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Egypt. J. Chem. **Vol. 64**, No 10 pp. 5693 – 5702 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Polyamide Coating as a Potential Protective Layer Against Corrosion of Iron Artifacts

Mohamed M. Megahed[1], Mohamed M. Abdelbar[2], El said M. Abouelez[3] and A. M. El-Shamy[4,*]

[1] Conservation Department, Faculty of Archaeology, Fayoum University, Al-Fayoum Governorate, Egypt
[2] Conservation Department, Faculty of Archaeology, Damietta University, Damietta El-Gadeeda City, Damietta Governorate, 34511, Egypt
[3] Conservator at ministry of tourism and antiquities, Tanta, Egypt
[4] Physical Chemistry Department, Electrochemistry and Corrosion Lab., National Research Centre, El-Bohouth St. 33, Dokki, P.O. 12622, Giza, Egypt

Abstract

Various tools were used in the investigation and analysis processes of the iron window grille of sabil Ramadan. Metallographic Microscope, SEM-EDS Microscope, Carbon-Sulfur, and XRD analysis indicated that the iron window grille was manufactured from low carbon steel. X-ray diffraction of corrosion products showed that they mainly consist of Magnetite Fe_3O_4, Goethite α-FeO(OH), and Akaganeite β-FeO(OH). Such information regarding the iron window may assist in the conservation process of this iron window. Coatings and inhibitors are used in a wide range in this field, where Special methods are required either for protection or treatment to stop or reduce corrosion rate. Experiments were performed on coupons simulating iron window to evaluate the efficiency of polyamide by using electrochemical techniques (electrochemical impedance spectroscopy (EIS) and polarization resistance (RP)). It gave sufficient protection and good results of the electrochemical measurements. Tannic acid diluted in 5% methyl alcohol (coating) and polyamide (inhibitor) applied to protect the iron window grille.

Keywords: Iron window grill; Surface characterization; Polyamide coatings; Electrochemical measurements.

1. Introduction

There are numerous decorative uses of steel in construction including staircases, window frames, doors, and door frames, elevator doors, railings, and window grilles. Iron window grilles were widely used on houses or public buildings for aesthetic purposes and ventilation [1, 2]. Iron window grilles are exposed to pollutants gas, acid rain, acid fog, salt, and dust, etc. caused by pollution of the atmospheric environment to be corroded more rapidly than indoor iron artifacts to cause damages, so inhibitors treatment preventing re-corrosion by quickly treating corrosion factors is important for iron window grilles exposed to the outdoors. Along with other amorphous iron corrosion materials, there is an inner layer of magnetite and an outer layer of iron hydroxide oxides, usually goethite and lepidocrocite. This could be found that iron corrosion happens above 60 percent relative humidity, the critical relative humidity for most metals is usually (50-70 percent) the critical relative humidity is the state under which multi-molecular layers of water vapor chemically adsorb from the atmosphere to the oxide – the metal surface. The iron oxide films can contain different oxides [3].

The first symptoms are relatively slow but after reaching a critical stage, corrosion follows very quickly. Once rust film starts to develop, the natural porosity of the corrosion products acts as a reservoir for moisture and pollution, resulting in an acceleration of the deterioration process. If this process is not stopped, it will continue until the iron is entirely consumed by corrosion, leaving nothing but rust [4]. There is a method employed for

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anticorrosive protection is the use of corrosion inhibitors, which contrast to industrial applications, since, in metal preservation, the addition of the inhibitor to the electrolyte is not mainly used. Inhibitors are applied directly on the surface to produce modifications, or they are mixed with the varnish. This change in concept and application is important for research on the use of inhibitors in the field of cultural heritage [5-7]. Some inhibitors are being widely used in the preservation and restoration treatments of copper, bronze, iron, and silver alloys [8].

However, the application of existing treatment methods is challenging at times, indicating that more diverse treatment materials and techniques are necessary. Therefore, in this study, a treatment method that employs polyamide rather than an anti-corrosion solution, for the conservation and management of iron window grille was used. Tannic acid and polyamide were used, and the results obtained confirmed that both showed an anti-corrosion effect. Small-sized iron artifacts allow for impregnation, but for large iron artifacts such as iron window grilles, coating treatment is carried out because it is so bulky that impregnation is not possible.

