemical corrosion parameters derived from these Tafel lines are summarized in Table 2, it illustrates a lower corrosion current and corrosion rate of the cast iron coated with Permalac or Permalac EF. This behavior is observed for passive materials, it indicates that the corrosion rate decreases with these organic coatings. From Figure 5, it is clear that, the corrosion rate of cast iron coated with different inhibitors decreases compared with uncoated cast iron, as represented in Table 2.

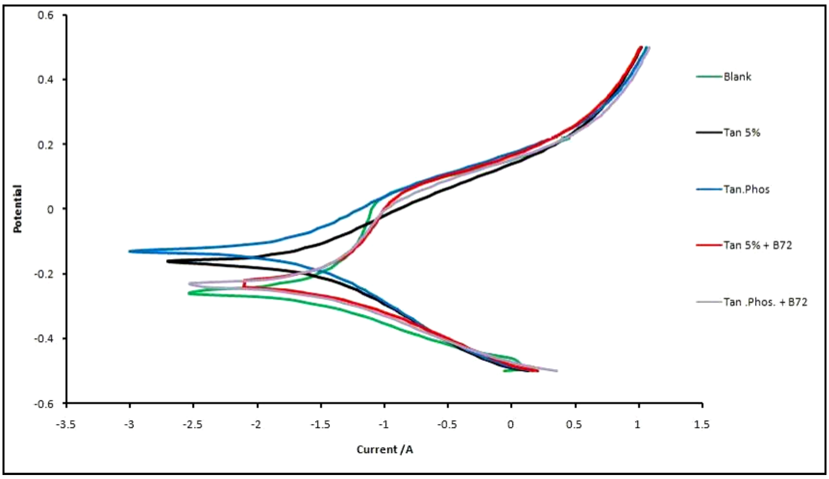


Fig. 5. Polarization curves of cast iron samples treated with different inhibitors compared with untreated sample.

As we can see, the best corrosion resistance (0.5429 mm/y) was observed with Tannic acid mixed with phosphoric acid followed by the layer of paraloid B 72 3% in acetone. Table 3 illustrates the protection degree (%) of the selected protection, by polarization resistance measurements.

Table 2. Electrochemical parameters derived from Tafel lines for the protected and unprotected cast iron coupons at 1mV s^{-1} in 0.6M NaCl at 25 °C.

Specimens type	E_{corr} (V)	I_{corr} (A/cm^2)	R_p (Ohm)	C. Rate (mm/y)
Blank	-0.2958	3.326E-5	1249	2.024
Permalac	-0.0459	1.865E-6	6.108E4	0.1135
Permalac EF	-0.1045	7.762E-6	5301	0.4724
Poligen® CE 9	-0.2311	4.883E-5	1519	2.972
Tannic acid 5%	-0.1712	3.004E-5	1589	1.828
Tannic acid mixed with phosphoric acid	-0.1076	1.775E-5	2394	1.08
Tannic acid 5% + B-72 3% in acetone	-0.1072	1.281E-5	4191	0.7796
Tannic acid mixed with phos. acid + B 72 3% in acetone	-0.1655	6.92E-6	3847	0.5429

Table 3. The protection degree (%) of the selected protection systems, by Tafel electrochemical measurements.

Tan 5%	Tan. Phos	Tan. Phos + B72	Tan 5% + B72	Permalac	Per EF	Poligen
19.60 %	46.64 %	73.17 %	61.48 %	99.43 %	76.66 %	- 46.83 %

Electrochemical impedance spectroscopy

While electrochemical techniques have a long tradition in conservation-restoration treatments for metallic cultural heritage, the evaluation of protective coatings using electrochemical impedance spectroscopy (EIS) has only been used very recently. EIS is a very well established method to investigate metal coatings for general purposes, and has many advantages that make it especially suitable for testing coatings for metallic works of art [25].

Electrochemical impedance measurements of uncoated and coated cast iron electrodes were performed in 0.6M NaCl solution. Analysis of the experimental EIS spectra was made by the best fitting led to the corresponding equivalent circuit model $R_s(R_pCp)$ for samples in 0.6M NaCl. The Nyquist plots of these investigated samples are shown in Figure 6 (a and b). From Figure 6a, it can be seen that in the absence of coating R_s, which represents the ohmic resistance between the working electrode and the reference electrode, and R_p, which represents the polarization resistance related to the corrosion reaction at open circuit potential, are very low. This Nyquist plot do not yield perfect semicircle as expected from the theory of EIS, this indicates that the corrosion process occurs under diffusion control.

