Development of new non-toxic corrosion inhibitors for cultural property made of iron and copper alloys

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Metal cultural heritage objects are often stored or displayed in uncontrolled environmental conditions, suffering from indoor atmospheric corrosion leading to their increased corrosion. A protection treatment could be used to insulate them from this corrosive environment. However, such a treatment must be reversible, and not affect the aesthetic appearance of the object. Corrosion inhibitors could fill these particular conditions. Within the framework of the European project PROMET, new protection solutions based on long chain carboxylic acids were investigated. These solutions are known to have good inhibition properties on many metals. Moreover, they are environmentally friendly, cheap, easy-to-use, and reversible. These inhibitors were tested on iron and copper coupons prepared within the project. Electrochemical measurements were carried out to evaluate the performances of the corrosion inhibitor solutions against aqueous corrosion, as well as the behaviour of protected iron and copper samples in a corrosive electrolyte. Artificial aging in climatic chamber proved the good performances of the treatments against atmospheric corrosion. Surface characterisation of treated samples by X-ray diffraction and Raman spectroscopy proved that the inhibitive effect is due to the formation of a thin hydrophobic film of metallic carboxylate on the metal surface.

Keywords: carboxylic acid, copper, corrosion inhibitors, electrochemical measurements, iron

1. INTRODUCTION

In many cases, metal cultural heritage objects are stored or displayed in uncontrolled environmental conditions. In theory, objects could be packed, using a microclimate to control their conditions. However, lots of objects are in open display in museums, where the environmental conditions cannot be controlled, such as the Royal Armoury collection (Valletta, Malta) or all the objects on display in the Egyptian museum. Due to ambient temperature and humidity fluctuations, these objects are exposed to cyclic wet and dry periods and suffer indoor atmospheric corrosion. Thus, the corrosion process occurs and leads to their degradation.

To avoid it, the development of new protection treatments must be promoted. This research is also motivated by large request of curators responsible for metallic collections, who try to avoid systematic and expensive restoration works. These protection treatments must respect the conservation rules in law in the cultural heritage domain. They should be applied without significant modification of the surface aspect and be easily removable. Soft treatments like application of corrosion inhibitors could satisfy those two conditions. Moreover, the protection systems which are currently being used can lead to some problems. For example, an uneven film can cause further damage to the objects. The use of corrosion inhibitors as a method of protecting the surface is preferred since such problems cannot occur.

Previous work have shown that saturated linear carbon carboxylates of sodium of general formula $CH_3(CH_2)_{n-2}COONa$ with $7 \le n \le 11$, noted NaC_n , have good inhibitor properties on many metals [1, 2, 3, 4, 5]. They are nowadays used in industry as temporary protection for the storage or transport of metallic pieces. The aim of this work is to determine the best conditions to use these new non-toxic inhibitors in the context of the protection of metallic artefacts.

This work is realised within the framework of the European project named "PROMET" with the goal to define a way to ensure the long-term protection of metal artefacts by using environmentally friendly corrosion inhibitors.

The efficiency of this inhibitor family was evaluated for the protection of iron and copper based artefacts. Different surface treatments have been studied. Their performances have been evaluated by electrochemical measurements. Surface characterisation of treated samples has also been carried out in order to improve our knowledge on the passivation mechanism. Development of new non-toxic corrosion inhibitors for cultural property made of iron and copper alloys

2. EXPERIMENTAL

Experiments have been carried out on iron and copper coupons, which have been pre-corroded within the project PROMET. The purpose was to get reproducible coupons, artificially corroded using accelerated ageing.



Figure 1 - iron (a) and copper-based (b) PROMET coupons

Iron coupons were artificially corroded inside an accelerated corrosion chamber. Conditions are given in Table 1. Coupon cleaning was performed thanks to cotton tipped bamboo skewers moistened with ethanol, and then a rotating natural fibre brush, in order to remove the non-adherent orange corrosion products from the surface.