2. Materials and methods

2.1 The iron window grille of Sabil Ramadan (case study)

Sabil Ramadan had been built in Abiar village, Kafr El-Zayyat, Gharbiah governorate (North of Cairo) during the Ottoman period in (1297 A.H. – 1879 A.D.) by Elsheikh Mohammed Hussein Ramadan. The iron window grille is located on the side overlooking the main street. Measures of the iron window grille are 285x140 cm. Visual observation is the first step in diagnosing the degradation state of a metal artifact. Documentation of the iron window grille was undertaken using drawing and photographic recording are shown in Fig. 1. All details were photographically documented to provide detailed information on the state of deterioration as presented in Fig. 2, 3.
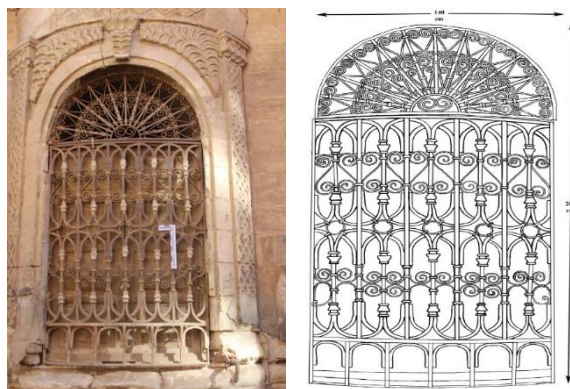

Fig. 1: Represents the iron window grille of sabil Ramadan and documentation by drawing of the window grille shows the twenty lead connections are still existed.
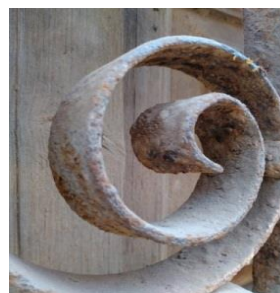

Fig. 2: showing corrosion products and dust particles accumulated on the iron surface of the window grille.
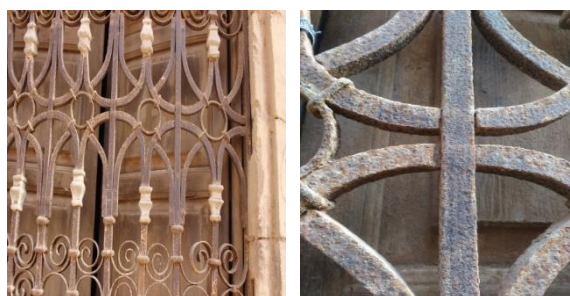
Fig. 3: Window grille components were joined by using iron collars, rivets, and connectors.

The cross-section was obtained to determine the alloy microstructure through an OLYMPUS BX41M-LED JAPAN metallographic microscope. A small sample from the window grill to prepare cross-section was embedded entirely in epoxy (EPOBOND) then ground and polished using 600, 800, and 1200 grit emery papers. The metallographic sample was etched using a 5% Nital etchant (5% HNO_3 and 95% Ethanol) for 30 seconds. The Same section prepared for metallographic examination was investigated for SEM and EDS analysis using a scanning electron microscope (Inspect S 50 HOLLAND,) FEI)). Carbon concentration in the iron alloy was detected using Carbon Sulfur analyzer ELTRA CS-2000. Corrosion products were analyzed with advanced PAN analytical X-Ray Diffraction equipment X, Pert PRO to determine the chemical composition and to understand corrosion mechanisms.

2.2. Corrosion Process

Many archaeologists try to multiply the samples before they are artificially damaged in research laboratory experiments. The electrochemical cell technique was performed according to what is known from the electrochemical cell that contains three reagents for work (an exposure area of 0.785), a platinum wire of 0.1 cm^2, a counter, and the reference electrode was (silver/silver chloride) where a standard calomel electrode was used directly connected with the test solution, where the tests were organized in a cell with a volume of 150 cm^3, all the electrolytes were prepared from pure chemicals used for the analysis. The tests were carried out in a stagnant solution. The experimental work was carried out in a solution consisting of 3.5% NaCl without polyamide and with different concentrations of polyamide as an anti-rust as indicated in the following diagram.

