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WEATHERING OF TREATMENTS FOR BRONZE CONSERVATION

Results of natural and artificial weathering

Work performed for the European Project ARTECH – Access, Research and Technology for the conservation of the European Cultural Heritage

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WEATHERING OF TREATMENTS FOR BRONZE CONSERVATION

Results of natural and artificial weathering

In this report, results of the natural and artificial weathering of treated patined bronze carried out with the objective of establishing the best conservation system applied are presented. The conservation treatments were developed in the frame of the European project ARTECH. The work developed comprehends the research activities that, during 2008, have been carried out in the Metallic Materials Division integrated in the ARTECH working group JRA1*: Development and evaluation of new treatments for the conservation-restoration of outdoor stone and bronze monuments*.

ENVELHECIMENTO DE TRATAMENTOS PARA CONSERVAÇÃO DO BRONZE

Resultados do envelhecimento natural e artificial

Neste relatório apresentam-se os resultados dos ensaios de envelhecimento natural e artificial de tratamentos para a conservação de bronze patinado, realizados com o objectivo de avaliar a eficácia dos sistemas aplicados. Os produtos de conservação em estudo foram desenvolvidos no âmbito do projecto europeu Eu-ARTECH. O trabalho desenvolvido foi realizado no Núcleo de Materiais Metálicos, durante 2008, no âmbito projecto Eu-ARTECH, inserido no grupo de trabalho *JRA1: Development and evaluation of new treatments for the conservation-restoration of outdoor stone and bronze monuments*.

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WEATHERING OF TREATMENTS FOR BRONZE CONSERVATION.

Results of natural and artificial weathering

1. INTRODUCTION

LNEC participates in the European project ARTECH - *Access, Research and Technology for the conservation of the European Cultural Heritage* – that is a consortium among thirteen international European infrastructures operating in the field of artwork conservation. The objective of Eu-ARTECH is to achieve a permanent interoperability among the participating infrastructures, establishing cooperation and exchange of knowledge with the other infrastructures in the field, in the perspective of structuring a common European research area. This is a five-year project and its activity program is developed through the following activities: networking, access and joint research. The joint research activities, which are devoted to improve the performances of the participating infrastructures and the quality of the access offered to the scientific community, are divided in two parts [1]:

- JRA1: Development and evaluation of new treatments for the conservation-restoration of outdoor stone and bronze monuments;
- JRA2: New methods in diagnostics: Imaging and spectroscopy.

LNEC has an active part in JRA1 activities, which have started in the end of 2004 and will go on till the end of the project in 2009.

This report presents the work carried out by the Metallic Materials Division, in 2008, for the JRA1 activities - bronze working group – of Eu-ARTECH , concerning Tasks 4 and 5, relative to assessment of patina conservation treatments performance. The work developed had the objective of making a comparison between new and traditional conservation treatments adequate to patinated bronze and to contribute to assess the best system applied.

The patina developed in bronze and in other copper alloys exposed outdoors is a unique material consisting in a thin layer of mainly copper corrosion products, usually very stable and adherent, that protects the metal underneath against corrosion. The degree of anticorrosive protection afforded by the patina depend on its thickness and composition. Thickness depends on the time of exposure, usually longer exposures lead to thicker patinas. Its composition is dependent on the type of corrosive agents present on the environment surrounding the alloy, namely, on the type of pollutants present, for example: SO_2 gases are typical of urban and industrial atmospheres, while marine atmospheres are rich in chlorides. Consequently, bronze (old) urban patinas are usually constituted mainly by copper sulphates, and bronze marine patinas by copper chlorides.

Because of that, the conservation treatments under study were applied in bronze or copper tests specimens with marine and urban patinas. Consequently, the weathering conditions were different accordingly to patina type: natural weathering in a marine site for the specimens with marine patina and artificial weathering simulating an urban environment for the specimens with urban patinas, because natural weathering in this case would take too much time to produce results.

The marine site, located at Cabo Raso (Portugal), is the same site where the marina patina was previously developed, through the natural exposition of new, unpatinated, bronze test specimens for 1 year. This site is very corrosive for copper alloys, being of corrosivity class C5 to copper (ISO methodology). The artificial weathering test conditions were established in a previous research work [3], needed because the existing standardized tests procedures for conducting accelerated corrosion tests were developed for testing paints and varnishes (organic coatings) or for metals and alloys in general, and also there was almost no information available in literature about weathering procedures specific for patinated bronze materials.

2. MATERIALS AND EXPERIMENTAL PROGRAM

2.1. Patinated specimens

For application and testing of treatments, three types of patinated test specimens were selected/prepared. The description of patinas properties and its genesis, and type of subtract is presented in Table 1.

Table 1 – Patinated test specimens: patina and substrate characteristics

Name	**Patina characteristics**				**Substrate type**
	Type	*Process of formation*	*Average thickness*	*Composition (main product)*	
UN	Urban	Natural exposure for 80 years in Munich (Germany)	19 µm	*brocantite* $Cu_4(SO_4)(OH)_6$	Copper sheet
UA	Urban	Artificial process (Pichler's)	79 µm	*brocantite* $Cu_4(SO_4)(OH)_6$	Bronze plate
MN	Marine	Natural exposure for 1 year in Cabo Raso (Portugal)	29 µm	*paracatamite* $(Cu_2(OH)_3Cl)$	

2.2. Conservation treatments

The treatments under study were developed within the research program that has being carried out by the ARTECH - JRA1 partners to be applied in the conservation-restoration of outdoor bronze monuments. These treatments are of different nature:

- silane type (two products – **T1S** (fluorinated) and **T2S**);
- cuprite deposition – **T3S** (inorganic);
- Incralac –**Tref** (organic, to be used as reference for the comparison with the silanes);
- 5% limewater solution – **I1S** (inorganic) as passivation agent to be compared with the traditional corrosion inhibitor benzotriazole;
- Benzotriazole (BTA) – **Iref** (organic).

Test specimens with no treatment applied are generically designated by **blank**.

2.3. Weathering conditions

To evaluate the (potential) efficacy of the conservation treatments, they should be applied in representative test specimens and subjected to an accelerated weathering.

2.3.1. Natural weathering

For testing the treatments applied in the marine patinated (MN) bronze samples, it was decided to expose it in the high corrosive marine site Cabo Raso for 18 months. This exposition started in April of 2007 and it ended in October 2008. This site is located close to sea, has an extremely wet and high chloride atmosphere what makes it a “natural accelerated” atmosphere. It has been classified according to ISO methodology with a class $\tau 4$ for TOW and S3 for chloride salinity, which gives an estimated atmospheric corrosivity class of C5 (ISO 9223). During 2004, its corrosivity to copper was measured by weigh loss and it was found to be slightly superior to C5 (ISO 9226).

For the exposure of the bronze specimens an exposure rack was designed according to EN ISO 8565 [4]. The rack was built in anodized aluminium and stainless steel. The angle of exposure is 30º and they are facing the sea direction. A total of 21 bronze test specimens (samples), 3 samples for each treatment under study plus 3 blank (with none treatment applied), were exposed (Figure 1).

2.3.2. Artificial weathering

For testing the treatments applied in the urban patinated (UN and UA) samples, it was decided to carry out an artificial weathering in laboratory, because in a natural urban environment the corrosion would be too slow, thus no significant results could be obtained within ARTECH project duration.

Due to the different nature of the treatments under study the artificial weathering had two parts: (I) UV radiation exposition to promote degradation of treatments and (II) a salt solution exposition in a salt fog chamber to promote corrosion. After discussion among Eu-ARTECH partners and preliminary tests [2], the following procedure was established: the first part (UV exposure) was carried out according to the standard EN ISO 11341 [5] in a Xenon-arc radiation chamber, for the second part, a salt spray chamber was used for the acid salt solution exposure, following the standard ISO 9227 [6] exposure conditions definition and the sprayed solution had the following composition: NaCl (0,5 g/L + $(NH_4)_2SO_4$ (3,5 g/L), with a pH close to 4,5 in order to be approximated to the urban rain water composition.

The treated samples were exposed alternatively to the UV radiation and to the salt solution, for periods of two weeks in each test chamber, till having reached a total of 2000 h of exposition. A total of 21 samples with urban natural (UN) patina (3 samples for each treatment plus 3 blank) plus 15 samples with urban artificial (UA) patina (3 for each treatment excluding inhibitor treatments, plus 3 blank), were weathered.

3. EXPERIMENTAL RESULTS

3.1 Natural weathering in a marine environment

The exposure of the treated marine patinas samples (MN) in Cabo Raso (P) has completed 18 months in last October. During this time, visual observations and thickness of surface layer (patina + treatment) measurements have been done for different times of exposure. Also for evaluation of the anticorrosion protective action of treatments applied, electrochemical impedance (EIS) measurements were performed in selected MN treated bronze samples and also in one not treated (blank) before and after 18 months exposure.

Figure 1 – View of the Cabo Raso test site and visual aspect of all the samples on the exposure rack after 18 months of exposure.

3.1.1. *Visual changes*

The natural marine (MN) patina is very irregular, heterogeneous and does not cover completely all the surface, where the bronze metal is still visible in some spots. After application of treatments there was very small changes in the surface aspect. Therefore, all the samples had a very similar visual aspect before exposure (Figure 2).

