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Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary

THE EFFECTIVENESS OF WAX IN PROTECTION OF BRONZES COVERED WITH ARTIFICIAL PATINA IN OUTDOOR EXPOSURE

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ABSTRACT. Lately there is a major concern about the preservation of artificial patina applied on the art objects made of bronze. These studies are important in the restoration and conservation of bronze monuments exposed outdoor. In this context the present work aims studying the efficiency of wax-based films (WF) on the protection of two artificial patina (brown and golden) in a solution containing Na_2SO_4 and $NaHCO_3$ (pH 5) simulating an acid rain. The protective effect of the artificial patina with / without wax-based films was investigated by electrochemical and non-electrochemical methods. The chemical composition of the golden artificial patina/ Carnauba wax layer was determined by X - ray fluorescence analysis, and the morphology was determined by SEM - EDX cartographies. The results have shown that both artificial patinas exerted an anticorrosion protective effect on bronze and the wax improved even more the corrosion resistance. The protection conferred by the golden artificial patina was significantly improved by using Carnauba wax (Cw) and a corrosion inhibitor (2 - mercapto - 5 acetylamino - 1, 3, 4 - thiadiazole).

Key words: *bronze, artificial patina, corrosion inhibitor, Carnauba wax.*

INTRODUCTION

Outdoor bronze artworks have aesthetic and often historic value. It is therefore necessary to protect them against aggressive agents. Long

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term conservation of outdoor bronze sculptures involves formation of artificial patinas on bronze surface, which additionally confer to artistic objects a pleasant aesthetic aspect [1, 2]. For more protection are used corrosion inhibitors [3 - 9], waxes and lacquers [10, 11] which are applied on the surface of patinated bronze. The advantage of the wax-bases films is that they do not modify the patina color [11], while some corrosion inhibitors such as benzotriazole change and blacken it [12].

In order to confer a pleasant esthetical aspect to bronze surfaces, in the past the sculptors prepared artificial patina by using flowers of sulphur (for dark brown color), copper nitrate (for light green) and copper sulphate (for reddish color). In a previous study [13] the authors examined the electrochemical behavior of bronze treated with these compounds in an environment that simulated acid rain. Accelerated corrosion tests revealed that the investigated patinas have a limited protection effect on bronze corrosion. The patina layers were not enough compact and uniform. Moreover, after the corrosion tests, the patina showed limited adherence to the bronze surface.

In this context, in order to improve the corrosion resistance of patinated bronze, the aim of this paper was to investigate comparatively the protective effect of two new artificial patinas (brown and golden) prepared by chemical methods on bronze CuSn8 surface, in the absence and in the presence of wax-based films (WF). Additionally, the efficiency of golden patina was investigated in the presence of Carnauba wax (Cw) and two corrosion inhibitors (benzotriazole (BTA) and 2 - mercapto - 5 acetylamino - 1, 3, 4 – thiadiazole (MAcT)). The anticorrosion effect of the all protective layers was investigated by electrochemical methods in a solution containing Na_2SO_4 + $NaHCO_3$ (pH 5) that simulated an acid rain in urban environment. The protective effect of artificial patinas was comparatively investigated by electrochemical and non - electrochemical methods.

RESULTS AND DISCUSSION

To conduct the studies, a contemporary bronze CuSn8 was selected, of the following composition: 90.18 % copper, 8 % tin, 0.8 % zinc, 1 % lead and 0.02 % aluminum.

Polarization measurements

Firstly the electrochemical behavior of electrodes covered with brown and golden patina has been studied. To determine the kinetic parameters of the corrosion process, polarization curves were recorded in the potential range of ± 200 mV *vs.* ocp (Figure 1-a). Secondly, the Tafel polarization curves for bronze electrodes covered with artificial patina in presence of

WF protection (Figure 1-b) were recorded. Finally, the electrodes covered with golden patina in the presence of Carnauba wax and corrosion inhibitors (BTA and MAcT) (Figure 1-c) were investigated.

The the corrosion kinetic parameters values were determined from the polarization curves by Tafel interpretation and the results are presented in Table 1. The polarization resistance R_p values for each electrode, calculated as the inverse of the slope of linear polarization curves (± 20 mV *vs.* OCP), are also shown in Table 1.