2.2.2. Procedure to Check Corrosion

To test the treatment that prevents rust as in the case of rust inhibitors, a composition containing active iron chloride $FeCl_2$ was used as a product of

the rust products of iron and its alloys. The sample of thickness of 1 mm according to the British standard that recommends that the size be is not less than 25 cm^2, but it was found that this sample size is very large, as the available room humidity during the test cannot take care of large samples of this size. Samples were cut to a size of 20 x 50 x 1 mm using a guillotine, as this sample size allows for the treatment of a larger number of samples in a single test, and thus helps in replicating the experimental results. The measurements used in the samples must be controlled to remove the difference in rusted surface. It is difficult to evaluate the explanations for changes in the levels of rust after the occurrence of rust because many other complex and complex factors must be considered.

2.2.3. Corrosion Items Analyzed on the Test Samples

The analysis was done with X-ray diffraction to analyze the components of the resulting powder and the components of the rust products present on the samples. In a solution of iron chloride, one sample was taken after rust and dried at a temperature of 50 °C under an infrared lamp for 5 minutes, then exposure to a temperature of 105 °C in an oven for 30 minutes and then exposed to 95% RH for 24 hours and then another sample is taken from the same sample. The sample was examined with X-ray diffraction by a Siemens X-ray diffractometer, D5000, where the sample was taken from iron dichloride, where it indicates the presence of a polyamide compound, where the sample turned and was classified as an iron compound with polyamide, a piece was taken for metallographic examination

To examine the layers of rust before and after exposure to the polyamide layer at 100% relative humidity, the piece of the sample before exposure to rust showed a layer with a thickness of 20-25 micrometers of polyamide on top of the iron sample, where this was covered with a layer 5-10 micrometers thick, which appears as a powder. Red from Fe_2O_3 iron dioxide.

2.3. Calculation of Inhibition of Corrosion

To estimate the efficiency of the rust inhibitor, the rust prevention has been estimated by the following formula:

$$I.E, \% = \frac{uninhibited\ corrosion\ rate\ -\ inhibited\ corrosion\ rate}{uninhibited\ corrosion\ rate} X100$$

The rate of non-prevention of rust is the weight of the rust product after completion at the time of exposure of the sample without treatment (the polyamide covering the sample is not treated with an anti-rust compound as it is exposed to 100% relative humidity

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at normal temperature for a period of 24 hours). The rust prevention rate is the comparison rate for the sample treated with the antirust after exposure 24 hours at room temperature at 95% RH.

3. Results and Discussion
3.1. Corrosion Results
3.1.1. Polarization Curves

The effect of the polyamide concentration on the iron polarization activity is shown as in Fig. 4 and based on the experimental results resulting from the concentrations, the presence of polyamide reduces the rate of decomposition of the anode at a rate of 3-4 times of the required. Since the anode is a negative (inert) region. As a result of the formation of a protective layer of iron (II) polyamide compound, the negative (inert) region stops at the voltage so that E_b falls after the current is expanded upward, where the voltage becomes more positive. The surge of current occurs due to the erosion of the protective layer, so a rise occurs over the E_b region due to local rust, and because the polyamide concentration raises the melt voltage as E_b becomes more suitable, and the current in the negative (inert) region reduces the possibility of a more stable layer.

The effect of sulfide ions in the anti-rust solution of polyamide is shown in the polarization curves. The sulfide ions have a clear negative effect on the induced negativizes of the polyamide, as the HS-ions have the following effects: Reducing the corrosion by hundreds of mV depending on the concentration, Increase the negative zone current and the electrode melt rate by the required amounts. The free rust voltage changes by hundreds of mV in the direction of the cathode. It has been observed that the concentration of low sulfide ions (10) -5 mol, i.e., 32 parts per million of sulfur raises the iron polarization curve in the presence of 2% of polyamide, this concentration of polyamide is 1000 times more sulfide ions but unable to repel the sulfide attack.
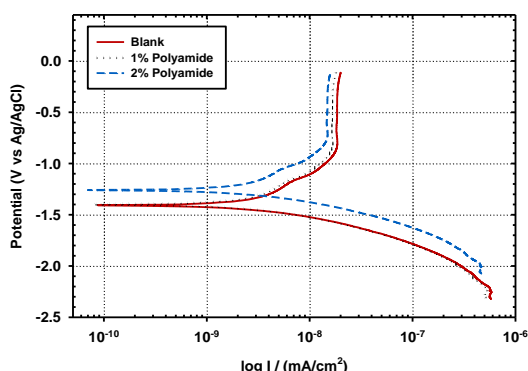

Fig. 4: Plots of potentiodynamic polarization curves for iron at a scan rate of 1 mV s−1 in a 3.5 % NaCl

solution in the presence of a gradual concentration of polyamide at 30 °C.

