

# Corrosion inhibitors for bronze protection in polluted atmosphere

*Amela Keserović<sup>1</sup>, Helena Otmačić Ćurković<sup>2</sup>, Ema Stupnišek-Lisac<sup>2</sup>, Katarina Marušić<sup>2</sup>,  
Alla Furman<sup>3</sup>, Margarita Kharshan<sup>3</sup>*

<sup>1</sup> *GlaxoSmithKline Research Centre, Zagreb, Croatia*

<sup>2</sup> *Faculty of Chemical Engineering and Technology, Zagreb, Croatia*

<sup>3</sup> *Cortec Corporation 4119 White Bear Parkway, St. Paul, 55110 MN, USA*

## Abstract

The aim of this work was to investigate the possibility of bronze protection in atmospheric conditions by three protective systems. Two of them were based on environmentally friendly corrosion inhibitors: 4-methyl-1-(*p*-tolyl)imidazole and a vapor phase corrosion inhibitor. The third protective system was water - based acrylic primer containing the mixture of non - toxic corrosion inhibitors.

The research was carried out in the solution of  $0.2 \text{ g dm}^{-3} \text{ NaNO}_3$ ,  $0.2 \text{ g dm}^{-3} \text{ Na}_2\text{SO}_4$  and  $0.2 \text{ g dm}^{-3} \text{ NaHCO}_3$  at pH 3. This electrolyte simulated the composition of acid rain characteristic for polluted urban environment. Measurements were performed by the means of electrochemical methods – Tafel extrapolation method, linear polarization method and electrochemical impedance spectroscopy. Stability of the applied protection was also tested in humidity chamber at two temperatures (25 °C and 35 °C).

Results of the investigation showed that each of the applied corrosion inhibitors provided protection to bronze in the tested conditions. However, the maximum inhibiting efficiency of 4-methyl-1-(*p*-tolyl)imidazole was about 68 %, that of vapor phase inhibitor about 98 %, while acrylic coating containing corrosion inhibitor had an efficiency of almost 100 % .

**Keywords:** bronze, acid rain, corrosion inhibitors, electrochemical methods, humidity chamber

## 1. Introduction

Bronze is a copper alloy known for over 3,000 years. Because of its good physical and chemical properties, especially resistance to corrosion, it is widely used as a construction material, in industries, for making tools, weapons, artworks etc. One of the particular properties of bronze is the formation of natural patina, corrosion products that form on the bronze surface turning it to green color. Not only that patina contributes to the beautiful appearance of bronze, but it also helps to protect it against further corrosion.<sup>1</sup> That is why it is so highly valued in statuary. But in the last few decades due to the increase of air pollution and acid rain, outdoor artifacts made of bronze are subject to sever corrosion. Because of their great significance and value they should be additionally protected.<sup>2,3</sup>

One of the methods for metal protection is using corrosion inhibitors. Most of commercially available corrosion inhibitors that have been known as highly effective are toxic and, therefore, dangerous for the environment.<sup>4</sup> Thus they need to be replaced with non-toxic compounds that can protect metal with the same high effectiveness. This research was aimed to investigate the possibility of bronze protection with three environmentally friendly systems. The toxicity of the 4-methyl-1-(*p*-tolyl)imidazole was tested measuring the inhibition of bacterial growth while toxicity testing for vapor phase inhibitor was determined orally on rats. Its LD50 value is 7500 mg/kg which is significantly higher than the LD50 of benzotriazole (560 mg/kg), common corrosion inhibitor for copper and its alloys.

Methods used in this investigation are electrochemical methods – Tafel extrapolation method, linear polarization method and electrochemical impedance spectroscopy. Stability of the applied protection was also tested using accelerated methods in a humidity chamber at two temperatures (25 °C and 35 °C).

## **2. Experimental**

### **2.1. Chemicals**

#### *2.1.1. Electrolyte*

The studies were performed in the solution of 0.2 g dm<sup>-3</sup> NaNO<sub>3</sub>, 0.2 g dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> and 0.2 g dm<sup>-3</sup> NaHCO<sub>3</sub> acidified to pH 3. This solution simulated acid rain in urban environment.

#### *2.1.2. Inhibitors*

Three inhibiting systems were examined in this research. All of them have shown a very low toxicity and, therefore, are environmentally acceptable.

*Inhibitor 1*, 4-methyl-1-(*p*-tolyl)imidazole, is an imidazole derivative, well-known for its ability to protect copper<sup>5-10</sup> and copper alloys because of its strong adsorption on the metal surface.<sup>2,11</sup>

*Inhibitor 2* is a vapor phase compound completely soluble in water. It creates a transparent, thin and soft lubricating film on metal surface. It is biodegradable and does not contain nitrites and phosphates.