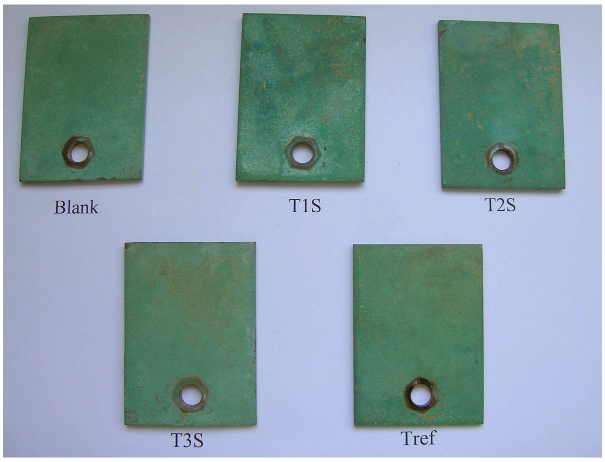
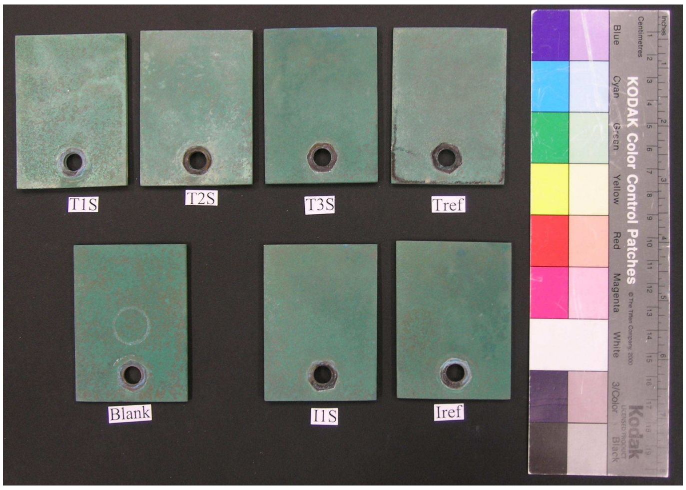


Figure 2 - Visual aspect of selected treated and non treated (blank) MN samples before exposure in Cabo Raso (P).



Treatment	*Surface changes*
None (Blank)	Slightly darker
T1S, T2S	Lighter, whitish and stained
T3S	Similar Blank, smoother
Tref	Lighter, whitish
I1S, Iref	Similar to Blank, smoother

Figure 3 - Visual aspect and visual changes of MN bronze samples from Cabo Raso after 18 months exposure (samples selected to perform EIS measurements).

After 18 months exposure (Figure 3, Figure A1) by visual observation in laboratory it was found out that the bronze samples with silane-type treatments (T1S, T2S) are those that presented more significant changes of aspect, having become whitish and stained. Also Tref (Incralac) became lighter. The not treated patina (blank) sample hasn’t evidenced great change in colour and products distribution, but showed a denser, more consistent aspect, as result of the continuous growing of the patina. The surface changes visually observed for the samples treated with inhibitors (I1S, Iref) and cuprite (T3S) were very similar to blank, but these patinas presented a smoother, relatively more uniform aspect.

3.1.2. Thickness changes

Thickness measurements of surface layer of the exposed MN bronze samples were carried out in all samples by a non destructive method (EN ISO 2360) after 18 months exposure. The results are shown in the next figure along with those from 1, 6 months and 1 year of exposure. It was found that there was a generalized increase of the surface layer thickness with exposure.

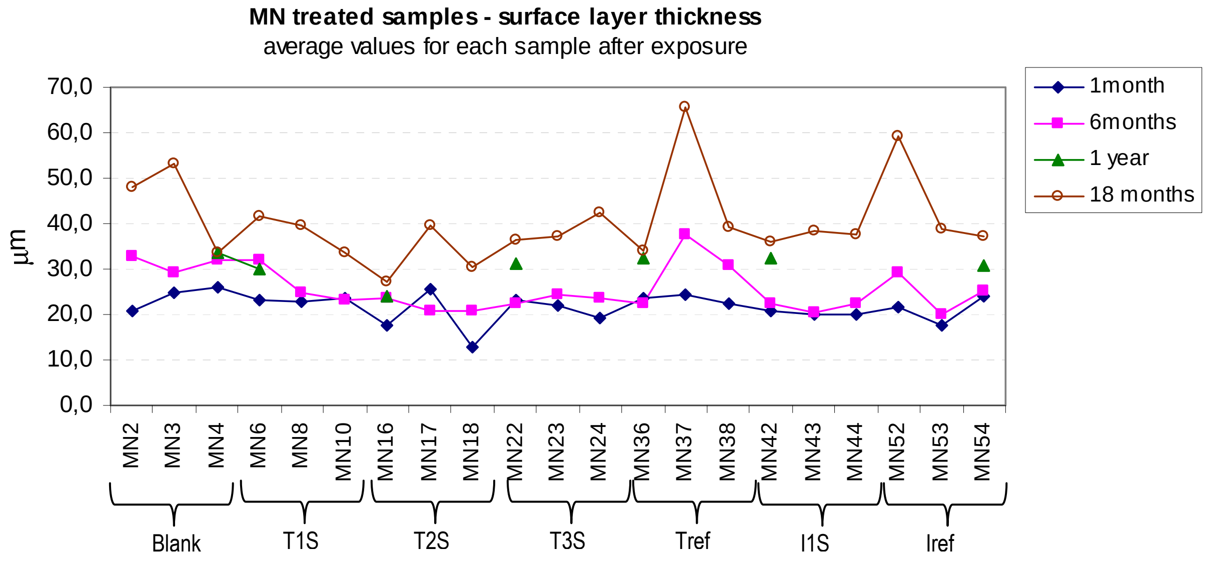


Figure 4 - Eddy current thickness measurements of marine natural (MN) treated and not treated bronze samples exposed in Cabo Raso (P) during 18 months.

3.1.3. Electrochemical Impedance Spectroscopy (EIS) measurements

AC impedance measurements were performed in one sample of each treatment and also in one not treated (blank) before and after the exposure (18 months) in Cabo Raso (P). Measurements were carried out after 30 min in distilled water, using a three-electrode configuration with a saturated calomel electrode (SCE) as reference electrode, using the set up presented in the next figure. Impedance diagrams were made over the frequency range 100 kHz to 10mHz under controlled potentiostatic conditions, at the open-circuit potential. A Frequency Response Analyser (FRA, Solartron 1255) and a potentiostat (Solartron 1287) were used for these measurements.

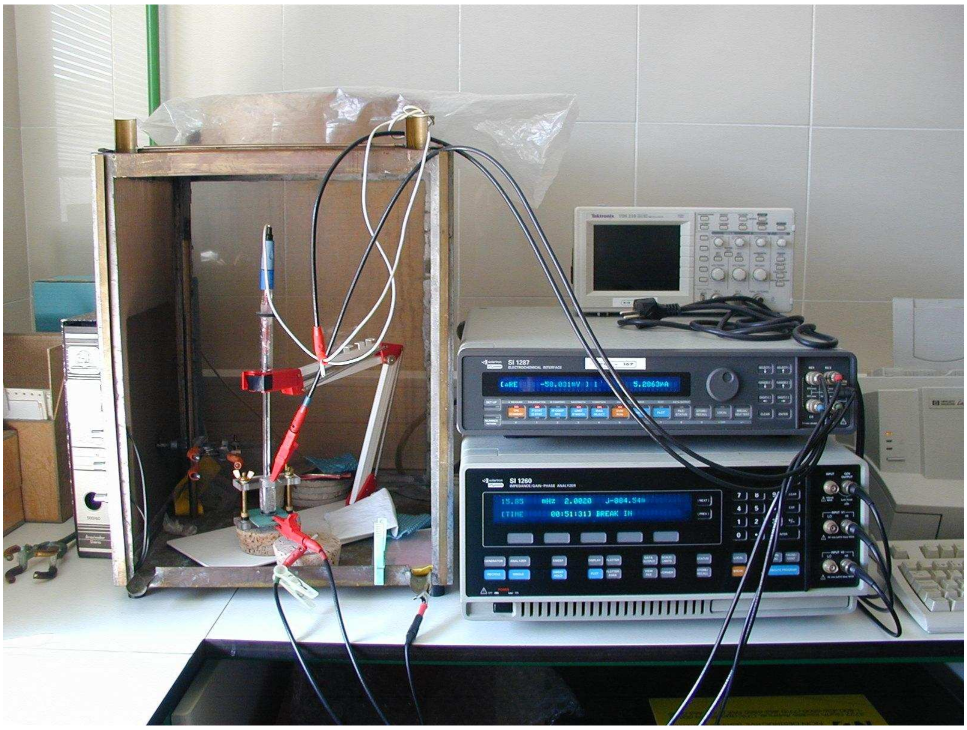


Figure 5 – EIS equipment and electrochemical cell

EIS measurements were carried out in two zones for each one of the selected bronze samples (representative of all the treatments under study plus the blank). In the next figure, EIS results (Nyquist and Bode plots), relative to test zone A, obtained after the 18 months of exposure in Cabo Raso (P) presented .