3.1.2. Polarization Resistance

With the passage of time, an increasing decrease in the current rate occurs, as shown in Fig. 5, where we note that the blocking efficiency of the polyamide improves over time. The impedance spectra were calculated after the different stages of immersion in the polyamide inhibitor medium. These spectra were examined before and after the sulfide ions injection, as we have seen before. The study demonstrated that the resistance is inversely proportional to the rust rate, as K represents a constant with each device, and the electrical resistance appears with the immersion time, where the constant rise in the polarization resistance (R_P) is observed with the immersion time before the sulfide ions are injected, where This is consistent with the results of previous work. The obvious anti-effect of iron ions was also observed in decreasing the polarization resistance (RP) and thus increasing the risk of rust, as the sulfide ions have a very rapid effect.
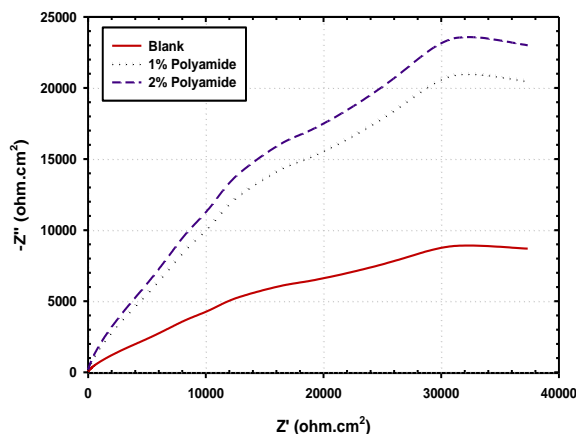

Fig. 5: The polyamide and its inhibiting efficacy improve over time and its effect after sulphide injection.

3.2. Case study

The iron window grille of Sabil Ramadan is exposed to atmospheric agents where the surface was covered with dirt and dust above the corrosion products. By visual examination, it can be noted that components of the iron window grille were joined using mechanical joins (collars, rivets) A rivet is essentially a flat-headed pin that grips two pieces of metal together through the middle, and collars achieve a similar result by wrapping tightly around two or more parallel pieces [9]. Cast iron is often joined using bolts or leaded sockets, whereas riveting indicates either wrought iron or steel [10]. The iron

window grille contains twenty lead connectors, divided into four rows. There are some missing pieces (Man-made deterioration) in the lower part. The metallographic investigation proved that the iron window grill was manufactured from low carbon steel consisting of ferrite grains (a light constituent) and pearlite (a dark constituent) [11]. Also contains impurities (slag), (a glassy phase or mixture of phases usually to be found in ancient or historic wrought or steel), Slags generally follow the direction of processing [12].

The EDS qualitative analyses indicate that the sample contains (Fe, C, Mn, P, and Al) (Fig. 6 and Table 1). Fe and C indicate to the main component of low carbon steel, while other elements such as (Mn, P, and Al) indicate slag. Low carbon steel may include phosphorus, sulfur, manganese, silicon, aluminum, copper, titanium, molybdenum, and nickel [13, 14]. Scott indicated that the ironworker first had to heat the iron and hammer it to weld the mass together and expel as much of the slag as possible. Not all the slag particles can be removed from iron; these remain as slag inclusions in iron artifacts [14]. These slag inclusions are numerous in most of the substrate and contribute to the structural heterogeneity of the metal [15]. The data obtained from the carbon-sulfur analyzer showed that the iron alloy contains 0.11 wt. % carbon and 0.023 wt.% sulfur.