*Inhibitor 3* is a water-based acrylic primer containing the mixture of non-toxic corrosion inhibitors.

### **2.2. Materials**

Electrochemical measurements were performed in a three-electrode cell, filled with 300 ml of electrolyte solution. As the working electrode was used bronze electrode, the reference electrode was saturated calomel electrode and the counter electrode was platinum

plate. Bronze electrode was insulated with epoxy resin so that surface exposed to aggressive media was  $A = 1 \text{ cm}^2$ . Its composition is shown in the *Table 1*.

*Table 1.* Composition of the bronze electrode

wt %	Sn	Pb	Zn	Fe	P	Cu
	6.10	0.01	0.10	0.02	0.11	93.66

Bronze panels that were used in humidity chamber were made of phosphorus bronze whose composition is presented in *Table 2*. Bronze panels were 2.54 cm x 5.08 cm x 0.0813 cm with a diameter  $d = 0.476$  cm hanging hole.

*Table 2.* Composition of the bronze panels

wt %	Sn	Pb	Zn	Fe	P	Cu
	5.80	0.05	0.30	0.10	0.35	93.40

Before each measurement bronze electrode/specimens were wet abraded with 1500 and 2000 grit sandpaper, polished with  $\text{Al}_2\text{O}_3$  particles diameter  $d = 0.5 \text{ }\mu\text{m}$ , degreased with methanol and rinsed with deionized water.

### 2.3. Methods

In this research measurements were performed by the means of electrochemical methods, while the stability of the applied protection was also tested in a humidity chamber at two temperatures (25°C and 35 °C).

#### 2.3.1. Electrochemical measurements

Electrochemical methods used in this work were Tafel extrapolation method, linear polarization method and electrochemical impedance spectroscopy (EIS). Polarization measurements were performed on VersaStat, EG&G instrument controlled with 352/252 SoftCorr™ Corrosion Software, while EIS measurements on Gamry PCI4 Potentiostat/Galvanostat/ZRA with EIS300 software.

Polarization measurements were performed in the wide potential range  $E_{\text{corr}} \pm 150 \text{ mV}$  (Tafel extrapolation method) and in the narrow potential range  $E_{\text{corr}} \pm 20 \text{ mV}$  (linear polarization method) at scan rate 0.166 mV/s. EIS measurements were performed at open circuit potential with the amplitude of perturbing signal of 10 mV and in the frequency range 100 kHz to 10 mHz.

Due to its high polarization resistance, *Inhibitor 3* was not tested using electrochemical methods.

### 2.3.2. Humidity chamber

Accelerated methods used for testing the stability of the applied protection on bronze specimens were conducted in a Q-Fog Cyclic Corrosion Chamber at two temperatures (25°C and 35°C) in three cycles (144, 240 and 336 hours) at 100 % relative humidity. A week spent in this humidity chamber is approximately six months of exposing the samples to the actual corrosive atmosphere. Bronze specimens were first immersed in an inhibitor solution (*Inhibitors 2 and 3* are in liquid form while *Inhibitor 1* was dissolved in ethanol) and then put in the chamber that was saturated with the studied electrolyte (0.2 g dm<sup>-3</sup> NaNO<sub>3</sub>, 0.2 g dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> and 0.2 g dm<sup>-3</sup> NaHCO<sub>3</sub>). For comparison, unprotected samples were also exposed to the same aggressive conditions. After each cycle, panels were analyzed visually and gravimetrically.

## 3. Results and discussion

### 3.1. Polarization resistance determination

Optimum concentration of each examined inhibitor was determined from polarization resistance measurements.