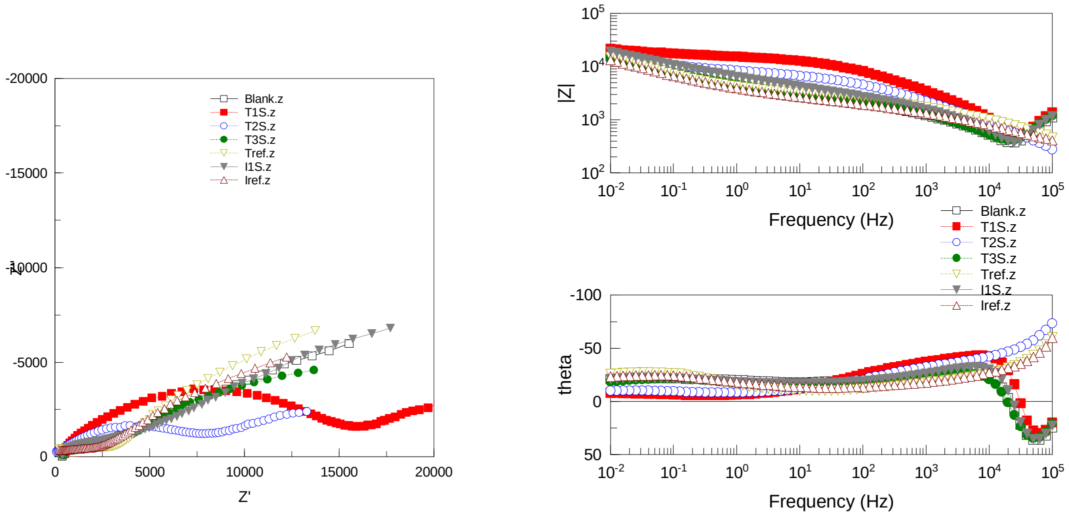


Figure 6 - EIS results for MN samples treated and untreated (blank) after exposure.

For comparison of protective coatings behaviour, the respective EIS results can be analysed in a quick and simplified form through the low frequency value of impedance modulus,

$|Z|_{10mHz}$. Generically, this parameter is directly related with the barrier properties of the coating, them the higher it value more protective is the coating under evaluation. The next figure resumes the values of this parameter, obtained before, during and after 18 months weathering, for all the treatments applied to MN patina samples and also for the blank sample.

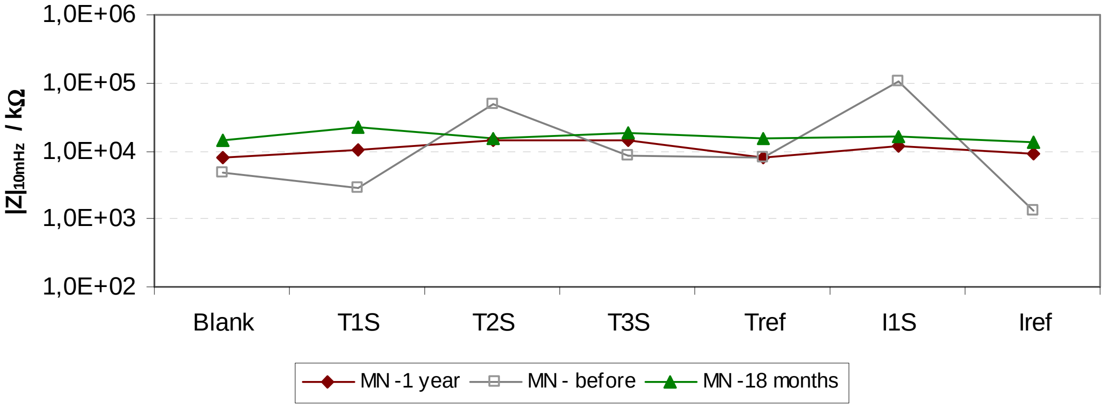


Figure 7 - $|Z|_{10mHz}$ values measured by EIS for treated and untreated (blank) MN samples before, during and after exposure in Cabo Raso (P). ($|Z|_{10mHz}$ values are averaged from the EIS results obtained in two different points.).

The low impedance modulus values obtained after 18 months of exposure, which are close to the ones obtained after one year, revealed a slight impedance increase for the untreated MN patina sample (Blank), consistent with the denser aspect and increase in patina thickness. The same was verified for T3S (cuprite) and Tref (Incralac) treatments, while T1S (fluorinated silane) and Iref (BTA) treatments showed higher impedance increases with exposure. T2S (silane) and I1S (limewater) treatments exhibited a significant impedance decrease after exposure, loosing their initial advantage. After weathering all the treatments converge to similar impedance values (taking $|Z|_{10mHz}$ as reference) and close to the value obtained for the blank.

When coatings are damaged and corrosion processes are active on the surface, however, the $|Z|_{10mHz}$ value would not depend only on the coating properties, namely its barrier effect, but results from several contributions. In this case, the estimation of remaining coating resistance by adjusting equivalent electric circuits could lead to more realistic information about coatings performance. Similarly, higher resistances mean more protective coatings. In the next figure, the values of $|Z|_{10mHz}$ obtained after 18 months exposure are presented together with the estimated resistance of the protective treatments: R_{coat} for those resulting from a coating application like T1S, T2S, Tref and Iref, or R_{patina} for those treatments resulting from chemical deposition of a substance on the patina and also for the blank.

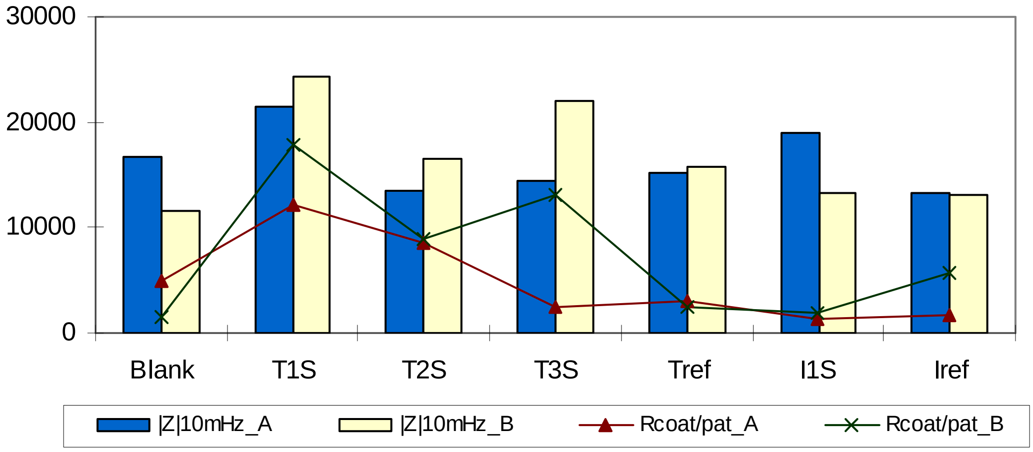
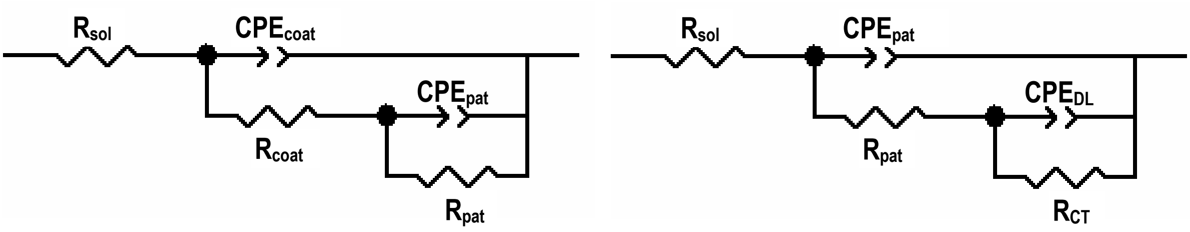


Figure 8 - EIS parameters of treated and untreated (blank) MN samples after weathering in Cabo Raso (P), measured in two points (A, B) of each sample.

Considering the specificities of the different protective systems under study, the following equivalent circuits were used to estimate coating/patina resistances:



I – T1S, T2S, Tref, Iref

II – Blank, T3S, I1S

Figure 9 – Equivalents circuits used to fit EIS results to obtain coating/patina resistances and the type of treatment they apply.

The equivalent circuit I applies to the treatments involving a coating (silanes – T1S, T2S, Incralac – Tref and also BTA-Iref), it assumes two resistive responses: one from the coating (R_{coat}) and other from the patina (R_{pat}), due to a certain degree of degradation of the coating that makes it porous, allowing some water penetration through it till the patina underneath. This patina is porous and irregular, but because of the coating sealing effectt, this process should have small extension so the patina still affords protection and corrosion processes are not yet detectable. In the case of samples with obtained by chemical deposition of other products on the patina, like T3S and I1S, and also for the blank, there is no coating protecting the patina that is totally exposed to the aggressive agents, then due to its not fully protective nature, the corrosion proceeds in time and the equivalent circuit II applies – the parameters CPE_{Dl} (related with double layer capacitance) and R_{CT} (charge transfer resistance) are corrosion process parameters.