Results confirmed that the iron window grill was manufactured from low carbon steel. Steels are divided according to composition into three types; Low carbon steels contain from (0.09 % carbon to 0.2%) medium carbon steels contain 0.2 - 0.4% carbon, and high carbon steels more than 0.4% carbon [12]. X-ray diffraction of corrosion products showed that they mainly consist of magnetite Fe_3O_4, goethite α-FeO(OH), and akaganeite β-FeO(OH) besides calcite $CaCO_3$ as dust particles as presented in Fig. 7 and Table 2. In general, iron artifacts are highly affected by atmospheric corrosion anticipated to the development of protective panes of rust products, which reduce the level of attack. The thickness and configuration of the rust products layer formed are governed by the relative humidity and pollution of the environment Magnetite Fe_3O_4 is an iron corrosion product, that happens when iron contact with dry oxygen. It oxidizes to various degrees and therefore three iron oxides appear successively.

The oxidation begins with the formation of a compact layer of iron (III) oxide. Further access to oxygen gradually changes this oxide into magnetite, and later into iron (III) oxide [16]. Goethite α-FeO(OH) is an important primary corrosion product of iron objects in a wide range of environmental milieux and may form the principal corrosion product of freshly rusted surfaces or of iron artifacts that have

been entirely converted to corrosion products. Akaganeite β-FeO(OH) bubbles located on archaeological iron were formed at higher RH levels [17]. Akaganeite formation is an indication of active corrosion of iron under a layer of corrosion products. Chloride ions can be implanted into the tunnels of the crystal lattice of akaganeite, stabilizing its structure [18].

The destructive effect of akaganeite consists of its potential to release chloride ions, and of its increased volume during crystallization, which can also be applied for other ferric oxyhydroxides. The damage caused by akaganeite is mainly of physical character, e.g., spalling and cracking, indicated by remaining orange needle-shaped crystals [19]. Regarding calcite $CaCO_3$, the presence of this compound could be due to pollution by the dust coming from the surrounding walls and the binders which are deposited on the iron surface [20].
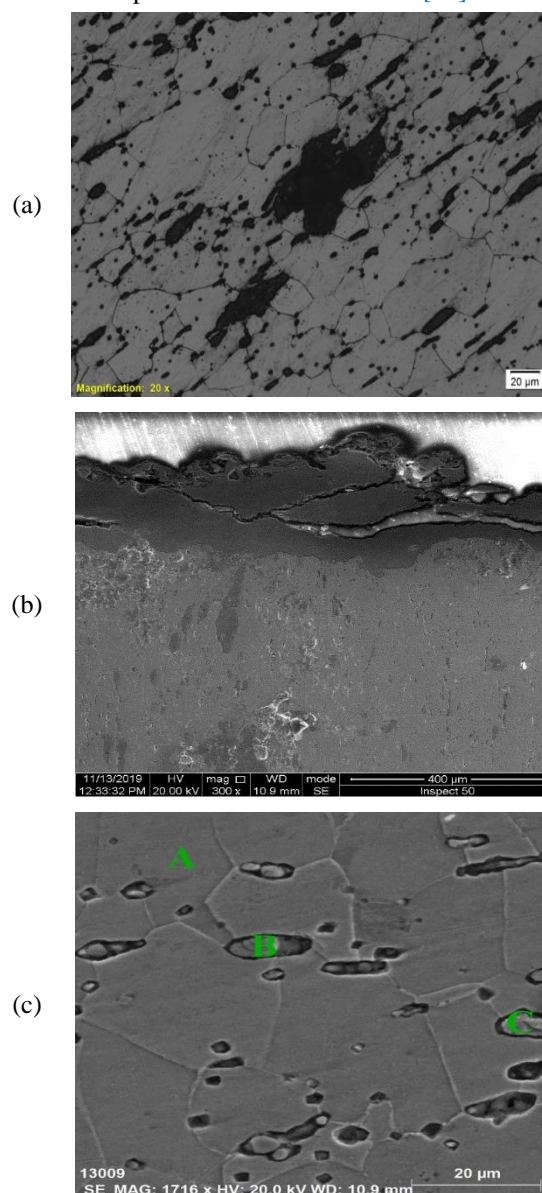

(a)

(b)

(c)

Fig. 6: (a) Micrograph of low-carbon steel showing a matrix of ferrite grains (a light constituent) and pearlite (a dark constituent) and slag, etched in 5% Nital, 500x. (b) SEM investigations, cross-section sample showing the iron surface covered with corrosion products. And (c) SEM-EDS analysis which (A, B, C) indicates to Spectrum spots.

Table 1: Results of EDS analysis of different spots in the iron alloy.