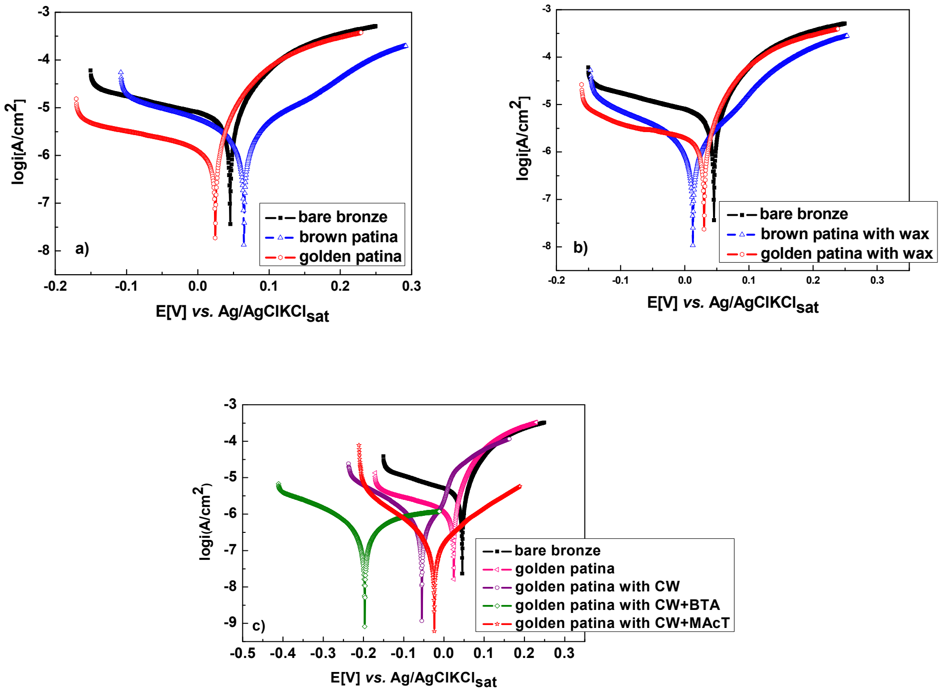


Figure 1. The polarization curves (± 200 mV *vs.* OCP) for the bronze covered with: brown and golden artificial patina (a); artificial patina (brown and golden) with WF (b); golden artificial patina with Cw in the absence and in the presence of inhibitors (c); Experimental conditions: corrosion solution, Na_2SO_4 + $NaHCO_3$ (pH 5); potential scan rate, 10 mV / min.

The protection efficiencies (PE) conferred by different treatments (artificial patinas and waxes) were calculated from the corrosion current densities (i_{corr}) according to the equation:

$$PE[\%] = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} x100$$

where: i^0_{corr} - represents the corrosion current density for bare bronze and i_{corr} -represents the corrosion current density for bronze covered with artificial patina / WF / inhibitor.

Table 1. Corrosion process parameters for the examined samples in 0,2 g/L $NaSO_4$ + 0,2 g/L $NaHCO_3$ (pH = 5)

Electrode	E_{corr} [mV *vs* Ag/AgCl]	i_{corr} [μA/cm^2]	$β_a$ [mV/decade]	- $β_c$ [mV/decade]	R_p [kΩcm^2]	PE [%]
Bare bronze	46	5.36	46	284	2.06	-
Brown patina	65	2.75	85	134	5.38	48.69
Golden patina	25	1.54	27	188	5.60	71.26
Brown patina / WF	13	1.69	71	111	4.39	68.47
Golden patina / WF	30	1.46	33	224	3.39	72.76
Golden patina / Cw	-55	0.22	53	56	3.60	95.90
Golden patina / Cw / BTA	-197	0.32	243	159	32.26	**94.03**
Golden patina / Cw / MAcT	-24	0.08	83	72	148	**98.51**

$β_a$ and $β_c$ are the Tafel coefficients

Artificial patinas

As expected, the lowest corrosion resistance, was obtained in case of bare bronze (R_p = 2.06 kΩcm^2, i_{corr}= 5.36 μA/cm^2, Table 1). The results have shown that both artificial patinas (brown and golden) improve the corrosion resistance of bronze, but their protection efficiencies are not spectacular. The best protection efficiency was exerted by the golden patina (71.26 %).

Artificial patinas with WF

In the presence of WF, it is observed in all cases a slight improvement in the protective properties of the patina layers and a decrease of the corrosion current density. Thus, the results reveal that the highest corrosion resistance was noticed in the case of the electrode coated with golden patina and WF (R_p=4.39 kΩcm^2, i_{corr}= 1.46 μA/cm^2), followed by the electrode covered with brown patina and WF (Table 1). By comparing these results with those recorded for bronze covered only with artificial patina layers, it can be concluded that the wax plays a role of barrier against corrosion enhancing the protective effect exerted by the patinas.