Time	Temp. (°C)	Relative humidity	
		(%)	
24 h	30	100	
24 h	25-30	50-60	
24 h	30	100	

Table 1- Accelerated corrosion protocol for iron

Artificial patination of copper was carried out by applying an aqueous solution of $Cu(NO_3)_2(80 \text{ g}) + NH_4OH(3 \text{ ml})$ by brush twice a day for 3 days and then by immersion twice a day for 2 days. The accelerated conditions are given in Table 2. The samples were exposed for two 24 hours cycles.

Time	Temp. (°C)	Relative humidity (%)	Corrosion stimulator
8 h	40 ± 3	100	SO_2
16 h	20 ± 3	50 ± 5	-

Table 2 - Accelerated corrosion conditions for copper

In order to carry out electrochemical measurements, several basic electrolytic solutions were prepared by adding to ASTM reference water (ASTM D1384-87 solution, noted "ASTM water") sodium at 0.05 and 0.1 mol.l⁻¹. Their pH was measured to be between 7.6 and 8.2 for solutions containing the NaC₁₀, and 8.5 for pure ASTM water. All these solutions were transparent without the presence of insoluble acidic compounds. Other treatments have been tested in the case of the PROMET iron coupons. They are solutions at pH 4-5 called "carboxylatation" treatments. The solutions were prepared by mixing in a hydro-organic medium, a carboxylic acid HC_n (n= 10, 12) at 30g.L⁻¹ with an oxidant agent at 0.1 mol.l⁻¹ : sodium perborate NaBO₃ or hydrogen peroxide H₂O₂.

Electrochemical tests were performed in a three-electrode electrochemical cell connected to a Gamry PCI4/300 potentiostat, driven by a computer and controlled by the software DC105 for the stationary techniques and EIS300 for the electrochemical impedance spectroscopy. A circular and horizontal working electrode (3.14 cm^2) was placed at the bottom of the cell under a Pt-disk electrode. The reference electrode was a KCl-saturated calomel electrode (Hg/Hg₂Cl₂, E=+0.242 V /SHE), and all potentials are given versus this reference electrode. The electrochemical data were recorded by Gamry Framework software.

Then climatic chamber tests have been realised in a LIEBISCH - KSE 300 chamber. The treated samples have undergone the FKW test cycle: 8 hours at 100% humidity, using twice-distilled water heated to 40°C, then 16 hours under the room conditions.

Solid iron decanoate and copper decanoate were synthesised by mixing an iron nitrate aqueous solution (copper nitrate aqueous solution in the case of the copper decanoate) with a sodium carboxylate solution. The precipitates were filtered, rinsed with distilled water and dried in an oven for a few hours at temperatures between 60 and 70°C.

After the inhibiting treatments, surface analysis was performed by X-ray diffraction on a D8 advance - Bruker AXS diffractometer by the conventional θ -2 θ method whose data have been recorded with the DiffracPlus #1 software. Surface characterisation has also been carried out by Raman spectroscopy on a Jobin Yvon LabRam Infinity spectrometer, with a Nd:YAG laser emitting at 532 nm coupled to a microscope Olympus allowing the sample micrometric observation.

3. RESULTS AND DISCUSSION

3.1 Electrochemical measurements and artificial ageing 3.1.1 Evaluation of the performances of the solutions on PROMET iron-based samples

First tests were carried out in an electrolyte containing ASTM corrosive water added or not with basic solutions of sodium decanoate.



Fig. 2 – Potentiodynamic curves of PROMET steel samples measured after 8 hours of immersion in different electrolytes

Potentiodynamic curves of iron were recorded after 8h of immersion in the different electrolytes (Figure 2). The addition of NaC_{10} to the corrosive medium induces a systematic increase of the corrosion potential and a decrease of the corrosion current density. A weak current density close to 10^{-5} A/cm² was also observed on the anodic branch. These results confirm that decanoate sodium solutions are effective for PROMET samples.

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Impedance spectra of iron were measured after different immersion times in ASTM water added with $0.05M \text{ NaC}_{10}$ (Figure 3) and are compared to the blank. An increase of impedance modulus with the immersion time was observed at low frequencies.



Figure 3 – Impedance modulus vs. frequency of PROMET steel samples in ASTM water added with 0.05M NaC₁₀.