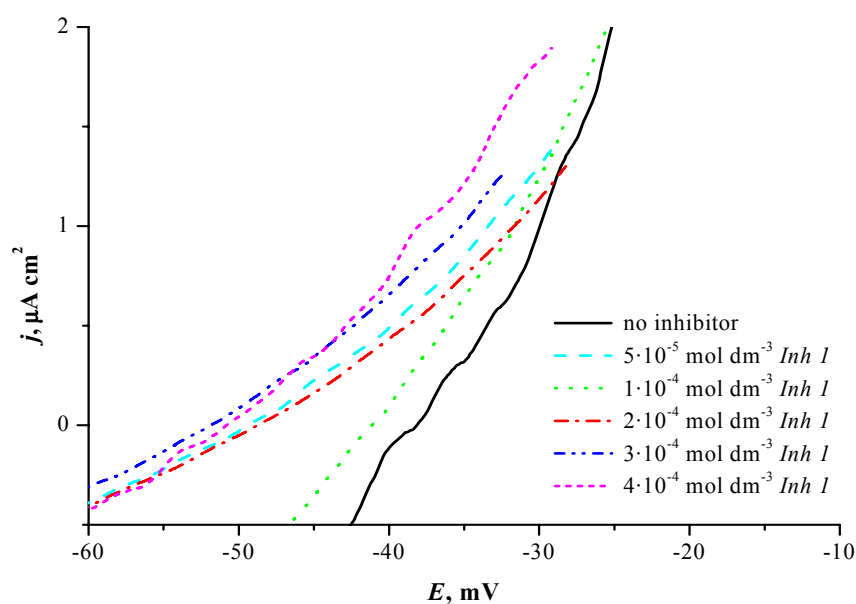


Figure 1. Polarization curves of bronze for various concentrations of *Inhibitor 1*

Corrosion parameters determined from the polarization curves recorded in the narrow potential range are presented in *Table 3*. The inhibitor efficiency was calculated using the relation

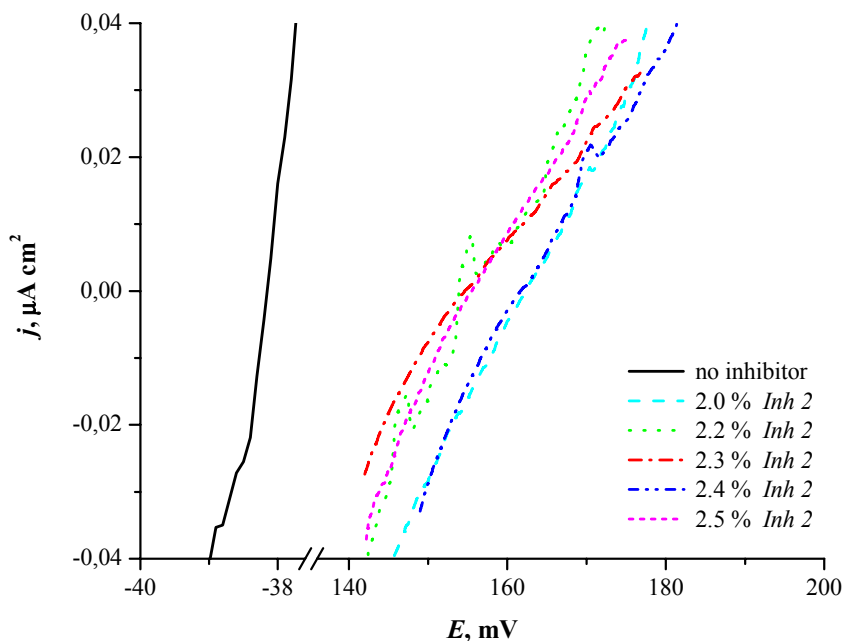
$$z = \frac{j_{corr}^0 - j_{corr}^{inh}}{j_{corr}^0} \cdot 100\%$$

where  $j_{corr}^0$  is a current density in a solution without an inhibitor and  $j_{corr}^{inh}$  current density in a solution with an inhibitor. It can be seen that the polarization resistance increases in the presence of inhibitor and that it is the highest for the inhibitor concentration  $2 \cdot 10^{-4} \text{ mol dm}^{-3}$  in the examined interval of concentrations. The efficiency of the inhibitor in this case is 62 %. It is interesting to note that an increase in inhibitor concentration causes shift of corrosion potential towards more negative values which indicates that *Inhibitor 1* has stronger influence on cathodic reaction than on the anodic reaction.

*Table 3.* Corrosion parameters of bronze in the solution of *Inhibitor 1* obtained by polarization resistance determination

$c_{inh}$ $\text{mol dm}^{-3}$	$j_{corr}$ $\mu\text{A cm}^{-2}$	corrosion rate $\text{mm y}^{-1}$	$E_{corr}$ $\text{mV}$	$R_p$ $\text{k}\Omega \text{ cm}^2$	$z$ $\%$
0	1.32	$1.55 \cdot 10^{-2}$	-38	9.91	0
$5 \cdot 10^{-5}$	0.60	$7.07 \cdot 10^{-3}$	-50	22.50	54
$1 \cdot 10^{-4}$	1.18	$1.39 \cdot 10^{-2}$	-41	10.50	11
$2 \cdot 10^{-4}$	0.50	$5.90 \cdot 10^{-3}$	-49	24.25	62
$3 \cdot 10^{-4}$	0.53	$6.25 \cdot 10^{-3}$	-52	21.86	60
$4 \cdot 10^{-4}$	0.77	$9.05 \cdot 10^{-3}$	-51	17.81	42

Polarization curves of bronze recorded in the presence of various concentrations of *Inhibitor 2* are presented in *Figure 2*, while corrosion parameters obtained by polarization resistance determination are given in *Table 4*.