Golden patina with Carnauba wax (Cw)

A comparison of the results obtained with two different waxes applied on the same type of patina was performed in the case of golden patina. The analysis of data obtained in this case (Table 1) shows that by applying a layer of Cw on the bronze surface covered with golden patina, there is a considerable improvement of anticorrosion properties. It should be also mentioned that Carnauba wax exerted a more pronounced inhibiting effect than WF.

In order to explore the possibility of improving even more the corrosion resistance of the bronze samples, a thiadiazole derivative (MAcT) was dissolved in the corrosion solution in a concentration of 1mM / L [14]. In this case, the bronze covered with golden patina and Cw gave the best results (R_p = 148 kΩcm^2, i_{corr}= 0.08 μA/cm^2) confirming that the thiadiazole derivative acts as an effective corrosion inhibitor. The spectacular rise of resistance polarization in this case is not only due to the fact that Cw layer forms a physical barrier against corrosion, but also to the synergistic effect that appear in the simultaneous presence of the inhibitor and the Cw layer on the bronze surface covered with golden patina. This synergistic effect may be due to chemical reactions that take place between participants and creates on the bronze surface covered with golden patina an effective barrier.

It should also be noted that the MAcT was proved to be a better corrosion inhibitor than BTA, which is a remarkable fact, given its non-toxic nature and its accessibility.

Morphological characterization

The SEM image of the bare bronze surface (Figure 2) shows that the surface is homogeneous, without slag inclusions or foreign material. However, there are some points with Pb segregation (see arrow).

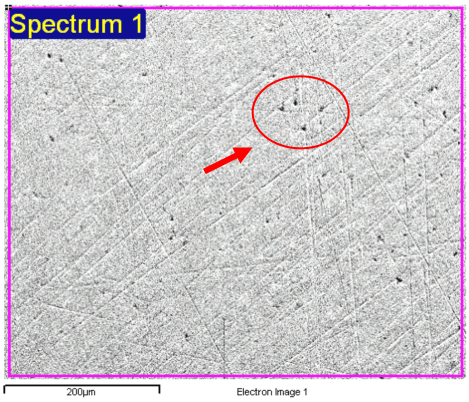


Figure 2. SEM image obtained on surface of bronze before the application of artificial patina