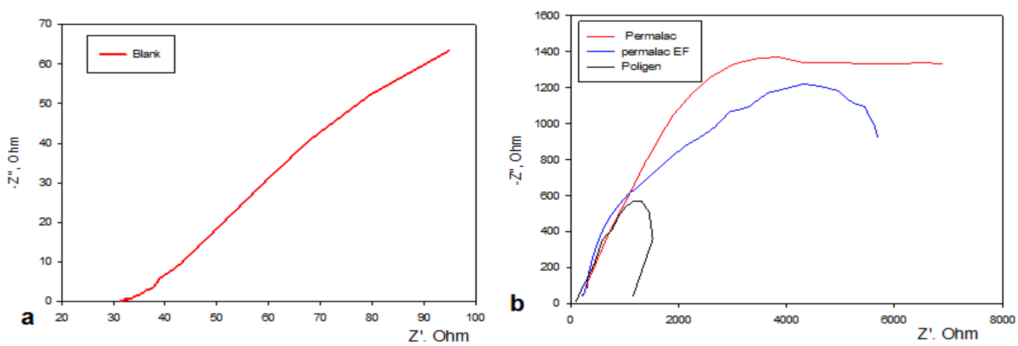


Fig. 6. Electrochemical impedance spectroscopy (EIS) of: **a)** uncoated cast iron, **b)** cast iron coated with Permalac, Permalac EF and poligen at open circuit potential at 25 °C.

From this obtained data, it is clear that the corrosion rate of uncoated cast iron is very high in 0.6M NaCl solution. On the other hand, the polarization resistance values (R_p) calculated from EIS data in Figure 6b and Table 4 increased as the organic coating covered the electrodes, and the highest corrosion resistance value was recorded for cast iron coated with Permalac (5308 Ohm cm^{-1}). The EIS as Nyquist plots displays arcs shape, and its diameters are increasing with the increase of polarization resistance. The most pronounced effect was observed in presence of Permalac organic coatings. The order of inhibition obtained using R_p values is Permalac> Permalac EF> Poligen.

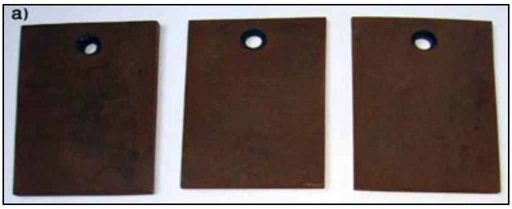
Table 4. Electrochemical impedance spectroscopic data (EIS) for cast iron uncoated and coated samples in 0.6M NaCl at 25 °C.

Sample	R_s, Ohm cm^{-2}	R_p Ohm cm^{-2}	C_{dl}, μFcm^{-2}	n	IE %
Blank	36.54	110.4	1.094 x10^5	0.986	----
Permalace	1019	5308	7.22	0.976	97.92
Permalac EF	304	1565	703.4	0.979	92.94
Poligen	208.8	1202	181.3	0.979	90.1

Long Term-Testing

Digital Photography

Digital photographs recorded the monitoring of coupons after various times (once a month) of exposure to atmospheric corrosion, as shown in Figure 7.

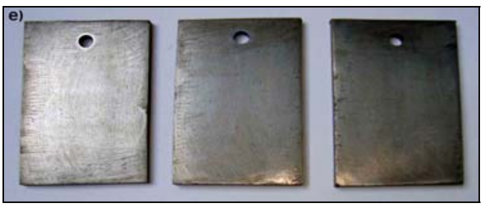


a) Tannic acid 5%

b) Tan. Phos.

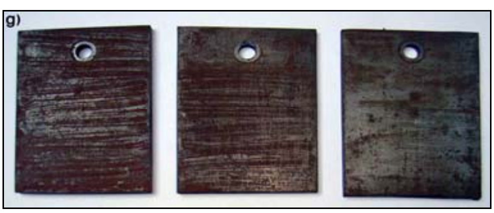
c) Tannic acid 5% + B72

d) Tan. Phos. + B72



e) Permalac

f) Permalac EF



g) Poligen

h) Blank

Fig. 7(a- h). Macrographs show assessment of the behavior of the protection systems after eight months of exposure.