*Figure 2.* Polarization curves of bronze for various concentrations of *Inhibitor 2*

Table 4. Corrosion parameters of bronze in the solution of *Inhibitor 2* obtained by polarization resistance determination

$c_{inh}$ vol %	$j_{corr}$ $\mu\text{A cm}^{-2}$	corrosion rate $\text{mm y}^{-1}$	$E_{corr}$ mV	$R_p$ $\text{k}\Omega \text{cm}^2$	$z$ %
0	1.32	$1.55 \cdot 10^{-2}$	-38	9.91	0
2.0	0.05	$6.10 \cdot 10^{-4}$	162	481.00	96
2.2	0.04	$5.16 \cdot 10^{-4}$	155	328.90	97
2.3	0.02	$2.81 \cdot 10^{-4}$	155	656.50	98
2.4	0.03	$3.52 \cdot 10^{-4}$	162	525.10	98
2.5	0.05	$5.39 \cdot 10^{-4}$	156	498.10	96

The maximum increase in polarization resistance is noticeable for 2.3 % inhibitor concentration followed by the efficiency of 98 %. This compound shifts corrosion potential towards more positive values which indicates that *Inhibitor 2* has a stronger effect on anodic reaction.

### 3.2. Tafel extrapolation method

Polarization measurements were performed in a wide potential range to observe more clearly influence of corrosion inhibitors on anodic and cathodic polarization curves (Fig. 3.). Measurements were performed with optimum concentration of *Inhibitor 1* and *Inhibitor 2*. As it was previously evaluated from the extent of shift of the corrosion potential, *Inhibitor 1* has more influence on cathodic reaction, while *Inhibitor 2* shows much greater influence on anodic reaction.

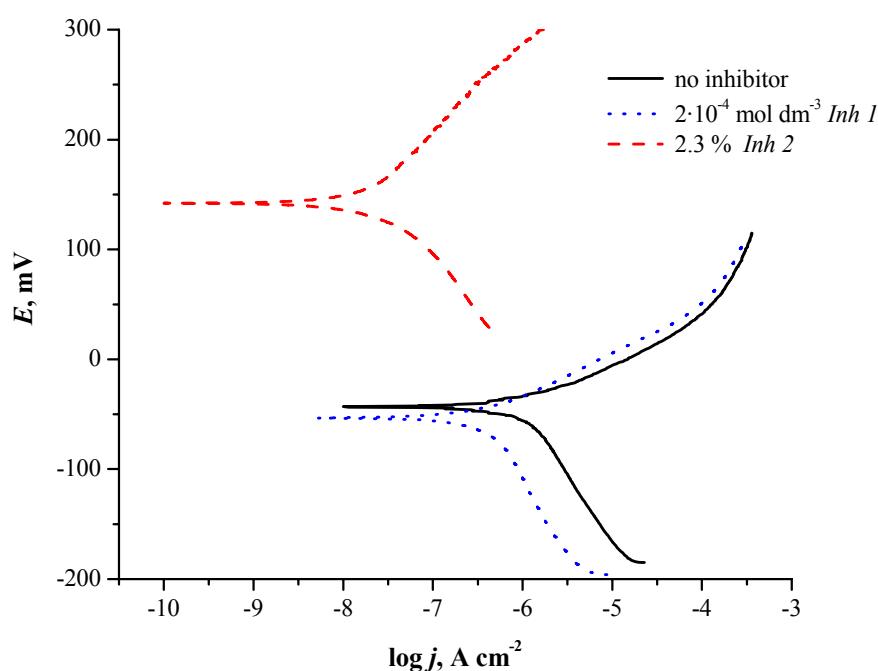


Figure 3. Polarization curves of bronze in the solution with and without the addition of examined inhibitors in optimal concentrations

Table 5. Corrosion parameters of bronze obtained for the optimal concentrations of *Inhibitor 1* and *Inhibitor 2* determined by Tafel extrapolation method

<i>Inh</i>	$c_{inh}$	$j_{corr}$ $\mu\text{A cm}^{-2}$	<i>corrosion rate</i> $\text{mm y}^{-1}$	$E_{corr}$ $\text{mV}$	$b_k$ $\text{mV dec}^{-1}$	$b_a$ $\text{mV dec}^{-1}$	$z$ $\%$
-	0	1.10	$1.29 \cdot 10^{-2}$	-43	-127	40	0
Inh 1	$2 \cdot 10^{-4}$ M	0.35	$4.06 \cdot 10^{-3}$	-53	-98	39	68
Inh 2	2.3 vol %	0.02	$2.34 \cdot 10^{-4}$	144	-62	88	98

### 3.3. Electrochemical impedance spectroscopy

EIS measurements were performed for the same inhibitor concentrations as used for polarization measurements. The obtained impedance spectra were analyzed with the equivalent circuit presented in *Figure 4*.