The corrosion rates of PROMET iron in immersion in corrosive water with different concentrations of sodium decanoate were calculated using the Tafel method (Fig. 4). An important decrease of the corrosion rate was observed when NaC_{10} is added to the ASTM water. These results confirm the efficiency of the NaC_{10} solutions for protecting iron against corrosion.



Figure 4 – Corrosion rate (µm/year) of PROMET samples after 8 hours of immersion in different electrolytes.

Another method of treatment was investigated, which allows the formation of thicker metallic carboxylate layers. Solutions containing carboxylic acid and an oxidising agent were prepared. Here, the carboxylatation treatment assumes that a more acidic pH should allow the release of a larger amount of iron cations. During iron immersion, as the concentration of Fe cations increases it allows the precipitation of iron carboxylate. Electrochemical experiments were carried out on coupons after immersion in several protection solutions. Considering the corrosiveness of this test, performances of the carboxylate coatings can only be evaluated for short immersion times in the electrolyte (2 to 3 hours- chosen electrolyte is NaCl 0.1M). During immersion of PROMET samples in the corrosive medium (0.1M NaCl), their potential corrosion and polarisation resistance have been measured. The OCP (fig.5) of treated samples are going from -400 mV to -520mV (/SCE) after 8-hours of immersion. These potentials are higher than the values recorded in the reference solution (-600mV).



Figure 5 – Ecorr vs. time of PROMET steel samples treated with different protection systems, measured in 0.1M NaCl electrolyte.

Polarisation resistance values of the treated samples (Fig. 6) gave better values than those obtained for the untreated sample during all the duration of measurements. However, the values slowly decreased after 60 to 80 minutes, because the electrolyte is very corrosive and the film cannot be restored during this aggressive immersion. In the case of $H_2O_2+HC_{10}$, Rp is 3 orders of magnitude higher than those recorded for the reference coupon.





Artificial ageing was carried out in climatic chamber using the same protection treatments. The coupons were treated by immersion in different inhibitive solutions and then underwent the FKW cycles. Surface examination of the coupons was performed for different cycles to allow a Development of new non-toxic corrosion inhibitors for cultural property made of iron and copper alloys

rating of the protection systems tested. Photos were taken after 3, 6, 15 and 22 cycles; they are shown in annex. The best results were obtained with the following treatments: NaC₁₀, HC₁₀ + H₂O₂, and HC₇ + H₂O₂.

3.1.2 Evaluation of the performances of NaC₁₀ solutions on PROMET copper-based samples

The efficiency of sodium decanoate solutions on copper has also been evaluated on PROMET coupons. Like in the case of iron, the first tests were carried out in a corrosive ASTM water (blank), then added with different amounts of NaC₁₀. Potentiodynamic curves of PROMET copper based alloys recorded after 8h of immersion are presented in Figure 7.



Figure 7 – Potentiodynamic curves of PROMET copper samples measured after 8 hours of immersion in different electrolytes.

When adding sodium carboxylate to the corrosive medium, a slight increase of the corrosion potential was observed. Nevertheless, at the anodic domain curves an important decrease of the current density was noted. The values obtained for NaC₁₀ were around 10^{-6} A/cm² on the main part of the anodic branch. These values are almost two decades lower than those recorded for the ASTM solution.

Impedance spectra measured at open circuit potential were recorded after different times of immersion in a 0.1M solution of NaC_{10} . The Bode plots (fig. 8) displayed that with the addition NaC_{10} in the corrosive electrolyte, the impedance modulus at low frequencies were one decade higher than that of the corrosive medium (ASTM solution).



Figure 8 – Impedance modulus vs. frequency of PROMET copper samples in ASTM water added with 0.1M NaC₁₀.

Moreover, the impedance modulus is increasing with the immersion time in ASTM water + $0.1M \text{ NaC}_{10}$, which can be correlated to an increase in the coating thickness.

Corrosion rates measured for the samples in immersion in 2 different solutions are presented in figure 9.