The criteria for the characterization of surfaces using visual examination included evaluation of blisters, active corrosion on the surface and visually recognizable faults and changes. Preliminary visual examination showed that Permalac offered the best protection after 8 months of exposure in atmospheric conditions. In addition, tannic acid mixed with phosphoric acid and followed by paraloid B72 gave quite satisfactory result. While tannic acid followed by paraloid B72, tannic acid mixed with phosphoric acid, tannic acid alone and poligen respectively, were unstable and showed clear evidence of failure as coating material.

Weight Loss Measurements

After 12 months of exposure, the test specimens were removed and weighed once a month. After eight months of exposure, the protection degree (%) of the selected protection systems was measured as given in Table 5. and Figure 8. The results proved that permalac and permalac EF gave the best result. In addition, tannic acid mixed with phosphoric acid and followed by a layer of paraloid B72 gave quite satisfactory result.

Table 5. The protection degree (%) of the selected protection systems after eight months of exposure, calculated by weight loss measurements

Tan 5%	Tan. Phos	Tan. Phos + B72	Tan 5% + B72	Permalac	Per EF	Poligen
8.89 %	40.45 %	72.16 %	63.57 %	98.76 %	96.57 %	62.41 %

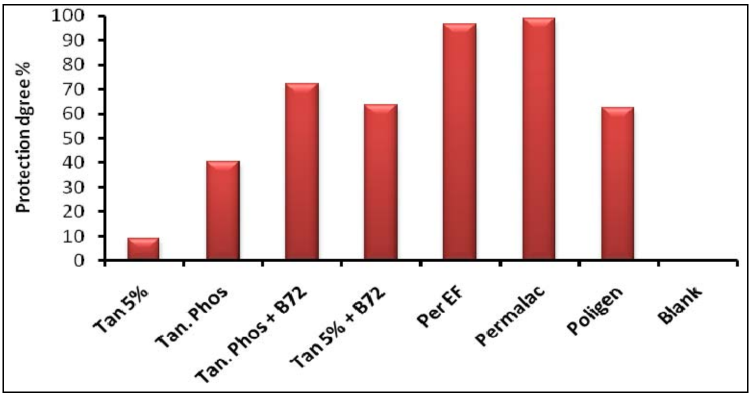


Fig.8. The protection degree (%) of the selected protection systems after eight months of exposure.

Colour Measurements

The color alteration of the selected protection systems recorded on the coupons during the exposure period. The results proved that permalac and permalac EF give the best result, Also tannic acid or tannic acid mixed with phosphoric acid and followed by a layer of paraloid B72 gave quite satisfactory result, as shown in Table 6.

Table 6. The color changes observed on the coupons during the exposure period.

Samples	ΔE None	ΔE after two months	ΔE after four Months	ΔE after six Months	ΔE after eight Months
Blank	0.0	27.36	27.19	28.39	29.09
Tan 5%	0.0	22.49	25.44	25.38	25.09
Tannic acid mixed with phosphoric acid	0.0	10.64	17.15	17.99	20.25
Tan 5%+ B 72	0.0	6.67	11.17	15.18	14.72
Tannic acid mixed with phosphoric acid + B 72	0.0	6.20	9.23	9.80	10.74
Permalac	0.0	1.04	3.14	3.22	4.65
Permalac EF	0.0	2.84	4.05	3.86	5.48
Poligen	0.0	5.15	9.10	14.76	22.41

Environmental Monitoring - RH and Temperature

Datalogger was installed next to the rack and T and RH were monitored during the whole exposure period. Figure 9 (a, b and c) presents the corresponding graph.