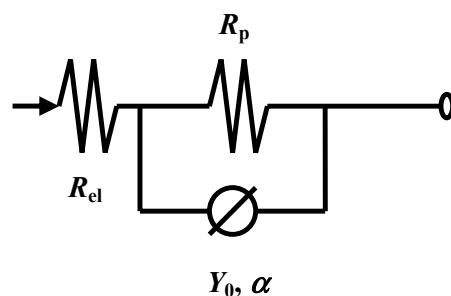


Figure 4. Equivalent electrical circuit representing studied system

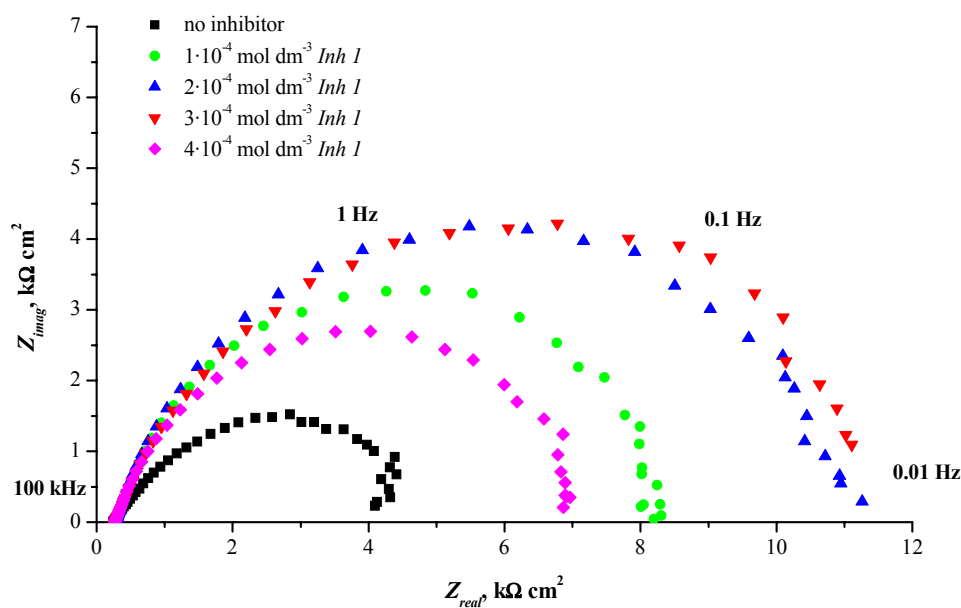


Figure 5. Nyquist impedance spectra of bronze electrode in the solution without inhibitor and for various concentrations of *Inhibitor 1*

Measurements conducted on the bronze in the solution containing *Inhibitor 1* (Fig. 5.) gave slightly higher impedance for  $3 \cdot 10^{-4}$  mol dm<sup>-3</sup> inhibitor concentration than for  $2 \cdot 10^{-4}$  mol dm<sup>-3</sup> concentration in contrary to polarization resistance measurements.

The EIS parameters obtained by fitting the experimental results for *Inhibitor 1* to proposed model are given in Table 6. They show the increase of polarization resistance in the presence of inhibitor while, at the same time, the influence on the value of the constant phase element  $Y_0$  that is related to double layer capacitance is less pronounced.

Table 6. Impedance parameters for bronze in the solution with and without *Inhibitor 1*

$c_{inh}$ mol dm <sup>-3</sup>	$R_{el}$ kΩ cm <sup>2</sup>	$R_p$ kΩ cm <sup>2</sup>	$Y_0$ S·s <sup>α</sup> cm <sup>-2</sup>	$α$
0	0.25	4.60	$1.18 \cdot 10^{-4}$	0.64
$1 \cdot 10^{-4}$	0.29	8.22	$0.49 \cdot 10^{-4}$	0.76
$2 \cdot 10^{-4}$	0.28	11.05	$0.56 \cdot 10^{-4}$	0.85
$3 \cdot 10^{-4}$	0.28	11.81	$1.06 \cdot 10^{-4}$	0.84
$4 \cdot 10^{-4}$	0.27	7.05	$0.89 \cdot 10^{-4}$	0.83

Impedance spectra obtained for *Inhibitor 2* are presented in Figure 6. The largest diameter of the impedance loop was observed for 2.4 % inhibitor concentration with corresponding impedance of almost 50 kΩ cm<sup>2</sup>. This was also confirmed with the values of polarization resistance and constant phase element given in Table 7. where the decrease of  $Y_0$  shows the presence of inhibitor on metal surface.