Figure 9 – Corrosion rate (μm/year) of copper PROMET samples after 8 hours of immersion in different electrolytes.

The values confirm that the addition of NaC₁₀ leads to an important decrease of the corrosion current. The inhibitive efficiency calculated from the expression: *Inhibitive efficiency* (%) = $[(i_{corr}-i^{inh}_{corr}) / i_{corr}] \times 100$ reaches almost 85% for the tested sodium carboxylate solution. Like for iron samples, the sodium carboxylate can be considered as an anodic inhibitor as no change on the cathodic reaction was observed.

For a second time, the polarisation resistance of some treated samples have been recorded versus time. PRO-MET copper coupons have been immersed in NaC_{10} solutions for 3 hours and electrochemical measurements were made in a 0.1M NaCl electrolyte (Fig.10).



Figure 10 – Resistance polarization vs. time of PROMET bronze samples treated with different protection systems, measured in 0.1M NaCl electrolyte

The Rp of protected coupons were better than the values for the untreated sample.

3.2 Characterisation of the protective layers **3.2.1** Iron PROMET samples

A treated iron sample was immersed in NaC_{10} (0.1 mol.L⁻¹) for 15 days and SEM examination was performed in order to identify the mechanism responsible for the inhibitive properties observed. Figure 11 indicates the pres-

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ence of crystallites on the treated coupons, which appear to grow in an upwards direction from rust points.





A PROMET steel sample was immersed for 15 days in a $0.1M \operatorname{NaC}_{10}$ solution, and then rinsed with distilled water. Both this sample and the synthesised powder of iron decanoate were characterised by Raman spectroscopy (Fig. 12). This spectrum of the treated corroded sample shows the peaks of several iron oxides and hydroxy-oxides: lepidocrocite (bands at 254, 300, 380, 530, 660 and around 1300 cm⁻¹), a bit of goethite (bands at 250, 300, 385, around 685 and around 1300 cm⁻¹), and a bit of magnetite (bands at 308, 540 cm⁻¹, peak at 670 cm⁻¹). Its comparison with the spectra of the synthetic powder also confirms that iron carboxylate is found at the sample surface after its immersion in the NaC₁₀ solution (small peak at 230 cm⁻¹, bands between 2850 and 2950 cm⁻¹).



Figure 12 – Raman spectra of the synthetic iron decanonate (a) and a PROMET iron sample treated in 0.1 M NaC₁₀ (b)

3.2.2 Copper-based PROMET samples

A characterisation of the surface of a PROMET coupon was realised after its immersion in a NaC_{10} solution.



Figure 13 – diffraction pattern of a bronze coupon treated in a NaC_{10} solution

The diffraction pattern (fig.13) shows a large diffraction peak with low theta values, which confirms that a carboxylate based compound exists on the metal surface. The characterisation of the surface by XRD confirmed that the protection is due to the precipitation of a copper carboxylate layer.

4. CONCLUSIONS

The use of sodium decanoate solutions as a corrosion inhibitor provides iron and copper-based PROMET samples with good protection against corrosion in an aggressive electrolyte. The best corrosion inhibitor solutions investigated by this study seem to be aqueous solutions of NaC_{10} at 0.05 or 0.1M. This inhibitive effect is linked to the formation of a layer of a metallic carboxylate on both iron and copper PROMET coupons. In the case of iron, the protective layer is on a nanometric-scale, although it is observable only when it upwards from rusted pits; whereas it is found on a micrometric-scale on copper. Aging tests prove that NaC_{10} neutral solutions gave very promising results, and can be proposed as a temporary protection measure for this kind of samples.

Carboxylatation solutions also gave good results for the electrochemical and artificial aging tests, allowing the formation of thicker metallic carboxylates layers.

Characterisation of the layers formed by carboxylatation treatments on this kind of surface (PROMET coupons) will be carried out using SEM, XRD, and Raman spectroscopy in forthcoming work.

Furthermore, the corrosion inhibitors will be tested on real artefacts in natural aging conditions on site. A treatment protocol will be established so as to allow conservators implement easily such treatments on their collections.

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Appendix: Climatic chamber tests

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