The high heterogeneity of the MN patina is patent in the results obtained by EIS (Figure 8), specially in those from the blank, it naturally influences the corrosion response, leading to the existence within the same sample of zones with different corrosion states. In spite of that, from the results obtained, resumed in the figure above, silane type treatments (T1S, T2S) are the ones that more consistently present a relative better resistance, thus better barrier properties and consequently better protective action, probably due to a synergic effect between coating and patina. The other treatments, according to EIS measurements didn't improve much, or even nothing, the corrosion resistance of patina with weathering in comparison to the patina without treatment (blank). Some exception, however, could be possible in the case of TS3 treatment, in which one of the tested zones also yielded a relative high resistance, but more studies would be needed to clarify its performance.

3.2. Artificial weathering

The samples with urban patinas were exposed alternatively to the UV radiation and to the salt solution, for periods of two weeks in each test chamber, till having reached a total of 2000 h of exposition (3 complete cycles of exposure). Treatments T1S, T2S, T3S and Tref were tested in both urban patinas (UN, UA), but the inhibitor treatments (I1S and Iref) were not tested in the urban artificial (UA) patina. The artificial weathering started in February 2008 and ended in July 2008.

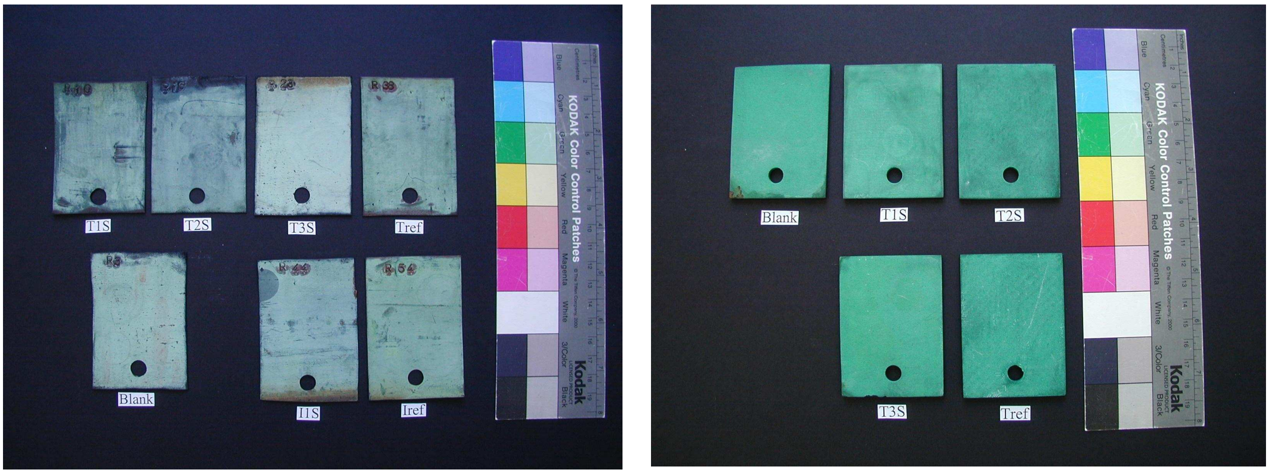
a) b)

Figure 10 - View of the mounting set up for artificial weatheringof treated urban patinas (UN, UA) in a) UV (Xenon-arc) chamber and in b) salt spray chamber.

3.2.1. Visual changes

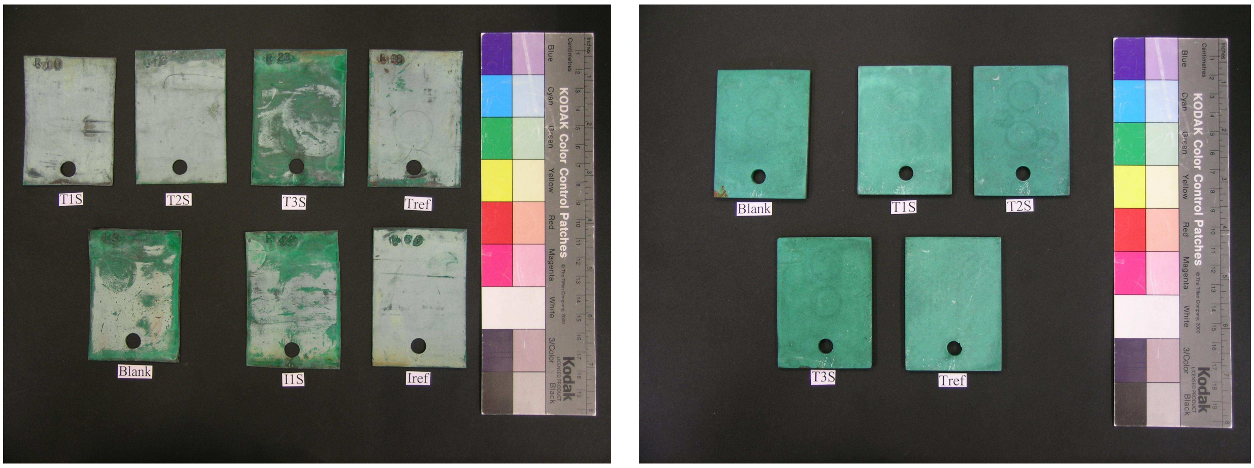
The urban natural patina is light green being relatively homogenous (some stains are visible) and continuous, covering all the metal surface although with some thickness variations. The application of the conservation treatments, namely silanes (T1S, T2S) and Incralac (Tref), led to slight visual modifications of surface aspect.

The urban artificial patina (UA) is vivid green being very homogenous and thicker. The application of conservation treatments practically hasn't change the visual aspect of surface.



UN samples **UA samples**

Figure 11 - Visual aspect of the urban patinas (UN, UA) copper/bronze samples selected to perform EIS measurements before artificial weathering.



UN samples **UA samples**

Figure 12 - Visual aspect of the urban patinas (UN, UA) copper/bronze samples selected to perform EIS measurements after artificial weathering.

Table 2 – Surface change of treated an untreated urban patinas after artificial ageing.

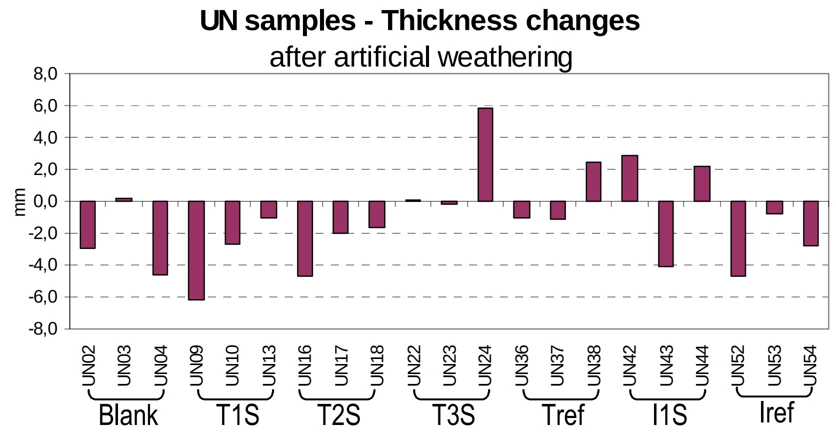
Treatments	UN samples	UA samples
Blank	Highly stained (vivid green stains)	Minor changes
T1S, T2S	Lighter and slightly greyish	Slightly whitish
T3S	Similar to blank	Similar to Blank
Tref	Minor changes, yellowish	Slightly whitish
I1S	Similar to blank	
Iref	Similar to Tref	

Globally, urban natural patina (UN) samples have showed more significant visual changes after weathering than the urban artificial patina (UA) samples that remain almost with the same aspect (Figures 12, A2 and A3). Urban natural patina samples with treatments resulting from a chemical deposition, like T3S (cuprite) and I1S (limewater) treatments, were the most visually affected by the artificial weathering, in a way similar to the untreated patina (blank). UN samples with silane treatments (T1S, T2S) and Incralac (Tref) became lighter and whitish but not in the same extent that was observed before for the natural exposed marine patina (MN) samples. This whitish aspect was also observed in the UA samples with those treatments, but in a lesser extent.

3.2.2. Thickness and mass changes

Thickness measurements of the surface layer were carried out in all the aged UN/UA samples by a non destructive method (EN ISO 2360) - Figure 13. Also mass changes after weathering were measured for all the samples - Figure 14.

It was found that there was tendency of the surface layer thickness to decrease with weathering in UN samples and to increase in UA samples, although less pronounced in this last group for the samples treated with silanes (T1S, T2S). Concerning mass changes, in the case of UN samples, those with treatments T3S and I1S, and the untreated (blank) exhibited mass gains with weathering (they had also the same visual changes). The other treatments showed minor changes (<10 mg) like the silanes (T1S, T2S), or small (Tref - Incralac) to moderate mass losses (Iref – BTA inhibitor).