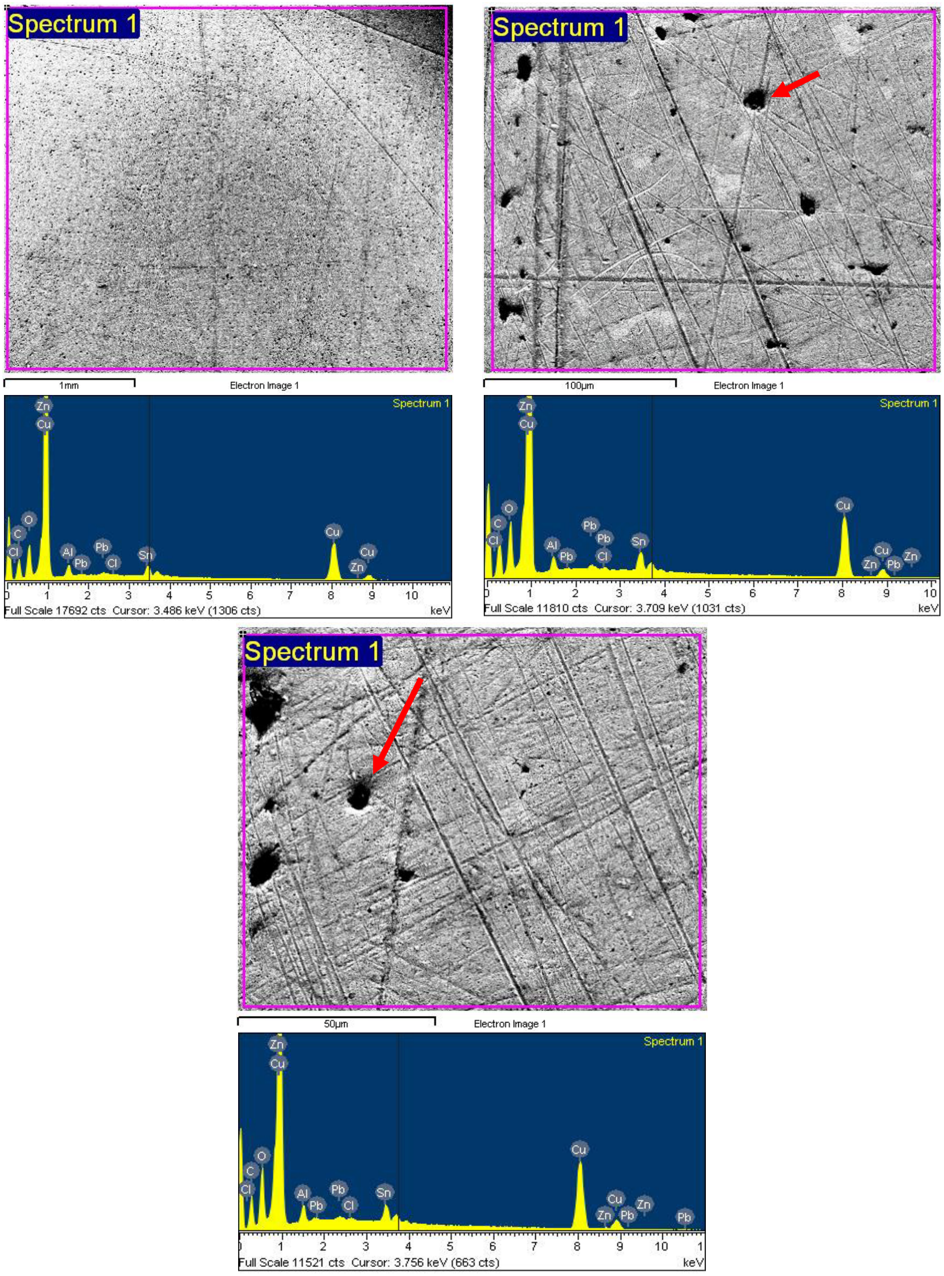


Figure 3. SEM / EDX results obtained on the bronze surface covered with golden artificial patina, after corrosion tests

The chemical treatment applied to form the golden patina led to a sparingly soluble and adherent film (Table 3, last column). After the corrosion tests, the bronze surface covered with golden patina has not suffered major depreciations and its color has not significantly changed (results not shown).

In order to determine the morphology and the chemical composition of the golden patina layer after one hour of immersion SEM - EDX analysis was performed at different points of the bronze's surface and results are presented in Figure 3 and Table 2.

Analyzing the SEM images from Fig. 3 it can be observed a uniform distribution of the corrosion products all over the surface and the existence of some black points (see arrow) in the patina layers, existing on bare bronze too (Fig. 2). As already mentioned, these points are due to lead segregation during casting. The bronze surface is not covered with a thick corrosion products layer and compared with bare bronze‘s surface there are not major modifications.

As can be seen from Table 2, the distribution of the chemical elements in the corrosion products all over the surface is uniform. The EDX analysis in different points indicated the presence of copper, oxygen, carbon, zinc and tin, whereas Al, Pb and Cl were present as minor elements. The presence of O and C in high concentrations led to the conclusion that the corrosion products layer is mainly composed of oxides and carbonates. The presence of zinc in the corrosion products layer in higher concentration than in the bronze substrate is due to the phenomenon of bronze dezincification [15] which is explained elsewhere [16].

Table 2. Elemental composition [%] of the corrosion products formed at different points of the bronze surface covered with golden artificial patina, determined by EDX analysis

	C [%]	**O** [%]	**Al** [%]	**Cl** [%]	**Cu** [%]	**Zn** [%]	**Sn** [%]	**Pb** [%]
1	15.09	9.82	1.63	-	64.76		5.53	0.96
2	15.29	9.36	1.38	0.21	65.19	2.03	5.69	0.85
3	13.50	9.16	1.45		68.02	2.16	4.83	0.70

The uniform distribution of the chemical elements on the bronze surface covered with golden patina after the corrosion tests can be also observed in Figure 4.

Based on SEM / EDX analysis it can be concluded that the thin, continuous, adherent and chemically homogenous corrosion products layer formed in the presence of golden patina is responsible for the better corrosion resistance of the bronze samples covered with this type of patina.