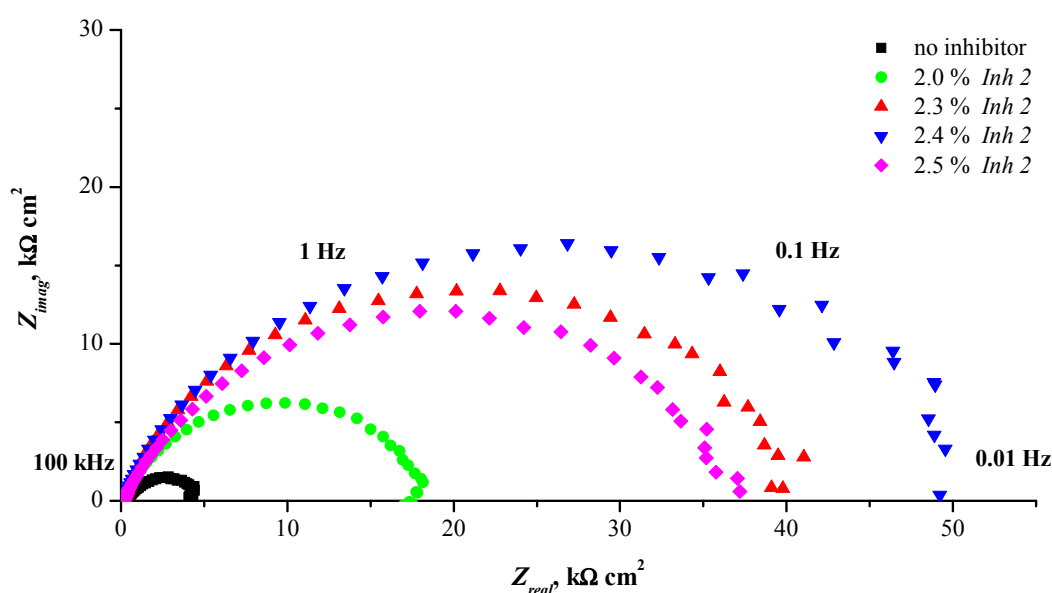


Figure 6. Nyquist impedance spectra for bronze electrode in the solution without inhibitor and for various concentrations of *Inhibitor 2*



Table 7. Impedance parameters for bronze in the solution with and without *Inhibitor 2*

$C_{inh}$ vol %	$R_{el}$ $k\Omega\ cm^2$	$R_p$ $k\Omega\ cm^2$	$Y_0$ $S\cdot s^\alpha\ cm^{-2}$	$\alpha$
0	0.25	4.60	$1.18\cdot 10^{-4}$	0.64
2.0	0.12	18.17	$0.12\cdot 10^{-4}$	0.75
2.3	0.15	40.15	$0.12\cdot 10^{-4}$	0.77
2.4	0.16	49.47	$0.10\cdot 10^{-4}$	0.76
2.5	0.15	37.16	$0.14\cdot 10^{-4}$	0.73