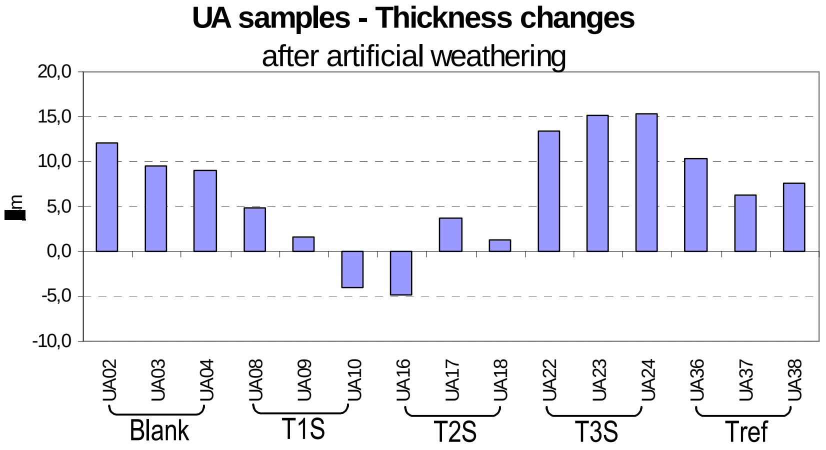
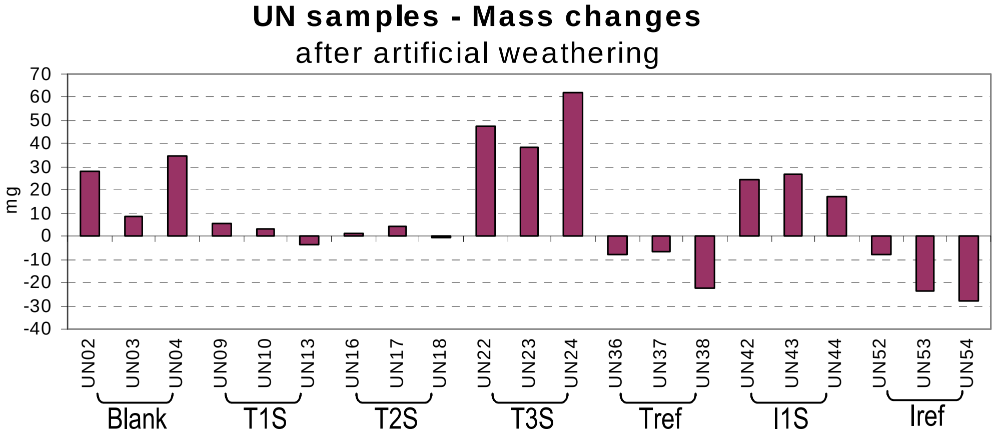


Figure 13 - Eddy current thickness measurements of urban natural (UN) and urban artificial (UA) treated and not treated samples after artificial ageing. (standard deviation: UN samples – 2,8 µm; UA samples – 6,9 µm).

In the case of UA samples, the artificial weathering led to moderate mass losses for the samples treated with coatings (T1S, T2S – silanes, Tref – Incralac), a little less for the non treated (blank), and small mass gains for the T3S treatment (cuprite). This behaviour may result from the mass balance between unprotected backside (bare bronze) losses and upper surface (treated) gains due to reactions with salt spray reagents, mainly sulphate. Thus, the relative higher mass losses of silane treated samples would result from less extension of upper surface reactions due to protection afforded by these treatments.



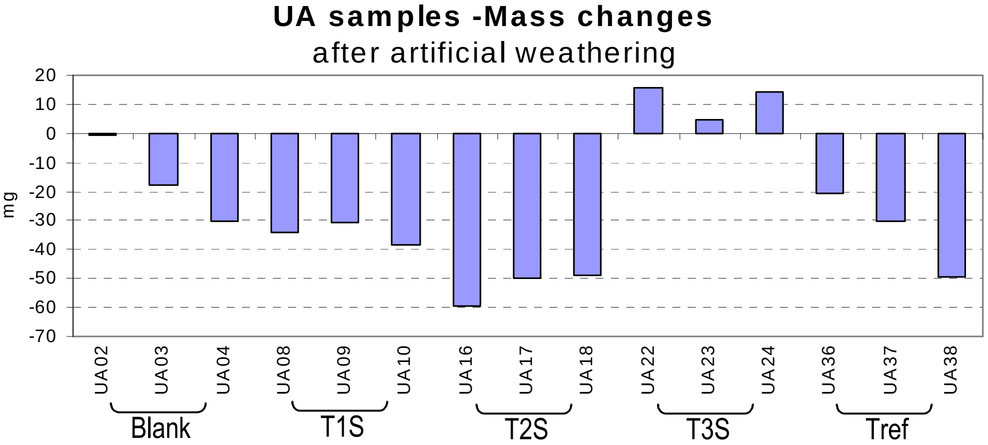
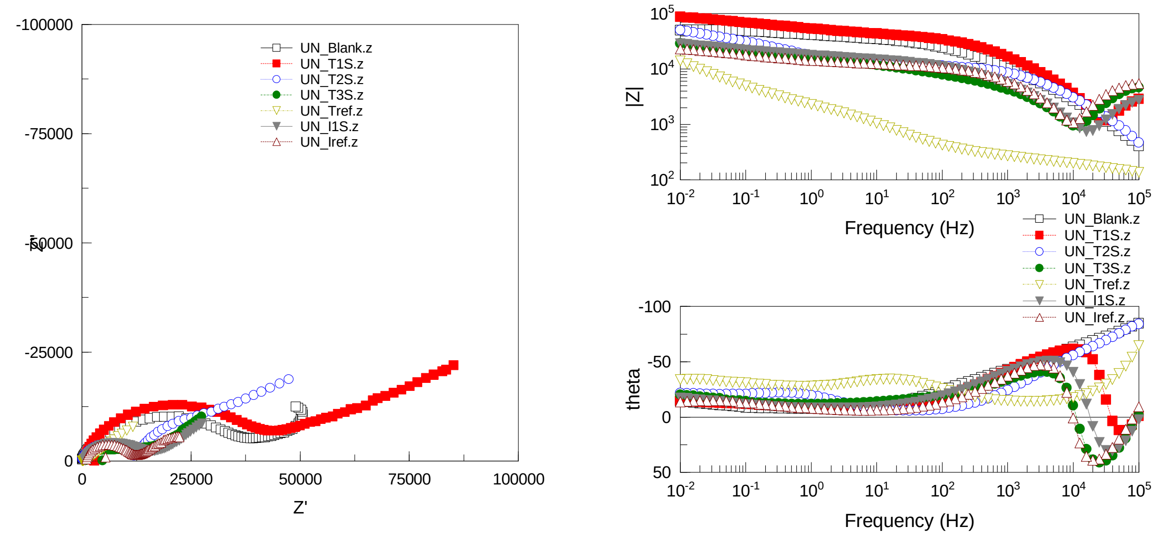


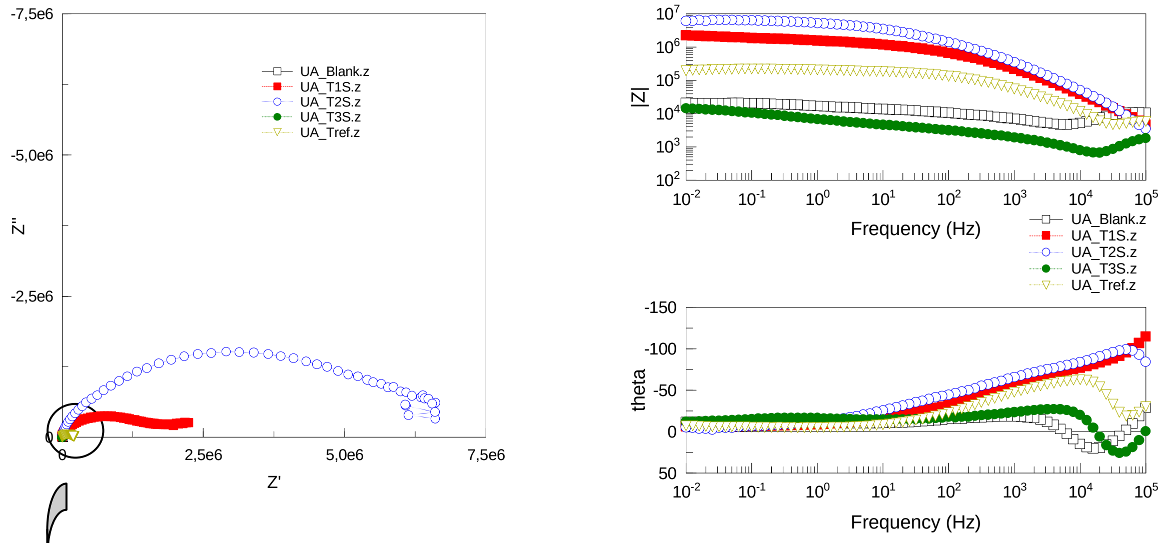
Figure 14 - Mass changes of urban natural (UN) and urban artificial (UA) treated and not treated samples after artificial ageing.