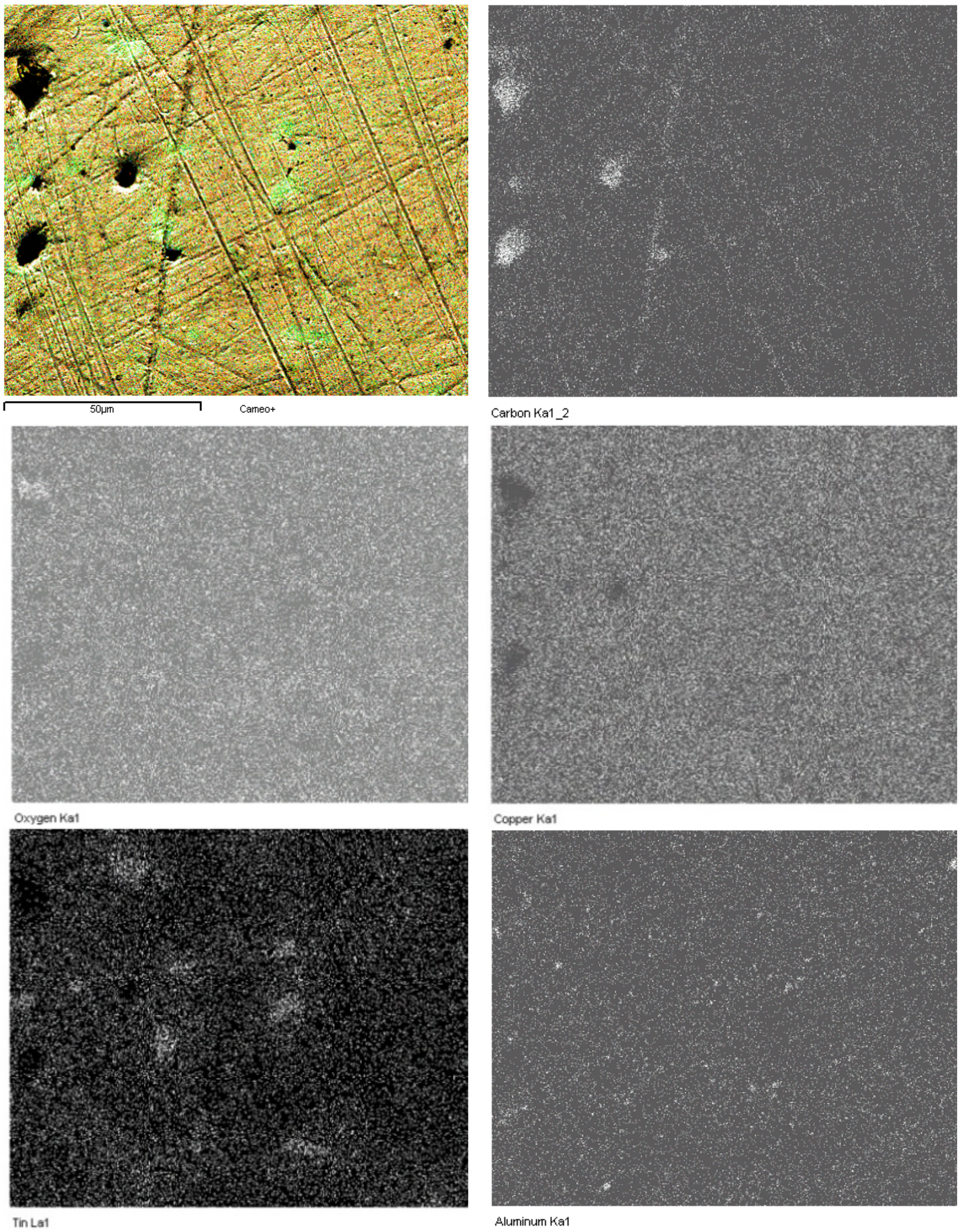


Figure 4. Mapping results obtained on surface of bronze electrode covered with gold artificial patina, after corrosion tests. X-ray maps for C, O, Cu, Sn, Al.

CONCLUSIONS

The corrosion properties of bronze covered with brown and golden artificial patinas (chemically formed on bronze surface) were investigated in a solution of Na_2SO_4 and $NaHCO_3$ (pH 5) which simulated an urban acid rain. The artificial patinas (brown and golden) were applied by chemical methods. For additional protection wax-based films were used.

Based on SEM / EDX analysis it can be concluded that in the presence of golden patina the corrosion products layer formed is thin, continuous, adherent and chemically homogenous and is mainly composed of copper and tin compounds (oxides and carbonates).