### 3.4. Humidity chamber

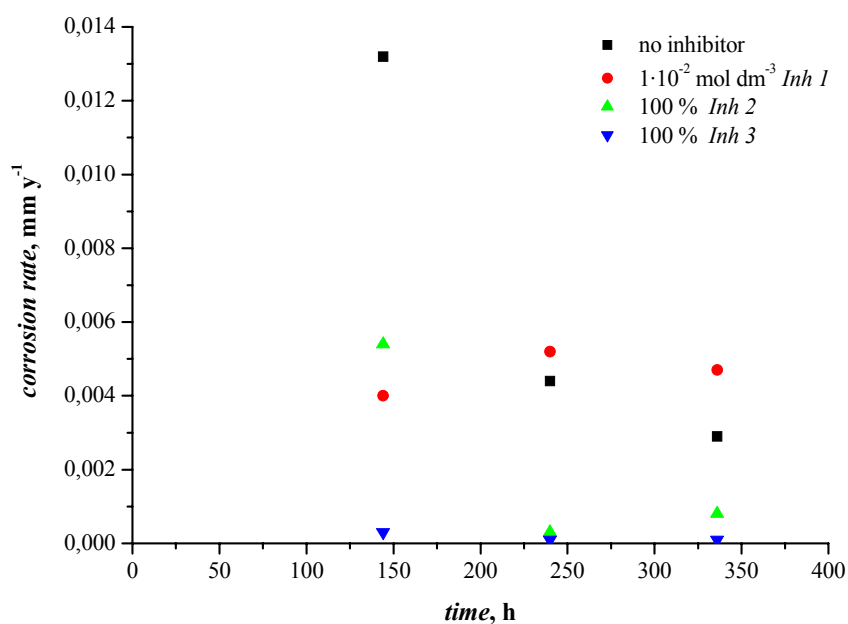


Figure 7. Changes in corrosion rate of an unprotected panel and protected panels with time at 25 °C

Results obtained in the humidity chamber at 25 °C are shown in *Figure 7*. The highest corrosion rate after the first cycle is observed for an uninhibited panel. During the next cycles, corrosion rate decreases due to the formation of corrosion products on the metal surface. It is noticeable that among the examined inhibitors, *Inhibitor 1* shows much weaker protection than the other two inhibitors (*Fig. 8*).

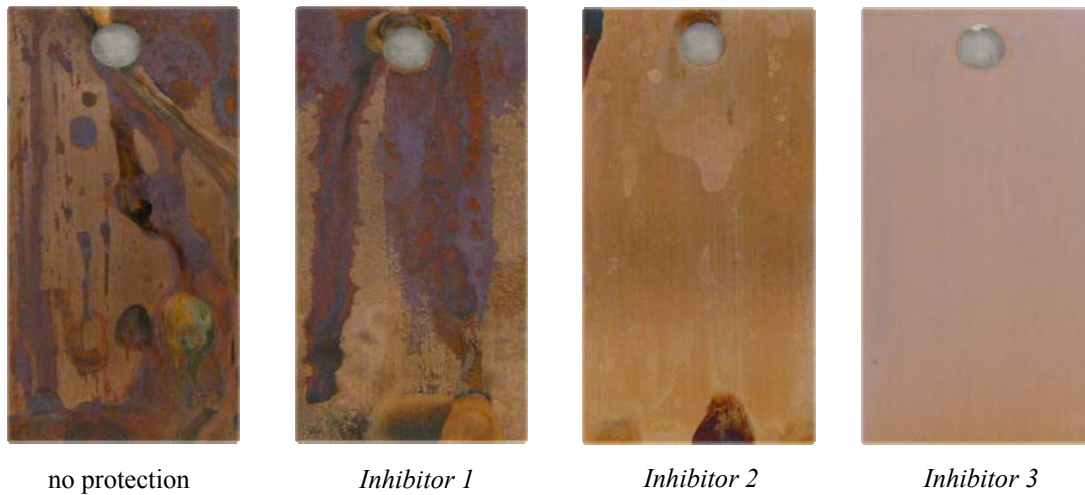


Figure 8. Bronze panels after 336 hours in humidity chamber at 25 °C

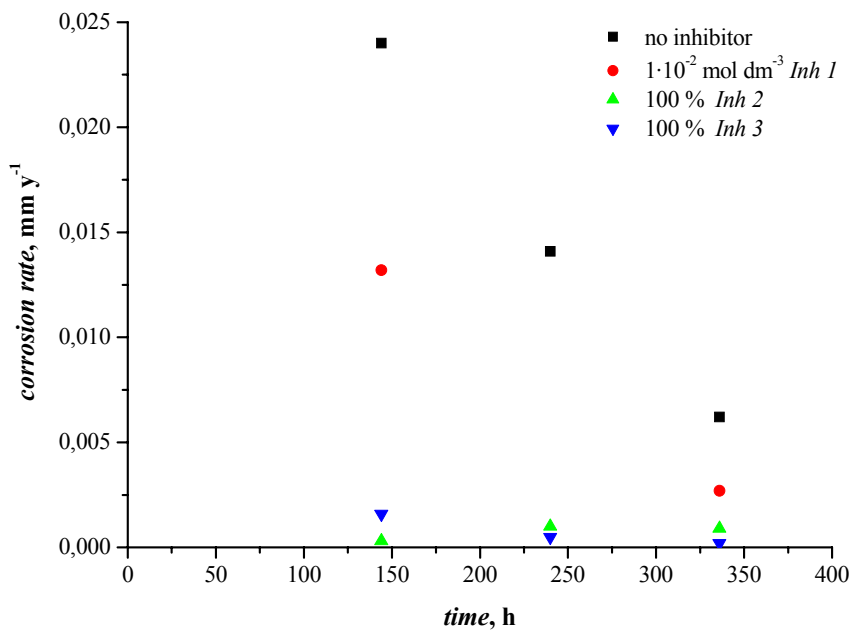


Figure 9. Changes in corrosion rate of an unprotected panel and protected panels with time at 35 °C