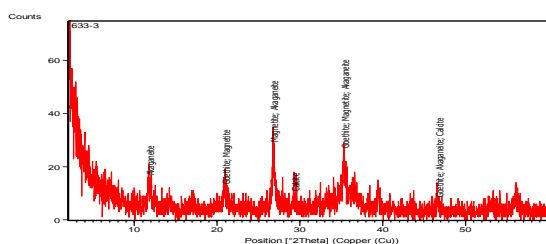| Element	Fe	C	Mn	P	Al
Spectrum A	93.87	5.79	-	0.34	-
Spectrum B	90.53	7.68	0.79	-	-
Spectrum C	91.01	6.85	0.32	0.12	0.20

Fig. 7: XRD diagram of corrosion products in the iron window grille

Table 2: The compounds which analyzed by XRD.

Minerals	Abbreviation	Chemical Composition	Ref. Code	
Magnetite	Mag.	Fe_3O_4	01-074-4121	Maj.
Akaganite	Aka.	$\beta\text{-FeO(OH)}$	01-080-1770	Min.
Goethite	Goe.	$\alpha\text{-FeO(OH)}$	01-073-6522	Min.
Calcite	Ca.	$CaCO_3$	01-083-0578	traces

3.2. Mechanism of film breakdown

In the relative stability of iron sulfide and the protective iron layer with the NH_2 group, the reason for the interaction of the sulfide ions can be observed. Although iron sulfide has high stability, the iron disulfide polyamide has medium stability, these assumptions are due to the fact that the sulfide ions are struggling to reach To the iron ions under the driving force greater than the polyamide, where the iron ions can separate from the iron polyamide compound due to the sulfide ions, the first step is to break the iron polyamide which is the protective layer under the influence of the sulfide ions, this reaction contributes to the disappearance of the protective layer of the polyamide iron, as well as the presence of iron sulfide, weakens the protective layer and rust begins to form on the surface.

3.3. Mode of Action

An electrical potential between the Fe, in the attendance of water, oxygen, and other impurities causes an exchange of electrons resulting in inter-granular corrosion, which weakens the iron and makes it especially susceptible to stress damage. Any attempt to reshape iron, such as dent removal or straightening, without prior heat treatment will result in distortion and damage, especially if corrosion-related micro-fissures already exist. Because iron must be heat-treated before working, any specific orientation in the substance due to original manufacturing techniques will be obliterated [21-24].

3.4. Conservation Treatments

3.4.1. Cleaning

Cleaning is one and only of the extremely familiar operations in conservation. The choice of method for cleaning depends on what is required from the item, what is made of, and the condition. It is known that the mechanical cleaning of metals is the preferred technique for eliminating disfiguring corrosion. It permits extra control and has less influence on the metallic alloy surface. Finally, all the objects were isolated with 2% polyamide.

Should be taken into the account avoid making any scratches on the iron surface during cleaning processes [25]. It was necessary to do cleaning to remove heavy dust layers, atmospheric deposits, and corrosion layers by using hand tool cleaning such as scalpels, brushes, sandpapers, and needles, as can be seen in Fig. 8.
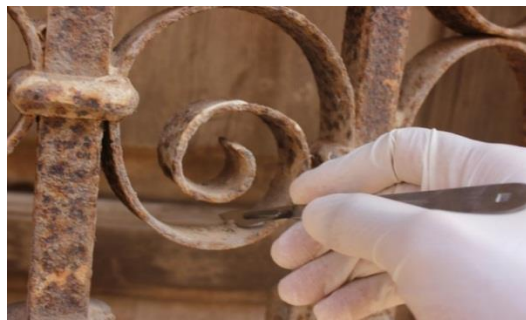
Fig. 8: Scalpels and needles were used to remove dust layer and corrosion products which disappear iron window grille details.

3.4.2. Applying the inhibitor

After finishing the cleaning processes, good surface preparation is the first stage in ensuring fresh coatings perform well. If the surface has not been correctly prepared to receive the coat, the new coating will be less effective and may even fail. If there is any moisture within the iron (due to rainfall, dew, or even high relative humidity) this will be trapped beneath fresh layers of coating and is likely to cause corrosion within a short period of time. So, the surface was cleaned with ethyl alcohol to remove any moisture, dust, and corrosion powder. The surface dried by a cold air dryer to confirm the most suitable surface for the coating layer. The iron window grille was coated on unclouded days to avoid rainy or windy days, as damp conditions and low temperatures can hinder the curing of the coating.