3.2.3. Electrochemical Impedance Spectroscopy (EIS) measurements

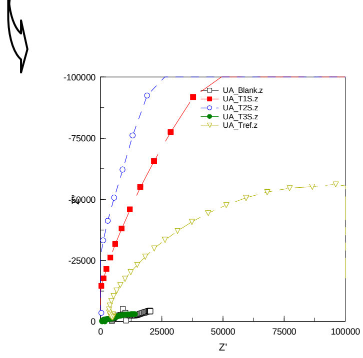
Electrochemical impedance measurements were carried out using the same EIS. Two measurements for each patina/treatment system were done, the results (Nyquist and Bode plots), relative to test zone A, obtained after complete artificial weathering are presented in the following figures for each patina type. From the observation of these EIS plots is clear that, in the case of UN samples, the impedance response yield by the several treatments under study after weathering is much more similar than for the UA samples, which present significant differences in terms of impedance values between silanes (T1S, T2S) and the other treatments applied. This is also evident by the low frequency impedance modulus values before and after weathering, determined for both patina type samples similarly to what was done for the MN samples, that are presented in Figure 16



UN samples



UA samples



Detalhe das altas frequências

Figure 15 - EIS results for UN and UA samples treated and untreated (blank) after artificial weathering.

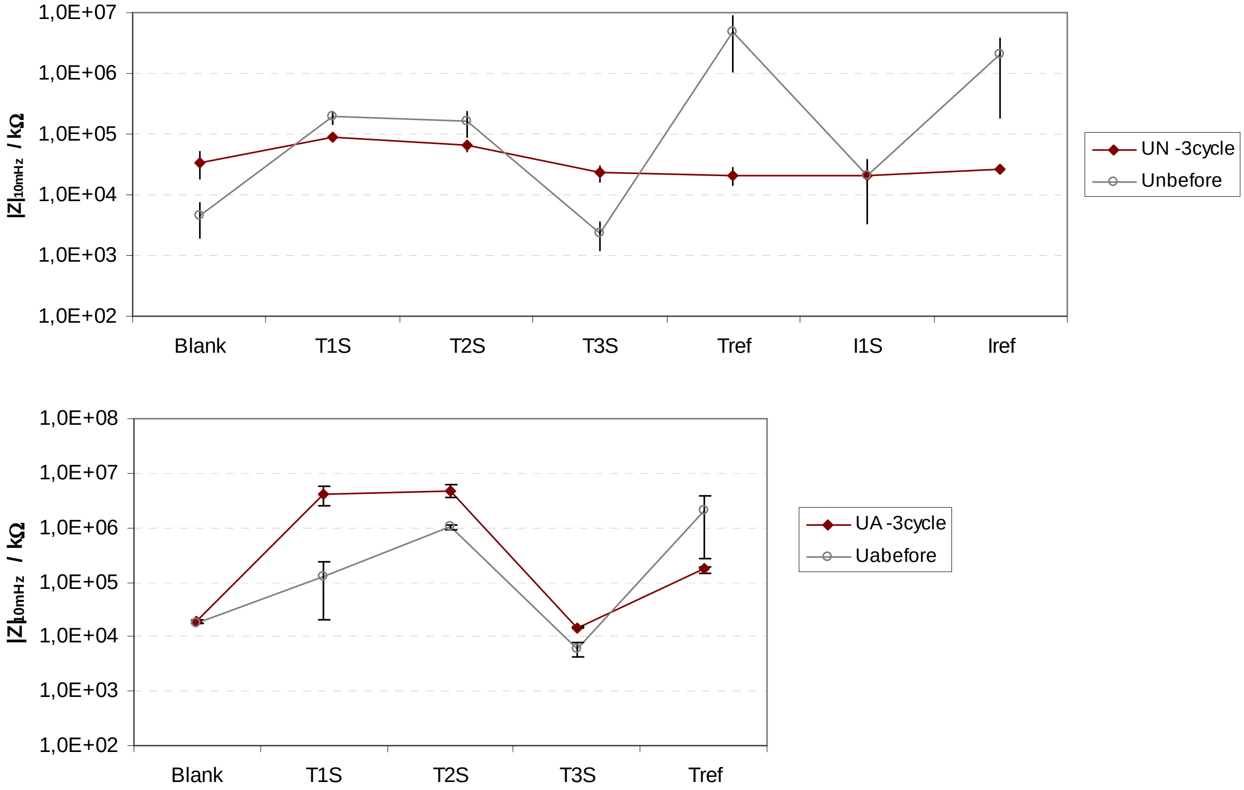
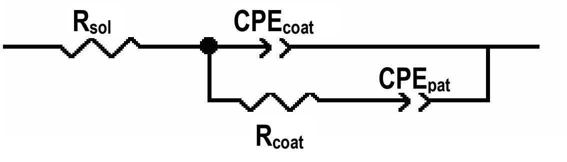
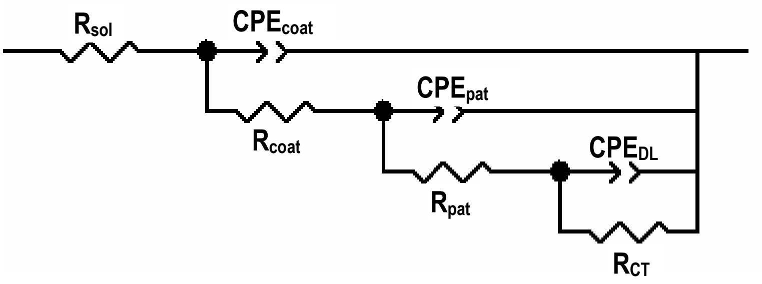


Figure 16 - $|Z|_{10mHz}$ values measured by EIS for treated and untreated (blank) UN and UA samples before and after weathering. ($|Z|_{10mHz}$ values are averaged from the EIS results obtained in two different points . The vertical stick represent the range of variation).

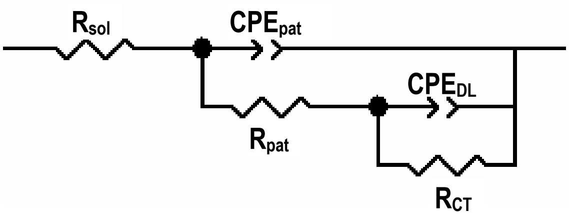
The estimative of coating/patina resistances was also done by fitting equivalent circuits to the impedance plots. The models used were the following:



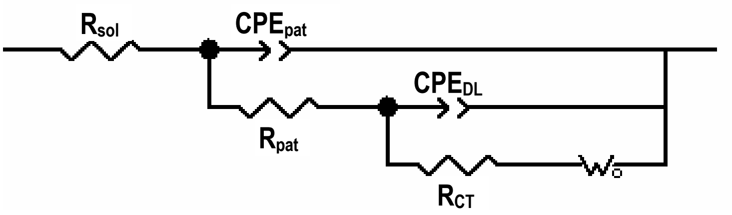
I – T1S, T2S, Tref, Iref



II – T2S (UN test spot B)



III - Blank



IV – T3S, I1S, Blank (UN test spot B)

The equivalent circuit model I applies to the coatings T1S, T2S (silanes), Tref (Incralac) and also to Tref (BTA), which exhibited a behaviour similar to a coating. The EIS plots of these treatments (with the exception of one of the UN-T2S test zones) had only one resistive response, corresponding to the coating resistance. Unlike MN patinas, the resistive response of UN patina with these treatments is not present because it should still be very high (they are more homogenous and dense than MN patinas). However in the case of one of the UN T2S test zones, a larger defect in the coating should have developed and some corrosion processes took place in spite of the protective nature of the patina, so the equivalent circuit model II was used.

For the UN and UA blank samples, the equivalent circuit model III (similar to the one used for MN patina) is valid. It represents the impedance response of the patina plus the occurrence of corrosion processes, because the urban patinas although being consistent and continuous, they are porous and reactive in some extent, so they do not completely protect the metal. The same applies to the urban patinas with I1S and T3S treatments, to whose EIS results the equivalent circuit model IV applies. This is very similar to model III used for the blank EIS results, it just adds a Warburg component, W, representing the occurrence of a diffusion path within the patina that limits the development of corrosion processes.

The results of the application of the equivalent circuits to estimate coating/patina resistances are represented in the next figures.

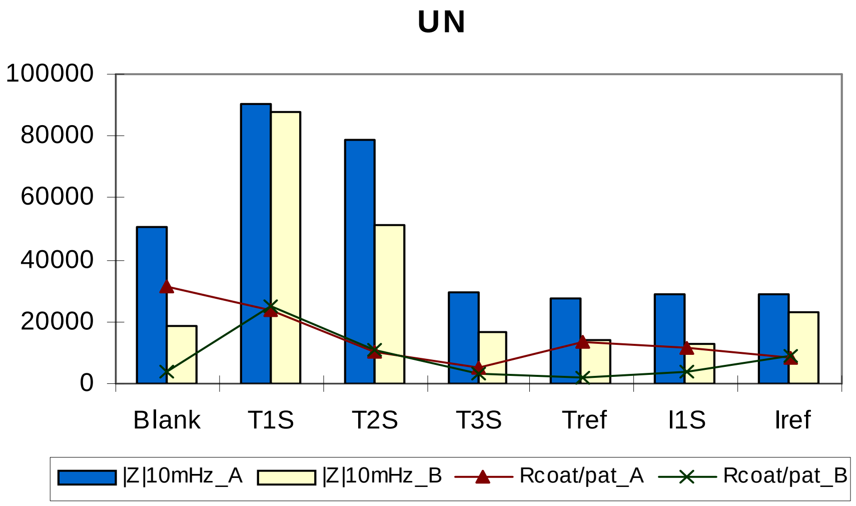


Figure 17 - EIS parameters of treated and untreated UN samples after artificial, measured in two points (A, B) of each sample.