Results of the chamber testing at 35 °C (Fig. 9.) are indicating on much higher corrosion rates than at the lower temperature. It is obvious that the metal surface has corroded significantly in comparison to the previous testing (Fig. 10.). In this case the applied protection of the inhibitors 2 and 3 shows much greater protection unlike the *Inhibitor 1*.



Figure 10. Bronze panels after 336 hours in humidity chamber at 35 °C

#### 4. Conclusion

In the present study the possibility of bronze protection of corrosion in urban atmospheric conditions was investigated. As the protective system three non - toxic corrosion inhibitors were examined.

The research was carried out in the solution of  $0.2 \text{ g dm}^{-3} \text{ NaNO}_3$ ,  $0.2 \text{ g dm}^{-3} \text{ Na}_2\text{SO}_4$  and  $0.2 \text{ g dm}^{-3} \text{ NaHCO}_3$  acidified to pH 3. Measurements were performed by the means of electrochemical methods – Tafel extrapolation method, linear polarization method and electrochemical impedance spectroscopy. Due to its high polarization resistance, *Inhibitor 3* was not tested using electrochemical methods. Stability of the applied protection using all three inhibitors was also tested in humidity chamber at two temperatures (25 °C and 35 °C).

Results obtained using linear polarization method showed that the polarization resistance increases in the presence of *Inhibitor 1* and *Inhibitor 2*. The highest efficiency of 62 % was achieved at  $2 \cdot 10^{-4} \text{ mol dm}^{-3}$  concentration of *Inhibitor 1*, while the *Inhibitor 2* showed the highest decrease in the current density of 98 % for 2.3 % concentration.

Tafel extrapolation method was used to examine inhibitor behavior in concentrations that showed optimum results. This method confirmed the results obtained by linear polarization method. Both inhibitors have a positive effect on slowing down the corrosion process, although *Inhibitor 1* has a stronger influence on cathodic reaction, while the *Inhibitor 2* retards more significantly anodic dissolution of bronze electrode.

Measurements performed by the use of electrochemical impedance spectroscopy also showed corrosion resistance improvement in the system that contained inhibitor. Highest efficiency of *Inhibitor 1* was at the concentration of  $3 \cdot 10^{-4} \text{ mol dm}^{-3}$  and for *Inhibitor 2* at the concentration of 2.4 %. The value of the impedance at optimal concentration of *Inhibitor 2* was multiply higher than the impedance at optimal concentration of *Inhibitor 1*. According to that *Inhibitor 2* provides much greater protection than *Inhibitor 1*.

Results of the testing the stability of these inhibitors using accelerated methods in humidity chamber showed that *Inhibitor 2* and *Inhibitor 3* provide better protection to bronze panels than *Inhibitor 1*.

Results of the investigation indicate that each of the studied compounds provides protection to bronze in the tested conditions. However, because of their extremely high efficiency and environmentally non - toxic chemical properties, *Inhibitor 2* and *Inhibitor 3* can present as an alternative to the toxic inhibitors.

### **Acknowledgements**

*The authors wish to express their gratitude to Mr. Boris A. Miksic, FNACE in whose laboratories presented measurements were performed.*

### **List of symbols**

$b_a$	Tafel anodic slope, mV dec <sup>-1</sup>
$b_k$	Tafel cathodic slope, mV dec <sup>-1</sup>
$c_{inh}$	inhibitor concentration, mol dm <sup>-3</sup>
$E_{corr}$	corrosion potential, mV
$j_{corr}$	corrosion current density, A cm <sup>-2</sup>
$R_{el}$	electrolyte resistance, $\Omega$ cm <sup>2</sup>
$R_p$	polarization resistance, $\Omega$ cm <sup>2</sup>
$Y_0$	constant phase element, S·s <sup>a</sup> cm <sup>-2</sup>
$z$	inhibitor efficiency, %
$Z_{imag}$	imaginary component of impedance, $\Omega$ m <sup>2</sup>
$Z_{real}$	real component of impedance, $\Omega$ m <sup>2</sup>
$\alpha$	coefficient representing depressed feature in Nyquist diagram

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