Lead connectors were covered by polyethylene to prevent staining from the tannic acid solution. Then, two layers of tannic acid dilute in alcohol 3% (as a pre-treatment) were applied by brush on the iron surface, a layer of tannic acid interacts with iron to form iron tannates. Small brushes were used to confirm penetrating the coating to all the details and the coating is free of any breaks which might expose the iron window grille to the agents of deterioration as seen in Fig. 9. Coatings have been applied in thin layers, allowing each to dry thoroughly before the next coating is applied. This prevents solvents from evaporating from the layer underneath and damaging subsequent coatings applied on top [26-28].
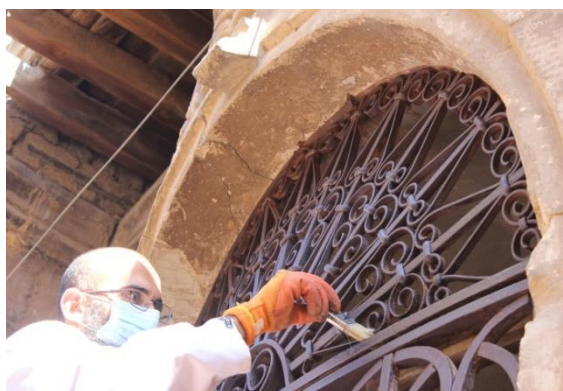

Fig. 9: iron window grille was coated by tannic acid dilutes in alcohol 3% by brush.

After the tannic acid layer was dried, the inhibitor layer (polyamide 2%) coated on the iron window grille surface by using a brush which gave the best results in the experimental study to prevent further corrosion in the future. Small brushes were used to confirm penetrating the inhibitors to all the details and the coating is free of any breaks which might expose the iron window grille to the agents of deterioration. It has been applied two layers by brush: one from the top to down and another from right to left, as shown in Figs. 10,11 [29-33].

Fig. 10: The iron window grille after conservation treatments

Fig. 11: The iron window grille was coated with polyamide 2% which applied in two layers by brush, from top to down and another layer from right to left

Conclusions

Chloride ions decrease the polyamide inhibitory activity against iron corrosion in chloride media. The magnitude of the effect depends on both species' relative concentrations. The real transients show complex associations on the iron surface between the injected sulfide ions and the polyamide. An order of magnitude increases in sulfide ion concentration at a given concentration of polyamide increases the sulfide attack rate by more than one order of magnitude. On the opposite, an order of magnitude increase in polyamide concentration lowers sulfide attack rate by only around one-third. Extended iron surface pre-passivation in the presence of polyamide does not increase its resistance to attack by sulfides.

SEM and XRD results show the occurrence of selective localized or general corrosion phenomena induced also by the separation of the alloy formation elements, which creates reactive electrochemical areas. The morphology of the surfaces and the elemental compositions of the rust products depends strongly on the chemical arrangement of the alloys. It is a great need to study corrosion phenomena of metal artifacts by simple and accelerating test procedures to develop proper methodologies to arrest or avoid further deterioration. There is a need for continued research on inhibitors for controlling corrosion and on methods to improve their adherence to a metal substrate especially for both patinated and unpatinated iron and to find new non-toxic and effective compounds to be used instead of toxic corrosion inhibitors. A successful way to evaluate quantitatively newly selected compounds for arresting the cycle of $FeCl_2$ corrosion was noticed to be the test procedure using iron coupons covered with a coating of polyamide to assess iron corrosion

inhibitors. Such treatment disadvantages may be found on iron coupons that are artificially corroded, making it unnecessary to initially apply new compounds to batches of archeological products.

This rapid corrosion check is a preliminary screening tool on ancient iron and its alloys for prospective restoration treatments. It helps, too. Scientists quantitatively compare the usefulness of inhibitor therapies or coating schemes. For this corrosion check, more compounds will be evaluated in the future to be capable to substitute polyamide for an inhibitor that causes less color change and is more successful on objects containing significant quantities of iron chloride corrosion.

Conflicts of interest

In accordance with our policy on Conflict of interest please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that "There are no conflicts to declare".

Formatting of funding sources

Not applicable

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