(a)

(b)

(c)

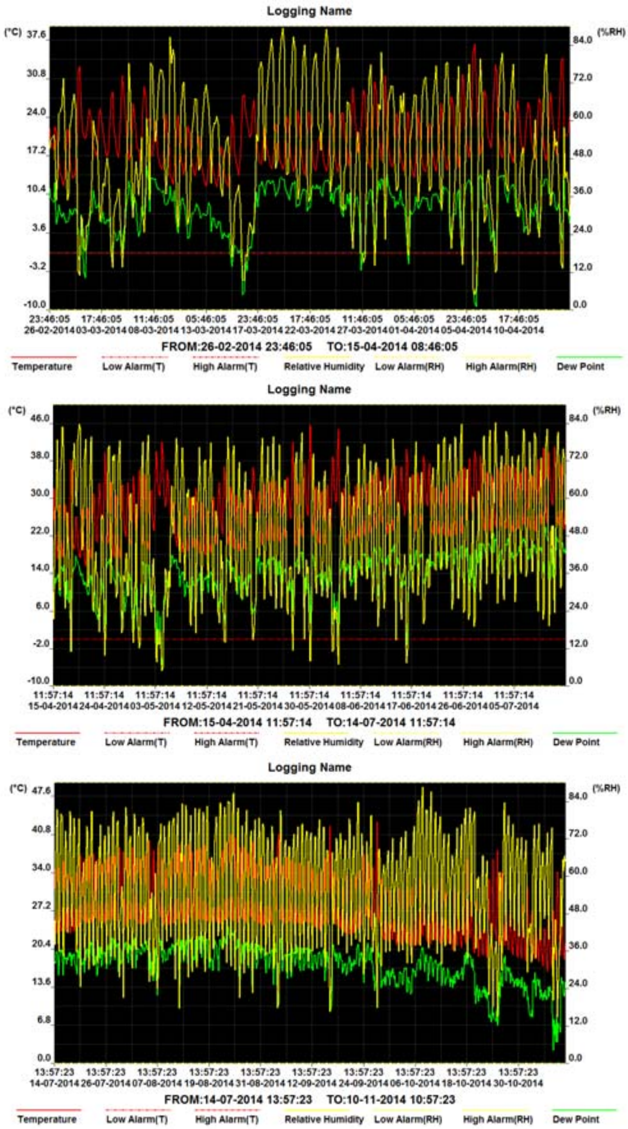


Fig. 9. (a, b, c) : T and RH measurements during the first eight months of the exposure period.

Complementary results to those obtained during electrochemical testing were obtained by long-term testing on the different protection systems used. Visual examination of the unprotected coupons shows that, new localized corrosion developed during the first month (end of the winter period). New overall corrosion developed between three and six months (spring time) as shown in Figure 7. During that period, the indoor RH level increased, as shown in Figure 9 (a-b-c).

The results obtained by visual examination, color measurements and weight lose after 8 months of exposure in atmospheric conditions, proved that permalac gave the best result. After this period, a small area of localized corrosion products was observed firstly at the edge of the coupons coated with permalac and permalac EF (edge effect) [11]. Whereas those coated with the poligen show localized corrosion all over the coupons. Although poligen increased the corrosion rate in electrochemical testing, but it behaved well in long term-testing, this may be due to its application on a bar metal surface.

Tannic acid 5% did not offer any protection, beyond three months the corrosion products developed much faster and covered the entire surface of the coupons. Tannic acid mixed with phosphoric acid is better than tannic acid alone, this is due to the addition of sufficient concentrated phosphoric acid H_3PO_4 and achieving a pH of at least 2.4 [26]. Applied a layer of paraloid B72 over tannic acid or tannic acid mixed with phosphoric acid gave quite satisfactory result. Poligen isn't good for ornamental cast ironwork exposed outdoors in uncontrolled environment, after three months of exposure, the corrosion products progressed slower (patchy areas) [11]. The results show that both permalac and permalac EF offered significant protection against atmospheric corrosion. The role of dust particles seemed to accelerate the corrosion progress on the unprotected coupons and the Tannic acid solution.

Conclusions

Electrochemical techniques (Rp and EIS) are a very well established method to investigate metal coatings for metallic works of art. Visual and colorimetric evaluation allowed choosing the protective coatings with minor aesthetic impact for the cleaned surface.

Permalac was certainly the most interesting protection system tested by this study, for the protection of cast ironworks. It gave sufficient protection during long term testing and thus confirmed the good results of the electrochemical testing. The protection of tannic acid is less effective than tannic acid mixed with phosphoric acid, Tannic acid mixed with phosphoric acid and followed by Paraloid B72 gave quite satisfactory result. Poligen is not an option for ornamental cast ironworks exposed outdoors in uncontrolled environments; since the corrosion resistance offered by this innovative coating isn't good like permalac.

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