The artificial patinas improve the corrosion resistance of bronze. Both types of patinas can be recommended for protection of works of art, especially in the presence of wax-based films.

The best protection efficiency was exerted by golden patina with Cw when corrosion inhibitors (BTA and MAcT) were used. The maximum protective effect was noticed in case of the golden patina with Cw in presence of MAcT (98.51 %).

EXPERIMENTAL

Electrodes

The working electrodes made of bronze CuSn8, cylindrically shaped, were placed in a PVC tube, while the sealing was assured with epoxy resin. In this way, the surface of the electrode exposed to the solution was disk - shaped, with a surface $S = 2.00$ cm^2. For electrical contact, a metal rod was attached. On these electrodes, patina was applied chemically.

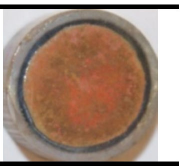
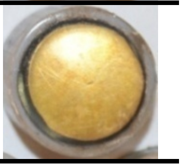
Patinas

Artificial patinas were prepared (on the polished bronze surface) in several steps, using the solutions mentioned in Table 3.

The stages in the patination process were:

- Polishing the electrode surface;
- Degreasing in acetone
- Immersion in solution (see Table 3) (T, t);
- Washing with distilled water;
- Drying with ethyl alcohol;
- Applying of a protective solution (wax - based)

Table 3. Substances used to create artificial patina

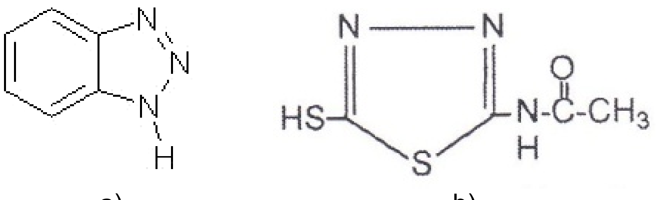
Patina color	Chemical composition of the solution	Chemical formula	Quantity [g/L]	Duration of imersion / temperature	The working electrode
Brown	Copper sulphate	$CuSO_4$	60	3 - 5 minutes / 90 - 100 ºC	
	Potassium permanganate	$KMnO_4$	7		
Golden	Sodium hydroxide	NaOH	50	7 - 15 minutes / 30 ºC	
	Oxalic acid	$C_2H_2O_4$	30		
	Copper sulphate	$CuSO_4$	50		

Wax – based films (WF)

For an additional protection of all artificial patinas a mixture of beeswax (25 %) and anticorrosive oil (75 %) was used. In the case of golden patina Carnauba wax (Cw) was also used. To apply the Cw on bronze surface the wax was melted around 85 ºC and mixed with „white spirit" [1].

Corrosion inhibitors

The inhibitors used in the experiments were benzotriazole (BTA) (Sigma Aldrich) and a non - toxic thiadiazole derivative, respectively 2 - mercapto - 5 acetylamino - 1, 3, 4 - thiadiazole (MAcT, from Sigma Aldrich). The molecular structure of the two compounds is shown in Figure 5. The inhibitors were dissolved in the corrosion solution at a concentration of 1mM / L, considered optimal according to some studies [14, 17].



a) b)

Figure 5. The molecular structure of the a) benzotriazole, b) 2 - mercapto - 5 acetylamino - 1, 3, 4 – thiadiazole

Experimental investigation

The morphology of corrosion products layer formed on the electrodes surface was examined with a scanning electron microscope (SEM; Scanning Jeol JEM5510LV (Japan) coupled with Oxford Instruments EDX Analysis System Inca 300 (UK) at 15kV and spot size 39 μm).

The electrochemical corrosion measurements were performed on a PC – controlled electrochemical analyzer AUTOLAB - PGSTAT 10 (Eco Chemie BV, Utrecht, The Netherlands) using a three electrodes cell containing a working electrode (bronze), an $Ag/AgCl/KCl_{sat}$ electrode as reference electrode and a platinum counter electrode. Anodic and cathodic polarization curves were recorded in a potential range of ± 20 mV (for Rp determination) and of ± 200 mV *vs.* the value of the open circuit potential (for Tafel interpretation), with a scan rate of 10 mV / min, after 1 hour immersion in the corrosive solution.

The electrolyte solution for corrosion measurements was 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ acidified to pH = 5 by the addition of a dilute sulphuric acid at room temperature.

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