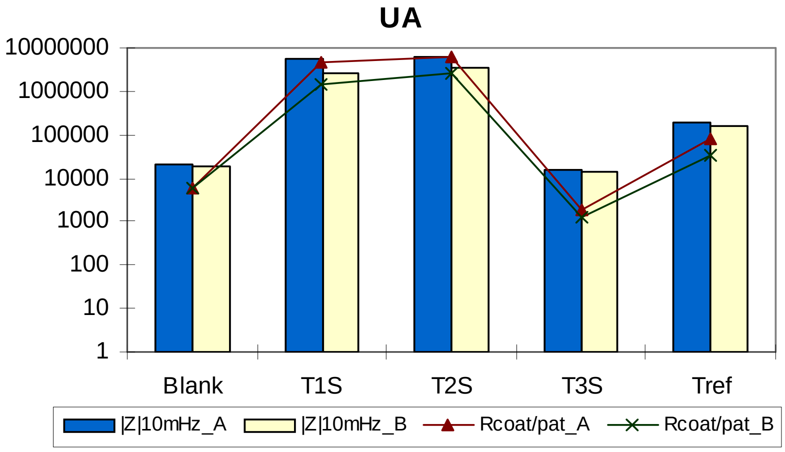


Figure 18 - EIS parameters of treated and untreated UA samples after artificial, measured in two points (A, B) of each sample.

The EIS results reflect the difference between the homogeneity of the two patinas types involved in this study: UN samples (Figure 17), having a naturally formed patina, present heterogeneous zones with different corrosion behaviour, sometimes rather dissimilar. This can be seen in the blank results and in less extent in the results from T3S an I1S treatments. Also, in the case of UN samples treated with coatings (T1S, T2S – silanes; Tref – Incralac) and with BTA (Iref), only $|Z|_{10mHz}$, which is influenced by patina properties, varies with the tested zone while coating resistance, R_{coat}, do not. These differences are not present in the UA samples results (Figure 18). The artificially formed patina is much more homogeneous, chemically stable and also, what is very important in corrosion protection, thicker. UA patina is less prone to degradation with weathering, in opposition to the UN patina, which chemically reacts with corrosive agents present in the artificial atmosphere, as it was seen in tests carried previously[2], causing the appearance of the vivid green stains.

Based in the $|Z|_{10mHz}$ parameter changes, the results obtained show, in the case of UN samples (like MN samples), that weathering led to a convergence of all treatments to similar impedance values and close to the value obtained from the blank. Tref (Incralac) and Iref (BTA) treatments exhibited a significant decrease of impedance values after weathering, loosing their initial advantage, silanes (T1S, T2S) impedance showed a slight decreased, while blank and T3S (cuprite) treatment showed increased impedance, probably due to the higher patina thickness, while I1S (limewater) treatment impedance remained practically the same.

In the case of UA samples, taking $|Z|_{10mHz}$ as reference, the impedance of the blank hasn't changed with weathering, attesting the stability of this patina type. Additionally, the initial relative positions of treatments impedance are kept after weathering although some changes in the $|Z|_{10mHz}$ values has occurred. After weathering, silane treatments (T1S, T2S) have increased impedance and have significant higher values and coating resistances than the other treatments tested in these patinas, including Incralac (Tref) which comes in second, although it has suffered a significant impedance decreased, and then T3S (cuprite) treatment being similar to blank.

4. CONCLUSIONS

The weathering of the several treatments for bronze conservation with marine and urban patinas was achieved. From the observations and tests carried out for the evaluation of treatments behaviour some conclusions arise:

- After 18 months of exposure in the marine environment of Cabo Raso (P) – natural weathering – T1S (Fluorinated silane) resulted to be the most protective treatment applied to the natural marine (MN) patinas. The T2S (silane) treatment comes in second. Silanes showed relative better protective properties than the other treatments, namely than the coating used as reference (Tref-Incralac), however, they undergone visual changes with weathering that could have a significant impact in aesthetics. The other treatments had not a decisive contribution to the corrosion protection of the MN patina.

- In the artificial ageing, T1S (fluorinated silane) and T2S (silane) treatments showed the best protective behaviour for both urban patinas. Tref (Incralac) was highly affected by weathering, it showed a significant decrease of protective properties in both urban patinas, losing initial advantages, for both urban patinas. Iref (BTA inhibitor) had a performance similar to Tref. T3S (cuprite) showed a impedance increase for both urban patinas and behaved similarly to blank. Aesthetically, all the artificial urban (UA) patina samples remain the same. The urban natural (UN) patina samples with treatments T3S (cuprite) and I1S (limewater) were the most visually changed, similarly to blank, while T1S and T2S treatments (silanes) presented less significant visual changes.

On the overall, the silane coating treatments (T1S, T2S) were those that exhibited the best anticorrosive performance, probably due to a synergistic effect between the patina and these two coatings: silanes seal patina natural porosity and patina promotes adherence and prevents/retards corrosion of the metal surface in the places where the coating has defects (porous, scratches, etc.). Silanes could establish chemical bonds with the products constituents of bronze/copper patinas surface that contain hydroxide groups, what provides an excellent linkage between these type of coatings and patinated bronze. This characteristic is probably the reason of their better protective behaviour in comparison to Incralac (Tref).

However, when dealing with objects of art, the aesthetics also have to be taken in consideration. In the application of silanes there is a possibility of aesthetic problems arising in longer exposures in natural environment rich in chlorides. From the results obtained in the artificial weathering that intended to simulate an urban environment, it seems that the risk of visual changes is less probably in this type of environment.

Collaborations: This work had the collaboration of Nuno Garcia, Ana Paula Melo and Nuno Silva in the experimental part.

Lisboa, Laboratório Nacional de Engenharia Civil, December of 2008

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[6] EN ISO 9227:2006 - Corrosion tests in artificial atmospheres. Salt spray tests (ISO 9227:2006).

[7] EN ISO 2360:2004 - Non-conductive coatings on non-magnetic electrically conductive basis materials - Measurement of coating thickness - Amplitude-sensitive eddy current method (ISO 2360:2003)

ANNEX A

Visual aspect of treated and non treated patined samples after natural (MN) and artificial (UN, UA) weathering

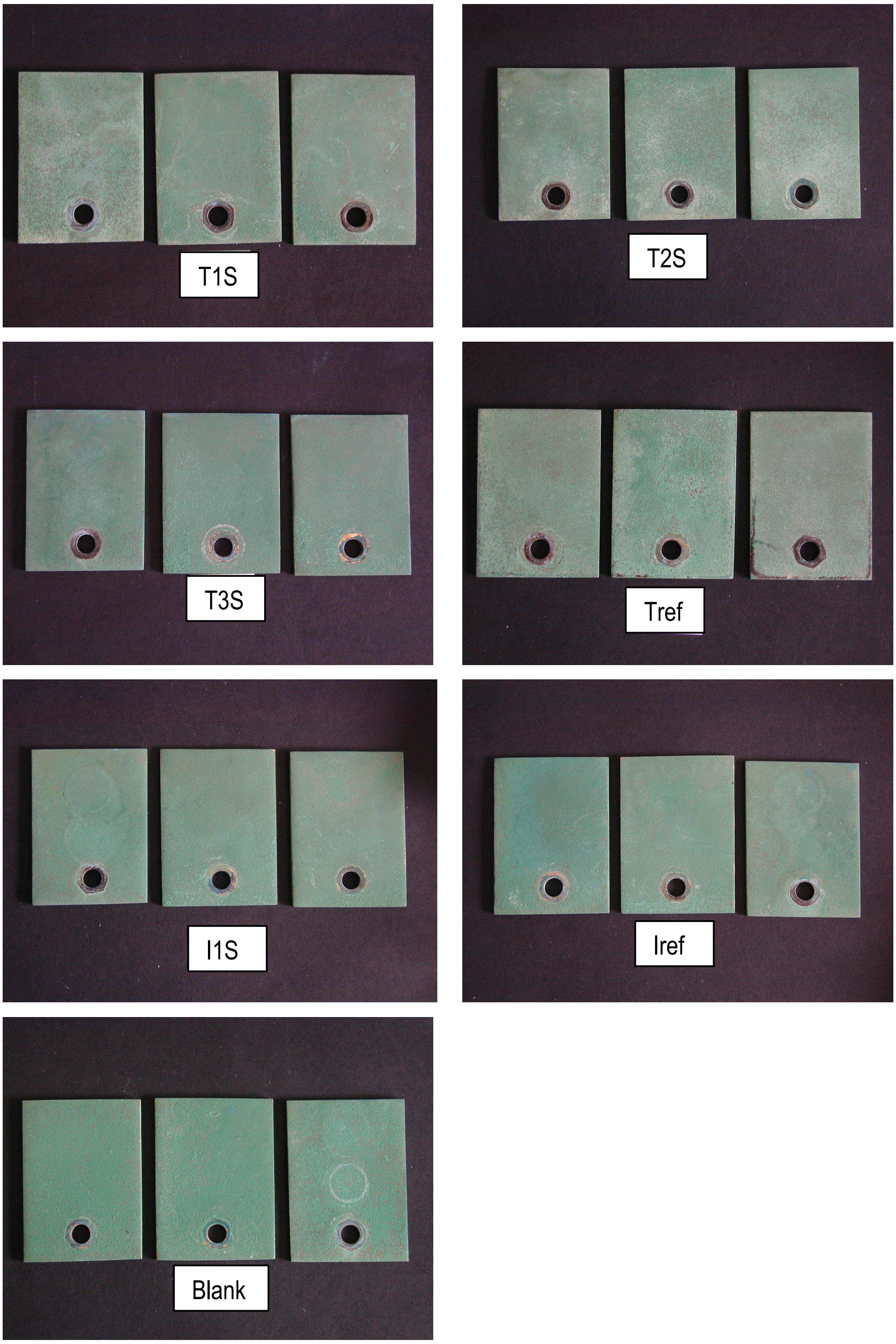

Figure A1 – Visual aspect of all marine natural (MN) bronze samples, treated and non treated (blank) after 18 months exposure in the marine site Cabo Raso (P).

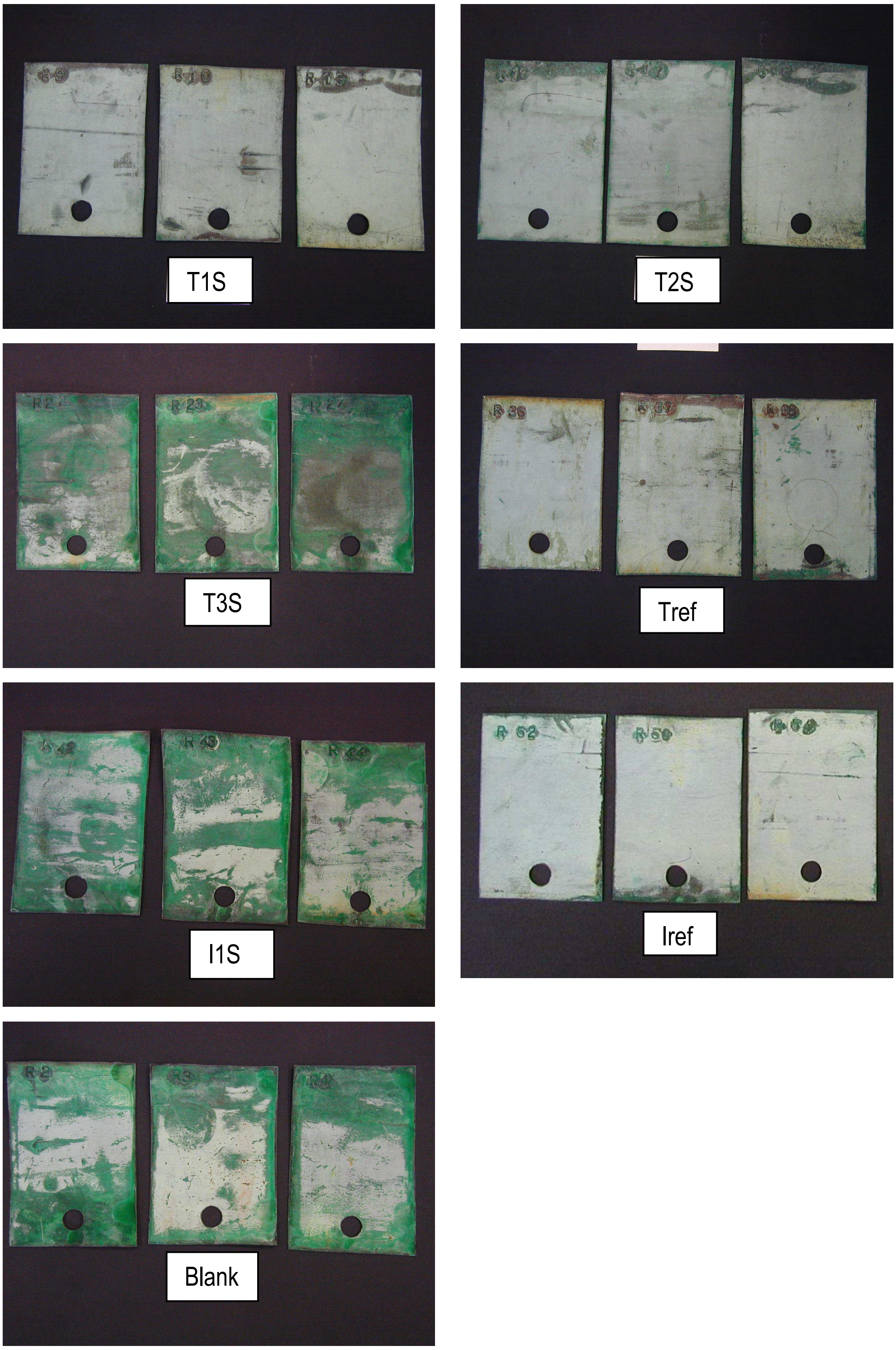

Figure A2 – Visual aspect of all urban natural (UN) bronze samples, treated and non treated (blank), after artificial weathering.

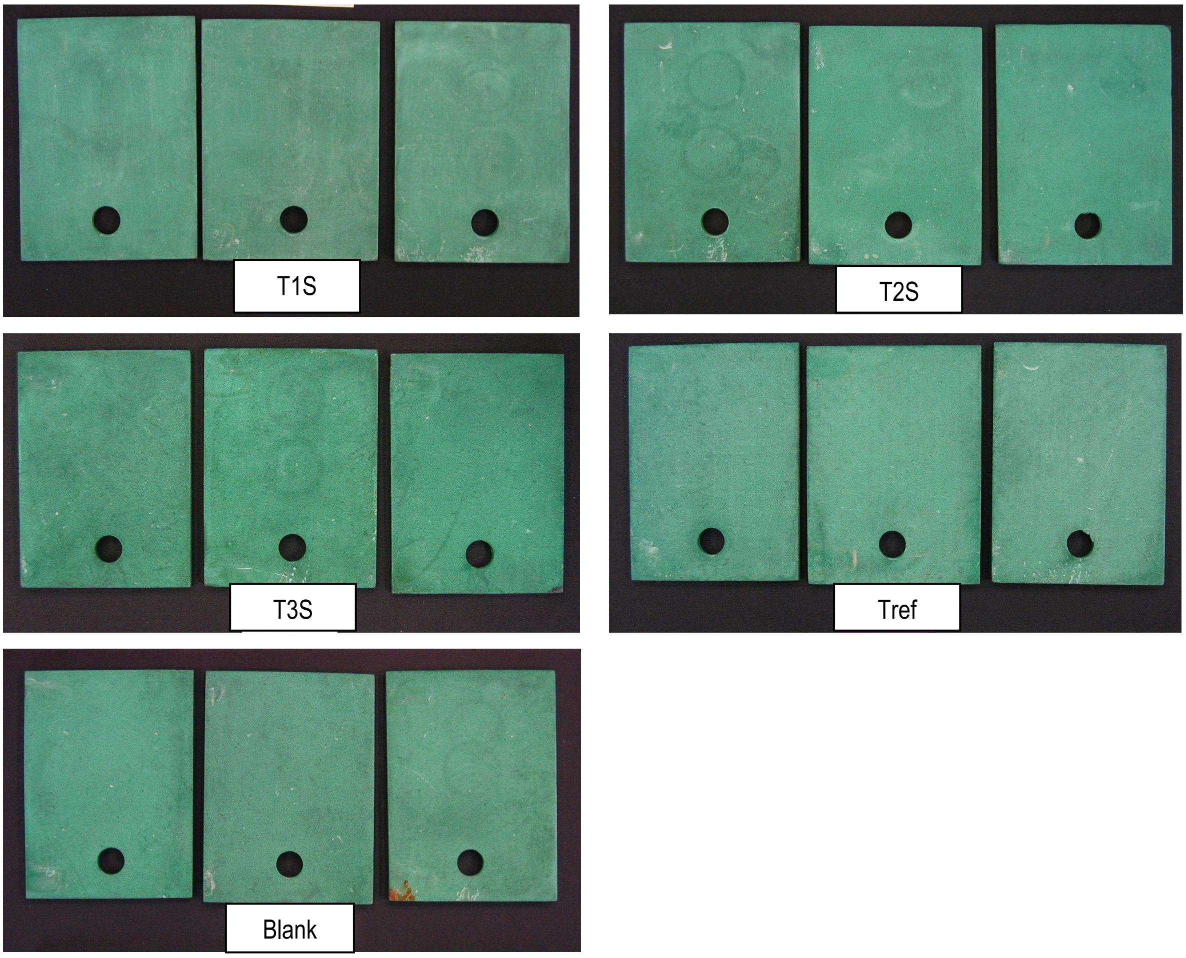

Figure A3 – Visual aspect of all urban artificial (UA) bronze samples, treated and non treated (blank), after artificial weathering.